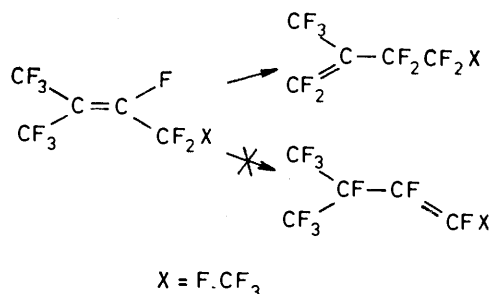




The but-1-ene (5) reacted more readily than (1) with chlorine [reaction complete after 1 day, *cf.* 10% of (1) recovered after 4 days<sup>4</sup>], giving 1,2-dichloro-2,3-dimethylbutane quantitatively. Potassium fluoride regenerated (1) from (5), in accord with the well-known rearrangement of terminal fluoro-olefins.<sup>10</sup>

Similar, but considerably slower, rearrangements were observed when perfluoro-2-methylbut-2-ene or perfluoro-2-methylpent-2-ene were irradiated, to give after 8–16 weeks irradiation, perfluoro-2-methylbut-1-ene and perfluoro-2-methylpent-1-ene respectively as sole products, formed essentially quantitatively by migration of fluorine to the :CFR<sub>F</sub> group from either of the (CF<sub>3</sub>)<sub>2</sub>C: trifluoromethyl groups. This rearrangement is evidently preferred to migration of fluorine to the (CF<sub>3</sub>)<sub>2</sub>C: group, which would have given perfluoro-3-methylbut-1-ene and perfluoro-4-methylpent-2-ene respectively; these olefins were not detectable in the reaction mixtures.



U.v. irradiation of perfluorobut-2-ene (a mixture of *cis*- and *trans*-isomers) did not result in any detectable formation of the but-1-ene.

No isomerisation of perfluoro-2-methylbut-1-ene by caesium fluoride was detected by n.m.r. as the reactants warmed from  $-196$  to  $-25$  °C, but by the time the sample had warmed to  $55$  °C, the but-2-ene was detectable and the reaction then proceeded readily. In the presence of dry diglyme and caesium fluoride, formation of the but-2-ene was complete after 6 h at  $34$  °C, the only other product being 2*H*-2-trifluoromethyloctafluorobutane (*ca.* 5%) presumably formed by reaction of the carbanion C<sub>2</sub>F<sub>5</sub>C(CF<sub>3</sub>)<sub>2</sub> with traces of moisture.

The u.v.-initiated rearrangement of the internal olefins can be represented as a suprafacial [1,3] sigmatropic shift of fluorine, which would be expected to be photochemically allowed,<sup>11</sup> but the driving force for the reaction, apart from a possible relief of steric strain in the internal olefin, which would be in accord with the observed reactivity order (R<sub>F</sub>)<sub>2</sub>C=C(R<sub>F</sub>)<sub>2</sub> > (R<sub>F</sub>)<sub>2</sub>C=CFR<sub>F</sub> > R<sub>F</sub>CF=CFR<sub>F</sub>, is not yet known.

#### EXPERIMENTAL

I.r. spectra were recorded on Perkin-Elmer 257 or 621 spectrophotometers, mass spectra on an A.E.I. MS902 spectrometer, and <sup>19</sup>F n.m.r. spectra on Perkin-Elmer R10 (56.46 MHz) or Varian HA100 (94.1 MHz) instruments. Chemical shifts have positive values to low field of external trifluoroacetic acid. <sup>19</sup>F N.m.r. parameters are available as Supplementary Publication No. SUP 22663 (3 pp).\*

Irradiations were with a Hanovia 500 medium pressure arc lamp with the reactants sealed *in vacuo* in silica tubes.

*The Reaction of Trifluoroiodomethane with Hexafluorobut-2-yne.*—Trifluoroiodomethane (162 g, 0.83 mol) and hexafluorobut-2-yne (66.6 g, 0.41 mol) were kept at  $350$  °C (indicated temperature) (4 days) in a Hastelloy-lined autoclave (250 ml) to give a fraction (60 g) shown by its i.r. spectrum (strong C:C at  $\tilde{\nu}_{\max}$  1730 and 1748 cm<sup>-1</sup>) to contain impurities as well as perfluoro-2,3-dimethylbut-2-ene. Distillation (Haage spinning-band column, 1 m) gave a series of fractions, b.p.  $48.3$ – $53.5$  °C, containing varying proportions of perfluoro-2,3-dimethylbut-2-ene and perfluoro-2,3-dimethylbuta-1,3-diene, which were finally separated by g.l.c. (2 m silicone elastomer 30, room temp.) and identified spectroscopically (*cf.* ref. 12). In another experiment, a fraction (34.5 g), b.p.  $54$ – $56$  °C, shown by g.l.c. to contain *ca.* 5% of the diene, was shaken (4½ days,  $80$  °C) *in vacuo* with methanol (30 ml). After addition of water (50 ml) the lower layer was dried and distilled to give pure (1) (30 g).

*Dehalogenation of Perfluoro-2,3-dimethylbut-2-ene.*—(a) *With iron.* The olefin (12.7 g, 42.3 mmol) was kept *in vacuo* at  $375$  °C in a Hastelloy autoclave (50 ml) packed with iron wool (6 days) to give as volatile products (11.54 g) the original olefin contaminated by perfluoro-2,3-dimethylbuta-1,3-diene (*ca.* 1%).

(b) *With copper.* Freshly prepared dry copper powder (2.4 g) and the olefin (0.30 g, 1.0 mmol) were kept *in vacuo* (40 ml tube) at  $325$  °C (62 h) to give silicon tetrafluoride (0.23 mmol) and a mixture of the original olefin (0.16 g, 53%) and perfluoro-2,3-dimethylbuta-1,3-diene (0.11 g, 40%).

*Pyrolysis of Tetrakis(trifluoromethyl)dithietan.*—(a) *In glass.* The dithietan (1.84 g, 5.0 mmol), prepared in 94% yield by the reaction of hexafluoropropene with sulphur and potassium fluoride in dry nitrobenzene in a Magnadrive stirred autoclave (*cf.* ref. 6), was kept at  $325$  °C (4 days) in a 70 ml Pyrex tube to give perfluoro-2,3-dimethylbut-2-ene (1.44 g, 96%) and sulphur.

(b) *In steel.* The dithietan (90.8 g, 0.25 mol) was kept at  $300$ – $325$  °C (25 h) in a stainless steel autoclave (500 ml) to give perfluoro-2,3-dimethylbut-2-ene (67.1 g, 90%) and sulphur. A coating, presumed to be ferric sulphide, on the surface of the autoclave was readily removed.

*Photochemical Reaction of Tetrakis(trifluoromethyl)thiiran.*—Tetrakis(trifluoromethyl)thiiran (3.15 g, 9.5 mmol), prepared from the dithietan by oxidation and thermal elimination of sulphur dioxide (*cf.* ref. 3), was irradiated (6 days) to give perfluoro-2,3-dimethylbut-2-ene (0.43 g, 15%), perfluoro-2,3-dimethylbut-1-ene (2.42 g, 85%) (Found: C, 23.7; H, 0.1%; *M*<sup>+</sup>, 300. C<sub>8</sub>F<sub>12</sub> requires C, 24.0; H, 0.0%; *M*, 300), b.p.  $54.8$ – $55.0$  °C;  $\tilde{\nu}_{\max}$  1730 cm<sup>-1</sup> (C:C), characterised by its n.m.r. spectrum, and sulphur (0.30 g, 100%).

*Photochemical Isomerisation of Perfluoro-2,3-dimethylbut-2-ene.*—Perfluoro-2,3-dimethylbut-2-ene (2.50 g, 8.3 mmol) was sealed *in vacuo* in a 240 ml silica tube, and the combined liquid and vapour phases were irradiated (17 days, 5 cm from the lamp) to give perfluoro-2,3-dimethylbut-1-ene (2.47 g, 99%).

*Reaction of Perfluoro-2,3-dimethylbut-1-ene with Chlorine.*—The olefin (1.50 g, 5.0 mmol) and chlorine (0.57 g, 8.0 mmol) were irradiated (12 in, 25 h) to give, after removal of the excess of chlorine (Hg), 1,2-dichloroperfluoro-2,3-dimethyl-

\* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1979, Index issue.

butane (1.82 g, 98%) (Found: C, 19.0; H, 0.1.  $C_6F_{12}Cl_2$  requires C, 19.4; H, 0.0%), b.p. (isoteniscope) 119 °C.

*Reaction of Perfluoro-2,3-dimethylbut-1-ene with Potassium Fluoride.*—The olefin (0.10 g) and dry potassium fluoride (ca. 0.1 g) were kept *in vacuo* in a Pyrex tube (ca. 5 ml) at 130 °C (3 days) to give perfluoro-2,3-dimethylbut-2-ene quantitatively.

*Action of Heat on Perfluoro-2,3-dimethylbut-1-ene.*—The olefin (1.26 g, 4.2 mmol) was recovered unchanged after being kept *in vacuo* (70 ml tube) at 260 °C (18 h).

*Photochemical Reactions of Perfluoro-2,3-dimethylbut-2-ene.*—(a) *With 2-methylpropane.* Irradiation of the olefin (0.54 g, 1.8 mmol) and 2-methylpropane (0.21 g, 3.6 mmol) *in vacuo* (5 cm, 325 ml tube, 6 days) gave perfluoro-2,3-dimethylbut-1-ene (0.54 g, 100%), 2-methylpropane (0.21 g, 100%), and two very small impurities detected by g.l.c. (each  $\leq 0.5\%$ ).

(b) *With benzophenone.* The olefin (0.60 g, 2.0 mmol) and benzophenone (1.0 g, 5.5 mmol), irradiated (3 cm, 7 days, 40 ml tube) *in vacuo*, gave a mixture of the but-1-ene (0.56 g, 94%) and the original olefin (0.04 g, 6%) as the only volatile products.

(c) *With benzene.* The olefin (1.53 g, 5.1 mmol) and benzene (0.60 g, 7.7 mmol), irradiated (3 cm, 6 days, 40 ml tube) *in vacuo*, gave a mixture (1.48 g, 97%) of the original olefin (98%) and the but-1-ene (2%).

*Action of Heat on Perfluoro-2,3-dimethylbut-2-ene.*—After 33 days *in vacuo* at 300 °C (70 ml tube), the olefin (0.58 g, 1.9 mmol) was recovered essentially quantitatively. Traces ( $< 0.1$  mmol) of silicon tetrafluoride and perfluoro-2,3-dimethylbuta-1,3-diene were detected, but the but-1-ene was absent.

*Photochemical Rearrangement of Perfluoro-2-methylbut-2-ene.*—Perfluoro-2-methylbut-2-ene (0.35 g, 1.4 mmol), containing perfluoro-2-methylbut-1-ene (4%), was irradiated in a 2 mm i.d. silica n.m.r. tube (3 cm). N.m.r. spectra showed the following concentrations of the original but-2-ene, with corresponding increases in the but-1-ene concentration: 1 day, 91%; 10 days, 45%; 26 days, 16%; 60 days, 3%; 72 days, undetectable. The tube was then opened to give perfluoro-2-methylbut-1-ene (0.34 g, 99%) (Found: C, 24.3; H, 0.3%;  $M$ , 250.  $C_5F_{10}$  requires C, 24.0; H, 0.0%;  $M$ , 250),  $\tilde{\nu}_{max}$  1 756  $cm^{-1}$  (C:C), characterised by its n.m.r. spectrum.

*Reaction of Perfluoro-2-methylbut-1-ene with Caesium Fluoride.*—(a) *Without solvent.* The olefin (0.35 g, 1.4 mmol) and dry caesium fluoride (0.050 g, 0.33 mmol) were sealed *in vacuo* in a 2 mm i.d. n.m.r. tube and warmed to  $-25$  °C, then slowly (6 h) to 55 °C. After  $2\frac{1}{2}$  days at 55 °C, the pro-

duct was perfluoro-2-methylbut-2-ene ( $> 99\%$ ), and the original olefin was undetected.

(b) *In diglyme.* Perfluoro-2-methylbut-1-ene (0.035 g, 0.14 mmol), anhydrous caesium fluoride (0.005 g, 0.03 mmol), and sodium-dried diglyme (0.3 ml) were kept at 34 °C as above to give, after 6 h, perfluoro-2-methylbut-2-ene (96%) and 2H-2-trifluoromethyloctafluorobutane (5%), identified by its n.m.r. spectrum and subsequently prepared unambiguously.<sup>13</sup>

*Photochemical Rearrangement of Perfluoro-2-methylpent-2-ene.*—The olefin (0.90 g, 3.0 mmol) was irradiated (6 cm) in a silica n.m.r. tube to give perfluoro-2-methylpent-1-ene, in the following concentrations: 1 month, 12%; 2 months, 50%; 4 months, 90%, the remainder being starting material. G.l.c. separation (7.5 m Kel-F 10, 30 °C) gave pure perfluoro-2-methylpent-1-ene (0.51 g, 57%)  $\tilde{\nu}_{max}$  1 742  $cm^{-1}$  (C:C), characterised by its n.m.r. spectrum.

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