473. *The Addition of Free Radicals to Unsaturated Systems. Part I. The Direction of Radical Addition to* 3 : 3 : 3-*Trifluoropropene.*

By R. N. Haszeldine.

The photochemical or thermal addition of hydrogen bromide and of trifluoroiodomethane to 3 : 3 : 3-trifluoropropene yields exclusively $CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}Br$ and $CF_3{\cdot}[CH_2{\cdot}CH(CF_3)]_n{\cdot}CH_2{\cdot}CHI{\cdot}CF_3$. Dehydroiodination of the compound where $n = 0$ yields *trans*-$CF_3{\cdot}CH{=}CH{\cdot}CF_3$. The conversion of this into $CF_3{\cdot}C{\equiv}C{\cdot}CF_3$ and the preparation of several chloro- and bromo-hexafluoro-butanes and -butenes are described. The hydrogenation of CF_3I, $CF_3{\cdot}CH{=}CH_2$, *cis*- and *trans*-$CF_3{\cdot}CH{=}CH{\cdot}CF_3$, and $CF_3{\cdot}C{\equiv}C{\cdot}CF_3$ is considered. Infra-red and ultra-violet spectra of certain fluorine compounds are reported.

This paper records the beginning of a study of the factors influencing the direction of addition of free radicals to unsaturated systems, *i.e.*, to determine how the direction of addition of a radical or atom Y to an unsaturated system $R_1R_2C{=}CR_3R_4$, $R_1C{\equiv}CR_2$, etc., is influenced by the nature of R_1, R_2, R_3, and R_4 (= H, halogen, alkyl, etc.), and to determine if variation of Y leads to changes in the direction of addition.

The study of the peroxide effect has led to the hypothesis that under free-radical conditions hydrogen bromide reacts by a chain mechanism initiated by a bromine atom (Mayo and Walling, *Chem. Reviews*, 1940, **27**, 351). If this is true, then the direction of addition of the bromine atom to a variety of olefins is known from the work of Kharasch and his co-workers. The addition of free alkyl radicals to unsaturated systems is less clearly defined, although recently Kharasch and his co-workers (various papers in *J. Amer. Chem. Soc.* and *J. Org. Chem.*) have studied the attack of a CCl_3 radical on olefins.

In the early papers of this series will be described the direction of addition of the trifluoromethyl and similar radicals derived from fluoroiodides to unsaturated compounds of various types. The reaction of perfluoroalkyl iodides with ethylene, tetrafluoroethylene, and acetylene has been described previously (Haszeldine, *J.*, 1949, 2856; 1950, 2789; 1951, 588).

The advantages of using trifluoroiodomethane as the source of a free radical are: (1) homolytic fission of the carbon–iodine bond is readily achieved by ultra-violet light or by heat, peroxide initiators are not required, and side reactions involving free radicals from the initiator are thus eliminated; (2) the addition to unsaturated systems proceeds smoothly and with few side-reactions; (3) the structure of the product and hence the direction of addition is often readily ascertained, and in this connection the stabilising influence of trifluoromethyl groups and the volatility of compounds which contain trifluoromethyl groups help considerably in the manipulation of the products; and (4) the initiation of reactions by an iodine atom may be assumed to be less probable than initiation by the much more reactive trifluoromethyl radical. In connection with (4) it may be noted that Mayo and Walling (*loc. cit.*), from a consideration of heats of addition of halogen acids to double bonds, conclude that the addition of an iodine atom to a double bond does not proceed readily. The photochemical addition of iodine to unsaturated compounds can occur *via* iodine atoms (Berthoud and Mosset, *J. Chim. phys.*, 1936, **33**, 272; Forbes and Nelson, *J. Amer. Chem. Soc.*, 1937, **59**, 693; Ghosh and Bhattacharyya, *Science and Culture*, 1937, **3**, 120, *Chem. Abs.*, 1938, **32**, 414; Bhattacharyya, *J. Indian Chem. Soc.*, 1941, **18**, 257; Ghosh, Murthi, and Gupta, *Z. physikal. Chem.*, 1934, *B*, **26**, 258; Schumacher and Wiig, *ibid*, 1930, *B*, **11**, 45; Schumacher and Stieger, *ibid.*, 1931, *B*, **12**, 348; Tamblyn and Forbes, *J. Amer. Chem. Soc.*, 1940, **62**, 99; Arnold and Kistiakowsky, *J. Chem. Phys.*, 1933, **1**, 166) and chain mechanisms have been put forward. The reverse reaction involving loss of iodine from the di-iodides also occurs readily. Iodine atoms are known to be much less reactive than alkyl radicals (Howe and Noyes, *J. Amer. Chem. Soc.*, 1935, **57**, 1262). Furthermore, if it were assumed that iodine atoms from trifluoroiodomethane could initiate a polymerisation reaction of the type described earlier (Haszeldine, *loc. cit.*), then, since ethylene or tetrafluoroethylene yield exclusively $CF_3\cdot[CX_2\cdot CX_2]_n\cdot I$ (X = H or F) with trifluoroiodomethane, a chain mechanism of the type

$$I\cdot \xrightarrow{C_2X_4} I\cdot CX_2\cdot CX_2\cdot \xrightarrow{C_2X_4} I\cdot[CX_2]_3\cdot CX_2\cdot, \text{ etc.}$$
$$I\cdot[CX_2]_3\cdot CX_2\cdot + CF_3I \longrightarrow I\cdot[CX_2]_4\cdot CF_3 + I\cdot$$

would have to be postulated. This would involve attack of radicals of the type $I\cdot[CX_2]_n\cdot CX_2\cdot$ on the carbon atom of trifluoroiodomethane for the chain-transfer step, as distinct from the more usual reaction of free hydrocarbon radicals, *viz.*, abstraction of an atom *attached* to a carbon atom, for example, hydrogen in the case of hydrocarbons, alcohols, ethers, etc., and chlorine in the case of carbon tetrachloride (Banus, Emeléus, and Haszeldine, *J.*, 1950, 3041). Until further evidence becomes available therefore, it will be assumed that the trifluoromethyl radical and not the iodine atom initiates the addition reactions described earlier (Haszeldine, *loc. cit.*). It should be noted that, in reactions involving the photochemical addition of hydrogen bromide or bromotrichloromethane to unsaturated systems, initiation of reaction by hydrogen or bromine atoms can be eliminated with much less certainty.

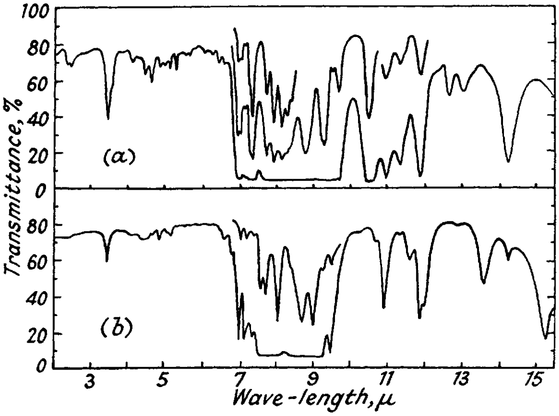


FIG. 1.
a, $CF_3\cdot CH_2\cdot CH_2Br$ (*liquid in* 0·1-*mm. cell and as capillary films*).
b, $CF_3\cdot CHI\cdot CH_2\cdot CF_3$ (*liquid in* 0·025-*mm. cell and as capillary films*).

The present communication (for preliminary results see Haszeldine and Steele, *Chem. and Ind.*, 1951, 684) describes the photochemical and thermal addition of hydrogen bromide and of trifluoroiodomethane to 3 : 3 : 3-trifluoropropene. The addition of hydrogen halides to the fluoropropene under conditions favouring an ionic reaction will be described later.

Hydrogen bromide does not react with 3 : 3 : 3-trifluoropropene in the dark, but on irradiation rapid addition occurs, giving exclusively 3-bromo-1 : 1 : 1-trifluoropropane. The reaction is, however, slower than the addition of hydrogen bromide to propylene which is very rapid in the vapour phase, even in Pyrex vessels (Vaughan, Rust, and Evans, *J. Org. Chem.*, 1942, **7**, 477). The 3-bromo-1 : 1 : 1-trifluoropropane is easily distinguished from its 2-bromo-isomer by a difference in boiling point of 14°, and its identity was confirmed by comparison of its infra-red spectrum (Fig. 1*a*) with that of a genuine specimen. If the bromine atom and not the hydrogen atom initiates the reaction then we have

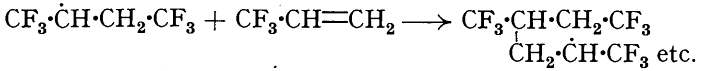
$$Br\cdot + CF_3\cdot CH{=}CH_2 \longrightarrow CF_3\cdot\dot{C}H\cdot CH_2Br$$
$$CF_3\cdot\dot{C}H\cdot CH_2Br + HBr \longrightarrow CF_3\cdot CH_2\cdot CH_2Br + Br\cdot \longrightarrow \text{etc.}$$

and, since 3-bromo-1 : 1 : 1-trifluoropropane is the only compound formed, there is apparently no tendency for the $CF_3\cdot CH\cdot CH_2Br$ radical to react with a second molecule of trifluoropropene.

Under the influence of light, 3 : 3 : 3-trifluoropropene reacts with a large excess of trifluoroiodomethane to give only one product, 1 : 1 : 1 : 4 : 4 : 4-hexafluoro-2-iodobutane, in almost theoretical yield; there is no reaction in the dark. The use of a moderate excess of trifluoroiodomethane leads to the formation of small amounts of the 1 : 2-adduct (1 : 1 : 1 : 6 : 6 : 6-hexafluoro-2-iodo-4-trifluoromethylhexane), fluoroform, 1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane, and traces of higher polymer. A similar mixture of products is formed on prolonged irradiation of trifluoropropene and excess of trifluoroiodomethane, or on heating in absence of light 3 : 3 : 3-trifluoropropene and a moderate excess of trifluoroiodomethane. The 1 : 3-adduct, 1 : 1 : 1 : 8 : 8 : 8-hexafluoro-2-iodo-4 : 6 bis(trifluoromethyl)octane, was isolated from the thermal reaction. Thus, if it is assumed that the CF$_3$ radical initiates the reaction, the suggested chain mechanism is :

$$CF_3I \xrightarrow[\text{or heat}]{h\nu} CF_3\cdot + I\cdot \qquad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$CF_3\cdot + CF_3\cdot CH{=}CH_2 \longrightarrow CF_3\cdot\dot{C}H\cdot CH_2\cdot CF_3 \qquad . \; . \; . \; . \; . \; . \quad (2)$$



$$CF_3\cdot\dot{C}H\cdot CH_2\cdot CF_3 + CF_3\cdot CH{=}CH_2 \longrightarrow \begin{array}{l} CF_3\cdot CH\cdot CH_2\cdot CF_3 \\ \qquad\; | \\ \qquad CH_2\cdot\dot{C}H\cdot CF_3 \text{ etc.} \end{array} \qquad . \; . \; . \; . \; . \quad (3)$$

$$CF_3\cdot\dot{C}H\cdot CH_2\cdot CF_3 + CF_3I \longrightarrow CF_3\cdot CHI\cdot CH_2\cdot CF_3 + CF_3\cdot \longrightarrow \text{etc.} \quad (4)$$

When a large excess of trifluoroiodomethane is present the chain-transfer reaction (4) excludes completely the chain-propagation reaction (3), and CF$_3$·CHI·CH$_2$·CF$_3$ is formed quantitatively. When less trifluoroiodomethane is used, however, the formation of small amounts of the 1 : 2- and 1 : 3-adducts CF$_3$·[CH$_2$·CH(CF$_3$)]$_n$·CH$_2$·CHI·CF$_3$ (n = 1 and 2) shows that the CF$_3$·$\dot{\text{C}}$H·CH$_2$·CF$_3$ radical can undergo reaction (3) to a certain extent. Prolonged photolysis cleaves the carbon–iodine bond in the 1 : 1-adduct and leads to hexafluorobutane by either disproportionation or hydrogen-abstraction from a hydrogen-containing molecule RH :

$$2CF_3\cdot\dot{C}H\cdot CH_2\cdot CF_3 \longrightarrow CF_3\cdot CH_2\cdot CH_2\cdot CF_3 + CF_3\cdot CH{=}CH\cdot CF_3$$

$$CF_3\cdot\dot{C}H\cdot CH_2\cdot CF_3 + RH \longrightarrow CF_3\cdot CH_2\cdot CH_2\cdot CF_3 + R\cdot$$

In the thermal reaction *trans*-1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-ene was formed in amount corresponding approximately to the hexafluorobutane isolated, but in the photochemical reactions no hexafluorobutene was detected. Thus either of the above routes to hexafluorobutane may apply. Fluoroform was a reaction product only when more stringent conditions were used, and clearly arises by attack of the CF$_3$ radical on RH. In this connection the hydrogenation of trifluoroiodomethane is reported. The fluoro-iodide and hydrogen yield fluoroform at 250° in absence of light : the photochemical reaction is slow at room temperature, but the rate is increased by addition of mercury which, by removal of iodine as mercuric iodide, prevents the primary recombination of the CF$_3$ radical and the iodine atom. Mercury-sensitised dissociation of hydrogen or of trifluoroiodomethane may also be involved. Trifluoromethylmercuric iodide is formed at room temperature, but only traces are found at 170° since it undergoes photolysis and hydrogenation under these conditions.

The ultra-violet absorption maxima of 1 : 1 : 1 : 4 : 4 : 4-hexafluoro-2-iodobutane and related compounds in ethanol are shown in the annexed Table. *n*-Aliphatic hydrocarbon iodides are characterised by a maximum at 255 mμ, which moves to longer wave-length with the *sec.*-isomers. Comparison of the spectrum of CF$_3$·CH$_2$·CH$_2$I with those of the *sec.*-iodides CF$_3$·CH$_2$·CHI·CH$_3$ and CF$_3$·CH$_2$·CHI·CF$_3$ shows a similar shift. The maxima of the last three fluoroalkyl iodides are at longer wave-lengths than those of the corresponding alkyl iodides, as was observed for trifluoroiodomethane vapour, and the further the polyfluoro-group is removed from the carbon–iodine bond the more does the absorption spectrum resemble that of the corresponding hydrocarbon.

	$\lambda_{\text{max.}}$ (mμ)		$\lambda_{\text{max.}}$ (mμ)
MeI	254·5	CF$_3$·CH$_2$·CH$_2$I	259—260
Pr^{n}I	254·5	CF$_3$·CH$_2$·CHI·CH$_3$	264
Bu^{n}I	255	CF$_3$·CH$_2$·CHI·CF$_3$	265
Pr^{i}I	261	CF$_3$I vapour	267
Bu^{s}I	259·5		

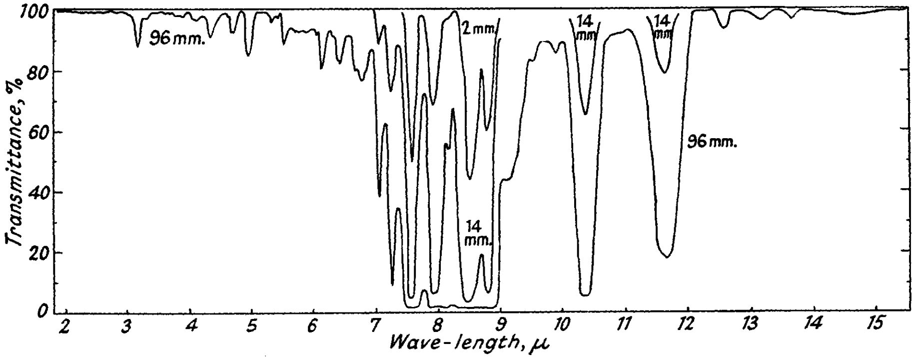
The infra-red absorption spectrum of 1 : 1 : 1 : 4 : 4 : 4-hexafluoro-2-iodobutane is recorded in Fig. 1*b*. Strong bands in the 7·6—9·0-μ region are associated with the carbon–fluorine stretching vibration, and the bands at 3·35 and 6·98 μ are due to carbon–hydrogen stretching and bending vibrations. Similar bands are apparent in the spectrum of 1-bromo-3 : 3 : 3-trifluoropropane (Fig. 1*a*).

That the direction of addition of the CF_3 radical to 3 : 3 : 3-trifluoropropene is actually as shown by (2) above and not as

$$CF_3\cdot + CF_3{\cdot}CH{=}CH_2 \longrightarrow (CF_3)_2CH{\cdot}CH_2\cdot \longrightarrow (CF_3)_2CH{\cdot}CH_2I$$

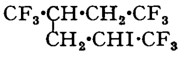
is shown by the conversion of the hexafluoro-iodobutane into *trans*-1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-ene by treatment with alcoholic potassium hydroxide. The infra-red spectrum of the fluorobutene is shown in Fig. 2. Presence of only one band in the 3-μ region (at 3·23 μ) shows that olefinic carbon–hydrogen bonds are present, and that CH_2 groups are absent. The absence of a band of moderate intensity in the 6-μ region of the spectrum (C=C stretching frequency) plus the presence of the strong band at 10·36 μ strongly support the formulation of the hexafluorobutene as the *trans*-isomer. In the hydrocarbon series, the 10·36-μ band is used diagnostically to distinguish between *cis*- and *trans*-isomers. In fluorine and halogeno-compounds the position of this strong carbon–hydrogen out-of-plane bending mode in *trans*-olefins is more variable but can still be used diagnostically (*Nature*, 1951, **168**, 1028, and unpublished work) (cf. Table). The preparation of *cis*-1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-ene is described below; its infra-red spectrum has the expected band in the 6-μ region (5·95 μ) for the C=C stretching frequency. The isomeric hexafluoroiodobutane $(CF_3)_2CH{\cdot}CH_2I$ would have given the butene $(CF_3)_2C{=}CH_2$, and the spectrum of this compound would show a C=C stretching band in the 6-μ region. Chemical verification of the structure of the *trans*-hexafluorobutene is its hydrogenation to 1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane (also obtained by hydrogenation of the *cis*-isomer), and its oxidation to 1·7 mols. of trifluoroacetic acid. Under comparable conditions the *cis*-isomer gave 1·75 mols. of trifluoroacetic acid. Oxidation of $(CF_3)_2C{=}CH_2$ would have yielded hexafluoroacetone which has been obtained by an independent route (*Nature*, *loc. cit.*) and is decomposed by alkali to fluoroform and alkali trifluoroacetate. The absence of fluoroform and hexafluoroacetone, and the production of more than one mol. of trifluoroacetic acid on oxidation, clearly eliminate the possibility of $(CF_3)_2CH{\cdot}CH_2I$ having been formed from trifluoroiodomethane and trifluoropropene.

FIG. 2. trans-$CF_3{\cdot}CH{=}CH{\cdot}CF_3$ (*vapour in 50-mm. cell*).



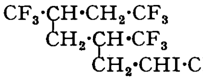
trans-Compound		*trans*-Compound	
$CF_3{\cdot}CH{=}CH{\cdot}CF_3$	10·36	$CF_3{\cdot}CH{=}CHBr$	10·71
$CF_3{\cdot}CH{=}CH{\cdot}CO_2H$	10·28	$CF_3{\cdot}CH{=}CHI$	10·64
$CF_3{\cdot}CH{=}CHCl$	10·70	$CH_2Cl{\cdot}CH{=}CHCl$	10·66
		$CH_3{\cdot}CH{=}CHBr$	10·74

The 1 : 2- and 1 : 3-adducts from trifluoroiodomethane and trifluoropropene are (I) and (II), and not (III) or (IV), since infra-red spectroscopic examination of the dehydroiodinated



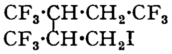
$$\begin{array}{l} CF_3\cdot CH\cdot CH_2\cdot CF_3 \\ \;\;\;\; CH_2\cdot CHI\cdot CF_3 \end{array}$$

(I)



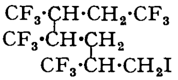
$$\begin{array}{l} CF_3\cdot CH\cdot CH_2\cdot CF_3 \\ \;\;\;\; CH_2\cdot CH\cdot CF_3 \\ \;\;\;\;\;\;\;\; CH_2\cdot CHI\cdot CF_3 \end{array}$$

(II)



$$\begin{array}{l} CF_3\cdot CH\cdot CH_2\cdot CF_3 \\ CF_3\cdot CH\cdot CH_2I \end{array}$$

(III)



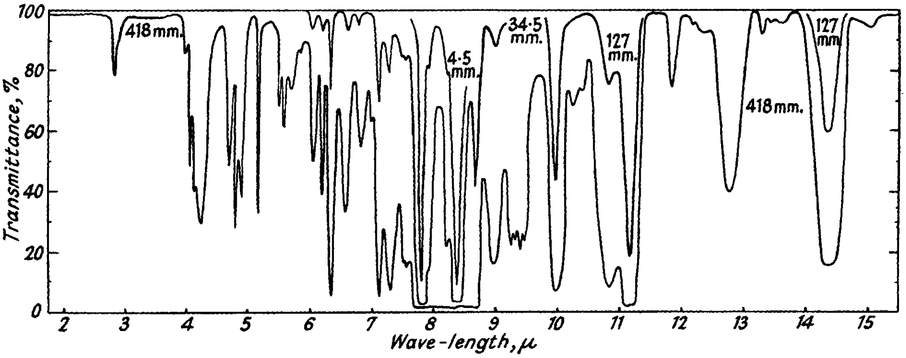
$$\begin{array}{l} CF_3\cdot CH\cdot CH_2\cdot CF_3 \\ CF_3\cdot CH\cdot CH_2 \\ \;\;\;\;\;\;\;\; CF_3\cdot CH\cdot CH_2I \end{array}$$

(IV)

material showed the presence of *trans*-CH=CH– groups and the absence of $>C=CH_2$ groups. Furthermore, trifluoroacetic acid was liberated on oxidation, as expected for compounds containing the $CF_3\cdot CH=CH-$ groups, and a trifluoromethyl ketone (or fluoroform, its hydrolysis product), which would arise by oxidation of compounds containing the $CF_3\cdot C=CH_2$ group, was not detected.

The structure of 1 : 1 : 1 : 4 : 4 : 4-hexafluoro-2-iodobutane is supported by a series of reactions described below, and the direction of addition of trifluoroiodomethane to 3 : 3 : 3-trifluoropropene is established. Still on the assumption that with trifluoroiodomethane and hydrogen bromide the trifluoromethyl radical and the bromine atom are the attacking entities, it follows that in both cases attack is on the terminal CH_2 group of $CF_3\cdot CH=CH_2$, *i.e.*, that the secondary radicals $CF_3\cdot\dot{C}H\cdot CH_2Br$ and $CF_3\cdot\dot{C}H\cdot CH_2\cdot CF_3$ are more stable than the primary radicals $CF_3\cdot CHBr\cdot CH_2\cdot$ and $(CF_3)_2CH\cdot CH_2\cdot$. In corresponding reactions with propylene, the CF_3 radicals and bromine atom also become attached to the terminal CH_2 group (Haszeldine and Steele, *loc. cit.*). The addition of HX to 3 : 3 : 3-trifluoropropene yields exclusively $CF_3\cdot CH_2\cdot CH_2X$ (X = F, Cl, Br, or OMe) (Henne and Kaye, *J. Amer. Chem. Soc.*, 1950, **72**, 3369; unpublished data from this laboratory), thereby indicating that in ionic reactions the trifluoropropene molecule is polarised as $F_3C \leftarrow \overset{\delta-}{CH}=\overset{\delta+}{CH_2}$. The polarisation for addition of HX to propylene is $CH_3-\overset{\delta+}{CH}=\overset{\delta-}{CH_2}$, so that, if it is *assumed* that the 3 : 3 : 3-trifluoropropene and the propylene molecules are polarised during reactions involving free radicals in the same direction as they are during reactions involving ionic intermediates, then it follows that the direction of addition of the trifluoromethyl radical or the bromine atom is not affected by the polarity of the double bond but depends on other factors, for example, the relative stability of the intermediate radicals. The factors affecting the stability of free radicals outlined earlier (Haszeldine and Steele, *loc. cit.*) with full discussion of the facts and validity of the assumptions made in the last sentence and elsewhere in this paper will be the subject of a later communication in this series.

FIG. 3. $CF_3\cdot C\equiv C\cdot CF_3$ (*vapour in* 64-*mm. cell*).



When 1 : 1 : 1 : 4 : 4 : 4-hexafluoro-2-iodobutane was treated with bromine or chlorine in the presence of light, high yields of the 1 : 1 : 1 : 4 : 4 : 4-hexafluoro-2-bromo- and -chloro-butane were obtained ($CF_3\cdot CH_2\cdot CHI\cdot CF_3 \longrightarrow CF_3\cdot CH_2\cdot CHX\cdot CF_3$). Dehydroiodination of these compounds also yielded *trans*-1 : 1 : 1 : 4 : 4 : 4-hexafluorobutene.

Addition of bromine to *trans*-hexafluorobutene followed by treatment with alcoholic potassium hydroxide yielded 2-bromo-1 : 1 : 1 : 4 : 4 : 4-hexafluorobutene. Reaction with chlorine followed by dehydrochlorination similarly yielded 2-chloro-1 : 1 : 1 : 4 : 4 : 4-

hexafluorobutene. In both cases, a small amount of hexafluorobut-2-yne (first prepared by Henne and Finnegan, *J. Amer. Chem. Soc.*, 1949, **71**, 298, from 2 : 3-dichloro-1 : 1 : 1 : 4 : 4 : 4-hexafluorobutene) was formed by removal of two molecules of hydrogen halide. Further treatment of the hexafluoro-2-halogenobutenes with powdered alkali gave hexafluorobut-2-yne but the yield from the chloro-compound was low. It is clear that $(CF_3)_2CH\cdot CH_2I$ could not have yielded an acetylene by the sequence used. The infra-red spectrum of hexafluorobut-2-yne is shown in Fig. 3; since the molecule is symmetrical, there is no band corresponding to the $-C{\equiv}C-$ stretching vibration (4·65 μ in 3 : 3 : 3-trifluoropropyne; Haszeldine, *J.*, 1951, 2495).

An alternative procedure giving better yields for the conversion of *cis-* or *trans-*hexafluorobut-2-ene into hexafluorobut-2-yne is :

$$CF_3\cdot CH{=}CH\cdot CF_3 \xrightarrow{X_2} CF_3\cdot CHX\cdot CHX\cdot CF_3 \xrightarrow{-HX} CF_3\cdot CH{=}CX\cdot CF_3 \xrightarrow{X_2}$$
$$CF_3\cdot CHX\cdot CX_2\cdot CF_3 \xrightarrow{-HX} CF_3\cdot CX{=}CX\cdot CF_3 \xrightarrow[\text{or AcOH}]{\text{Zn, EtOH}} CF_3\cdot C{\equiv}CCF_3$$

Each step can be effected in high yield if dehydrohalogenation is carried out at low temperature; higher temperatures bring about solvolysis of the allylic trifluoro-groups. Thus, as noted (*J.*, 1951, 2495) for the synthesis $CF_3\cdot CH{=}CH_2 \longrightarrow CF_3\cdot C{\equiv}CH$, the formation of a triple bond adjacent to a CF_3 group is best achieved by removal of the two halogen atoms from adjacent carbon atoms, $CF_3\cdot CX{=}CX- \longrightarrow CF_3\cdot C{\equiv}C-$ rather than by removal of an adjacent halogen as hydrogen halide, $CF_3\cdot CX{=}CH-$ or $CF_3\cdot CH{=}CX- \longrightarrow CF_3\cdot C{\equiv}C-$.

The stepwise hydrogenation of hexafluorobut-2-yne proceeds smoothly, to yield exclusively the *cis*-hexafluorobut-2-ene and 1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane reported by Henne and Finnegan (*loc. cit.*), who deduced that the configuration was *cis* from its appreciable dielectric constant of 20·8 at 20°. Further proof of the configuration of the olefin is given by its infra-red spectrum since, although the olefinic C–H stretching vibration is at 3·23 μ as in the *trans*-isomer, a clear distinction between the isomers can be made by the band due to the $C{=}C$ stretching vibration at 5·95 μ in the *cis*-isomer. The large difference in boiling point between *cis-* (33·5°) and *trans* hexafluorobut-2-ene (8·5°) (cf. *cis-* and *trans*-but-2-ene, b. p. 3·7° and 0·9°) suggests that their heats of hydrogenation should differ appreciably.

Electrophilic addition to olefins containing a polyfluoro-group adjacent to a double bond is difficult, and nucleophilic addition often involves side-reactions. Thus, hydrogen fluoride, chloride, bromide, and iodide can be added to 3 : 3 : 3-trifluoropropene and to 1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-enes only with difficulty (unpublished data). Henne, Smook, and Pelley (*J. Amer. Chem. Soc.*, 1950, **72**, 4756) recently showed that base-catalysed addition of ethanol to 3 : 3 : 3-trifluoropropene yielded some $CF_3\cdot CH_2\cdot CH_2\cdot OEt$, but that the main reaction was solvolysis of the CF_3 group, and Campbell, Knobloch, and Campbell (*ibid.*, p. 4380) report that sodium methoxide, primary amines, and sodiomalonic esters do not add to olefins of the type $CF_3\cdot CH{=}CHR$. It becomes increasingly evident, however, that the addition of free radicals or of atoms to such olefins can proceed more smoothly than reactions involving ionic intermediates, although at a somewhat slower rate than to the corresponding hydrocarbon olefins. Thus, hydrogenation of 3 : 3 : 3-trifluoropropene, hexafluorobut-2-yne, and 1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-enes proceeds readily under mild conditions, and addition of chlorine or bromine to these unsaturated compounds is facilitated by ultra-violet light rather than by polar catalysts.

Further papers in this series will deal with the addition of trifluoroiodomethane to a variety of unsaturated compounds.

EXPERIMENTAL

Preparation of 3 : 3 : 3-*Trifluoropropene.*—This compound was prepared from 1 : 1 : 1-trifluoro-3-iodopropane (Haszeldine, *J.*, 1951, 2495) or from 1 : 1 : 1-trifluoro-3-chloro- or -3-bromo-propane. The last two compounds were products of the treatment of 3-bromo-1 : 1 : 1-trichloropropane with antimony trifluoride (unpublished). Dehydrohalogenation was effected in >90% yields.

Hydrogenation of 3 : 3 : 3-*Trifluoropropene.*—Trifluoropropene (5·0 g.) was treated with hydrogen at 30°/10 atm. in the presence of Raney nickel. Hydrogen absorption was rapid and the yield of 1 : 1 : 1-trifluoropropane (4·9 g.) (*M*, 98), b. p. −13°, was practically quantitative.

Hydrogenation of Trifluoroiodomethane.—Trifluoroiodomethane (3·0 g.) in a series of sealed Pyrex tubes was irradiated at 170° with ultra-violet light in the presence of mercury and a slight excess of hydrogen. Mercuric iodide and traces of trifluoromethylmercuric iodide (Emeléus and Haszeldine, *J.*, 1949, 2948) were deposited. After 24 hours the yield of fluoroform was 81%; 15% of the trifluoroiodomethane was recovered.

When heated with a slight excess of hydrogen to 250° for 48 hours in the absence of light, trifluoroiodomethane (2·0 g.) gave an 89% yield of fluoroform.

There was little reaction when trifluoroiodomethane (2·0 g.) and excess of hydrogen were irradiated in 50-ml. silica vessels at room temperature. A slow reaction took place in the presence of mercury, to give after 72 hours fluoroform (12%), trifluoromethylmercuric iodide (5%), and unchanged trifluoroiodomethane (71%).

Addition of Hydrogen Bromide to 1 : 1 : 1-*Trifluoropropene.*—Trifluoropropene (3·20 g., 0·033 mole) and pure, dry hydrogen bromide (5·40 g., 0·067 mole) were sealed in two silica tubes which had been carefully cleaned and dried to remove traces of materials which might act as catalysts. After 48 hours in the dark at room temperature, no reaction had occurred. The tubes were then irradiated at a distance of 20 cm. by a Hanovia lamp with filter removed. An immediate reaction was apparent at room temperature, and after 18 hours the contents of the tubes were distilled, to give 3-bromo-1 : 1 : 1-trifluoropropane (5·71 g., 97%), b. p. 62—62·5°, n_D^{25} 1·358 (Found: *M*, 176. Calc. for $C_3H_4BrF_3$: *M*, 177). McBee, Hass, Toland, and Truchan (*J. Amer. Chem. Soc.*, 1947, **69**, 944) report b. p. 62—62·5°, n_D^{25} 1·3572. The b. p. of 2-bromo-1 : 1 : 1-trifluoropropane is 49° (Swarts, *Bull. Soc. chim. Belg.*, 1929, **48**, 106; Haszeldine, *J.*, 1951, 2495, reports b. p. 48—50·5°, n_D^{25} 1·350). When the excess of hydrogen bromide was dissolved in water, no unchanged trifluoropropene could be detected.

Addition of Trifluoroiodomethane to 1 : 1 : 1-*Trifluoropropene.*—(a) *Under influence of light.* Trifluoropropene (9·60 g., 0·1 mole), sealed in a series of silica tubes with trifluoroiodomethane (29·4 g., 0·15 mole), was exposed to ultra-violet light at room temperature for 5 days. Reaction was soon apparent and continued steadily during the above period. Only a small amount of iodine was liberated in those tubes where the reaction products were shielded from direct radiation. Distillation of the combined products gave (1) fluoroform (0·30 g., 3%), b. p. *ca.* −80° (Found: *M*, 70. Calc. for CHF_3: *M*, 70), (2) trifluoroiodomethane (13·8 g., 47%), b. p. −22° (Found: *M*, 196. Calc. for CF_3I: *M*, 196), (3) 1 : 1 : 1-trifluoropropane (1·82 g., 19%), (4) 1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane (0·46 g., 3%), b. p. 24—25° (Found: *M*, 165. Calc. for $C_4H_4F_6$: *M*, 166), identical with that prepared below, (5) 1 : 1 : 1 : 4 : 4 : 4-*hexafluoro*-2-*iodobutane* (19·1 g., 65% based on trifluoropropene taken, 81% on trifluoropropene used), b. p. 87·5—88·0°, n_D^{25} 1·371 (Found: C, 16·3; H, 1·0; I, 43·0%; *M*, 290. $C_4H_3F_6I$ requires C, 16·4; H, 1·0; I, 43·5%; *M*, 292), (6) 1 : 1 : 1 : 6 : 6 : 6-*hexafluoro*-2-*iodo*-4-*trifluoromethylhexane* (0·99 g., 5%), b. p. 76—78°/75 mm. (Found: C, 22·1; H, 1·6; I, 32·9. $C_7H_6F_9I$ requires C, 21·6; H, 1·5; I, 32·7%), and (7) higher polymers (0·2 g.).

Trifluoroiodomethane and trifluoropropene have similar b. p.s (−22·5°, −22°), and were separated (fractions 2 and 3), after initial distillation, by treatment with chlorine and a small amount of aluminium trichloride in a sealed tube in the dark; the trifluoroiodomethane was unaffected by this treatment whereas the fluoropropane yielded 2 : 3-dichloro-1 : 1 : 1-trifluoropropane, b. p. 76—77°, the weight of which was used to estimate the amount of fluoropropene recovered.

When trifluoroiodomethane (29·4 g.) and trifluoropropene (4·8 g.) were sealed in a 50-ml. silica tube, and the vapour phase was irradiated for 3 days with the liquid phase shielded from light, the 1 : 1-adduct, 1 : 1 : 1 : 4 : 4 : 4-hexafluoro-2-iodobutane [absorption spectrum in ethanol, $\lambda_{max.}$ 265 mμ (ε 280); $\lambda_{min.}$ 230·5 mμ (ε 84)] was formed in 98% yield. Only a faint colour of iodine was apparent, and fractions (1), (3), (4), (6), and (7) were absent.

(b) *Under influence of heat.* Trifluoropropene (4·80 g.), in Carius tubes with trifluoroiodomethane (14·7 g.), was heated to 225° for 36 hours in the absence of light. More iodine was liberated than in the photochemical reaction. Distillation of the combined product gave fluoroform (0·05 g., 1%) (*M*, 70), trifluoroiodomethane (5·9 g., 40%) (*M*, 196), 1 : 1 : 1-trifluoropropene (0·2 g., 4%), 1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane (0·12 g., 1%), b. p. 22—26°, 1 : 1 : 1 : 4 : 4 : 4-hexafluoro-2-iodobutane (9·93 g.; 68% based on trifluoropropene taken, 71% on trifluoropropene used), b. p. 88—88·5°, n_D^{25} 1·369, 1 : 1 : 1 : 6 : 6 : 6-hexafluoro-2-iodo-4-trifluoromethylhexane (1·07 g., 11%), 1 : 1 : 1 : 8 : 8 : 8-*hexafluoro*-2-*iodo*-4 : 6-*bistrifluoromethyl* *octane* (0·32 g., 4%), b. p. *ca.* 90°/5 mm. (Found: C, 25·0. $C_{10}H_9F_{12}I$ requires C, 24·8%), higher polymer (0·2 g.), and (9) 1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-ene (0·1 g.). The trifluoroiodomethane and trifluoropropene were separated as described earlier.

Dehydroiodination of 1 : 1 : 1 : 4 : 4 : 4-*Hexafluoro-2-iodobutane*.—Cold 10% alcoholic potassium hydroxide (10% excess) was slowly run into the 1 : 1-adduct from the CF_3I–CF_3·CH═CH_2 reaction (2·91 g.) dissolved in ethanol (5 ml.) in a 20-ml. flask cooled to 10° and fitted with water-condenser and rubber connection to traps cooled in liquid air. After 20 minutes the flask was allowed to warm to 25°, then excess of 20% hydrochloric acid was added. No unchanged hexafluoroiodobutane formed as a lower layer. The volatile products in the flask were swept into the liquid-air traps by a stream of nitrogen and were then fractionated *in vacuo*, to give trans-1 : 1 : 1 : 4 : 4 : 4-*hexafluorobut-2-ene* (1·56 g., 95%), b. p. 8·5° (Found: C, 29·7; H, 1·8%; *M*, 164. $C_4H_2F_6$ requires C, 29·3; H, 1·2%; *M*, 164). A compound, b. p. 33·2°, believed to be the *cis*-isomer has been described by Henne and Finnegan (*loc. cit.*).

Oxidation and Hydrogenation of trans-1 : 1 : 1 : 4 : 4 : 4-*Hexafluorobut-2-ene*.—The olefin (1·0 g.) was oxidised with alkaline permanganate as described earlier (*J.*, 1950, 2789). The volatile products were carefully examined and fluoroform and hexafluoroacetone were absent. The trifluoroacetic acid formed was converted into the amide, m. p. 74°, corresponding to 1·7 mols. of acid per mol. of fluorobutene. Some fluoride ion was formed by the oxidation.

When treated with excess of hydrogen in the presence of Raney nickel at 80°/10 atm., *trans*-1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-ene was converted quantitatively into 1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane, identical with that obtained from the *cis*-isomer (see below).

Addition of Bromine and of Chlorine to trans-1 : 1 : 1 : 4 : 4 : 4-*Hexafluorobut-2-ene*.—The butene (1·23 g.), prepard by the method given above, was sealed in a Carius tube with a slight excess of bromine. After irradiation with ultra-violet light for 1 hour, the product was distilled over mercury, to give 2 : 3-*dibromo*-1 : 1 : 1 : 4 : 4 : 4-*hexafluorobutane* (1·96 g., 82%), b. p. 60°/120 mm., *ca.* 118°/760 mm. (Found: C, 15·1; H, 0·9. $C_4H_2Br_2F_6$ requires C, 14·8; H, 0·6%).

Treatment of the butene (1·23 g.) with a slight excess of chlorine, with irradiation for 15 minutes, gave 2 : 3-*dichloro*-1 : 1 : 1 : 4 : 4 : 4-*hexafluorobutane* (1·40 g., 79%), purified in the vacuum system, b. p. (micro) 78° (Found: C, 20·8; H, 0·8%; *M*, 231. $C_4H_2Cl_2F_6$ requires C, 20·4; H, 0·8%; *M*, 235).

Dehydrohalogenation of 1 : 1 : 1 : 4 : 4 : 4-*Hexafluoro*-2 : 3-*dihalogenobutanes*.—A 5% excess of 10% alcoholic potassium hydroxide, cooled to 0°, was added slowly to a stirred solution of 2 : 3-dibromo-1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane (3·22 g.; prepared as described above) in alcohol (3 ml.) at 5°, under a water condenser and with rubber connections to a trap cooled in liquid air. After 1 hour the material was heated at 40° and then at 70° for 10 minutes, cooled, and treated with excess of 20% sulphuric acid. The lower layer, washed with water, dried (phosphoric oxide), and distilled, gave 2-*bromo*-1 : 1 : 1 : 4 : 4 : 4-*hexafluorobut-2-ene* (1·41 g., 58%), b. p. 55° (Found: C, 19·5; H, 0·8%; *M*, 240. C_4HBrF_6 requires C, 19·7; H, 0·4%; *M*, 243), and a small residue of unchanged starting material.

Similar treatment of 2 : 3-dichloro-1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane (2·40 g.) gave 2-chloro-1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-ene (1·61 g., 80%), b. p. 34·5—35·5°, n_D^{25} 1·298 (Found: C, 24·0; H, 0·3%; *M*, 195. Calc. for C_4HClF_6: C, 24·2; H, 0·5%; *M*, 198·5). Henne, Hinkamp, and Zimmerschied (*J. Amer. Chem. Soc.*, 1945, **67**, 1907) report b. p. 34·4°, n_D^{25} 1·2999.

After removal of traces of bromo- and chloro-hexafluorobutenes from the liquid-air traps in the above experiments, the more volatile products were combined and distilled, to give 1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-yne (perfluorobut-2-yne) (0·4 g.) (*M*, 160), identical with a specimen prepared as described below.

The dehydrohalogenation described above led to formation of fluoride ion in solution.

Conversion of 1 : 1 : 1 : 4 : 4 : 4-*Hexafluoro-2-halogeno but-2-enes into* 1 : 1 : 1 : 4 : 4 : 4-*Hexafluorobut-2-yne*.—When the 2-bromohexafluorobutene (3·61 g.) was treated with a 300% excess of powdered potassium hydroxide at 10° and the temperature was then slowly raised to the b. p., the volatile product was 1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-yne (1·64 g., 68%), b. p. −24° (Found: *M*, 162. Calc. for C_4F_6: *M*, 162). Henne and Finnegan (*loc. cit.*) report b. p. −24·7° to −24·5°. Fluoride ion, but no unchanged bromofluorobutane, was found in the reaction vessel.

2-Chloro-1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-ene, similarly treated, gave perfluorobut-2-yne in 36% yield; 8% of the unchanged chloro-compound was recovered from the liquid-air traps.

In an alternative procedure, 2-bromo-1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-ene (2·00 g.) was treated with a slight excess of bromine in ultra-violet light, to give 2 : 2 : 3-*tribromo*-

1 : 1 : 1 : 4 : 4 : 4-*hexafluorobutane* (Found : C, 12·1. $C_4HBr_3F_6$ requires C, 11·9%) as an oil, b. p. 79°/45 mm., *ca.* 163°/760 mm. (after removal of excess bromine and a trace of unchanged starting material *in vacuo*). To the tribromohexafluorobutane cooled in ice was added a slight excess of ice-cooled 10% alcoholic potassium hydroxide. After 30 minutes the temperature was raised to 30°, then to 50°, then an excess of 20% sulphuric acid was added. The lower layer was dried and distilled, to give 2 : 3-*dibromo*-1 : 1 : 1 : 4 : 4 : 4-*hexafluorobut*-2-*ene* (2·07 g., 78%), b. p. 106°, n_{D}^{25} 1·396 (Found : C, 14·9%; *M*, 318. $C_4Br_2F_6$ requires C, 14·9%; *M*, 322). The dibromohexafluorobutene (1·98 g.) was treated with zinc (20 g.) and absolute alcohol (60 ml.) with vigorous stirring under reflux for 4 hours, giving 1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-yne (0·90 g., 90%) (*M*, 162).

Addition of chlorine to 2-chloro-1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-ene (2·5 g.) similarly gave 2 : 2 : 3-trichloro-1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane (92%), b. p. 104°. Treatment of this with 10% alcoholic potassium hydroxide at 20° readily gave 2 : 3-dichloro-1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-ene (see below) in 87% yield. Treatment with zinc and glacial acetic acid then gave the perfluorobutyne in 70% yield.

Bromination and Chlorination of 1 : 1 : 1 : 4 : 4 : 4-*Hexafluorobut*-2-*yne*.—In ultra-violet light, perfluorobutyne (1·61 g.) readily added bromine in the vapour phase, to give 2 : 3-dibromo-1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-ene (3·17 g., 98%), b. p. 105—106°, identical with the compound described earlier.

Mild irradiation of perfluorobutyne (1·60 g.) and chlorine (0·71 g.) gave a quantitative yield of 2 : 3-dichloro-1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-ene, b. p. 68°, n_{D}^{25} 1·344 (Found : *M*, 231. Calc. for $C_4Cl_2F_6$: *M*, 233). Henne, Hinkamp, and Zimmerschied (*loc. cit.*) report b. p. 67·8°, n_{D}^{25} 1·3459.

Hydrogenation of 1 : 1 : 1 : 4 : 4 : 4-*Hexafluorobut*-2-*yne*.—The butyne (2·45 g.) was sealed with hydrogen (1 mol. at 15 atm.) in the presence of Raney nickel catalyst (1 g.) and heated to 60° for 3 hours. Distillation gave the *cis*-1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-ene (91% yield), b. p. 33—33·5°, described by Henne and Finnegan (*loc. cit.*). A small amount of 1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane, b. p. 25°, was also formed.

cis-1 : 1 : 1 : 4 : 4 : 4-Hexafluorobut-2-ene yielded 1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane in almost theoretical yield when heated to 50° with hydrogen (20 atm.) and Raney nickel. The hexafluorobutane, b. p. 24—25° (Found : C, 29·0; H, 2·8%; *M*, 165. Calc. for $C_4H_4F_6$: C, 28·9; H, 2·4%; *M*, 166), was identical with that isolated from the reaction of trifluoroiodomethane with trifluoropropene.

Preparation and Dehydrohalogenation of 2-*Bromo- and* 2-*Chloro*-1 : 1 : 1 : 4 : 4 : 4-*hexafluorobutane*.—The iodine atom in 1 : 1 : 1 : 4 : 4 : 4-hexafluoro-2-iodobutane (2·31 g.) was replaced by bromine by treatment with a slight excess of bromine in the presence of ultra-violet light. The product was washed with water to remove iodine bromide, dried, and distilled over mercury, giving 2-*bromo*-1 : 1 : 1 : 4 : 4 : 4-*hexafluorobutane* (1·57 g., 81%) b. p. 70° (Found : C, 19·5; H, 1·3%; *M*, 242. $C_4H_3BrF_6$ requires C, 19·6; H, 1·2%; *M*, 245).

Similarly, treatment of the iodo-compound (2·31 g.) with chlorine gave iodine monochloride and 2-*chloro*-1 : 1 : 1 : 4 : 4 : 4-*hexafluorobutane* (1·21 g., 76%), b. p. 51°, n_{D}^{25} 1·298 (Found : C, 23·7; *M*, 200. $C_4H_3ClF_6$ requires C, 23·9%; *M*, 200·5).

A slight excess of ice-cold 10% alcoholic potassium hydroxide was added to 2-chloro-1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane (1·0 g.) in absolute alcohol (2 ml.), cooled in ice. The mixture was stirred and the temperature allowed to rise, volatile products passing through a water-condenser and being collected in a liquid-air trap. After heating to 50°, excess of 20% hydrochloric acid was added. No unchanged chloro-compound was found and the aqueous solution contained only a trace of fluoride ion. The volatile product (88% yield) was shown to be *trans*-1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-ene.

The 2-bromohexafluorobutane (1·4 g.), similarly treated, gave an 85% yield of the *trans*-olefin. The b. p. of the combined product was 8—9°.

Dehydroiodination of the 1 : 2- *and* 1 : 3-*Adducts of Trifluoroiodomethane and* 3 : 3 : 3-*Trifluoropropene*.—A 5% excess of 10% alcoholic potassium hydroxide was run at 0° into a solution of 1 : 1 : 1 : 6 : 6 : 6-hexafluoro-2-iodo-4-trifluoromethylhexane (0·6 g.) in absolute ethanol (1 ml.). After warming to 25°, the mixture was treated with excess of 10% hydrochloric acid, and the organic layer was separated and dried (phosphoric oxide). The 1 : 3-adduct, 1 : 1 : 1 : 8 : 8 : 8-hexafluoro-2-iodo-4 : 6-bistrifluoromethyloctane (0·2 g.), was similarly treated. Infra-red spectroscopic examination in the 6-μ and 9·5—15-μ region indicated the presence of a *trans*-$\cdot CH{=}CH\cdot$ double bond in each case (weak band at 5·9 μ and strong band at 10·3—10·4 μ), and the absence of $R_2C{=}CH_2$ (absence of strong bands at 6·0—6·1 and *ca.* 11·2 μ). Fusion with sodium showed that dehydroiodination had been complete. The unsaturated products were probably 1 : 1 : 1 : 6 : 6 : 6-hexafluoro-4-trifluoromethylhex-2-ene and 1 : 1 : 1 : 8 : 8 : 8-hexafluoro-4 : 6-bistrifluoromethyloct-2-ene. Each was oxidised by alkaline permanganate as described above and yielded trifluoroacetic acid, identified as the amide, m. p. 74°; fluoroform was not a product of reaction, and tests for ketones were negative.

Spectra.—Infra-red spectra were determined on a Perkin–Elmer Double Beam Spectrophotometer Model 21 with sodium chloride optics. Volatile compounds were contained in a gas-cell, of length indicated, with sodium chloride windows. Pressures were measured to 1 mm. Ultra-violet spectra were taken with Beckman Model DU and Unicam Spectrophotometers.

A. L. Henne and M. Nager report (personal communication) that they have recently added trifluoroiodomethane and bromotrichloromethane to trifluoropropene.

The author acknowledges the technical assistance of R. D. Elsey and E. Liddell in the determination of the infra-red and ultra-violet spectra.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, December* 18*th*, 1952.]