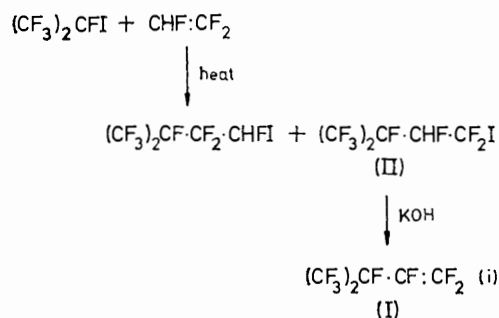


## Addition of Free Radicals to Unsaturated Systems. Part XXII.<sup>1</sup> Photochemical Addition of Trifluoroiodomethane and Iodine to Perfluoro-(3-methylbut-1-ene) and Photochemical Dimerisation of the Olefin

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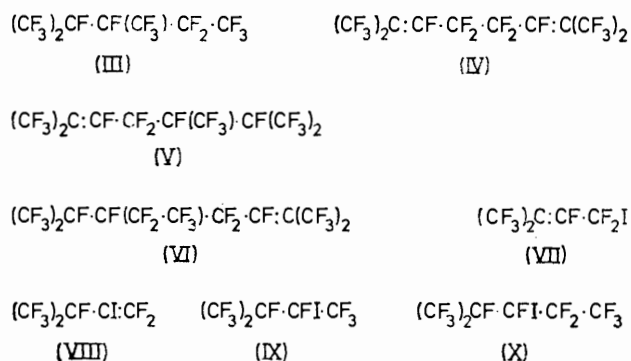
Photochemical reaction of trifluoroiodomethane with the title olefin gives the 1:1 adduct  $(CF_3)_2CF \cdot CFI \cdot CF_2 \cdot CF_3$  in low yield (22%), the perfluoroalkane  $(CF_3)_2CF \cdot CF(CF_3) \cdot C_2F_5$ , the iodo-compounds  $(CF_3)_2C \cdot CF \cdot CF_2I$  (VII),  $(CF_3)_2CF \cdot Cl \cdot CF_2$  (VIII), and  $(CF_3)_2CF \cdot CFI \cdot CF_3$  (IX), formed *via* the iodine adduct  $(CF_3)_2CF \cdot CFI \cdot CF_2I$ , and the unsaturated compounds  $(CF_3)_2C \cdot CF \cdot CF_2 \cdot CF_2 \cdot CF \cdot C(CF_3)_2$  (IV),  $(CF_3)_2C \cdot CF \cdot CF_2 \cdot CF(CF_3) \cdot CF(CF_3)_2$  (V), and  $(CF_3)_2C \cdot CF \cdot CF_2 \cdot CF(C_2F_5) \cdot CF(CF_3)_2$  (VI), which are considered to arise by combination reactions involving the allyl radical  $(CF_3)_2C \cdot CF \cdot CF_2$ . Under comparable conditions the reaction of iodine with the olefin yields the iodo-compounds (VII), (VIII), and (IX), the alkene (V), and the diene (IV). Irradiation of the olefin alone affords mainly the dimers (V) and  $(CF_3)_2CF \cdot CF(CF_3) \cdot C[CF(CF_3)_2] \cdot CF_2$ , together with small amounts of the dimer  $(CF_3)_2CF \cdot CF_2 \cdot CF_2 \cdot C[CF(CF_3)_2] \cdot CF_2$  and the diene (IV); dimer formation probably involves rearrangement of intermediate dimer diradicals.

PERFLUORO-(3-METHYLBUT-1-ENE) (I) has been prepared<sup>2</sup> by dehydroiodination of the major adduct (II) formed by free-radical addition of 2-iodoheptafluoropropane to trifluoroethylene [equation (i)].



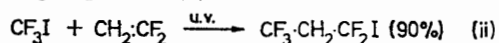
In a continuation of a study of the addition of free radicals to olefins, the photochemically initiated addition of trifluoroiodomethane to the olefin (I) has been investigated. Irradiation of a mixture of the iodoalkane and the olefin (2.9:1 molar ratio), for 65 h gave unchanged olefin (62% recovered), unchanged iodoalkane (83% recovered), a mixture of hexafluoroethane and silicon tetrafluoride, a mixture (2%) of four minor components, perfluoro-(2,3-dimethylpentane) (III) (5%), perfluoro-(2,7-dimethylocta-2,6-diene) (IV) (15%), perfluoro-(2,5,6-trimethylhept-2-ene) (V) (3%), a mixture of perfluoro-(5-ethyl-2,6-dimethylhept-2-ene) (VI) (12%) and an unknown compound (1%), 1,1,2,4,4,4-hexafluoro-1-iodo-3-trifluoromethylbut-2-ene (VII) (12%), 1,1,3,4,4,4-

hexafluoro-2-iodo-3-trifluoromethylbut-1-ene (VIII) (16%), 1,1,1,2,3,4,4,4-octafluoro-2-iodo-3-trifluoromethylbutane (IX) (2%), 1,1,1,2,2,3,4,5,5,5-decafluoro-3-iodo-4-trifluoromethylpentane (X) (22%), iodine, and higher boiling material (*ca.* 10%).



The structures of the products were established by i.r. and n.m.r. spectroscopy and mass spectrometry. An attempted thermal reaction at 230 °C gave unchanged reactants (94%), hexafluoroethane (trace), and a small amount of higher boiling material which was not characterised.

Trifluoroiodomethane generally reacts with fluoro-olefins to give 1:1 adducts as major products, and high yields can be obtained when the addend is present in excess, *e.g.* equation (ii).<sup>3</sup> However, with a number of

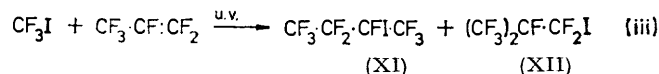


\* G. L. Fleming, R. N. Haszeldine, and A. E. Tipping, *J.C.S. Perkin I*, 1973, 574.

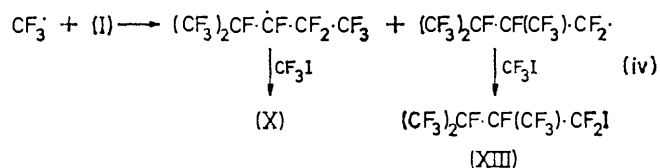
<sup>3</sup> R. N. Haszeldine, *J. Chem. Soc.*, 1953, 3761.

<sup>1</sup> Part XXI, R. N. Haszeldine, J. R. McAllister, and A. E. Tipping, *J.C.S. Perkin I*, 1974, 1203.

olefins initial bidirectional  $\text{CF}_3\cdot$  radical attack takes place, *e.g.* the reaction with hexafluoropropene<sup>4</sup> which gives adducts (XI) and (XII) in the ratio 80:20 [equation (iii)]. The reaction of trifluoroiodomethane with olefin

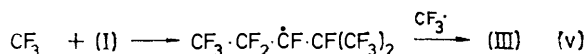


(I) under comparable conditions was expected similarly to afford a mixture of the adducts (X) and (XIII) [equation (iv)]. However, only adduct (X) was isolated



from the products and the only other isolated product formed *via*  $\text{CF}_3\cdot$  radical attack on the olefin (I) is the perfluoroalkane (III). It would be expected that  $\text{CF}_3\cdot$  radical attack on the olefin (I) would occur to a greater extent on the terminal  $\text{CF}_2$  group than on the same group in hexafluoropropene (80%), because of the greater steric hindrance to attack on the internal vinylic carbon atom in (I). In support of this it has been observed that, with the exception of hexafluoropropene,<sup>5</sup> almost identical 1:1 adduct ratios are obtained from free-radical addition of trifluoroiodomethane or the *N*-halogenobis(trifluoromethyl)amines to olefins. The greater amount (96%) of  $(\text{CF}_3)_2\text{N}\cdot$  radical attack on the terminal  $\text{CF}_2$  group in hexafluoropropene as compared with attack by the  $\text{CF}_3\cdot$  radical (80%) was suggested as being due to increased steric hindrance to attack on the central carbon atom of the olefin by the bulky  $(\text{CF}_3)_2\text{N}\cdot$  radical as compared with the  $\text{CF}_3\cdot$  radical.<sup>5</sup>

The absence of the adduct (XIII) in the products indicates that the alkane (III) is formed *via* exclusive initial  $\text{CF}_3\cdot$  radical attack on the terminal  $\text{CF}_2$  group of the olefin [equation (v)]. The formation of the alkane (III), to-



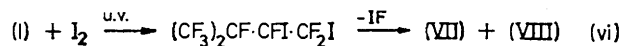
gether with the large amount of olefin (I) recovered unchanged, indicates that initial  $\text{CF}_3\cdot$  radical addition is slow. This results in a build-up of trifluoromethyl radicals and iodine atoms, and so other reactions take place. Thus the formation of the olefins (VII) and (VIII) indicates that iodine reacts with olefin (I), and the photochemical reaction of iodine with the olefin was therefore investigated. This gave unchanged olefin (31% recovered), compounds (IV) (19%), (V) (14%), (VII) (6%), (VIII) (22%), and (IX) (28%), and a higher boiling residue (*ca.* 10%). The iodo-olefins (VII) and (VIII) probably arise by addition of iodine across the double bond of

<sup>4</sup> R. N. Haszeldine, *J. Chem. Soc.*, 1953, 3559; J. Brown and R. N. Haszeldine, unpublished results.

<sup>5</sup> G. L. Fleming, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc. (C)*, 1971, 3833.

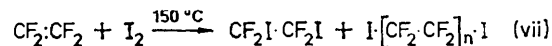
<sup>6</sup> R. N. Haszeldine, *J. Chem. Soc.*, 1949, 2948.

the olefin (I) followed by elimination of iodine monofluoride from the resultant adduct (XIV) [equation (vi)].

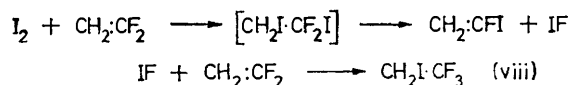


Elimination occurs by loss of tertiary fluorine, not of secondary fluorine to give  $(\text{CF}_3)_2\text{CF}\cdot\text{CF}\cdot\text{CFI}$ .

Thermal reaction of iodine with tetrafluoroethylene gives mainly the 1:1 adduct (76%), together with telomers<sup>6</sup> [equation (vii)]; 1:1 adducts are believed to be



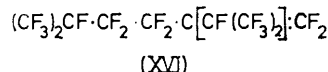
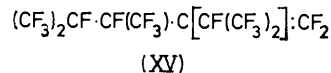
formed as intermediates when iodine reacts with other fluoro-olefins, *e.g.* equation (viii).<sup>7</sup> An attempted ther-



mal reaction of iodine with the olefin (I) at 150 °C afforded only unchanged reactants.

Compound (IX) is the iodine monofluoride adduct of the olefin (I), and ionic or radical mechanisms are possible, initiated by  $\text{F}^-$  or  $\text{F}\cdot$ , respectively. If the addition is ionic, the reaction of the carbanion  $(\text{CF}_3)_2\text{CF}\cdot\text{CF}\cdot\text{CF}_3$  to abstract iodine to give (IX) must be fast, since the carbanion is known to lose fluoride ion to give the olefin  $(\text{CF}_3)_2\text{C}:\text{CF}\cdot\text{CF}_3$ ,<sup>8</sup> which was not detected in the present investigation.

The formation of the diene (IV) and the dimer (V) of the olefin (I) prompted an investigation of the effect of u.v. irradiation on the olefin. After irradiation (43 h) the products were unchanged (I) (46% recovered), a dimer fraction (84%), and a higher boiling residue (16%). The dimer fraction was shown by g.l.c. to contain three major components in the ratio 10:56:34 and two minor components (*ca.* 4%) of longer retention times; the major components were separated and were identified as a mixture of the diene (IV) (6%) and an unidentified dimer (2%), the dimer (V) (46%), and a mixture of perfluoro-(2-isopropyl-3,4-dimethylpent-1-ene) (XV) (*ca.* 21%) and other dimers (*ca.* 7%), the major one of which was tentatively identified as perfluoro-(2-isopropyl-5-methylhex-1-ene) (XVI) (*ca.* 5%).

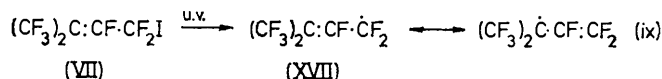


However, in the reactions of trifluoroiodomethane and iodine with the olefin (I), the diene (IV) was formed in much higher yield (19 and 15%, respectively), the dimer

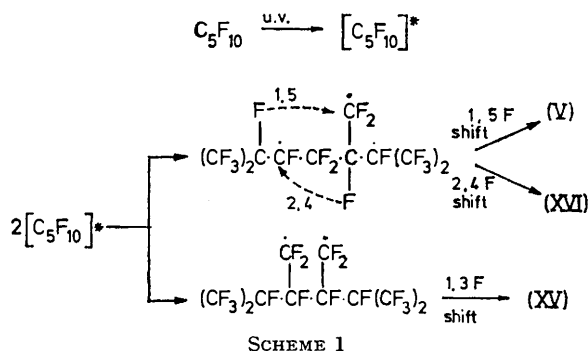
<sup>7</sup> M. Hauptschein, M. Braid, and F. E. Lawlor, *J. Amer. Chem. Soc.*, 1957, **79**, 2549; M. Braid and M. Hauptschein, U.S.P. 2,920,111/1960.

<sup>8</sup> R. N. Haszeldine, I.-ud.-D. Mir, and A. E. Tipping, unpublished results; M. G. Barlow, R. N. Haszeldine, and H. I. Jones, unpublished results.

(V) was formed in much lower yield (14 and 3%, respectively), and the dimers (XV) and (XVI) were not detected; (IV) and (V) are thus not formed *via* dimerisation reactions of the olefin (I) under these conditions, and hence the diene (IV) probably arises *via* dimerisation of the allyl radical (XVII) derived from the allyl iodide (VII) [equation (ix)]. Radical combination of the allyl

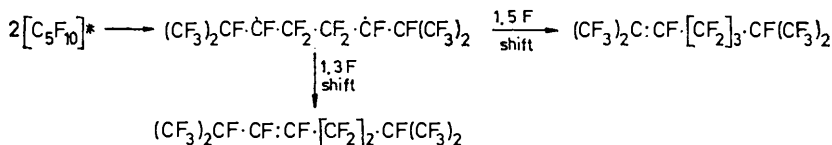


radical (XVII) with the radical  $(\text{CF}_3)_2\text{CF}:\dot{\text{C}}\text{F}:\text{CF}_3$  formed by photolysis of (IX) would yield the dimer (V), and combination with the radical  $(\text{CF}_3)_2\text{CF}:\dot{\text{C}}\text{F}:\text{CF}_2\cdot\text{CF}_3$ , the product of  $\text{CF}_3\cdot$  attack on the olefin (I), would give the



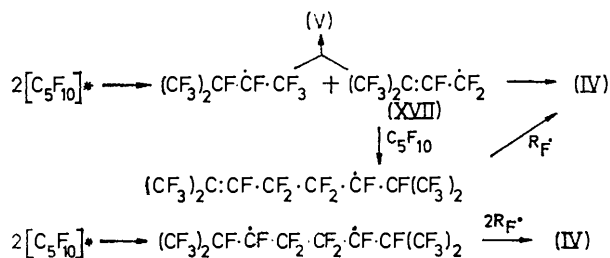
perfluoro-alkene (VI). The olefin  $(\text{CF}_3)_2\text{C}:\text{CF}:\text{CF}_2\cdot\text{CF}_3$ , which would result from combination of an allyl radical (XVII) and a trifluoromethyl radical, was surprisingly not detected in the products.

The dimers formed on irradiation of the olefin (I) alone may arise from excited olefin molecules *via* dimer diradicals which rearrange (Scheme 1). The dimer (V) can



SCHEME 2

also arise by radical combination (Scheme 3). Dimers formed by combination of two terminal carbon atoms

SCHEME 3  $\text{R}_F^*$  is any radical present in the system

were not isolated, but they may comprise the minor unidentified products (Scheme 2).

The formation of the diene (IV) by irradiation of the olefin (I) alone is surprising, since transfer of fluorine must occur at some stage (*e.g.* Scheme 3); the precise pathway to (IV) is not yet established.

## EXPERIMENTAL

Reactants and products were manipulated, where possible, in a conventional vacuum system. The photochemical reactions were carried out by using silica tubes (*ca.* 350 cm<sup>3</sup> unless stated otherwise) which were irradiated at *ca.* 15 cm from a Hanovia S500 medium-pressure u.v. lamp. Products were separated by fractional condensation *in vacuo* or by preparative-scale g.l.c. (columns as indicated in the text) and were identified by elemental analysis, molecular weight determination (Regnault's method), i.r. spectroscopy (Perkin-Elmer 257 spectrophotometer with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer R10 or Hitachi R20A spectrometer operating at 56.46 MHz for <sup>19</sup>F, or a Varian HA100 instrument operating at 94.1 MHz for <sup>19</sup>F and with external trifluoroacetic acid as reference), and mass spectrometry (A.E.I. MS902 spectrometer).\*

*Reactions of Perfluoro-(3-methylbut-1-ene).*—(a) *With trifluoroiodomethane.* A mixture of the olefin (2.30 g, 9.20 mmol) and trifluoroiodomethane (5.24 g, 26.7 mmol) sealed *in vacuo* and irradiated (65 h), gave after treatment of the volatile product with mercury to remove iodine, (i) a mixture (1.53 mmol) of hexafluoroethane, trifluoroiodomethane, and silicon tetrafluoride, which was washed with aqueous sodium hydroxide to give hexafluoroethane (0.04 g, 0.3 mmol, 2%) and unchanged trifluoroiodomethane (0.12 g, 0.6 mmol, 2% recovered), (ii) unchanged trifluoroiodomethane (4.24 g, 21.6 mmol, 81% recovered), (iii) unchanged perfluoro-(3-methylbut-1-ene) (1.42 g, 5.66 mmol, 62% recovered), and (iv) a mixture (1.07 g, 2.6 mmol) shown by g.l.c. (7.5 m SE30 oil at 50 °C) to contain 4 minor components (2% of fraction) and eight components of longer g.l.c. retention times present in the ratio 7:10:2:9:16:21:3:30. These eight components were separated by g.l.c. (7.5 m

SE30 oil at 80 °C) and were identified as (i) *perfluoro-(2,3-dimethylpentane)*\* (III) (0.07 g, 0.18 mmol, 5%) (Found: C, 21.9; F, 78.1.  $\text{C}_7\text{F}_{16}$  requires C, 21.6; F, 78.4%), b.p. (isoteniscope)  $84 \pm 0.5$  °C; (ii) *perfluoro-(2,7-dimethylocta-2,6-diene)*\* (IV) (0.12 g, 0.26 mmol, 15%) (Found: C, 25.7; F, 74.2%;  $M^+$ , 462.  $\text{C}_{10}\text{F}_{18}$  requires C, 26.0; F, 74.0%;  $M$ , 462), b.p. (isoteniscope)  $144.7 \pm 0.5$  °C; (iii) perfluoro-(2,5,6-trimethylhept-2-ene) (V) (0.02 g, 0.05 mmol, 3%); (iv) a mixture of perfluoro-(5-ethyl-2,6-dimethylhept-2-ene) (VI)\* (0.11 g, 0.21 mmol, 12%) and an unknown component\* (0.01 g, 0.02 mmol) in the ratio 90:10 (n.m.r.); (v) 1,1,2,4,4,4-hexafluoro-1-iodo-3-trifluoromethylbut-2-ene (VII) (see later) (0.15 g, 0.41 mmol, 12%); (vi) 1,1,3,4,4,4-

\* Spectroscopic data for compounds marked with an asterisk are available as Supplementary Publication No. SUP 21680 (8 pp.). For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1975 Index issue.

hexafluoro-2-iodo-3-trifluoromethylbut-1-ene (VIII) (see later) (0.19 g, 0.55 mmol, 16%); (vii) 1,1,1,2,3,4,4,4-octafluoro-2-iodo-3-trifluoromethylbutane (IX) (see later) (0.03 g, 0.08 mmol, 2%); and (viii) 1,1,1,2,2,3,4,5,5,5-decafluoro-3-iodo-4-trifluoromethylpentane \* (X) (0.35 g, 0.78 mmol, 22%) (Found: C, 16.0; F, 55.6%;  $M^+$ , 446.  $C_8F_{13}I$  requires C, 16.1; F, 55.4%;  $M$ , 446), b.p. (isoteniscope)  $99.7 \pm 0.5$  °C.

(b) *With iodine.* A mixture of the olefin (4.1 g, 18.05 mmol) and iodine (5.2 g, 20.5 mmol), irradiated (68 h), gave, after removal of the excess of iodine by shaking with mercury, (i) a mixture (0.21 g, 1.72 mmol;  $M$ , 125) of silicon tetrafluoride and an unknown compound \*; (ii) unchanged olefin (1.38 g, 5.54 mmol, 31% recovered); and (iii) a mixture (3.60 g, 9.01 mmol) which was separated by g.l.c. (7m Kel-F 10 oil at 80 °C) into its five components (ratio 9:29:39:13:10), identified as (i) 1,1,2,4,4,4-hexafluoro-1-iodo-3-trifluoromethylbut-2-ene \* (VII) (0.27 g, 0.76 mmol, 6%) (Found: C, 16.7; F, 47.4%;  $M^+$ , 358.  $C_5F_9I$  requires C, 16.8; F, 47.8%;  $M$ , 358); (ii) 1,1,3,4,4,4-hexafluoro-2-iodo-3-trifluoromethylbut-1-ene \* (VIII) (0.96 g, 2.69 mmol, 22%) (Found: C, 16.9; F, 48.3%;  $M^+$ , 358.  $C_5F_9I$  requires C, 16.8; F, 47.8%;  $M$ , 358); (iii) 1,1,1,2,3,4,4,4-octafluoro-2-iodo-3-trifluoromethylbutane \* (IX) (1.38 g, 3.50 mmol, 28%) (Found: C, 15.3; F, 53.1%;  $M^+$ , 396.  $C_8F_{11}I$  requires C, 15.1; F, 52.8%;  $M$ , 396); (iv) perfluoro-(2,7-dimethylocta-

2,6-diene) (IV) (0.54 g, 1.16 mmol, 19%); and (v) perfluoro-(2,5,6-trimethylhept-2-ene) (V) (0.45 g, 0.90 mmol, 14%).

(c) *Irradiation alone.* The olefin (2.16 g, 8.66 mmol), sealed *in vacuo* in a silica ampoule (*ca.* 100 cm<sup>3</sup>) and irradiated (43 h), gave (i) unchanged olefin (0.94 g, 3.97 mmol, 46% recovered), (ii) a volatile fraction (1.02 g), and (iii) a non-volatile oil (0.2 g, 16%), which remained in the reaction tube and was not examined further. The volatile fraction was separated by g.l.c. (7 m Kel-F 10 oil at 50 °C) into its three major components [2 minor components of longer retention times also present (*ca.* 4% of fraction)], present in the ratio 10:56:34 and shown to be (i) a mixture of perfluoro-(2,7-dimethylocta-2,6-diene) (IV) (0.06 g, 0.09 mmol, 6%) and an unidentified component \* (0.02 g, 0.03 mmol, 2%); (ii) perfluoro-(2,5,6-trimethylhept-2-ene) \* (V) (0.56 g, 1.12 mmol, 46%) (Found: C, 24.1; F, 75.5%;  $M^+$ , 500.  $C_{10}F_{20}$  requires C, 24.0; F, 76.0%;  $M$ , 500), b.p. (Siwoloboff) 137 °C; and (iii) a mixture \* (0.34 g, 0.675 mmol, 28%) (Found: F, 76.3%;  $M^+$ , 500. Calc. for  $C_{10}F_{20}$ : F, 76.0%;  $M$ , 500), of perfluoro-(2-isopropyl-3,4-dimethylpent-1-ene) \* (XV) (*ca.* 0.26 g, *ca.* 0.51 mmol, *ca.* 21%), perfluoro-(2-isopropyl-5-methylhex-1-ene) \* (XVI) (*ca.* 0.06 g, *ca.* 0.12 mmol, *ca.* 5%), and unidentified components \* (*ca.* 0.02 g, *ca.* 0.045 mmol, *ca.* 2%).

[5/1915 Received, 2nd October, 1975]