1216

J. Chem. Soc. (C), 1971

## Addition of Free Radicals to Unsaturated Systems. Part XIX.<sup>1</sup> The Direction of Radical Addition to 1,1,1-Trifluorobut-2-ene

By R. Gregory, R. N. Haszeldine,\* and A. E. Tipping, Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

The photochemical reactions of trifluoroiodomethane or hydrogen bromide with 1,1,1-trifluorobut-2-ene have been studied. Trifluoroiodomethane gives the 1:1 adducts 1,1,1-trifluoro-2-iodo-3-trifluoromethylbutane and 1,1,1-trifluoro-3-iodo-2-trifluoromethylbutane in high yield in the ratio 80:20, and the major adduct is a mixture of the erythro- and threo-isomers in the approximate ratio 1:2. Treatment of the 1,1,1-trifluoro-2-iodo-3-trifluoromethylbutane isomers separately with potassium hydroxide gives predominantly trans-1,1,1-trifluoro-3-trifluoromethylbut-2-ene from the threo-isomer and the corresponding cis-olefin from the erythro-isomer. 1,1,1-Trifluoro-3-iodo-2-trifluoromethylbutane similarly gives 1,1,1-trifluoro-2-trifluoromethylbut-2-ene in high yield. The 1:1 adducts 2-bromo- and 3-bromo-1,1,1-trifluorobutane are formed in the approximate ratio 65:35 in the reaction with hydrogen bromide, but trans-4-bromo-1,1,1-trifluorobut-2-ene is also a major product.

FOLLOWING a series of investigations into radical additions to unsymmetrical olefins it has been suggested that when the two intermediate radicals are of comparable stability and steric factors are of minor importance, the ratio of attack at either end of the double bond may be correlated with the relative electrophilicity of one attacking radical compared with another. Electronic effects in the olefin then help to determine the direction of radical addition. Thus with hexafluoropropene, which is polarised  $CF_3 \cdot CF \cdot CF_2$ , it is found that the highly electrophilic trichlorosilyl radical attacks the  $CF_3$ ·CF end of the olefin to the extent of 65% <sup>2</sup> while with the weakly electrophilic trimethylsilyl radical only ca. 15%<sup>3</sup> attack occurs at this end of the olefin.

The olefin 1,1,1-trifluorobut-2-ene should have a strong inductive polarisation in the direction  $CF_3 \cdot CH \cdot CH_3$ , and since the methyl and trifluoromethyl groups should stabilise a lone electron on adjacent carbon to a comparable degree, bidirectional radical addition to the olefin should be observed, and variation in radical electrophilicity should be reflected by changes in the ratio of attack at each end of the double bond. The photochemical reactions of trifluoroiodomethane and hydrogen bromide with this olefin have thus been investigated.

The photochemical reaction between trifluoroiodomethane and propene gave a 1:1 adduct fraction (91%), which on treatment with potassium hydroxide afforded trans-1,1,1-trifluorobut-2-ene (I) (72%), cis-1,1,1-trifluorobut-2-ene (II) (15%), and 2-trifluoromethylpropene (III) (4%).



The olefin ratio infers that in the original addition to propene the 1: 1 adducts 3-iodo-1,1,1-trifluorobutane and 3-iodo-1,1,1-trifluoro-2-methylpropane were formed in the approximate ratio 96:4 which is in reasonable

<sup>1</sup> Part XVIII, R. Gregory, R. N. Haszeldine, and A. E. Tipping, J. Chem. Soc. (C), 1970, 1750. <sup>2</sup> C. J. Attridge, R. N. Haszeldine, and M. J. Newlands,

unpublished results.

agreement with the ratio 90:10 found for a thermal addition at 200°.4

$$\begin{array}{c} CF_{3}I + CH_{2}:CH \cdot CH_{3} \xrightarrow{u.v.} \\ CF_{3} \cdot CH_{2} \cdot CHI \cdot CH_{3} + CF_{3} \cdot CHMe \cdot CH_{2}I \\ \downarrow & \downarrow & \downarrow & \downarrow \\ (I) + (II) & (III) \end{array}$$

The above olefin mixture was normally used for the reactions with trifluoroiodomethane and hydrogen bromide since the presence of a small amount of olefin (III) should not affect the additions to olefins (I) and (II).

Trifluoroiodomethane.--A preliminary photochemical reaction between trifluoroiodomethane and the olefin mixture gave six products in the ratio 40:25:8:22:2:2from which the four major products were separated (g.l.c.) and identified as 1:1 adducts (IV) [two stereoisomers (IVa) and (IVb)], (V), and (VI), respectively, by elemental analysis and molecular weight determination.

$$\begin{array}{c} CF_3 \cdot CHI \cdot CHMe \cdot CF_3 & CF_3 \cdot CH_2 \cdot CI(CF_3) \cdot CH_3 \\ (IV) & (V) \\ CH_3 \cdot CHI \cdot CH(CF_3)_2 \\ (VI) \end{array}$$

The identification of products (IVa) and (IVb) follows from their separate treatment with potassium hydroxide to give a mixture (80% and 65%, respectively) of cisand trans-1,1,1-trifluoro-3-trifluoromethylbut-2-ene (VIIa) and (VIIb). The n.m.r. spectra of the two

$$CF_{3} \cdot CHI \cdot CHMe \cdot CF_{3} \xrightarrow{KOH} CF_{3} \cdot CF_{3} + CF_{3} + CF_{3} \cdot CF_{3} + C$$

adduct isomers were in full agreement with the proposed structure and the mass spectra each showed a parent peak at m/e 306 (100%) and a peak at m/e 209 (ca. 3%) assigned to the ion CF<sub>3</sub>·CHI<sup>+</sup>.

<sup>3</sup> C. J. Attridge, G. W. Cross, R. N. Haszeldine, and M. J. Newlands, unpublished results. <sup>4</sup> R. N. Haszeldine, D. W. Keen, and A. E. Tipping, J. Chem.

Soc. (C), 1970, 414.

The identification of product (VI) follows from its reaction with potassium hydroxide to give 1,1,1-tri-fluoro-2-trifluoromethylbut-2-ene (VIII) (97%) as the

$$CH_3 \cdot CHI \cdot CH(CF_3)_2 \xrightarrow{KOH} CH_3 \cdot CH: C(CF_3)_2$$
  
(VIII)

only volatile product. In agreement with this the mass spectrum of (VI) contained a strong peak at m/e 155 (24%) assigned to the ion CH<sub>3</sub>·CHI<sup>+</sup>; the n.m.r. spectra were also in full agreement with the proposed structure.

In further experiments, in which the reactant olefin (III) was absent, it was observed that product (V) was not formed. Product (V) is thus considered to be 1,1,1-trifluoro-3-iodo-3-trifluoromethylbutane formed via trifluoromethyl radical attack on the terminal  $CH_2$  group of olefin (III).

The results from various photochemical additions of trifluoroiodomethane to 1,1,1-trifluorobut-2-ene are shown in Table 1.

In the addition to the *trans*-olefin [expt. (3)] no *cis*olefin was observed in the product mixture and thus are formed in each case the major elimination reaction probably takes place by an E2 mechanism.

Since the E2 mechanism is *trans*-stereospecific the *cis*-olefin (VIIa) would be formed from the *erythro*isomer and the *trans*-olefin (VIIb) from the *threo*-isomer. On this basis the major isomer (IVa) is assigned the *threo*-configuration and the minor isomer (IVb) the *erythro*-configuration.



Hydrogen Bromide.—A dark reaction with 1,1,1-trifluorobut-2-ene at  $20^{\circ}$  in the presence of aluminium bromide (425 hr.) gave only unchanged reactants, but a

TABLE 1
Addition of trifluoroiodomethane to 1,1,1-trifluorobut-2-ene

Olefin ratio		Irradiation	% Olefin	% Olefin recovered		% 1:1	Ratio of 1:1 adducts			
Expt.	trans	cis	period (hr.)	conversion	trans	cis	Adducts	(IVa)	(IVb)	(VI)
(1) *	82	18	96	<b>22</b>	83	53	90	46	29	25
(2)	87	13	170	60			95	50	28	<b>22</b>
(3)	100	0	100	<b>54</b>	46	0	90	57	26	17
				* Olefin (III) (4	<b>4%) also</b> pre	esent.				

little or no isomerisation of the olefin occurs; *cis-trans* isomerisation was also not observed when the *trans*-olefin was irradiated alone.

From experiment (1) it is apparent that the *cis*-olefin reacts faster than does the *trans*-olefin and as the percentage of *trans*-olefin in the reactant mixture increases this is accompanied by a parallel increase in attack on the  $CH_3$ ·CH group of the olefin. The overall variation in the three experiments is only between 75:25 and 83:17 and it is therefore considered that the average ratio of the three experiments, *i.e.* 80:20, is a reasonably accurate ratio for radical attack in the photochemical reaction of trifluoroiodomethane with 1,1,1-trifluorobut-2-ene.

The two diastereoisomers of structure (IV) gave different results on treatment with potassium hydroxide. The major adduct (IVa) gave the *cis*-olefin (VIIa) (10%), *trans*-olefin (VIIb) (70%), and an unknown olefin (3%), while the minor isomer (IVb) gave (VIIa) (40%), (VIIb) (25%), and the same unknown olefin (8%).

The formation of both isomeric olefins from each stereoisomer suggests that in part the reaction goes *via* an *E*1cB mechanism, but because different major olefins

$$CF_3 \cdot CHI \cdot CHMe \cdot CF_3 \xrightarrow{KOH} CF_3 \cdot CHI \cdot \overline{C}Me \cdot CF_3 \xrightarrow{-I^-} CF_3 \cdot CHI : CMe \cdot CF_3$$

preliminary photochemical experiment gave four major products in the ratio 35:26:5:34, the first three of which were identified as the 1:1 adducts 2-bromo-1,1,1-trifluorobutane (IX) (35%), 3-bromo-1,1,1-trifluorobutane (X) (26%), and 1-bromo-2-trifluoromethylpropane (XI) [86% based on olefin (III)].

$$\begin{array}{ccc} CF_3 \cdot CHBr \cdot CH_2 \cdot CH_3 & CF_3 \cdot CH_2 \cdot CHBr \cdot CH_3 \\ (IX) & (X) \\ CF_3 \cdot CHMe \cdot CH_2Br \\ (XI) \end{array}$$

Product (IX) was identified on the basis of its mass spectrum which showed bands at m/e 161 (0.5%), assigned to CF<sub>3</sub>·CHBr<sup>+</sup>, and at m/e 29 (54%), assigned to CH<sub>3</sub>·CH<sub>2</sub><sup>+</sup>, and its n.m.r. spectrum which was of the ABP<sub>3</sub>SX<sub>3</sub>-type. The reasonably large coupling (7.2 Hz) found between the fluorine nuclei (F<sub>x</sub>) and only one hydrogen nucleus suggests the presence of a CF<sub>3</sub>·CHXgrouping (where X is not H or F).

The n.m.r. spectrum of product (X) was also of the  $ABP_3SX_3$ -type and the large triplet splitting (10.4 Hz) observed for the fluorine nuclei (F<sub>x</sub>) suggests the presence of a  $CF_3$ ·CH<sub>2</sub>-grouping. This, taken in conjunction with the doublet splitting (6.6 Hz) observed for the three equivalent hydrogens (H<sub>P</sub>), which suggests the presence of a  $CH_3$ ·CHX-grouping (where X is not H or F),

provides conclusive evidence as to the structure of the adduct.

The minor adduct was found to be formed only when olefin (III) was present in the reactant mixture and is thus considered to be (XI) formed *via* bromine atom attack on the terminal  $CH_2$  group of olefin (III).

Chemical analysis and a molecular-weight determination on the fourth product of the reaction indicated the molecular formula  $C_4H_4BrF_3$  and the presence of a medium strength band at 5.92 µm. in the i.r. spectrum of the compound suggested that it was an olefin. The n.m.r. spectrum showed the presence of two vinylic hydrogen atoms ( $\tau$  3.40 and 4.10) and the large coupling (15.8 Hz) observed indicates that they are *trans* to one another. Thus the compound is identified as *trans*-4bromo-1,1,1-trifluorobut-2-ene (XII) (34%).

In a second experiment to high olefin conversion (95%) the products were a mixture (62%) of the 1:1 adducts (IX) and (X) in the ratio 74:26 and the allylic bromination compound (XII) (38%).

The 1:1 adduct ratios obtained in the two experiments vary considerably and so an accurate 1:1 adduct ratio could not be obtained, but a value of  $65 \pm 10:35 \mp 10$  represents the results obtained so far. The formation of compound (XII) does not affect the 1:1 adduct ratio because it is formed from a different intermediate to those which lead to the 1:1 adducts. Since hydrogen is formed in appreciable amount during the reaction molecular bromine is also probably formed in appreciable quantity and compound (XII) then arises as shown in the reaction scheme:



It is surprising that the corresponding cis-analogue of (XII) was not detected in the reaction products, especially in the first experiment where 18% of the cis-olefin (II) was present in the mixture of reactant olefins.

An attempt to prepare compound (XII) and its *cis*analogue by photochemical bromination of a mixture of olefins (I) and (II) failed because spontaneous addition of bromine to the double bond occurred in the dark (prior to irradiation) to give the *erythro-* and *threo*dibromides (96%).

## DISCUSSION

The 1:1 adduct ratio (80:20) obtained from the photochemical reaction of trifluoroiodomethane with 1,1,1-trifluorobut-2-ene indicates that the secondary

radical  $CF_3 \cdot \dot{C}H \cdot CH(CF_3) \cdot CH_3$  is more stable than the secondary radical  $CH_3 \cdot \dot{C}H \cdot CH(CF_3)_2$  even though the



former has only one hydrogen atom available for hyperconjugative stabilization of the type:

$$CF_3 \cdot CH \cdot CH(CF_3) \cdot CH_3 \longrightarrow CF_3 \cdot CH \cdot C(CF_3) \cdot CH_3$$
  
H·

while the latter has four hydrogen atoms available. Thus it would appear that such stabilisation is not important in this case and that the dominant factor is the greater stabilising effect on a lone electron by a trifluoromethyl group than by a methyl group. The adduct ratio is almost identical to that obtained from the addition of trifluoroiodomethane to hexafluoropropene (80% attack on  $\rm CF_2$  group)  $^5$  and to 1,3,3,3-tetrafluoropropene (75% attack on CHF group).^1 These ratios can be regarded as reflecting the greater stabilising power of a trifluoromethyl group than a fluorine atom for a lone electron. Thus, it would appear that for trifluoromethyl radical additions a methyl group stabilises a lone electron to approximately the same extent as a fluorine atom. This is supported by the observation 4 that the thermal additions of trifluoroiodomethane at 200° to vinyl fluoride and propene give the same 90: 10 ratio of adducts with major trifluoromethyl radical attack at the terminal CH<sub>2</sub> groups.

The direction of addition of a bromine atom to 1,1,1trifluorobut-2-ene is in direct contrast to that of trifluoromethyl radical addition and predominant attack occurs at the CF<sub>3</sub>·CH end of the olefin. The olefin 1,1,1-trifluorobut-2-ene is expected to be highly polarised as CF<sub>3</sub>·CH·CH·CH<sub>3</sub> and since the bromine atom is reported <sup>6</sup> to be more electrophilic than the trifluoro-

<sup>&</sup>lt;sup>5</sup> J. Brown and R. N. Haszeldine, unpublished results.

methyl radical, the predominance of bromine atom attack at the relatively electron-rich  $CF_3$ ·CH end of the olefin is in keeping with its higher electrophilicity.

1,1,1-Trifluorobut-2-ene thus appears to be an eminently suitable olefin with which to study radical electrophilicities because (i) steric effects should be comparable at both ends of the olefin, (ii) the olefin is highly polarised, and (iii) the intermediate radicals formed by initial radical addition have comparable stabilities.

## EXPERIMENTAL

Reactants and products were manipulated, where possible, in a conventional vacuum-system to avoid contamination with air or moisture. Photochemical reactions were carried out in 350-ml. silica tubes, unless stated to the contrary, at a distance of 10 cm. from a Hanovia S.500 lamp. The lower 5 cm. of the tubes were shielded from the radiation. Products were separated either by repeated fractional distillation in vacuo or by preparative scale gasliquid chromatography [g.l.c., Perkin-Elmer 116, 451, or 452 instruments with 2 m. or 4 m. columns packed with dodecyl phthalate (DDP, 30% by weight) on Celite]. The identities of products were established by molecular-weight determination (Regnault's method), elemental analysis, i.r. spectroscopy (Perkin-Elmer spectrophotometer model 21 with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer R10 spectrometer operating at 56.46 MHz for <sup>19</sup>F and 60.0 MHz for 1H), mass spectrometry (A.E.I. MS/2H spectrometer), g.l.c., and u.v. spectroscopy (Unicam SP 700 spectrophotometer).

Photochemical Reaction of Trifluoroiodomethane with Propene.—The iodo-compound (43.7 g., 0.224 mole) and propene (5.73 g., 0.134 mole), irradiated in four silica tubes (1400-ml. total capacity) for 160 hr., gave (i) unchanged trifluoroiodomethane (17.8 g., 91.0 mmoles, 41%) contaminated with small amounts of trifluoromethane and hexafluoroethane, and (ii) a higher boiling fraction (31.2 g.) which when fractionally distilled afforded mainly 1,1,1trifluoro-3-iodobutane (29.2 g., 0.123 mole, 91%) (Found: M, 236. Calc. for C<sub>4</sub>H<sub>6</sub>F<sub>3</sub>I: M, 238), b.p. 100—106° (lit.,7 b.p. 103.5°; lit.,<sup>4</sup> b.p. 101.6°).

Reaction of 1,1,1-Trifluoro-3-iodobutane with Potassium Hydroxide .--- The material prepared in the previous experiment (29.2 g.) when condensed onto powdered potassium hydroxide (ca. 150 g.) in vacuo and warmed to ca. 50° (30 min.), gave a mixture (12.6 g., 0.115 mole, 91%) (Found: M, 110. Calc. for  $C_4H_5F_3$ : M, 110) of three olefins (g.l.c., 4 m. DDP at 20°) in the ratio 79:17:4. The olefins were separated by g.l.c. (as above) and identified as (i) trans-1,1,1-trifluorobut-2-ene (I) (9.99 g., 90.8 mmoles, 72%) (Found: C, 43·3; H, 4·5%; M, 110.  $C_4H_5F_3$ requires C, 43.6; H, 4.5%; M, 110), b.p. (isoteniscope) 17.6°;  $\lambda_{\max}$  3.20w, 3.26m, 3.36s, 3.41s, 3.48m, 3.64w, 3.78w, 3.93w, 4.06w, 4.17w, 4.34w, 4.41w, 4.60w, 4.72w, 4.98w, 5.42w, 5.50w, 5.71w, 5.88 and 5.92s (C:C str.), 6.60w, 6.87s, 6.90s, 7.20s, 7.34s, 7.38s, 7.56vs, 7.87vs, 8.61vs, 8.72vs, 9.27s, 10.42s, 10.50s, 11.79m, 14.05w, 14.59s, 14.70s, and 14.82s µm., (ii) cis-1,1,1-trifluorobut-2-ene (II)  $(2\cdot15~\text{g.},~19\cdot5$  mmoles, 15%) (Found: C,  $43\cdot3;~H,~4\cdot5\%;$  $\dot{M}$ , 110), b.p. (isoteniscope) 16·0°;  $\lambda_{max}$ , 3·26m, 3·31m, 3·38m, 3·45m, 4·00w, 4·15w, 4·38w, 4·47w, 5·07w, 5·30w, 5.60w, 5.70w, 5.80m and 5.96s (C:C str.), 6.45w, 6.53w, 6.60w, 6.86s, 6.88s, 7.04s, 7.19s, 7.22s, 7.55s, 7.83vs, 8.08vs, 8.56vs, 8.70vs, 9.40s, 10.40w, 10.49w, 10.71m, 12.04m,

12·12m, and 14·03s (CF<sub>3</sub> def.)  $\mu$ m., and (iii) 2-trifluoromethylpropene (III) (0·51 g., 4·6 mmoles, 4%) (Found: M, 110. Calc. for C<sub>4</sub>H<sub>5</sub>F<sub>3</sub>: M, 110) identified by its i.r. spectrum which was identical to that reported.<sup>4</sup>

Photolysis of trans-1,1,1-Trifluorobut-2-ene.—The transolefin (0·21 g., 1·87 mmoles) contaminated with cis-1,1,1trifluorobut-2-ene (4 mole %), irradiated in a 100-ml. silica tube (70 hr.) gave a mixture of olefins (0·20 g., 1·82 mmoles, 97%) shown by g.l.c. (4 m. DDP at 20°) to be the trans- and cis-olefins in the ratio 96:4.

Photochemical Reaction of Trifluoroiodomethane with 1,1,1-Trifluorobut-2-ene.-(a) Reaction (1). Trifluoroiodomethane (21.0 g., 0.107 mole) and a mixture (5.88 g., 53.55 mmoles) consisting of (I) (4.66 g., 42.31 mmoles), (II) (1.00 g., 9.10 mmoles), and (III) (0.24 g., 2.15 mmoles), sealed in two 350-ml. silica tubes and irradiated (96 hr.), gave (i) a mixture of trifluoromethane (0.088 g., 1.20 mmoles) and hexafluoroethane (0.11 g., 0.75 mmole), (ii) unchanged trifluoroiodomethane (18.51 g., 94.6 mmoles, 88%), (iii) a mixture (4.51 g., 40.92 mmoles) of olefins shown by g.l.c. (4 m. DDP at 20°) to contain (I) (3.90 g., 35.42 mmoles, 83%), (II) (0.54 g., 4.89 mmoles, 53%), and (III) (0.07 g., 0.61 mmole, 28%), and (iii) a higher-boiling fraction (3.51 g.) shown by g.l.c. (2 m. DDP at 115°) to contain six components [(A)-(F)] in the ratio 40:8:22:25:2:2. The four major components [(A)-(D)] of this latter fraction were separated by g.l.c. (4 m. DDP at 120°) and identified as (i) threo-1,1,1-trifluoro-2-iodo-3-trifluoromethylbutane (IVa) (1.40 g., 4.58 mmoles, 41%) (Found: C, 19.9; H, 1.9%; M, 306.  $C_5H_5F_6I$  requires C, 20.0; H, 1.7%; M, 306), b.p. (isoteniscope) 107.5°;  $\lambda_{max}$  (vapour) 267—269 nm. ( $\varepsilon$  199),  $\lambda_{min.}$  234—235 nm. ( $\varepsilon$  26);  $\lambda_{max}$  3·30w, 3·34w, 6·80m, 6·95w, 7·21m, 7·51s, 7·55s, 7·82s, 7·92vs, 8·32vs, 8·44vs, 8·66vs, 8.94s, 9.10s, 9.27m, 9.47m, 9.85m, 10.38w, 11.73w, and 14·38m μm., (ii) 1,1,1-trifluoro-3-iodo-3-trifluoromethylbutane (V) (0.28 g., 0.92 mmole, 60%) (Found: C, 20.2; H, 2.0%; *M*, 304), b.p. (isoteniscope) 111.0°;  $\lambda_{\text{max}}$  3.34w, 3.38w, 6.85m, 6.96m, 7.14m, 7.30s, 7.51s, 7.61s, 7.83vs, 7.95vs, 8.22s, 8.38vs, 8.46vs, 8.65vs, 8.95s, 9.14s, 9.22m, 10.00m, 10.88w, 12.10w, 13.53w, 14.15w, and 14.88w µm., (iii) 1,1,1trifluoro-3-iodo-2-trifluoromethylbutane (VI) (0.77 g., 2.52mmoles, 23%) (Found: C, 20.3; H, 1.6%; M, 305), b.p. (isoteniscope) 98·1°;  $\lambda_{\rm max}$  3·31w, 3·36w, 6·83w, 6·87w, 7·16m, 7·52s, 7·60s, 7·78s, 7·96s, 8·18s, 8·35s, 8·55s, 8·65s, 8.94m, 9.13m, 9.48m, 10.04m, 10.50w, 10.90w, 11.20m, 12·10w, 13·52w, and 14·35m  $\mu m.,$  and (iv) erythro-1,1,1trifluoro-2-iodo-3-trifluoromethylbutane (IVb) (0.87 g., 2.87 mmoles, 26%) (Found: C, 20.2; H, 1.8%; M, 304), b.p. (isoteniscope) 116.3°;  $\lambda_{max}$  (vapour) 267—269 nm. ( $\varepsilon$  202),  $\lambda_{min}$  238 nm. ( $\varepsilon$  59);  $\lambda_{max}$  3.31w, 3.36w, 6.78m, 7.15m, 7.28s, 7.52s, 7.63s, 7.82vs, 7.96vs, 8.20s, 8.36vs, 8.46vs, 8.65vs, 8.90s, 9.14s, 9.44m, 9.87m, 10.50w, 10.88m, 11.23w, 11.94w, 13.52m, and 14.35m µm.

(b) Reaction (2). A similar reaction with an olefin mixture (I): (II) of 87:13 and irradiated (170 hr.) gave a 60% olefin conversion and a 95% yield of the 1:1 adducts (IVa), (VI), and (IVb) present in the ratio 50:22:28.

(c) Reaction (3) [with olefin (I)]. Trifluoroiodomethane (3.50 g., 17.4 mmoles) and trans-olefin (I) (0.22 g., 1.99 mmoles), sealed in a 100-ml. silica tube and irradiated (100 hr.), gave (i) hexafluoroethane (0.06 g., 0.42 mmole; M, 136) shown by i.r. spectroscopy to be contaminated with a trace of trifluoromethane, (ii) unchanged trifluoroiodomethane (3.05 g., 15.55 mmoles, 90%), (iii) unchanged (I)

7 R. N. Haszeldine and B. R. Steele, J. Chem. Soc., 1953, 1199.

(0.10 g., 0.91 mmole, 46%), and (iv) a higher-boiling fraction (0.30 g.) shown by g.l.c. (2 m. DDP at 115°) to contain (IVa) (0.17 g., 0.56 mmole, 52%), (VI) (0.05 g., 0.17 mmole, 15%), and (IVb) (0.08 g., 0.25 mmole, 23%).

Reaction of the Trifluoroiodo(trifluoromethyl)butanes with Potassium Hydroxide.—(a) Mixture of isomers. The mixture (2·49 g., 7·81 mmoles) of isomers consisting of (IVa) (1·17 g., 3·83 mmoles), (IVb) (0·65 g., 2·11 mmoles), and (VI) (0·53 g., 1·72 mmoles), condensed in vacuo onto powdered potassium hydroxide (ca. 20 g.) and warmed to ca. 50° (30 min.), gave (i) unchanged reactants (0·21 g., 0·69 mmole, 9%) and (ii) a more volatile fraction (1·08 g., 6·12 mmoles, 86%) (Found: M, 177. Calc. for C<sub>5</sub>H<sub>4</sub>F<sub>6</sub>: M, 178) shown by g.1.c. (4 m. DDP at 20°) to contain (0.37 mmole, 5%) was not identified and its i.r. spectrum showed bands at 3.40m, 3.55m, 5.80s (C:C str.), 6.98w, 7.92s, 8.16s, 8.32s, 8.58s, 9.52m, 9.72s, 12.60w, and 13.95w µm. Component (M) was identified as 1,1,1-trifluoro-2-trifluoro-methylbut-2-ene (VIII) [0.27 g., 1.53 mmoles, 89% of reactant (VI)] (Found: C, 33.9; H, 2.3%; M, 178. C<sub>5</sub>H<sub>4</sub>F<sub>6</sub> requires C, 33.7; H, 2.3%; M, 178), b.p. (isoteniscope) 53.7°;  $\lambda_{max}$ , 3.29w, 3.38m, 3.46w, 4.32w, 4.38w, 4.61w, 4.77w, 5.14w, 5.23w, 5.30w, 5.36w, 5.82m, 5.92s, 6.41w, 6.53w, 6.84m, 6.87m, 7.10vs, 7.21s, 7.60vs, 8.02vs, 8.19s, 8.49vs, 9.05vs, 9.39m, 9.75m, 10.09s, 10.56s, 11.56s, 13.05m, 14.02 triplet s, and 14.78w µm.

(b) 1,1,1-*Trifluoro-3-iodo-2-trifluoromethylbutane* (VI). The iodo-compound (0.51 g., 1.67 mmoles), condensed

19	F N.m.r. spectra;	chemical shifts,	coupling constants	, and assignments	
Compound	Inty.	Chemical shift (p.p.m.)	Multiplicity	Coupling constant $I$ (Hz)	Assignment
$\begin{array}{c} CF_3 \cdot CH(CH_3) \cdot CHI \cdot$		-10.4 -5.8	d d	8·4 8·4	$\begin{array}{c} F_{\mathbf{X}} \text{ or } F_{\mathbf{A}} \\ F_{\mathbf{A}} \text{ or } F_{\mathbf{X}} \end{array}$
CF <sub>3</sub> ·CH(CH <sub>3</sub> )·CHI·C X M P G (eryth	CF <sub>3</sub> 1 A 1 <i>iro</i> )	-14.3 -8.2	quin quin	8·2 8·2	$\begin{array}{c} F_{\mathbf{X}} \text{ or } F_{\mathbf{A}} \\ F_{\mathbf{A}} \text{ or } F_{\mathbf{X}} \end{array}$
$CF_3 \cdot CH(CF_3) \cdot CHI \cdot C$ X M A G	H <sub>3</sub> 1 P 1	-15.6 -12.6	quin quin	$\begin{array}{rll} \mathrm{A-MX} = & 9 \cdot 0 \\ \mathrm{X-AM} = & 9 \cdot 0 \end{array}$	$\mathbf{F}_{\mathbf{A}}$ $\mathbf{F}_{\mathbf{X}}$
CF₃·CHBr·CH₂·CH₃ S P		-4.9	dq	$\begin{array}{rcl} \mathrm{F-S} &=& 7\cdot 2 \\ \mathrm{F-P} &=& 0\cdot 9 \end{array}$	
CF3·CH2·CHBr·CH3		-13.0	t	10.4	
CF <sub>3</sub> •CHBr•CHBr•CH P S A (eryth	H <sub>3</sub> iro)	-9.9	dq	$\begin{array}{rcl} \mathrm{F}\text{-}\mathrm{P} &=& 7{\cdot}4\\ \mathrm{F}\text{-}\mathrm{A} &=& 0{\cdot}9 \end{array}$	
CF <sub>3</sub> ·CHBr·CHBr·CH P S A (that	H <sub>3</sub> reo)	-9.9	dq	$\begin{array}{rcl} \mathrm{F-P} &=& 7{\cdot}4\\ \mathrm{F-A} &=& 0{\cdot}7 \end{array}$	
CF <sub>3</sub> H A C=C H <sub>P</sub> CH <sub>2</sub> Br		-13.0	dq	$\begin{array}{rcl} F-A &=& 6 \cdot 0 \\ F-PX &=& 2 \cdot 0 \end{array}$	
CF <sub>3</sub> H C=C P CF <sub>3</sub>	1	-17.6	$\operatorname{dsep}$	$\begin{array}{rcl} X-A &=& 8\cdot 2 \\ X-PS &=& 1\cdot 9 \end{array}$	$F_{\boldsymbol{X}}$
A S	1	-5.3	quin	S-AX = 1.9	$\mathbf{F_8}$
CF <sub>3</sub> C=C H CF CH	1	-17.7	qqd	$\begin{array}{rcl} S-X &=& 7\cdot 2\\ S-P &=& 2\cdot 4\\ S-A &=& 1\cdot 1 \end{array}$	$\mathbf{F_s}$
S P	1	-11.6	qqđ	$X-S = 7\cdot 2$ $X-P = 2\cdot 3$ $X-A = 1\cdot 8$	$\mathbf{F}_{\mathbf{X}}$

TABLE 2

seven components [(F)-(M)] present in the ratio 0.5: 0.5: 57: 5: 6: 6: 25, the four major components, (H), (K), (L), and (M), of which were separated by g.l.c. Component (H) was identified as trans-1,1,1-trifluoro-3-trifluoromethylbut-2-ene (VIIb) [0.62 g., 3.49 mmoles, 59% of reactant (IV)] (Found: C, 33.7; H, 2.4%; M, 179. C<sub>5</sub>H<sub>4</sub>F<sub>6</sub> requires C, 33.7; H, 2.3%; M, 178), b.p. (isoteniscope) 31.4° (lit.,8 b.p. 31° for 1,1,1-trifluoro-3-trifluoromethylbut-2-ene);  $\lambda_{max}$  3.22w, 3.29w, 3.37w, 3.46w, 4.34w, 4.41w, 4.98w, 5.65w, 5.83 and 5.89m (CC str.), 6.86s, 6.94s, 7.16s, 7.28s, 7.61vs, 7.80vs, 8.38vs, 8.57vs, 9.20vs, 10.12s, 11.69s, 12.52w, 13.88m, 13.94m, and 14.01m µm. Component (K) [0.066 g., 0.37 mmole, 6% of reactant (IV)] was later identified as cis-1,1,1-trifluoro-3trifluoromethylbut-2-ene (VIIa);  $\lambda_{max}$  5.80w (C:C str.), 6.77m, 6.85m, 7.25m, 7.55s, 8.02m, 8.33m, 8.59s, 9.12m, 9.73m, 11.70m, 12.59w, and 14.20w µm. Component (L)

in vacuo onto powdered potassium hydroxide (ca. 5 g.) and left at  $20^{\circ}$  (20 min.), gave olefin (VIII) (0.29 g., 1.62 mmoles, 97%).

(c) threo-1,1,1-Trifluoro-2-iodo-3-trifluoromethylbutane. The iodo-compound (1.04 g., 3.40 mmoles) treated as in (b) at 20° did not react, but when heated at 100° (15 min.) gave (i) unchanged iodo-compound (0.33 g., 1.10 mmoles, 32%) and (ii) a more volatile fraction (1.90 mmoles, 83%) shown by g.l.c. (4 m. DDP at 20°) and i.r. spectroscopy to contain (VIIb) (0.28 g., 1.61 mmoles, 70%), (VIIa) (0.041 g., 0.23 mmole, 10%) contaminated with a small amount of an unknown component with strong i.r. bands at 4.90 (C:C:C asym. str.) and 6.72  $\mu$ m., and the unknown component (L) (0.07 mmole, 3%) from (a).

(d) erythro-1,1,1-Trifluoro-2-iodo-3-trifluoromethylbutane.

<sup>8</sup> P. Tarrant, M. L. Brey, and B. E. Grey, *J. Amer. Chem. Soc.*, 1958, **80**, 1711.

The iodo-compound (0.673 g., 2.20 mmoles), treated as in (c) gave (i) unchanged iodo-compound (0.154 g., 0.51 mmole, 23%), (ii) (VIIb) (0.075 g., 0.42 mmole, 25%), (iii) *cis*-1,1,1-trifluoro-3-trifluoromethylbut-2-ene (VIIa) (0.121 g., 0.68 mmole, 40%) (Found: M, 178. Calc. for  $C_5H_4F_6$ : M, 178), and (iv) unknown component (L) (0.14 mmole, 8%).

bromine by shaking with mercury, gave (i) unchanged (I) (0.23 g., 2.06 mmoles, 23%), (ii) unchanged (II) (ca. 0.005 g., 0.04 mmole, 2%), and (iii) a high-boiling fraction (2.25 g.) shown by g.l.c. (2 m. DDP at 100°) to contain 2 components in the ratio 80:20 which were separated and identified as erythro-2,3-dibromo-1,1,1-trifluorobutane [1.80 g., 6.67

<sup>1</sup> H N.	m.r. spectra;	chemical shifts, co	oupling constant	s, and assignments	
Compound $CF_3 \cdot CH(CH_3) \cdot CHI \cdot CF_3$ $X \cdot M \cdot P \cdot G \cdot A$ (three)	Inty. 1 1 3	Chemical shift ( $ au$ ) 5.40 7.64 8.70	Multiplicity q hep d	Coupling constant J (Hz) G-A = 8.4 M-PX = 8.0 P-M = 7.5	Assignment H <sub>G</sub> H <sub>M</sub> Ha
$CF_3 \cdot CH(CH_3) \cdot CHI \cdot CF_3$	1	5.54	qđ	$\begin{array}{ccc} \mathbf{G}-\mathbf{A} &=& 8\cdot 2\\ \mathbf{G}-\mathbf{M} &=& 3\cdot 0 \end{array}$	Hp H <sub>G</sub>
(erythro)	1	7.34	hepd	M - PX = 8.2 M - G = 3.0	$\mathbf{H}_{\mathbf{M}}$
	3	8.75	d	$P-M = 8 \cdot 1$	HP
$\underset{X M}{\operatorname{CF}_3} \cdot \underset{M}{\operatorname{CH}} (\operatorname{CF}_3) \cdot \underset{G}{\operatorname{CHI}} \cdot \underset{P}{\operatorname{CHI}} \cdot \underset{A}{\operatorname{CHI}} \cdot \underset{P}{\operatorname{CHI}} \cdot \underset{P}{$	1	5.45	$\mathbf{q}\mathbf{d}$	$\begin{array}{rcl} \mathrm{G-P} &=& 8\cdot 0\\ \mathrm{G-M} &=& 3\cdot 0 \end{array}$	H <sub>Q</sub>
	1	6.62	hepd	$\begin{array}{rcl} \mathrm{M-AX} = & 9 \cdot 0 \\ \mathrm{M-G} & = & 3 \cdot 0 \end{array}$	$\mathbf{H}_{\mathbf{M}}$
	3	7.96	d	P-G = 8.0	$H_{\mathbf{P}}$
CF₃•CHBr•CHH•CH₃ S AB P	1	6.00	dqd	$\begin{array}{rcl} \mathrm{S-F} & = & \begin{array}{c} 9 \cdot 3 \\ 7 \cdot 2 \\ 4 \cdot 3 \end{array}$	$H_{s}$
	$\frac{2}{3}$	7·98 8·88	$\operatorname{complex}$ tq	$PF = \begin{array}{c} 7 \cdot 3 \\ 0 \cdot 9 \end{array}$	$H_{AB}$ $H_{P}$
CF₃•CHH∙CHBr•CH₃ AB S P	$1 \\ 2 \\ 3$	5·82 7·05 8·23	sex complex d	$\begin{array}{rcl} 6{\cdot}6\\ \mathrm{P-S} &=& 6{\cdot}6 \end{array}$	H <sub>S</sub> H <sub>AB</sub> H <sub>P</sub>
$CF_3$ ·CHBr·CHBr·CH <sub>3</sub> P S A (erythro)	$\frac{2}{3}$	5·45 8·19	complex dq	A-S = 6.5 A-F = 0.9	${ m H_{PS}}{ m H_{X}}$
$CF_3$ ·CHBr·CHBr·CH <sub>3</sub> PSA ( <i>threo</i> )	$\frac{2}{3}$	5·67 8·22	complex dq	$\begin{array}{rcl} A-S &=& 6\cdot 5 \\ A-F &=& 0\cdot 7 \end{array}$	$H_{PS}$
$ \begin{array}{c} CF_3 \\ H \\ H \\ A \\ X \end{array} $ $ \begin{array}{c} H_P \\ CH_2Br \\ X \end{array} $	1	3.40	dtq	$\begin{array}{rcl} P-A &= 15.8 \\ P-X &= 6.8 \\ P-F &= 2.0 \end{array}$	H <sub>P</sub>
	1	<b>4</b> ·10	dqt	A-P = 15.8 A-F = 6.0 A-X = 1.0	$H_{A}$
	2	6.04	dqd	$\begin{array}{rcl} { m X-P} &=& 6\cdot 8 \\ { m X-F} &=& 2\cdot 0 \\ { m X-A} &=& 1\cdot 0 \end{array}$	$H_{\mathbf{X}}$
CF <sub>3</sub> H C=C P CE	1	3.81	qsep	$\begin{array}{rcl} A-X &=& 8\cdot 2\\ A-PS &=& 1\cdot 9 \end{array}$	$H_{\mathbf{A}}$
A S	3	7.91	quin	P-XA = 1.9	$H_{P}$
CF <sub>3</sub> H	1	3.14	q	A-P = 7.6	$H_{A}$
CF <sub>3</sub> CH <sub>3</sub> P	3	7.98	dsep	$\begin{array}{rcl} \mathrm{P-A} &=& 7{\cdot}6\\ \mathrm{P-SX} &=& 2{\cdot}3 \end{array}$	$H_{P}$

TABLE 3

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

Chemical shift (p.p.m.)

Group	Found	Reported	Ref.					
CF₃·C€	-4.9 to $-15.6$	-19.7 to $11.9$	10					
CF₃·Ċ=	-5.3 to $-17.7$	0 to -20	11					

Reaction of Bromine with 1,1,1-Trifluorobut-2-ene. Bromine (1.61 g., 10.0 mmoles) and a mixture of (I) (0.98 g., 8.82 mmoles) and (II) (0.21 g., 1.90 mmoles) reacted immediately in the liquid phase in the dark at *ca*. 0° and was left in the dark at 20° (8 hr.); removal of traces of mmoles, 98% of olefin (I) reacted] (Found: C, 18.0; H, 1.9%. C<sub>4</sub>H<sub>5</sub>Br<sub>2</sub>F<sub>3</sub> requires C, 17.8; H, 1.8%), b.p. (Siwoloboff) 135°;  $\lambda_{max}$  3.32w, 3.38w, 6.86w, 6.90w, 7.20w, 7.49s, 7.68w, 7.92s, 8.15m, 8.20m, 8.25m, 8.47s, 8.88s, 8.98s, 9.28w, 9.51m, 9.93m, 10.35w, 11.08w, 11.70m, 13.69m, and

14·13m µm., and threo-2,3-*dibromo*-1,1,1-*triftuorobutane* [0·45 g., 1·68 mmoles, 90% of olefin (II) reacted] (Found: C, 17·8; H, 1·7%), b.p. (Siwoloboff) 138°;  $\lambda_{max}$ . 3·33w, 3·40w, 6·84w, 6·92w, 7·20m, 7·28m, 7·40m, 7·65m, 7·81s, 7·92s, 8·10m, 8·23m, 8·47s, 8·90s, 9·51m, 9·93w, 10·52m, 11·73m, 12·20w, 12·51w, 13·36m, and 14·60w µm.

Reaction of Hydrogen Bromide with 1,1,1-Trifluorobut-2ene.—(a) Reaction (1) (dark). Hydrogen bromide and a mixture of the isomeric butenes (0.48 g., 4.33 mmoles), ponents (N)—(Q) present in the ratio 35:26:5:34 which were separated and identified as: (a) 2-Bromo-1,1,1-trifluorobutane (IX) (0.51 g., 2.67 mmoles, 35%) (Found: C, 25.4; H, 3.1%; M, 191. C<sub>4</sub>H<sub>6</sub>BrF<sub>3</sub> requires C, 25.2; H, 3.1%; M, 191), b.p. (isoteniscope)  $72.9^{\circ}$ ;  $\lambda_{max}$ . 3.33m, 3.38m, 3.45m, 3.61w, 4.45w, 4.71w, 5.05w, 6.00w, 6.52w, 6.82m, 6.90m, 7.16 and 7.18 dbt. m, 7.28s, 7.57s, 7.69s, 7.88vs, 8.24s, 8.41vs, 8.88vs, 9.34m, 9.61m, 9.66m, 10.76m, 10.82m, 11.72 triplet m, 12.28m, 12.87w, 13.37w, and

TABLE 4

Main mass-spectral bands

			Wan	mass-spectral bands				
	Peak intensity				Peak intensity			
m e	(IVa)	(IVĎ)	Assignment	m e	(V)	(VI)	Assignment	
306	`100´	100	$M^+$	306	64	100	$M^+$	
209	3.2	3.1	C.HF.I+	227	16	8.2	C.F.I+	
179	16	36	C.H.F.+	179	21	86	C.H.F.+	
160	11	9.2	C.H.F.+	159	$\bar{65}$	71	C.H.F.+	
159	$\overline{\overline{72}}$	77	C.H.F.+	155	17	24	C.H.I+	
139	16	22	C.H.F.+	139	15	11	C.H.F.+	
128	19	19	C.H.F.+ HI+	128	33	19	C.H.F.+. HI	+
120	19	27	1+	127	57	31	I+	
115	19	28	Ĉ.H.F.+	115	32	6.8	C.H.F.+	
109	7.8	11	C.H.F.+	113	23	14	$C_{a}HF_{a}^{4}$	
95	27	41	$C_{4}H_{4}F_{3}$	109		8.7	C.H.F.+	
80	ĩi	13	$C_{3}H_{2}F_{3}$	95	42	25	C.H.F.+	
88		12	$C_{4}H_{3}F_{2}^{+}$	91	100		C.H.F.+	
69	18	26	$C_{4}^{11}_{21}_{2}^{2}_{2}$	89	100	10	C.H.F.+	
65	15	20	$C_{13}$	69	63	30	$CE^{+131}_{-2}$	
64	3.7	6.3	$C_{1}H_{1}F_{1}^{+}$	65	23	7.0	C.H.F.+	
51	20	27	$CHE^+$	64	20	6.3	$C_{1}H_{1}F_{1}^{+}$	
47	2.3	11	CH <sup>5+</sup>	59		5.1	$C_{1}H_{1}F_{2}^{+}$	
30	7.1	1.8	$CH^{\pm}$	51	42	7.9	CHE +	
97	4.4	6.3	$C_{3}H_{3}^{++}$	47	27	89	C.H.F+	
2.	11	00	$\cup_{2^{11}3}$	43	21		$C_{2}F_{4}F_{4}$	
	(IX)	$(\mathbf{X})$		41	23		$C_{2}^{21}$	
192 190	28	26	$M^+$	39	$\frac{1}{27}$	10	C.H.+	
111	76	93	C.H.F.+	27	$\frac{20}{20}$	9.2	$C_{3}H_{3}$	
95	10	12	CaHaFa+	21		0 -	$\odot_{2^{*}1_{3}}$	
91	74	84	C.H.F.+		(X			
77	15	14	C.H.F.+	190, 188		32	$M^+$	
73	100		C.H.F+	171, 169	10		C.H.BrF.+	
69	13	53	CF.+	109	100		C.H.F.+	
64	14	14	C.H.F.+	90	13		C.H.F.+	
59	$\tilde{16}$		C.H.F+	89	40		C.H.F.+	
51	9.3	18	CHF.+	74	17		C <sub>2</sub> F <sub>2</sub> +	
47	58	100	C.H.F+	69	18		ČĚ.+	
45	28		C <sub>0</sub> H <sub>0</sub> F <sup>+</sup>	59	48		C.H.F+	
41	46	56	C.H.+	47	ĩĩ		C.H.F+	
40		49	C.H.+	45	-	32	C.H.F+	
$\overline{31}$	30	13	CF+	43	]	2	$C_{a}F^{+}$	
$\tilde{29}$	54	$\overline{21}$	C.H.+	39	4	3	C.H.+	
$\overline{28}$	$\overline{42}$	- 9·1	C.H.+	38	]	Ó	C.H.+	
$\overline{\overline{27}}$	33	39	C.H.+	32	ç	20	CHF+	
		••	6 <sup></sup> 4	31		33	$CF^+$	
				28		30	C.H.+	
				=•			24	

sealed in a 100-ml. Pyrex tube with aluminium bromide  $(1 \cdot 0 \text{ g.})$  and left in the dark at  $20^{\circ}$  (425 hr.), gave only unchanged reactants.

(b) Reaction (2) (photochemical). Hydrogen bromide (4.05 g., 50.0 mmoles) and a mixture of olefins consisting of (I) (2.33 g., 21.09 mmoles) ,(II) (0.50 g., 4.55 mmoles), and (III) (0.11 g., 1.04 mmoles), irradiated for 6 hr. and the bromine formed in the reaction removed by shaking with mercury, gave (i) hydrogen (0.0098 g., 4.92 mmoles) (Found: M, 2.0. Calc. for H<sub>2</sub>: M, 2.0), (ii) unchanged hydrogen bromide (2.79 g., 34.50 mmoles, 69%), (iii) unchanged olefins (2.05 g., 18.64 mmoles, 70%) shown by g.l.c. (4 m. DDP at 20°) to consist of (I) (1.90 g., 17.27 mmoles, 82%), (II) (0.08 g., 0.77 mmole, 17%), and (III) (0.07 g., 0.60 mmole, 58%), and (iv) a higher boiling fraction (1.46 g.) shown by g.l.c. (2 m. DDP at 70°) to contain four com14·74 triplet  $\mu$ m. (b) 3-Bromo-1,1,1-trifluorobutane (X) (0·38 g., 1·99 mmoles, 26%) (Found: C, 25·3; H, 3·1%; M, 191), b.p. (isoteniscope) 82·5° (lit.,<sup>9</sup> b.p. 84°);  $\lambda_{\max}$ 3·33m, 3·38m, 3·45m, 6·80m, 6·92m, 7·16m, 7·18m, 7·28s, 7·44s, 7·57s, 7·90vs, 8·41vs, 8·53vs, 8·74vs, 8·89vs, 9·34m, 9·65m, 9·84m, 10·47w, 10·84m, 11·38w, 11·44w, 11·66m, 11·72m, 11·78m, 11·96m, 12·28m, 13·37w, 14·14m, 14·74 triplet m, and 15·05m  $\mu$ m. (c) 1-Bromo-2-trifluoromethylpropane (XI) [0·073 g., 0·38 mmole, 86% based on reactant (III)] (Found: M, 190. Calc. for C<sub>4</sub>H<sub>6</sub>BrF<sub>3</sub>: M, 191);  $\lambda_{\max}$ , 7·36m, 7·70m, 7·92s, 8·33s, 8·43m, 8·67s, 8·88s, 8·97m,

<sup>9</sup> P. Tarrant, A. M. Lovelace, and M. R. Lilyquist, J. Amer. Chem. Soc., 1955, 77, 2783. <sup>10</sup> N. Muller, P. C. Lauterbur, and G. F. Svatos, J. Amer.

<sup>10</sup> N. Muller, P. C. Lauterbur, and G. F. Svatos, *J. Amer. Chem. Soc.*, 1957, **79**, 1807.

<sup>11</sup> Unpublished data from this department.

10.50m, 11.05w, 11.75w, 12.08m, 12.30w, and 14.23m  $\mu$ m.; main mass spectral bands at m/e 192 and 190 (C<sub>4</sub>H<sub>6</sub>BrF<sub>3</sub><sup>+</sup>, intensity 22%), 111 (C<sub>4</sub>H<sub>6</sub>F<sub>3</sub><sup>+</sup>, 84%), 91 (C<sub>4</sub>H<sub>5</sub>F<sub>2</sub><sup>+</sup>, 82%), 69 (CF<sub>3</sub><sup>+</sup>, 68%), 47 (C<sub>2</sub>H<sub>4</sub>F<sup>+</sup>, 79%), 41 (C<sub>3</sub>H<sub>5</sub><sup>+</sup>, 69%), 39 (C<sub>3</sub>H<sub>3</sub><sup>+</sup>, 66%), 31 (CF<sup>+</sup>, 63%), 29 (C<sub>2</sub>H<sub>5</sub><sup>+</sup>, 63%), 28 (C<sub>2</sub>H<sub>4</sub><sup>+</sup>, 100%), and 27 (C<sub>2</sub>H<sub>3</sub><sup>+</sup>, 56%). (d) trans-4-Bromo-1,1,1-trifluorobut-2-ene (XII) (0.50 g., 2.64 mmoles, 34%) (Found: C, 25.4; H, 2.1%; M, 190. C<sub>4</sub>H<sub>4</sub>BrF<sub>3</sub> requires C, 25.4; H, 2.2%; M, 189), b.p. (isoteniscope) 100.0°;  $\lambda_{\rm max}$ . 3.34m, 3.46w, 5.92m (C:C str.), 6.84m, 6.92 and 6.96 dbt. m, 7.18m, 7.27m, 7.50vs, 7.80vs, 7.99s, 8.24s, 8.42vs, 8.68vs, 8.92s, 9.45m, 9.88m, 10.86s, 11.05m, 11.15m, 11.36m, 11.42m, 11.71m, 12.31w, 14.15m, 14.30m, and 14.74 triplet  $\mu$ m.

(c) Reaction (3) (photochemical). The olefin mixture (2.05 g., 18.64 mmoles) and hydrogen bromide (2.79 g.,

34.50 mmoles) recovered from (b), irradiated for 19 hr., gave unchanged olefins (0.103 g., 0.93 mmole, 5%) and the products (IX), (X), and (XII) (3.35 g., 17.53 mmoles, 99%) in the ratio 46:16:38.

Nuclear Magnetic Resonance Spectra.—The data recorded in Tables 2 and 3 are relative to external  $CF_3 \cdot CO_2 H$  (<sup>19</sup>F) and internal Me<sub>4</sub>Si (<sup>1</sup>H); negative values are to low field.

Mass Spectral Data.—The main bands for the compounds prepared in the present work are shown in Table 4.

The authors wish to thank Dr. M. G. Barlow for help with the interpretation of the n.m.r. spectra and the S.R.C. for a Research Studentship (to R. G.).

[0/553 Received, April 8th, 1970]