#### The Addition of Free Radicals to Unsaturated Systems. Part XVI.<sup>1</sup> Α Reinvestigation of Radical Addition to 1,1,3,3,3-Pentafluoropropene

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Photochemical reaction of trifluoroiodomethane with 1,1,3,3,3-pentafluoropropene gives the 1:1-adducts 1,1,1,3,3-pentafluoro-3-iodo-2-trifluoromethylpropane and 1,1,1,2,2,4,4,4-octafluoro-3-iodobutane in 75-85% yield and in a 60:40 ratio. A thermal reaction gives the isomeric 1:1-adducts as the major components but by-product formation increases. Photochemical reaction of hydrogen bromide with the olefin is not very reproducible, but gives the 1:1-adducts 1-bromo-1,1,3,3,3-pentafluoropropane and 2-bromo-1,1,1,3,3-pentafluoropropane, and 1,2-dibromo-1,1,3,3,3-pentafluoropropane as the main products.

WE earlier reported<sup>2</sup> that trifluoromethyl radical attack on 1,1,3,3,3-pentafluoropropene took place to the extent of at least 90% on the  $CF_3$ ·CH group; no attack on the  $CF_2$  group was detected. This was in contrast with bromine atom attack which, though less certain, was mainly on the  $CF_2$  group of the olefin. The availability of g.l.c. and n.m.r. as analytical techniques allows isomer ratios to be determined with greater precision than was possible when the earlier work was done. A reinvestigation of radical attack on 1,1,3,3,3pentafluoropropene has been carried out particularly to enable proper comparison to be made with radical addition to hexafluoropropene (80% attack of  $\rm CF_3$ on the  $CF_2$  group).<sup>3</sup> The earlier result for trifluoromethyl radical attack now needs to be corrected to 60% attack on the CF<sub>3</sub>·CH group and 40% attack on the CF<sub>2</sub> group of the olefin. No meaningful conclusions can be reached concerning the ratio of bromine atom attack on the olefin, since the yields of the 1:1-adducts are insufficiently high.

Trifluoroiodomethane.-Photochemical reaction of trifluoroiodomethane with 1,1,3,3,3-pentafluoropropene gave the analytically pure 1:1-adducts 1,1,1,3,3-pentafluoro-3-iodo-2-trifluoromethylpropane (1)and 1,1,1,2,2,4,4,4-octafluoro-3-iodobutane (II) (ratio 55:45), the structures of which follow from spectroscopic and chemical evidence.

Compound (I) reacted with powdered potassium hydroxide *in vacuo* to give perfluoroisobutene (55%) as the only product, and this olefin can only be formed from (I).

$$(CF_3)_2CH \cdot CF_2I \qquad CF_3 \cdot CHI \cdot CF_2 \cdot CF_3$$
(I)
(II)

The n.m.r. spectrum of (I) is of the  $A_2PX_6$  type and the two  $CF_3$  groups, because of their equivalence, are inferred to be on the same carbon atom. The chemical shift (-37.4 p.p.m.) observed for the other fluorines is in the expected region for a  $CF_2I$  group <sup>1,4</sup> but not for a C-CF<sub>2</sub>-C grouping.<sup>1,5</sup> The mass spectrum shows a strong peak at m/e 177 (45%) from the ion CF<sub>2</sub>I<sup>+</sup>.

Part XV, R. Gregory, R. N. Haszeldine, and A. E. Tipping, J. Chem. Soc. (C), 1968, 3020.
 R. N. Haszeldine and B. R. Steele, J. Chem. Soc., 1955,

3005.

Compound (II) did not react with potassium hydroxide under similar conditions to those used for (I), and this infers that the compound does not contain vicinal hydrogen and iodine atoms. The <sup>19</sup>F n.m.r. spectrum showed four regions of absorption (intensities 3,3,1, and 1) and the <sup>1</sup>H spectrum one region of absorption; this is as expected for a spectrum of the  $ABLP_3X_3$ type. The two non-equivalent fluorines A and B must be geminal, since they exhibit a very large coupling constant ( $J_{AB}$  277 c./sec.), and the absence of coupling between  $F_A$  or  $F_B$  and one of the  $CF_3$  groups shows the presence of a  $CF_3 \cdot CF_2$  group.

From a series of experiments on the photochemical reaction of trifluoroiodomethane with pentafluoropropene (Table 1, Experimental section) at temperatures in the range 30-100°, and with varied light intensity and irradiation time, the yield of the 1:1-adduct fraction was 76—85% and the ratio of (I): (II) lay between 63:37 and 55:45, with an average near 60:40. The yield of the 1: 1-adducts is less than ideally desirable, and this raises the possibility that by-product formation might be removing one of the 1 : 1-adducts preferentially. With this limitation, the ratio of trifluoromethyl radical attack on pentafluoropropene may taken as 60% on the  $CF_3$ ·CH group and 40% on the  $CF_2$  group.

The 1: 1-adducts arise by a radical mechanism of the type proposed earlier,<sup>6</sup> e.g.,

$$(CF_3)_2 CH \cdot \dot{C}F_2 \xrightarrow{CF_3 I} (CF_3)_2 CH \cdot CF_2 I$$

$$\downarrow CF_3 \cdot + CF_3 \cdot CH : CF_2$$

$$\downarrow CF_3 \cdot \dot{C}H \cdot CF_2 \cdot CF_3 \xrightarrow{CF_3 I} CF_3 \cdot CH I \cdot CF_2 \cdot CF_3$$

and the minor products  $C_2F_6$ ,  $CHF_3$  etc. arise by combination, abstraction etc. Under the conditions used there was no evidence of chain propagation to give products  $CF_3 \cdot [C_3 HF_5]_n \cdot I$  with n > 1.

Thermal reaction of trifluoroiodomethane and 1,1,3,3,3-pentafluoropropene at 212° gave unchanged

<sup>4</sup> E. G. Brame, Analyt. Chem., 1962, 34, 591.

- <sup>5</sup> N. Muller, P. C. Lauterbur, and G. F. Svatos, J. Amer. Chem. Soc., 1957, 79, 1807. <sup>6</sup> R. N. Haszeldine and B. R. Steele, Chem. and Ind., 1951,
- 684; R. N. Haszeldine, J. Chem. Soc., 1952, 2504.

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<sup>&</sup>lt;sup>3</sup> R. N. Haszeldine, J. Chem. Soc., 1953, 3559; J. Brown and R. N. Haszeldine, unpublished results cited in J. Chem. Soc., 1963, 1083.

olefin (37%), perfluoroisobutene (ca. 23%), the 1:1 adducts (I) and (II) (36%) in the ratio 17:83, and several unknown components. Perfluoroisobutene is formed by dehydroiodination of (I) at the temperature used, and when this is taken into account the 1:1-adduct ratio is ca. 50:50, which is in reasonable agreement with that found for the photochemical addition, but not very meaningful since the total yield of the 1:1-adducts calculated in this way is only ca. 59%, and full allowance cannot be made for the other products, two of which are probably the compounds (CF<sub>3</sub>)<sub>2</sub>CH·CHF<sub>2</sub> and CF<sub>3</sub>·CH<sub>2</sub>·CF<sub>2</sub>·CF<sub>3</sub> formed by reduction of the 1:1 adducts (I) and (II) respectively, with hydrogen iodide.

Hydrogen Bromide.—The photochemical reaction of hydrogen bromide with 1,1,3,3,3-pentafluoropropene was reported <sup>2</sup> to give the 1: 1-adduct 1-bromo-1,1,3,3,3pentafluoropropane (III) (40%) and 1,2-dibromo-1,1,3,3,3-pentafluoropropane (IV) (60%); the isomeric adduct 2-bromo-1,1,1,3,3-pentafluoropropane (V) was not detected. The formation of (IV) as a major product

$$\begin{array}{ccc} CF_3 \cdot CH_2 \cdot CF_2 Br & CF_3 \cdot CHBr \cdot CF_2 Br & CF_3 \cdot CHBr \cdot CHF_2 \\ (III) & (IV) & (V) \end{array}$$

thus prevented any conclusions concerning the direction of bromine atom attack on the olefin, since it was not known whether  $CF_3 \cdot CH \cdot CF_2 Br$  or  $CF_3 \cdot CHBr \cdot CF_2 \cdot was$  the preferred precursor of (IV).

The reaction has been reinvestigated and, although a precise ratio of bromine atom attack on the olefin cannot be given, the formation of the 1 : 1-adduct (V) as well as of (III) and (IV) has now been established.

Pentafluoropropene and hydrogen bromide do not react in the dark at room temperature (either alone or in the presence of a trace of added bromine), but a slow photochemical reaction gave unchanged olefin (33%), the 1:1-adducts (III) and (V) (33%); present in the ratio 72:28), the dibromide (IV) (48%), 2,3-dibromotetrafluoropropene (VI) (1%), and a compound tentatively identified as 1,2-dibromo-1,1,3,3-tetrafluoropropane (VII) (5%).

The n.m.r. spectrum of (III) is of the AA'PP'X<sub>3</sub> type and the two hydrogen nuclei (P and P') and the two fluorine nuclei (A and A') are both almost identical, thus indicating that a CH<sub>2</sub> group and a CF<sub>2</sub> group are present. The mass spectrum shows strong bands at m/e 131 and 129 (52%) assigned to the ion CF<sub>2</sub>Br<sup>+</sup>.

The n.m.r. spectrum of product (V) is of the ABMSX<sub>3</sub> type and the different chemical shifts of the two hydrogen nuclei suggests that they are probably on different carbon atoms. The large coupling constant (55.0 c./sec.) observed between  $F_A$  or  $F_B$  and  $H_M$  indicates the presence of a CHF<sub>2</sub> group since only geminal H-F couplings give such large values. Strong peaks are present in the mass spectrum at m/e 163 and 161 (50%), assigned to CF<sub>3</sub>·CHBr<sup>+</sup>, and at m/e 51 (93%), assigned to the ion CHF<sub>2</sub><sup>+</sup>.

The dibromide (IV), also formed by the photochemical

addition of bromine to 1,1,3,3,3-pentafluoropropene,

$$CF_3 \cdot CH: CF_2 + Br_2 \xrightarrow{u.v.} CF_3 \cdot CHBr \cdot CF_2Br$$

had n.m.r. and mass spectra fully in agreement with its structure. Compound (VI) was identified by comparison with a known sample prepared by the reaction of tetrafluoroallene with bromine.

The product (VII) was not fully identified, but the mass spectrum showed main peaks at m/e 275, 273, and 271 (9%,  $P - H^+$ ), 224, 222, and 220 (27%,  $C_2F_2Br_2^+$ ), 145 and 143 (100%,  $C_2H_2F_2Br^+$ ), 129 and 131 (13%,  $CF_2Br^+$ ), 64 (15%,  $C_2H_2F_2^+$ ), and 51 (5%,  $CHF_2^+$ ); no peaks were observed with more than three carbon, four fluorine, two bromine, or two hydrogen atoms.

This infers that the molecule contains a  $CHF_2$  group and a  $CF_2Br$  group and that both the two bromine atoms and the two hydrogen atoms are on the same or on adjacent carbon atoms. The only structure which fits all these requirements is (VII). The compound was shown not to be the isomer 1,3-dibromo-1,1,3,3-tetrafluoropropane by i.r. and mass spectral evidence. The route by which compound (VII) is formed is not known, but dehydrofluorination of adduct (V) followed by radical addition of hydrogen bromide to the intermediate olefin is a possibility:

$$CF_{3} \cdot CHBr \cdot CHF_{2} \xrightarrow{-HF} CF_{2} \cdot CBr \cdot CHF_{2} \xrightarrow{HBr} CF_{2}Br \cdot CHBr \cdot CHF_{2}$$
(VII)

The minor product (VI) could arise from tetrafluoroallene, a possible, though undetected trace impurity (more than 2% would have been detected) in 1,1,3,3,3pentafluoropropene.

$$CF_{3} \cdot CH_{2} \cdot CF_{2}I \xrightarrow{KOH} CF_{3} \cdot CH : CF_{2} \xrightarrow{KOH} CF_{2} \cdot CF_{2} \cdot CF_{2} \xrightarrow{KOH} CF_{2} : CBr \cdot CF_{2}Br$$

$$CF_{2} : C:CF_{2} \xrightarrow{Br_{3}} CF_{2} : CBr \cdot CF_{2}Br$$

$$(VI)$$

Thus it has been observed that both trifluoromethyl radicals and bromine atoms add bidirectionally to the olefin 1,1,3,3,3-pentafluoropropene. Trifluoromethyl radical attack occurs mainly on the central carbon of the olefin even though this is the most sterically-hindered site. It is inferred that addition is governed by the greater stability of the tertiary radical  $(CF_3)_2CH\cdot CF_2$  (where tertiary refers to substituents other than hydrogen on the carbon carrying the lone electron) compared with the secondary radical  $CF_3\cdot CH\cdot CF_2\cdot CF_3$ .

### EXPERIMENTAL

Volatile materials were handled in a conventional highvacuum apparatus to avoid contact with air or moisture. Photochemical reactions were carried out in 350-ml. silica tubes at a distance of 15 cm. from a Hanovia S.500 lamp,

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unless stated otherwise, with the lower portion of the tubes (5 cm.) shielded from the radiation. Thermal reactions were carried out in 300-ml. Dreadnought glass tubes, unless stated otherwise. Pure products were separated either by repeated fractional condensation *in vacuo* or by g.l.c. [Perkin-Elmer 451 or 452 instruments using columns packed with dodecyl phthalate (D.D.P., 30%) on Celite], and were examined by i.r. spectroscopy (Perkin-Elmer 21 instrument with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer R10 instrument operating at 60.00 Mc./sec. for <sup>1</sup>H and 56.46 Mc./sec. for <sup>19</sup>F), mass spectroscopy (A.E.I. MS./2H instrument), or u.v. spectroscopy (Unicam S.P. 700 spectrophotometer).

1,1,3,3,3-Pentafluoropropene was prepared in 76% overall yield by the photochemical addition of trifluoroiodomethane to 1,1-difluoroethylene to give 1,1,1,3,3-pentafluoro-3-iodopropane followed by dehydroiodination of this 1:1-adduct with potassium hydroxide *in vacuo*.<sup>2</sup>

Photochemical Reaction of Trifluoroiodomethane with 1,1,3,3,3-Pentafluoropropene.—(a) Reaction 1. Trifluoroiodomethane (10.5 g., 53.7 mmoles) and the olefin (3.72 g., 28.1 mmoles), irradiated (265 hr.), gave (i) hexafluoroethane (0.10 g., 0.71 mmole) shown by its i.r. spectrum to be contaminated with traces of trifluoromethane and silicon tetrafluoride, (ii) unchanged trifluoroiodomethane (9.35 g., 47.7 mmoles, 89%), (iii) unchanged olefin (2.96 g., 22.5 mmoles, 80%), and (iv) a higher-boiling fraction (1.78 g.) shown by g.l.c. (2-m. D.D.P. at 90°) to contain seven components. The two major components of the higher-boiling fraction (A and B), present in the ratio 55 : 45, were separated by g.l.c. (2-m. D.D.P. at 80°).

Component A was identified as 1,1,1,3,3-pentafluoro-3-iodo-2-trifluoromethylpropane (I) (0.864 g., 2.63 mmoles, 47%) (Found: C, 14.4; H, 0.3%; *M*, 326. Calc. for  $C_4HF_8I$ : C, 14.6; H, 0.3%; *M*, 328), b.p. (isoteniscope) 79.8°;  $\lambda_{max}$  3.34w, 4.38w, 4.56w, 4.63w, 4.85w, 5.80w, 6.92w, 7.39vs, 7.78vs, 8.04vs, 8.22vs, 8.30vs, 8.43s, 8.60m, 8.98vs, 9.12vs, 9.73s, 10.30m, 10.48s, 10.92s, 11.41m, 11.68m, 12.36s, 13.50m, 13.85s, 14.14s, 14.54s, and 14.98s  $\mu$ .

Component B was identified as 1,1,1,2,2,4,4,4-octafluoro-3-iodobutane (II) (0.706 g., 2.15 mmoles, 38%) (Found: C, 14.8; H, 0.5%; M, 329. C<sub>4</sub>HF<sub>8</sub>I requires C, 14.6; H, 0.3%; M, 328), b.p. (isoteniscope) 71.0°;  $\lambda_{max}$  (vapour) 268—269 mµ ( $\varepsilon$  196); i.r. bands at 3.30w, 4.11w, 4.35w, 4.42w, 5.80w, 6.10w, 6.84w, 7.19m, 7.36s, 7.56vs, 7.88vs, 8.14vs, 8.27vs, 8.35vs, 8.60s, 9.10vs, 9.35s, 9.78vs, 11.34m, 11.65m, 12.00m, 12.90w, 13.44s, 13.93s, 14.45s, and 15.00s µ.

(b) Reaction 2.' Trifluoroiodomethane (10.5 g., 53.7 mmoles) and the olefin (3.88 g., 29.4 mmoles), sealed and irradiated (192 hr.) at a distance of 2 cm. from the lamp, gave (i) a mixture (0.20 g., 2.05 mmoles; M, 100) of hexa-fluoroethane, trifluoromethane, and silicon tetrafluoride which when washed with aqueous potassium hydroxide (2M) gave hexafluoroethane (0.07 g., 0.48 mmole) and trifluoromethane (0.05 g., 0.70 mmole, 8%), (ii) unchanged trifluoroiodomethane (8.63 g., 44.0 mmoles, 82%), (iii) unchanged olefin (2.71 g., 20.5 mmoles, 70%), (iv) a higherboiling fraction (2.43 g.) shown by g.l.c. (2-m. D.D.P. at 90°) to contain (I) (1.29 g., 3.95 mmoles, 44%), (II) (0.94 g., 2.86 mmoles, 32%), and the same five unknown components as in the previous reaction, and (v) a trace of iodine.

(c) Reaction 3. Trifluoroiodomethane (10.5 g., 53.7 mmoles) and the olefin (3.52 g., 26.7 mmoles), sealed and

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irradiated at 100° (216 hr.), gave (i) a mixture (0.23 g., 2.25 mmoles; M, 102) estimated by i.r., molecular-weight measurement, and washing with aqueous potassium hydroxide (2M) to contain hexafluoroethane (0.07 g., 0.48 mmole), trifluoromethane (0.04 g., 0.62 mmole, 5%), and silicon tetrafluoride (0.12 g., 1.15 mmoles), (ii) unchanged trifluoroiodomethane (8.20 g., 41.8 mmoles, 78%), (iii) unchanged olefin (1.97 g., 14.9 mmoles, 56%), (iv) a higher-boiling fraction (3.32 g.) shown by g.l.c. (as before) to contain (I) (1.89 g., 5.76 mmoles, 49%), (II) (1.11 g., 3.38 mmoles, 29%), and the same five unknown components as in the previous experiments, and (v) a trace of iodine.

(d) Reaction 4. Trifluoroiodomethane (10.5 g., 53.6 mmoles) and the olefin (3.52 g., 26.7 mmoles), sealed and irradiated at a distance of 2-cm. from a Hanovia 250w lamp (144 hr.), gave (i) a mixture (0.10 g., 1.05 mmoles; M, 99) of hexafluoroethane, trifluoroidomethane, and silicon tetrafluoride, (ii) unchanged trifluoroidomethane (9.63 g., 49.1 mmoles, 93%), (iii) unchanged olefin (2.93 g., 22.2 mmoles, 83%), (iv) a higher-boiling fraction (1.31 g.) shown by g.l.c. (as before) to contain (I) (0.71 g., 2.16 mmoles, 48%), (II) (0.47 g., 1.44 mmoles, 32%), and the same unknown components (as previously), and (v) a trace of iodine.

The results of the experiments are shown in Table 1.

TABLE 1

# Photochemical addition of trifluoroiodomethane to 1,1,3,3,3-pentafluoropropene

			-	-	-		
Irradi- ation time	Lamp	Dis- tance		Olefin conver- sion	1:1 Adducts	Rat 1 : 1-a	io of dducts
(hr.)	(w)	(cm.)	Temp.	%	(%)	<b>(I)</b>	(II)
265	500	8	<b>3</b> 0°	20	85	55	<b>45</b>
192	500	<b>2</b>	60	30	76	58	42
216	500	8	100	44	78	63	37
144	250	2	60	17	80	60	40

Thermal Reaction of Trifluoroiodomethane with 1,1,3,3,3-Pentafluoropropene.-Trifluoroiodomethane (6.29 g., 32.1 mmoles) and the olefin (2.12 g., 16.0 mmoles), heated at  $212^{\circ}$  (70 hr.), gave (i) a mixture (0.10 g., 1.52 mmoles; M, 66) of trifluoromethane, silicon tetrafluoride, and an unknown component with strong i.r. bands at 7.89, 8.17, 8.45, 9.32, and 10.30  $\mu$ , (ii) unchanged trifluoroiodomethane (4.45 g., 22.7 mmoles, 71%), (iii) unchanged olefin (0.79 g., 5.96 mmoles, 37%), (iv) perfluoroisobutene (0.46 g., 2.40 mmoles, 23%) identified by its i.r. spectrum, (v) a higherboiling fraction (1.45 g.) shown by g.l.c. (as before) to contain (I) (0.20 g., 0.61 mmole, 6%), (II) (0.99 g., 3.02 mmoles, 30%), and eleven unidentified components, five of which had the same g.l.c. retention times as the unidentified components found in the photochemical reactions, and (vi) a small amount of iodine and a black tar

Reaction of 1,1,1,3,3-Pentafluoro-3-iodo-2-trifluoromethylpropane (I) with Potassium Hydroxide.—The iodo-compound (0.75 g., 2.29 mmoles) condensed in vacuo onto powdered potassium hydroxide (ca. 5 g.) and left at 20° (30 min.), gave (i) unchanged iodo-compound (0.06 g., 0.18 mmole, 8%) and (ii) perfluoroisobutene (0.23 g., 1.15 mmoles, 55%) (Found: C, 24.1%; M, 200. Calc. for C<sub>4</sub>F<sub>8</sub>: C, 24.0%; M, 200) the i.r. spectrum of which was identical to that reported.<sup>7</sup>

<sup>7</sup> T. J. Brice, J. D. La Zerte, L. J. Hals, and W. H. Pearlson, J. Amer. Chem. Soc., 1953, **75**, 2698. Reaction of 1,1,1,2,2,4,4-Octafluoro-3-iodobutane with Potassium Hydroxide.—The iodo-compound (0.42 g., 1.28 mmoles) was recovered unchanged (97%) when treated with powdered potassium hydroxide as in the previous experiment.

Reaction of Bromine with 1,1,3,3,3-Pentafluoropropene.— Bromine (0.66 g., 4.12 mmoles) and the olefin (1.18 g., 8.90 mmoles), sealed in a 250-ml. Pyrex tube and left in the dark (16 hr.) did not react, but exposure to a 100 w bulb (10 hr.) gave, after removal of unchanged bromine by shaking with mercury *in vacuo*, unchanged olefin (0.82 g., 6.21 mmoles, 70%) and 1,2-dibromo-1,1,3,3,3pentafluoropropane (IV) (0.77 g., 2.64 mmoles, 98%) (Found: C, 12.5; H, 0.5%; *M*, 290. Calc. for C<sub>3</sub>HBr<sub>2</sub>F<sub>5</sub>: C, 12.3; H, 0.3%; *M*, 292), b.p. (Siwoloboff) 87° (lit., b.p. 87°; <sup>2</sup> 88° <sup>8</sup>);  $\lambda_{max}$ . 3:30w, 7.46s, 7.91s, 8.06 and 8.08db, s, 8.22s, 8:30s, 8.67m, 8:83s, 8:94s, 9.70s, 10.34s, 10.39s, 10.71w, 11.36m, 11.54m, 12.35m, 13.10m, 14.20m, and 15.32m  $\mu$ .

Reaction of Hydrogen Bromide with 1,1,3,3,3-Pentafluoropropene.—(a) In the dark. Hydrogen bromide (3.88 g., 48.01 mmoles) and the olefin (3.49 g., 26.40 mmoles) sealed in a 350-ml. silica tube and left in the dark (14 days) underwent no reaction. A similar reaction carried out in the presence of bromine (2 mole %) also gave only unchanged reactants.

(b) Photochemical. Hydrogen bromide (3.88 g., 48.01 mmoles) and the olefin (3.49 g., 26.40 mmoles), irradiated (48 hr.), gave, after shaking with mercury to remove bromine, (i) hydrogen (0.010 g., 5.13 mmoles; M, 2.0), (ii) unchanged hydrogen bromide (1.94 g., 23.58 mmoles, 49%), (iii) unchanged olefin (1.44 g., 10.90 mmoles 41%), (iv) an unidentified fraction (0.17 g., 1.03 mmoles; M, 167);  $\lambda_{max}$  3.40w, 5.68m, 7.06s, 7.28s, 7.49s, 7.84s, 7.92s, 8.22s, 8.48s, 8.86s, 9.30s, 9.70w, 10.00w, 10.40m, 10.70w, 11.20br,m, 11.70m, 12.38m, and 14.75m  $\mu$ , and (v) a higherboiling fraction (3.36 g.) which was shown by g.l.c. (2-m. D.D.P. at 80°) to contain five major components (C—G) present in the ratio 28 : 11 : 1 : 54 : 5 and three minor components (<1%) with shorter g.l.c. retention times; the major components were separated by g.l.c.

Component C was identified as 1-bromo-1,1,3,3,3-pentafluoropropane (III) (0.79 g., 3.72 mmoles, 24%) (Found: C, 16.9; H, 1.0%; M, 212. Calc. for  $C_3H_2BrF_5$ : C, 16.9; H, 0.9%; M, 213), b.p. (isoteniscope) 47.5° (lit.,<sup>9</sup> b.p., 47.0°);  $\lambda_{max}$ . 4.45w, 4.53w, 4.62w, 4.74w, 5.06w, 6.36w, 6.80m, 7.04s, 7.25vs, 7.38s, 7.50s, 7.84vs, 8.26vs, 8.50vs, 8.64vs, 9.01m, 9.23s, 9.75m, 10.08s, 10.50s, 10.75s, 11.09s, 11.89s, 11.95s, 12.49s, 13.90m, 14.50m, and 14.94br, s  $\mu$ .

Component D was identified as 2-bromo-1,1,1,3,3-pentafluoropropane (V) (0.31 g., 1.47 mmoles, 9%) (Found: C, 17.0; H, 1.1%; M, 214.  $C_3H_2BrF_5$  requires C, 16.9; H, 0.9%; M, 213), b.p. (isoteniscope) 56.1°;  $\lambda_{max}$  3.35m, 4.16w, 4.46w, 4.57w, 4.64w, 4.70w, 5.78w, 7.04m, 7.20 and 7.24 db,s, 7.39s, 7.56s, 7.81s, 7.96s, 8.26 and 8.32db,s, 8.89s, 9.10 and 9.14db,s, 9.45m, 10.25m, 10.50w, 11.45m, 11.71w, 12.55m, 12.89m, and 14.40br,s  $\mu$ .

Component E was identified as 2,3-dibromotetrafluoropropene  $CF_2Br\cdot CBr\cdot CF_2$  (0.04 g., 0.14 mmole, 1%) by a comparison of its i.r. and mass spectra with those of a pure sample prepared by the addition of bromine to tetrafluoroallene.

Component F was identified as the dibromide (IV) \* E. T. McBee, A. Truchan, and R. O. Bolt, J. Amer. Chem. Soc., 1948, 70, 2023. (2.15 g., 7.39 mmoles, 48%) by a comparison of its i.r. spectrum and g.l.c. retention time with those of a sample prepared by bromination of the olefin.

Component G was tentatively identified as 1,2-dibromo-1,1,3,3-tetrafluoropropane CF<sub>2</sub>Br·CHBr·CHF<sub>2</sub> (0.20 g., 0.73 mmole; 5%);  $\lambda_{max}$  7.05w, 7.49m, 7.92s, 8.05s, 8.21s, 8.55w, 8.64w, 8.82w, 8.99s, 9.10s, 9.31s, 9.70s, 10.08s, 10.38m, 10.68s, 11.50w, 12.45br,m, 13.13m, 13.23m, and 13.60m  $\mu$ . It had mass-spectral bands as listed in the discussion, and in addition bands at 193 and 191 (14%, C<sub>3</sub>F<sub>4</sub>Br<sup>+</sup>) and 69 (16%, CF<sub>3</sub><sup>+</sup>).

In a second reaction (140 hr. irradiation) all the olefin reacted and the major products were (IV) (*ca.* 60%) and the 1:1-adducts (III) (*ca.* 12%) and (V) (*ca.* 20%) present in the ratio 36:64.

(c) Photochemical in the presence of silver powder. Hydrogen bromide (1.36 g., 16.85 mmoles), the olefin (1.08 g.,

#### TABLE 2

## <sup>19</sup>F N.m.r. spectra; assignments, chemical shifts, and coupling constants

		1 0			
Compound (CF3)2CH•CF2I X A	Inty. 6	Chemical shift (p.p.m.) -15.2	Multi- plet struc <b>ture</b> td	Coupling constant J (c./sec.) X-A = 10.9 X-H = 7.3	Assign ment F <sub>X</sub>
	2	-37.4	sept. of d	A-X = 10.9 A-H = 10.0	$\mathbf{F}_{\mathbf{A}}$
CF <sub>3</sub> ·CFF·CHI·CF P AB X	3 3	-14.6	dddq	$\begin{array}{rl} 12 \cdot 7 \\ 8 \cdot 3 \\ \mathrm{X-H} = & 6 \cdot 9 \\ \mathrm{X-P} = & 5 \cdot 4 \end{array}$	$\mathbf{F}_{\mathbf{X}}$
	3	3.6	q	P-X = 5.4	$\mathbf{F}_{\mathbf{P}}$
	1	$25 \cdot 0$	ddq	A-B = 277 11.2 8.3	F▲
	1	36.0	d of quin,	$B-A = 277 \\ 12.7$	FB
CF <sub>3</sub> ·CHH·CFFBr X PP' AA'	$\frac{3}{2}$	$-\frac{13\cdot5\mathrm{br}}{-30\cdot5\mathrm{br}}$	t t	8·6 13·0	$\mathbf{F}_{\mathbf{X}}$ $\mathbf{F}_{\mathbf{AA}}$
CF <sub>3</sub> •CHBr•CHFF X S MAB	3	-7.7br	dt	8·7 7·7	$F_{\boldsymbol{X}}$
	1	43.6	d of quin.	$55.0 \\ 8.4$	$\mathbf{F}_{\mathbf{A}}$
	1	44.4	ddq	55·0 11·8 7·9	$F_{B}$
$\begin{array}{c} \mathrm{CF}_3 \cdot \mathrm{CHBr} \cdot \mathrm{CFFBr} \\ \mathrm{X} & \mathrm{AB} \end{array}$	3	-10.0	td	11·0 6·0	$\mathbf{F}_{\mathbf{X}}$
	2	-27.8	qd	11·0 8·7	FAB
CF <sub>3</sub> H	3	-16.8	ddd	$\begin{array}{ll} \mathrm{X-A} = 17.5 \\ \mathrm{X-P} = 11.4 \\ \mathrm{X-H} = 6.7 \end{array}$	Fx
	1	-2.5	dqd	$\begin{array}{l} \mathrm{A-H}=21{\cdot}7\\ \mathrm{A-X}=17{\cdot}5\\ \mathrm{A-P}=14{\cdot}2 \end{array}$	$\mathbf{F}_{\mathbf{A}}$
	1	2.7	dqd	$\begin{array}{ll} P-A &= 14 \cdot 2 \\ P-X &= 11 \cdot 4 \\ P-H &= 1 \cdot 6 \end{array}$	FP

Negative values are to low field of reference

8.20 mmoles), and silver powder (0.10 g.), sealed and irradiated (12 hr.), gave, after shaking the volatile products

<sup>9</sup> P. Tarrant, A. M. Lovelace, and M. R. Lilyquist, J. Amer. Chem. Soc., 1955, 77, 2783. with mercury to remove bromine, (i) hydrogen (0.0025 g., 1.25 mmoles), (ii) unchanged hydrogen bromide (1.15 g., 14.14 mmoles, 84%), (iii) unchanged olefin (1.06 g., 8.01 mmoles, 98%), and (iv) a higher-boiling fraction (0.046 g., 0.188 mmole) shown by g.l.c. (2-m. D.D.P. at 80°) to contain (III) (0.0090 g., 0.042 mmole, 22%), (IV) (0.0220 g., 0.076 mmole, 40%) and (V) (0.0149 g., 0.070 mmole, 37%), present in the ratio 22:40:37. A residue of silver bromide remained in the tube.

A further reaction (12 hr.) in the presence of silver powder (1.0 g.) gave unchanged reactants, hydrogen, and silver bromide.

N.m.r. Spectra.-The data in Tables 2 and 3 were recorded with trifluoroacetic acid as external reference and tetramethylsilane as internal reference, respectively.

TABLE 3	3
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<sup>1</sup>H N.m.r. spectra: chemical shifts and coupling constants

Compound (CF <sub>3</sub> ) <sub>2</sub> CH•CF <sub>2</sub> I X A	Chemical shift (7) 6.24	Multiplet structure t of sept.	Coupling constant J (c./sec.) H-A = 10.0 H-X = 7.3	Assign ment
$ \substack{ \mathrm{CF}_3 \text{\cdot} \mathrm{CF}_2 \text{\cdot} \mathrm{CHI} \text{\cdot} \mathrm{CF}_3 \\ \mathrm{X} } $	5.32	tq	$H-X = {\begin{array}{*{20}c} 12 \cdot 6 \\ 6 \cdot 9 \end{array}}$	
CF₃•CH₂•CF₂Br	6.78	tq	13·0 8·6	
CF <sub>3</sub> •CHBr•CHF <sub>2</sub> S M	<b>4</b> ·03	td	$M-S = \frac{55 \cdot 0}{3 \cdot 4}$	Н <mark>м</mark>
	5.68	ddqd	11·8 9·0 7·0	H <sub>8</sub>
			S-M = 3.4	
CF <sub>3</sub> •CHBr•CF <sub>2</sub> Br	5.38	tq	8·4 6·0	
CF <sub>3</sub> H	5.26	dqd	$\begin{array}{rl} \mathrm{H-A}=21{\cdot}7\\ \mathrm{H-X}=&6{\cdot}7\\ \mathrm{H-P}=&1{\cdot}6 \end{array}$	

<sup>19</sup>F Chemical shifts which have been established for various groups are as follows: vicel shift /

Chemical shift (p.p.m.)			
Found	Reported	Ref.	
-15.2 to $-7.7$	-19.7 to 0.0	5	
3.6	3.2 to 11.9	5	
$\left.\begin{array}{c}25\cdot0\\36\cdot0\end{array}\right\}$	21.9 to 57.8	5	
-30.5 and $-27.8$	ca22 to $-13$	10	
-37.4	ca20	4	
<b>43</b> ∙6 ો	<i>ca</i> . 65	4	
<b>44</b> ∙ <b>4</b> ∫	<b>20</b> to 70	11	
-16.8	-20 to 0	11	
	Found $-15\cdot2 \text{ to } -7\cdot7$ $3\cdot6$ $25\cdot0$ $36\cdot0$ $-30\cdot5 \text{ and } -27\cdot8$ $-37\cdot4$ $43\cdot6$ $44\cdot4$ $-16\cdot8$	$ \begin{array}{c c} \text{Found} & \text{Reported} \\ \hline & -15\cdot2 \text{ to } -7\cdot7 & -19\cdot7 \text{ to } 0\cdot0 \\ \hline & 3\cdot6 & 3\cdot2 \text{ to } 11\cdot9 \\ \hline & 25\cdot0 \\ \hline & 36\cdot0 \end{array} \right\} & 21\cdot9 \text{ to } 57\cdot8 \\ \hline & -30\cdot5 \text{ and } -27\cdot8 & ca22 \text{ to } -13 \\ \hline & -37\cdot4 & ca20 \\ \hline & 43\cdot6 \\ \hline & 44\cdot4 \end{array} \right\} & ca. 65 \\ \hline & 44\cdot4 \\ \hline & 20 \text{ to } 70 \\ \hline & -16\cdot8 & -20 \text{ to } 0 \end{array} $	

Mass Spectral Data .-- The main mass spectral bands of the compounds prepared are shown in Table 4.

	1	ABLE 4	
	Main mas	s spectral band	ls
	(CF <sub>a</sub> ) <sub>a</sub> CH•CF <sub>a</sub> I	CF. CF. CHI C	F.
m e	Ion inty.	Ion inty.	Assignment
328	10	100 <sup>°</sup>	Parent
			$(C, HF, I^+)$
258		15	Č,F,ľ+
208		10	$C_{2}F_{3}I^{+}$
201	100	1.2	C₄HF <sub>8</sub> +
177	<b>45</b>		CF <sub>2</sub> I+
163		8.1	$C_4 HF_6^+$
127	22	34	I+
113	17	20	$C_3HF_4^+$
82	2.0	5.3	$C_2HF_2^+$
69	62	26	$CF_3^+$
	CF, CH, CF, Br	CF <sub>3</sub> ·CHBr·CH	F,
m e	Ion inty.	Ion inty.	Assignment
214.212	2.0	100	Parent
•			$(C_3H_2F_5Br^+)$
195, 193	10	13	C <sub>3</sub> H <sub>2</sub> F₄Br+
163, 161		50	$\tilde{C_2HF_3Br^+}$
144, 142		<b>26</b>	$C_2HF_2Br^+$
133	100	4.8	$C_{3}H_{2}F_{5}^{+}$
131, 129	52	11	$CF_2Br^+$
113	9.0		$C_{3}HF_{4}^{+}$
112		8.0	$C_{3}F_{4}^{+}$
112, 110		11	CFBr+
69	85	10	$CF_3^+$
51	$4 \cdot 2$	92	$CHF_{2}^{+}$
<b>45</b>	14	11	$C_2H_2F^+$
31	14	20	$CF^+$
	CF.	CHBr•CF <sub>•</sub> Br	
	m/e I	on inty.	Assignment
274,	272, 270	4.1	$C_3F_4Br_2^+$
2	13, 211	100	C <sub>3</sub> HF <sub>5</sub> Br+
14	44, 142	$6 \cdot 2$	$C_2HF_2Br^+$
13	31, 129	48	$CF_{2}Br^{+}$
	113	12	$C_{3}HF_{4}^{+}$
	82	<u>6</u> ∙0	$C_2HF_3^+$
1	81, 79	7.9	Br <sup>+</sup>
	69	67	CF <sub>3</sub> +
	51	4.9	CHF <sub>2</sub> +
	31	14	CHT

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<sup>10</sup> J. Lee and L. H. Sutcliffe, *Trans. Faraday Soc.*, 1958, 54, 308; 1959, 55, 880.
 <sup>11</sup> Unpublished data from this department.