

$C_5F_{10}Br_2$ 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, [$M - (CF_3)_2CF$]⁺}, 181 (74, $C_4F_7^+$), 131 and 129 (90, CF_2Br^+), 93 (47, $C_3F_3^+$), and 69 (100, CF_3^+); ^{19}F n.m.r. δ -7.5 [6 F, dm, (CF_3)₂CF, $J_{CF_3,F}$ 12.6 Hz], -22.0 (2 F, AB m, CF_2Br , J_{AB} 174 Hz), 49.0 (1 F, m, CFBr), and 93.0 [1 F, m, (CF_3)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. $C_5HF_{10}Br$ requires C, 18.1; H, 0.3% M , 331), b.p. (isoteniscope) 79.7 ± 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], ^{19}F n.m.r. δ -17.6 (2 F, m, CF_2Br), -4.0 and -0.6 [6 F, m, (CF_3)₂CF], 109.3 [1 F, m, (CF_3)₂CF], and 120.0 (1 F, dm, CHF), and the dibromide (2) (4.06 g, 9.90 mmol, 53%).

(c) *With N-bromobis(trifluoromethyl)amine.* 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*-bis(trifluoromethyl)amine (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 ($C\equiv N$ 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), tetrakis(trifluoromethyl)hydrazine (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-1,1,2,3,4,4,4-heptafluoro-3-trifluoromethylbutyl-*NN*-bis(trifluoromethyl)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 CF₂⁺], 181 (39, $C_4F_7^+$), 114 (38, $C_2F_4N^+$), and 69 (100, CF_3^+); ^{19}F 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, (CF_3)₂CF], 5.7 (2 F, AB m, CF_{AFB} , J_{AB} 228 Hz), 55.7 (1 F, m, CFBr), and 94.7 [1 F, dm, (CF_3)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), ^{19}F n.m.r. δ -20.4 [6 F, (CF_3)₂N], -4.8 (3 F, CF_3), -1.8 (3 F, CF_3), 33.9 (2 F, CF_2), 52.2 (1 F, CF), and 108 (1 F, CF), and (iv) a non-volatile 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. $C_6H_4F_{10}S$ requires, C, 24.2; H, 1.35%; M , 298), b.p. 117 °C; m/e 298 (28%, M^+), 181 (25, $C_4F_7^+$), 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, $J_{H,F}$ (*gem*) 42.0, $J_{H,F}$ (*vic*) 12.0, J_{H,CF_2} 8.0 Hz] and 7.78 (3 H, s, SMe), ^{19}F δ -4.4 (3 F, m, CF_3), -0.74 (3 F, m, CF_3), 10.1 (2 F, AB m, CF_{AFB} , J_{AB} 230 Hz), 109.0 [1 F, m, (CF_3)₂CF], 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 1,1,2,3,4,4,4-heptafluoro-3-trifluoromethylbutyltrimethylsilane (7) (2.36 g, 7.3 mmol, 87%) (Found: C, 30.0; H, 3.4; F, 58.1. $C_6H_{10}F_{10}Si$ requires C, 29.7; H, 3.1; F, 58.6%), b.p. (Siwoloboff) 142 °C; m/e 231 [2%, ($M - SiMe_3 - HF$)⁺], 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, $J_{H,F}$ 43.8 Hz) and 6.55 (9 H, s, Me_3Si) p.p.m. to high field of external benzene, ^{19}F δ -4.4 (3 F, m, CF_3), -1.0 (3 F, m, CF_3), 49.6 (2 F, AB m, CF_{AFB} , 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 2*H*-2-trifluoromethyloctafuorobutane (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-2-ene (8) (0.06 g, 0.24 mmol, 6%); and (iii) 2*H*-2-trifluoromethyloctafuorobutane (10) (0.78 g, 2.9 mmol, 73%) (Found: C, 22.3; H, 0.5. C_6HF_{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],

^{19}F δ -14.6 [6 F, m, $(\text{CF}_3)_2\text{C}$], 8.5 [3 F, septet, $J_{\text{CF}_3,(\text{CF}_3)_2\text{C}}$ 5.7 Hz], and 38.0 [2 F, octet, CF_2 , $J_{\text{CF}_2,(\text{CF}_3)_2\text{C}}$ 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 cm³) 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.); 3*H*-2-trifluoromethyloctafluorobutane (11) (0.08 g, 0.33 mmol, 4%), *m/e* 251 [3%, $(M - \text{F})^+$], 250 [8, $(M - \text{HF})^+$], 181 (46, C_4F_7^+), 131 (25, C_3F_5^+), 113 (13, C_3HF_4^+), and 69 (100, CF_3^+), ^1H n.m.r. τ 5.29 [dq, CHF , $J_{\text{H,F}}$ (*gem*) 43.5, $J_{\text{H,F}}$ (*vic*) 6.0, $J_{\text{H,CF}_3}$ 6.0 Hz], ^{19}F δ -3.6 [3 F, m, CF_3 in $(\text{CF}_3)_2\text{C}$], -1.4 [3 F, m, CF_3 in $(\text{CF}_3)_2\text{C}$], 0.5 (3 F, m, CF_3), 111.6 [1 F, m, $(\text{CF}_3)_2\text{CF}$], and 135.5 (1 F, dm, CHF); an unknown compound (0.03 g, 0.12 mmol); and 2*H*-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 2*H*-2-trifluoromethyloctafluorobutane (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. $\text{C}_6\text{H}_3\text{F}_9\text{O}$ requires C, 27.5; H, 1.15; F, 65.3%; M , 262), b.p. (isoteniscope) 82.7 ± 0.5 °C, λ_{max} 6.03s, (C:C str.) μm ; *m/e* 262 (44%, M^+), 243 [46, $(M - \text{F})^+$], 209 (40, $\text{C}_5\text{F}_7\text{O}^+$), 193 (29, $\text{C}_5\text{H}_3\text{F}_8\text{O}^+$), 184 (38, $\text{C}_6\text{HF}_5\text{O}^+$), 178 (27, $\text{C}_4\text{F}_6\text{O}^+$), 159 (100, $\text{C}_4\text{F}_5\text{O}^+$), 131 (45, $\text{C}_3\text{H}_3\text{F}_4\text{O}^+$), 100 (29, C_2F_4^+), 93 (30, C_3F_3^+), 91 (23, $\text{C}_3\text{HF}_2\text{O}^+$), 81 (25, C_2F_3^+), 78 (42, $\text{C}_2\text{F}_2\text{O}^+$), 69 (83, CF_3^+), 59 (28, C_2FO^+), and 31 (40, CF^+ and MeO^+); ^1H n.m.r. τ 6.45 (s, OMe), ^{19}F δ -18.92 [3 F, qq, CF_3 , $J_{\text{CF}_3, \text{CF}_3}$ (*cis*) 14.4, $J_{\text{CF}_3, \text{CF}_3}$ (*gem*) 10.0 Hz], -16.60 [3 F, q, CF_3 , $J_{\text{CF}_3, \text{CF}_3}$ (*gem*)], and -11.80 [3 F, q, =C(CF_3)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 $\text{C}_6\text{H}_4\text{F}_{10}\text{O}$: 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 °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 pentoxide 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) 3*H*-2-trifluoromethyloctafluorobutane (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%, $(M - \text{H})^+$], 251 [3, $(M - \text{OMe})^+$], 181 (21, C_4F_7^+), 113 (14, $\text{CF}_3 \cdot \text{CH} \cdot \text{OMe}^+$), 69 (100, CF_3^+), and 31 (18, MeO^+); ^1H n.m.r. τ 6.84 (m, $\geq\text{CH}$ and OMe), ^{19}F δ -2.9 (3 F, m, CF_3), -2.0 (3 F, m, CF_3), -0.5 (3 F, m, CF_3), and 112.0 [1 F, m, $(\text{CF}_3)_2\text{CF}$]; (iv) an unidentified methyl ester (0.6 mmol, ca. 12%), *m/e* 159 (5%, $\text{C}_2\text{F}_4 \cdot \text{CO}_2\text{Me}^+$), 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 H, m), ^{19}F δ -0.4 (6 F, 2 CF_3) and 0.5 (1 F); (v) 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, λ_{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 , $J_{\text{H,F}}$ (*gem*) 42.6, $J_{\text{H,CF}_3}$ 8.0, $J_{\text{H,F}}$ 4.0 Hz], ^{19}F δ -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, $\geq\text{CF}$), and 132.9 (1F, dm, CHF), *m/e* 263 (12%, $\text{C}_6\text{HF}_9\text{OMe}^+$), 229 (7, $\text{C}_6\text{HF}_8\text{O}^+$), 213 (6, $\text{C}_4\text{HF}_7\text{OMe}^+$), 131 (8, C_3F_5^+), 113 (19, $\text{C}_2\text{HF}_3\text{OMe}^+$), 81 (100, $\text{CF}_2 \cdot \text{OMe}^+$), 69 (63, CF_3^+), and 31 (10, OMe^+); and (viii) 1-methoxy-1,1,2,2,4,4,4-heptafluoro-3-trifluoromethylbutane (17) (0.08 g, 0.29 mmol, 6%) (Found: C, 26.0; H, 1.4. $\text{C}_6\text{H}_4\text{F}_{10}\text{O}$ requires C, 25.6; H, 1.5%), *m/e* 263 [30%, $(M - \text{F})^+$], 201 (33, C_4HF_8^+), 181 (17, C_4F_7^+), 131 (27, $\text{C}_2\text{F}_4\text{OMe}^+$), 113 (48, C_3HF_4^+), 81 (100, $\text{CF}_2 \cdot \text{OMe}^+$), 69 (65, CF_3^+), 47 (19, CFO^+), and 31 (13, MeO^+); ^1H n.m.r. τ 6.48 (1 H, m, $\geq\text{CH}$) and 6.62 (3 H, s, OMe), ^{19}F δ -13.15 [6 F, tdt, $(\text{CF}_3)_2\text{C}$, $J_{\text{CF}_3, \text{CF}_3}$ 11.8, $J_{\text{CF}_3, \text{H}}$ 7.5, $J_{\text{CF}_3, \text{CF}_3}$ 5.5 Hz], 16.9 (2 F, m, $\text{CF}_2 \cdot \text{OMe}$), and 38.5 (2 F, m, CF_2).

(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, λ_{max} 5.62m (C=O str.) and 5.94m (C:C str.) μm , 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, $J_{\text{H,CF}_2}$ 11.7, $J_{\text{H,CF}_3}$ 8.2 Hz) and 4.22 (6 H, m, Me_2N) p.p.m. to high field of external benzene, ^{19}F δ -15.6 [6 F, tdt, $(\text{CF}_3)_2\text{C}$, $J_{\text{CF}_3, \text{CF}_3}$ (*vic*) 11.7, $J_{\text{CF}_3, \text{CF}_3}$ 6.8 Hz], 24.6 (2 F, m, CF_2N), and 33.2 (2 F, octet, C- CF_2 -C), 2,2,4,4,4-pentafluoro-*NN*-dimethyl-3-trifluoromethylbutylamide (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, Me_2N) p.p.m. to high field of external benzene, ^{19}F δ -14.6 [6 F, td, $(\text{CF}_3)_2\text{C}$, $J_{\text{CF}_3, \text{CF}_3}$ 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.

(l) *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), 3*H*-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 non-volatile 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. $\text{C}_5\text{H}_2\text{F}_{10}$ requires C, 23.8; H, 0.8%), *m/e* 233 [1%, ($M - \text{F}$)⁺], 182 [14, ($M - \text{CHF}_3$)⁺], 113 (38, C_3HF_4^+), 95 (19, $\text{C}_3\text{H}_2\text{F}_3^+$), 83 (81, $\text{CHF}\cdot\text{CHF}_2^+$), 69 (91, CF_3^+), 51 (100, CHF_2), and 32 (40, CHF^+), ¹H n.m.r. τ 4.40 [1 H, tt, CHF_2 , $J_{\text{H,F}_2}$ (*gem*) 54.0, $J_{\text{H,F}}$ (*vic*) 5.0,

$J_{\text{H,H}}$ (*vic*) 5.0 Hz] and 5.52 [1 H, dm, CHF, $J_{\text{H,F}}$ (*gem*) 44.0 Hz], ¹⁹F δ -2.5 (3 F, m, CF_3), 0.1 (3F, m, CF_3), 51.8 (2 F, dm, CHF_2), 111.5 (1 F, dm, CHF), and 112.5 (1 F, m, CF).

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