

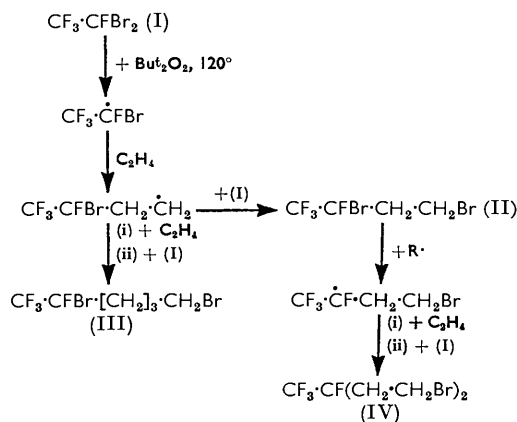
The Peroxide-initiated Addition of 1,1-Dibromotetrafluoroethane to Ethylene, Propene, and 2-Methylpropene

By P. Piccardi,* M. Modena, and E. Santoro, Montecatini Edison S.p.A., Centro Ricerche Bollate, via S. Pietro, 50-20021 Bollate (Milano), Italy

1,1-Dibromotetrafluoroethane has been found to give simple addition products with ethylene, propene, and 2-methylpropene in the presence of di-*t*-butyl peroxide. The products of dehydrohalogenation of the adducts are described and their structures elucidated by spectroscopic methods.

THE free-radical addition of polyfluorobromoalkanes such as CF_2Br_2 or $\text{CF}_2\text{Br}\cdot\text{CFBrCl}$ to simple olefins is known¹ to give 1:1 addition products, which are valuable intermediates in the synthesis of reactive molecules. For example tetrafluoroallene has been prepared by dehydrobromination² of the monoadduct of CF_2Br_2 and vinylidene difluoride. Generally compounds of the type $\text{R}_\text{F}\text{CFXY}$ (with $\text{X} = \text{Br}, \text{Cl},$ or I and $\text{Y} = \text{Br}$ or I) should be more versatile than the familiar $\text{R}_\text{F}\text{CF}_2\text{Y}$ compounds in the synthesis of dienes and allenes, because they have two halogen atoms, X and Y , that can easily be removed from the monoadducts with α -olefins. Thus 1,1-dibromotetrafluoroethane (I), obtained from the commercially available 1,2-dibromotetrafluoroethane by refluxing[†] with less than 2% by weight of aluminium bromide, is more reactive and yields more versatile products than the 1,2-isomer. We report here the products of addition of compound (I) to ethylene, propene, and 2-methylpropene and the dehydrohalogenation reactions of these adducts.

The reaction of compound (I) with ethylene, initiated by di-*t*-butyl peroxide, yields the 1:1 adduct (II) as the major product and smaller amounts of both the isomeric 1:2 adducts (III) and (IV). The ratio between the 1:2

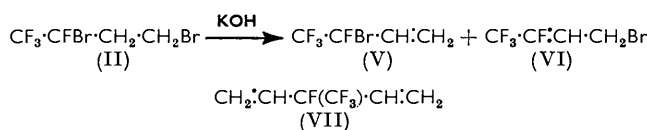


adducts (III) and (IV) (13:1) was obtained from the ratio of the CF_3 signals in the ^{19}F n.m.r. spectrum of the mixture. The presence of the latter (IV) shows that the 1:1 adduct (II) is sufficiently active to compete with (I) in the chain transfer. In a separate reaction products

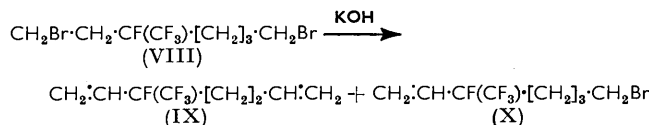
† A small amount of residual 1,1,1-tribromo-2,2,2-trifluoroethane may remain.

* G. Sosnovsky, 'Free Radical Reactions in Preparative Organic Chemistry', MacMillan, New York, 1964.

of the type $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CF}(\text{CF}_3)\cdot[\text{CH}_2]_n\cdot\text{CH}_2\text{Br}$ ($n = 1, 3, 5,$ etc.) have been obtained from the adduct (II) and ethylene, showing that the transfer reaction takes place preferentially at the CFBr group. By treating the adduct (II) with potassium hydroxide in butane-1,4-diol a mixture of the isomeric olefins 3-bromo-3,4,4,4-tetrafluorobutene (V) and 4-bromo-1,1,1,2-tetrafluorobut-2-ene (VI) was produced (1.2:1.0 molar ratio).



Examination of olefin (VI) by g.l.c. and n.m.r. spectroscopy showed that only one isomer was present. The $\text{CH}:\text{CF}$ coupling constant was 28.9 Hz and so fell in the known³ range of values for *trans*-isomers. The complete dehydrobromination of the 1:2 adduct (IV) was carried out by use of an excess of solid potassium hydroxide, and gave 3-fluoro-3-trifluoromethylpenta-1,4-diene (VII), isomer of the 3,3,4,4-tetrafluorohexa-1,5-diene obtainable⁴ from the symmetrical diadduct of 1,2-dibromotetrafluoroethane and ethylene. The reaction of 1,7-dibromo-3-fluoro-3-trifluoromethylheptane (VIII) with potassium hydroxide pellets was also studied. Two major products were formed (g.l.c.), which were identified as 3-fluoro-3-trifluoromethylhepta-1,6-diene (IX) and 7-bromo-3-fluoro-3-trifluoromethylheptene (X).



The absence, at least under these reaction conditions, of 7-bromo-5-trifluoromethylheptene shows the strong acidity of a hydrogen atom adjacent to a fluorinated group.

Free-radical addition of compound (I) to propene yielded only 1,4-dibromo-1,1,1,2-tetrafluoropentane (XI) as two stereoisomers in the ratio of about 2:1. G.l.c. and n.m.r. analysis did not show any evidence of the 1:1 'anti-Kharasch' adduct found⁵ in other cases;

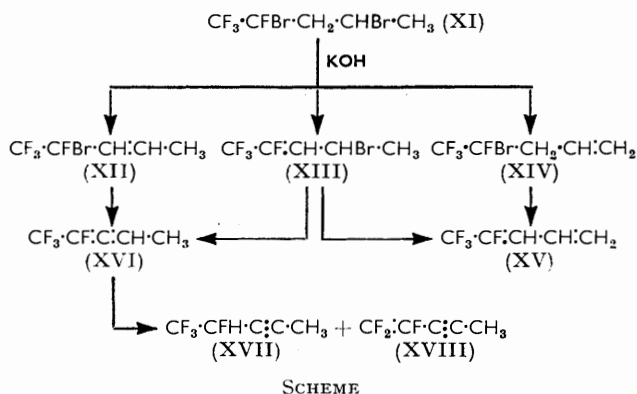
² R. E. Banks, M. G. Barlow, W. D. Davies, R. N. Haszeldine, and D. R. Taylor, *J. Chem. Soc. (C)*, 1969, 1104.

³ J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy', Pergamon Press, Oxford, 1966, vol. 2, p. 911.

⁴ N. O. Brace, U.S.P. 3,055,953/1962.

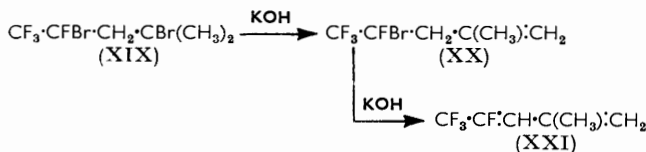
⁵ R. N. Haszeldine, D. W. Keen, and A. E. Tipping, *J. Chem. Soc. (C)*, 1970, 414, and references cited therein.

also higher telomers were not detected. Dehydrobromination of the adduct (XI) by use of potassium hydroxide in ethylene glycol gave a mixture of seven components (g.l.c.). The main products were 4-bromo-4,5,5,5-tetrafluoropent-2-ene (XII) and *trans*-4-bromo-1,1,1,2-tetrafluoropent-2-ene (XIII) (3.5:1.0 molar ratio). Examination of olefin (XII) by g.l.c. and n.m.r. spectroscopy showed that the *trans*-isomer was still predominant. The other five products were separated by g.l.c. and identified by physical methods as 4-bromo-4,5,5,5-tetrafluoropentene (XIV), 4,5,5,5-tetrafluoropenta-1,3-diene (XV), 1,1,1,2-tetrafluoropenta-2,3-diene (XVI), 4,5,5,5-tetrafluoropent-2-yne (XVII), and 1,1,2-trifluoropent-1-en-3-yne (XVIII) (see Scheme). The



alkynes (XVII) and (XVIII) are presumably formed by isomerisation of the allene (XVI) in the alkaline medium.

Treatment of compound (I) with 2-methylpropene yielded 2,4-dibromo-1,1,1,2-tetrafluoro-4-methylpentane (XIX), which was dehydrobrominated to 4-bromo-4,5,5,5-tetrafluoro-2-methylpentene (XX). The formation of this terminally unsaturated compound was not unexpected, since an olefin of this type has been isolated before.⁶ Compound (XX) was easily dehydrobrominated to 4,5,5,5-tetrafluoro-2-methylpenta-1,3-diene (XXI).



EXPERIMENTAL

Techniques.—Products were identified by elemental analysis, i.r. spectroscopy (Perkin-Elmer 225 grating spectrophotometer), ¹H and ¹⁹F n.m.r. spectroscopy [Varian HA-100 instrument; the ¹⁹F figures quoted are chemical shifts in p.p.m. from internal trichlorofluoromethane and the ¹H figures are τ values (internal tetramethylsilane standard)], and mass spectrometry (Hitachi-Perkin-Elmer RMU/6E instrument). Analytical g.l.c. was carried out with a column (4 m × 4 mm) packed (25%) with Apiezon L on Chromosorb or a column (6 m × 4 mm) packed (25%) with dinonyl phthalate on Celite; temperatures were 40–150°.

Addition of 1,1-Dibromotetrafluoroethane (I) to Ethylene.—A typical experiment is described. Compound (I) (540 g, 2.078 mol) mixed with 0.46% (w/w) of di-*t*-butyl peroxide

was placed in a 400 ml stainless steel autoclave. After evacuation ethylene was added by means of an injection system to give a pressure of 50 kg cm⁻² at 120°. The autoclave was rocked at 120° for 2 h; whenever the pressure dropped to 45 kg cm⁻² ethylene was added to restore the original pressure; **Caution:** addition of ethylene more frequently (at 48–50 kg cm⁻² for instance) causes a violent reaction. The autoclave was cooled and the pressure released. Low-boiling material, mostly ethylene, was condensed in a cold trap. Fractionation of the residual liquid gave, besides unchanged starting material (I), 2,4-dibromo-1,1,1,2-tetrafluorobutane (II) (156.2 g, 0.542 mol, 26%) (Found: C, 16.7; H, 1.3; Br, 55.4. C₄H₄Br₂F₄ requires C, 16.69; H, 1.40; Br, 55.51%), b.p. 130.6° at 750 mmHg, and a fraction (18 g, 0.057 mol, 2.7%) boiling at 82° and 14 mmHg and shown by g.l.c. and n.m.r. spectroscopy to be a 93:7 mixture of 2,6-dibromo-1,1,1,2-tetrafluorohexane (III) and 1,5-dibromo-3-fluoro-3-trifluoromethylpentane (IV) (its properties are reported later) [Found (for mixture): C, 22.9; H, 2.6. C₆H₈Br₂F₄ requires C, 22.8; H, 2.55%].

Spectra. Adduct (II), ¹H n.m.r. τ (CCl₄) 6.5 (2H, m, CH₂Br) and 7.2 (2H, m, CH₂); ¹⁹F n.m.r. φ* 81.5 [3F d, J (CF₃-F) 8.0 Hz, CF₃] and 126.5 (1F, m, CFBr); adduct (III), ¹H n.m.r. τ (CCl₄) 6.5 (2H, m, -CH₂Br) and 7.4–8.3 (6H, m, [CH₂]₃); ¹⁹F n.m.r. φ* 81.4 [3F, d, J (CF₃-F) 8.0 Hz, CF₃] and 125.3 (1F, complex, CFBr).

Addition of Compound (I) to Propene.—By a similar procedure compound (I) (546 g, 2.101 mol) and di-*t*-butyl peroxide (4 g) were heated at 124°. Propene was added to give a pressure of 10 kg cm⁻² and more was frequently injected in order to maintain constant pressure (9–10 kg cm⁻²) during the run (124°; 7 h). Fractionation of the products gave 2,4-dibromo-1,1,1,2-tetrafluoro-3-methylbutane (XI) (435.7 g, 1.443 mol, 68.7%) (Found: C, 19.9; H, 1.8. C₅H₆Br₂F₄ requires C, 19.9; H, 2.0%), b.p. 143.8° at 755 mmHg, and no residue. The n.m.r. spectra of the product (XI) showed the presence of two stereoisomers (XIa and b) in the approximate ratio 2:1 (from integration of the CF₃ and CH₃ signals): ¹H n.m.r. τ (CCl₄) of the stereoisomers gave resonances at 5.3–5.8 (m; -CHBr-), 6.8–7.6 (m, CH₂), 8.15 [d, J 6.65 Hz, Me of (XIa)], and 8.16 [d, J 6.65 Hz, Me of (XIb)]; ¹⁹F n.m.r. φ* 81.5 [d, J (CF₃-F) 7.6 Hz, CF₃ of (XIb)], 82.13 [d, J (CF₃-F) 7.6 Hz, CF₃ of (XIa)], 127.19 [m, CFBr of (XIa)], and 128.31 [m, CFBr of (XIb)].

Addition of Compound (I) to 2-Methylpropene.—Compound (I) (400 g, 1.539 mol), di-*t*-butyl peroxide (3 g), and 2-methylpropene (60 g, 1.069 mol) were heated in an autoclave at 120° for 5 h with constant rocking. Distillation of the products yielded, besides unchanged (I) and 2-methylpropene, 2,4-dibromo-1,1,1,2-tetrafluoro-4-methylpentane (XIX) (145.5 g, 0.461 mol, 29.9%) (Found: C, 22.8; H, 2.4. C₆H₈Br₂F₄ requires C, 22.81; H, 2.56%), b.p. 94° at 100 mmHg, and no residue. In the ¹H n.m.r. spectrum of product (XIX) (in CCl₄) the methylene groups gave rise to a characteristic ABX pattern, analysis of which gave the following data: |J_{AB}| 15.9 Hz, |J_{AX}| 6.9 Hz, |J_{BX}| 32.9 Hz, τ_A 6.63, τ_B 6.83; other signals: τ 7.89 (3H, s, Me) and 8.00 (3H, d, J 2 Hz, Me); ¹⁹F n.m.r. φ* 82.68 [3F, d, J (CF₃-F) 8.3 Hz, CF₃] and 127.87 (1F, complex m, CFBr).

Addition of 2,4-Dibromo-1,1,1,2-tetrafluorobutane (II) to Ethylene.—By use of the same procedure as in addition of compound (I) to ethylene, compound (II) (268 g, 0.931 mol)

⁶ P. Tarrant and J. P. Tandon, *J. Org. Chem.*, 1969, **34**, 864.

and di-*t*-butyl peroxide (2.7 g) were heated to 120°. Ethylene was added to give a pressure of 50 kg cm⁻² and frequently injected to maintain the pressure constant (48—50 kg cm⁻²) during the run (6 h). The combined products of two such runs were fractionally distilled to give 1,5-dibromo-3-fluoro-3-trifluoromethylpentane (IV) (29.2 g, 0.092 mol, 5%) (Found: Br, 50.5. C₆H₉Br₂F₄ requires Br, 50.58%), b.p. 80.7° at 10 mmHg; 1,7-dibromo-3-fluoro-3-trifluoromethylheptane (VIII) (38.8 g, 0.113 mol, 6%) (Found: Br, 46.5. C₈H₁₂Br₂F₄ requires Br, 46.46%), b.p. 123.6° at 10 mmHg; and a high-boiling unexamined residue (11.1 g).

Spectra. Adduct (IV), ¹H n.m.r. τ (CCl₄) 6.57 (2H, complex t, *J* 8.3 Hz, CH₂Br) and 7.53br (2H, m, CH₂); ¹⁹F n.m.r. φ* 79.8 [3F, d, *J* (CF₃-F) 6.2 Hz, CF₃] and 172.8 (1F, complex m, CF); adduct (VIII), ¹H n.m.r. τ (CCl₄) 6.6 (4H, complex m, CH₂Br), 7.4—7.7 (2H, m, CF·CH₂·CH₂-Br), and 8—8.5br (6H, m, CH₂); ¹⁹F n.m.r. φ* 79.9 [d, *J* (CF₃-F) 6.2 Hz, CF₃] and 172.5 (complex, CF).

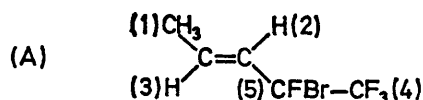
Dehydrohalogenation of 2,4-Dibromo-1,1,1,2-tetrafluorobutane (II) with Potassium Hydroxide.—A solution of potassium hydroxide (50 g, 0.891 mol) in water (50 ml) and butane-1,4-diol (100 ml) was added during *ca.* 2 h under nitrogen to a stirred mixture of the adduct (II) (241.7 g, 0.839 mol) and butane-1,4-diol (100 ml) at 100°; the products were continuously distilled off. After washing and drying (MgSO₄), the products (180 g) were fractionated to give 3-bromo-3,4,4,4-tetrafluorobutene (V) (62.1 g, 0.300 mol, 35.8%) (Found: Br, 38.5. C₄H₃BrF₄ requires Br, 38.6%), b.p. 55.4° at 749 mmHg; 4-bromo-1,1,1,2-tetrafluorobut-2-ene (VI) (51.9 g, 0.251 mol, 29.9%) (Found: Br, 38.5. C₄H₃BrF₄ requires Br, 38.6%), b.p. 81° at 749 mmHg; and unchanged (II).

Spectra. Product (V), λ_{max} 6.10 μm (C:C), ¹H n.m.r. τ 3.65—4.54 (complex, CH=CH₂), ¹⁹F n.m.r. φ* 81.32 [3F, complex d, *J* (CF₃-F) 9.3 Hz, CF₃] and 133.73 (1F, m, CF); product (VI), λ_{max} 5.83 μm (C:C str.), ¹H n.m.r. τ (CCl₄) 4.15 [1H, dtq, *J* (H-F *trans*) 29.0, *J* (H-CH₂) 8.5, *J* (H-CF₃) 0.7 Hz, C=CH], and 6.04 [2H, ddq, *J* (CH₂-H) 8.5, *J* (CH₂-F) 2.0, *J* (CH₂-CF₃) 1.4 Hz, CH₂Br]; ¹⁹F n.m.r. φ* 74.33 [3F, ddt, *J* (CF₃-F) 11.6, *J* (F-H) 0.7, *J* (F-CH₂) 1.4 Hz, CF₃] and 131.80 [1F, dqt, *J* (F-H *trans*) 29.2, *J* (F-CF₃) 11.6, *J* (F-CH₂) 2.0 Hz, CF=C].

Dehydrohalogenation of 2,4-Dibromo-1,1,1,2-tetrafluoro-3-methylbutane (XI) with Potassium Hydroxide.—A solution of potassium hydroxide (40 g, 0.713 mol) in water (20 ml) and ethylene glycol (75 ml) was added during *ca.* 2 h under nitrogen to a stirred mixture of compound (XI) (196.2 g, 0.650 mol) and ethylene glycol (120 ml) at 100—110°; the products were continuously distilled off. After washing with water and drying (MgSO₄), the products (139 g) were distilled to give fractions (i), b.p. 40—90° (5.5 g); (ii), b.p. 92—93° (94 g); (iii) b.p. 93—95° (1.6 g); and (iv), b.p. 95° (27.6 g); and pot liquid. G.l.c. analysis of fraction (i) showed the presence of five new main products, which were separated by g.l.c. and identified by their spectroscopic properties as 4,5,5,5-tetrafluoropenta-1,3-diene (XV) (1.2 g, 8.6 mmol, 1.3%), 1,1,1,2-tetrafluoropenta-2,3-diene (XVI) (2.6 g, 18.6 mmol, 2.9%), 4,5,5,5-tetrafluoropent-2-yne (XVII) (0.5 g, 3.6 mmol, 0.5%), 1,1,2-trifluoropent-1-en-3-yne (XVIII) (0.4 g, 3.3 mmol, 0.5%), and 4-bromo-4,5,5,5-tetrafluoropent-2-ene (XII). G.l.c. analysis of fraction (ii) showed that it was essentially product (XII) with small amounts of a substance (about 1%) whose mass spectrum gave a highest mass peak corresponding to C₅H₃BrF₄⁺

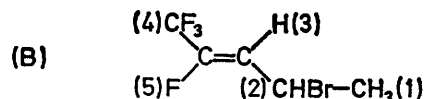
(probably 4-bromo-4,5,5,5-tetrafluoropentene) and product (XIII) (*ca.* 1%). The yield of product (XII) (95.6 g, 0.432 mol, including estimates on fore- and after-runs) was 66.6% (Found: C, 27.3; H, 2.2. C₅H₃BrF₄ requires C, 27.15; H, 2.3%), b.p. 92.6° at 750 mmHg. G.l.c. analysis of fraction (iii) showed about equal amounts of products (XII) and (XIII). Fraction (iv) gave pure 4-bromo-1,1,1,2-tetrafluoropent-2-ene (XIII) (27.6 g, 0.125 mol, 19.2%) (Found: Br, 36.1. C₅H₃BrF₄ requires Br, 36.15%), b.p. 95° at 752 mmHg.

Spectra. Product (XII), λ_{max} 5.99 μm (C:C str.); n.m.r. chemical shifts (p.p.m.) and coupling constants (Hz) are shown below formula (A).



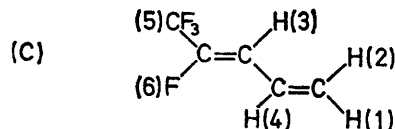
δ₁ 1.9, δ₂ 5.7, δ₃ 6.3, φ₄* 81.5, φ₅* 130.0, |*J*_{1,2}| 1.5, |*J*_{1,5}| 1.5, |*J*_{2,4}| 0.6, |*J*_{4,5}| 8.8, |*J*_{1,3}| 6.4, |*J*_{2,3}| 14.9, |*J*_{2,5}| 17.7.

Product (XIII), λ_{max} 5.86 μm (C:C str.); n.m.r. chemical shifts (p.p.m.) and coupling constants (Hz) are shown below formula (B).



δ₁ 1.8, δ₂ 4.9, δ₃ 5.8, φ₄* 73.7, φ₅* 132.2, |*J*_{1,2}| 6.8, |*J*_{2,3}| 10.2, |*J*_{2,5}| 0.5, |*J*_{3,5}| 29.5, |*J*_{1,5}| 0.5, |*J*_{2,4}| 0.6, |*J*_{3,4}| 0.6, |*J*_{4,5}| 10.8.

Product (XV), λ_{max} 5.9 and 6.1 μm (C:C str.); n.m.r. chemical shifts (p.p.m.) and coupling constants (Hz) are shown below formula (C).

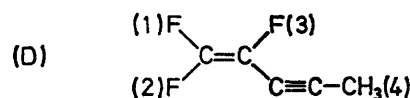


δ₁ 5.38, δ₂ 5.47, δ₃ 6.03, δ₄ 6.60, φ₅* 73.1, φ₆* 133.2, |*J*_{1,4}| 10.6, |*J*_{3,4}| 10.6, |*J*_{3,6}| 31.0, |*J*_{4,6}| 0.7, |*J*_{2,4}| 16.9, |*J*_{3,5}| 0.6, |*J*_{4,5}| 0.7, |*J*_{5,6}| 11.4.

Product (XVI), λ_{max} 5.05 μm (C:C); ¹H n.m.r. τ 3.70 [1H, qdq, *J* (H-CH₃) 7.48, *J* (H-F) 0.7, *J* (H-CF₃) 2.91 Hz, C:C:CH] and 8.05 [3H, ddq, *J* (CF₃-F) 8.26, *J* (CH₃-H) 7.48, *J* (CH₃-CF₃) 0.35 Hz, CH₃]; ¹⁹F n.m.r. φ* 70.9 [3F, ddq, *J* (CF₃-F) 17.5, *J* (CF₃-H) 2.9, *J* (CF₃-CH₃) 0.35 Hz, CF₃] and 158.9 [1F, qdq, *J* (F-CF₃) 17.5, *J* (F-CH₃) 8.26, *J* (F-H) 0.7 Hz, CF=C].

Product (XVII), λ_{max} 4.5 μm (C:C); ¹H n.m.r. τ 4.82 [1H, dqq, *J* (H-F) 46.40, *J* (H-CF₃) 5.25, *J* (H-CH₃) 2.25 Hz, CFH:C:C] and 8.07 [3H, ddq, *J* (CH₃-F) 7.00, *J* (CH₃-H) 2.25, *J* (CH₃-CF₃) 0.27 Hz, C:C-CH₃]; ¹⁹F n.m.r. φ* 80.3 [3F, ddq, *J* (CF₃-F) 14.96, *J* (CF₃-H) 5.25, *J* (CF₃-CH₃) 0.27 Hz, CF₃] and 188.9 [1F, dqq, *J* (F-H) 46.40, *J* (F-CF₃) 14.96, *J* (F-CH₃) 7.00 Hz, CFH:C:C].

Product (XVIII), λ_{max} 4.4 (C:C str.) and 5.7 μm; (C:C) n.m.r. chemical shifts (p.p.m.) and coupling constants (Hz) are shown below formula (D).



φ₁* 93.9, φ₂* 115.0, φ₃* 171.9, δ₄ 2.05, |*J*_{1,2}| 53.8, |*J*_{1,4}| 1.9, |*J*_{2,4}| 1.9, |*J*_{1,3}| 28.9, |*J*_{2,3}| 115.8, |*J*_{3,4}| 5.2

Dehydrohalogenation of 2,4-Dibromo-1,1,1,2-tetrafluoro-4-methylpentane (XIX) with Potassium Hydroxide.—A solution of potassium hydroxide (20.2 g, 0.360 mol) in water (20 ml) and ethylene glycol (50 ml) was added during 1 h under nitrogen to a stirred mixture of compound (XIX) (121.4 g, 0.384 mol) and ethylene glycol (150 ml) at 130 °C; products were continuously distilled off. After washing with water and drying (MgSO₄), the products (88.2 g) were distilled to give 4,5,5,5-tetrafluoro-2-methylpenta-1,3-diene (XXI) (4.5 g, 0.029 mol, 7.6%) (Found: C, 46.8; H, 3.7. C₆H₆F₄ requires C, 46.75; H, 3.95%), b.p. 63.5° at 752 mmHg; 4-bromo-4,5,5,5-tetrafluoro-2-methylpentene (XX) (52.9 g, 0.225 mol, 58.6%) (Found: Br, 33.9. C₆H₇BrF₄ requires Br, 34.0%), b.p. 106.2° at 752 mmHg; and residual liquid [unchanged (XIX)].

Spectra. Product (XX), λ_{max} 6.05 μm (C:C); ¹H n.m.r., τ 4.91 (1H, m, =CHH), 5.08 (1H, m, =CHH), 6.8—7.5 (2H, m, CH₂C:C), and 8.12 (3H, m, CH₃C:C); ¹⁹F n.m.r. φ* 81.28 (3F, dt, J 7.6 and 0.6 Hz, CF₃) and 124.92 (1F, complex m, CF); product (XXI), λ_{max} 5.92 and 6.19 μm (C:C); ¹H n.m.r. τ 4.05 (1H, complex d, J_{HF} 35.9 Hz, trans-CF=CH), 4.84 (2H, complex m, =CH₂), and 7.97 (3H, m, CH₃); ¹⁹F n.m.r. φ* 73.07 [3F, d, J (CF₃-CF) 11.1 Hz, CF₃] and 133.74 (1F, d of complex q, J 35.9 and 11.1 Hz, trans-FC=CH).

Dehydrohalogenation of 1,5-Dibromo-3-fluoro-3-trifluoromethylpentane (IV) with Potassium Hydroxide.—Compound (IV) (22.4 g, 70.9 mmol) was dropped slowly into potassium hydroxide (85%) (11.2 g, 0.2 mol) at 120° with stirring under nitrogen. Low-boiling material distilled directly from the mixture as it was formed. After washing with water and drying (MgSO₄) the product was distilled to give 3-fluoro-3-trifluoromethylpenta-1,4-diene (VII) (8.7 g, 56.4 mmol, 79.5%) (Found: C, 46.7; H, 3.8. C₆H₆F₄ requires C, 46.75; H, 3.9%), b.p. 59.4° at 754 mmHg, λ_{max} 6.10 μm (C:C); τ 3.8—4.6 (complex, vinylic protons); ¹⁹F n.m.r. φ* 81.29 [3F, d, J (CF₃-CF) 8.6 Hz, CF₃] and 173.59 (1F, m, CF).

Dehydrohalogenation of 1,7-Dibromo-3-fluoro-3-trifluoromethylheptane (VIII) with Potassium Hydroxide.—Compound (VIII) (19.5 g, 57.7 mmol) was heated with potassium hydroxide pellets (2.5 g, 0.45 mol) at 140—160°; low-

boiling material (6.5 g) distilled directly from the mixture. G.l.c. showed the presence of two products, peak area ratio 1.8:1. These were separated by g.l.c. and identified by spectroscopic properties as 3-fluoro-3-trifluoromethylhepta-1,6-diene (IX), λ_{max} 6.09 μm (C:C), and 7-bromo-3-fluoro-3-trifluoromethylheptene (X), λ_{max} 6.06 μm (C:C).

Spectra. Product (IX), ¹H n.m.r. τ 4.0—4.6 (4H, complex m, CF-CH=CH₂ and CH₂-CH=CH₂), 4.9—5.1 (2H m, CH₂-CH=CH₂), and 7.93br (4H, m, CH₂·CH₂); ¹⁹F n.m.r. φ* 81.82 [3F, d, J (CF₃-CF) 6.7 Hz, CF₃] and 179.74br (1F, m, CF); product (X), ¹H n.m.r. τ 4.0—4.6 (3H, complex m, -CH=CH₂), 6.67 (2H, t, J 6.5 Hz, -CH₂Br), and 7.9—8.6 (6H, complex m, [CH₂]₃); ¹⁹F n.m.r. φ* 81.80 [3H, d, J (CF₃-CF) 7 Hz] and 179.34br (1F, m, CF).

Mass Spectra.—The major mass spectral bands and assignments are listed in SUP No. 20336 (5 pp., 1 microfiche).^{*} Compounds containing bromine atoms exhibit rather intense molecular ion peaks, except (XIX) because of its chain branching. The most important fragmentation involves cleavage of a bromine atom from the parent ions. If another bromine atom is present, loss of HBr occurs with formation of the ion (M - Br - HBr)⁺, which is usually the base peak or a strong one. This cleavage almost always occurs with production of the corresponding metastable peak. For the unsaturated compounds, the characteristic fragmentation at the position β to the double bond allows an easy identification of the isomers. Thus both compounds (V) and (XI) give an ion (M - CF₃)⁺, whose signal is stronger than that of the corresponding ion arising from (VI) and (XIII). Olefins containing allylic bromine atoms [(V), (VI), (XII), and (XIII)] give spectra that can easily be interpreted and exhibit base peaks formed by bromine atom removal. The favoured cleavage also indicates the structures of the isomers (XV), (XVI), and (XVII): (XVII) has a base peak at m/e 71 (M - CF₃)⁺, whereas (XV) and (XVI) have the molecular ion as the predominant peak and give rise to a fragment at m/e 139 (M - H)⁺ that is completely absent in (XVII).

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^{*} For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue no. 20.