716. *Addition of Free Radicals to Unsaturated Systems. Part V.* The Direction of Addition to* 1 : 1-*Difluoroprop*-1-*ene,* 3 : 3 : 3-*Trifluoro*-2-*trifluoromethylprop*-1-*ene, and* 3-*Chloro*-3 : 3-*difluoro*-2-*trifluoromethylprop*-1-*ene.*

By R. N. Haszeldine.

Attack on 1 : 1-difluoroprop-1-ene by a CF_3 or CCl_3 radical or by a bromine atom is exclusively on the $:CH\cdot$ group, thus showing that radical addition can take place in the opposite direction to that predicted only from steric factors. Radical attack on $CF_3\cdot CR:CH_2$ ($R = CF_3$ or CF_2Cl) is on the CH_2 group. Theories of free-radical stability are discussed briefly, and in at least one example the hyperconjugative stabilisation of a radical by hydrogen on the β-carbon atom in $C\cdot\overset{\beta}{C}\cdot\overset{\alpha}{C}\cdot$ is shown to be of less importance than replacement of hydrogen on the α-carbon atom by any other atom or group. On this basis radical stability decreases in the order tertiary > secondary > primary, where the terms tertiary, secondary, and primary indicate the number of atoms or groups other than hydrogen attached to the α-carbon atom, *i.e.*, $\geqslant C\cdot$ $>CH\cdot$, and $-CH_2\cdot$, and do not necessarily refer to the carbon skeleton.

Syntheses for the olefins $CF_3\cdot CMe:CF_2$, $CCl_3\cdot CMe:CF_2$, $CClF_2\cdot CMe:CCl_2$, $CF_3\cdot CMe:CCl_2$, $(CF_3)(CClF_2)C:CH_2$, $(CF_3)_2C:CH_2$, $(CF_3)(CF_3\cdot CH_2)C:CF_2$, and $(CF_3)_2C:CH\cdot CF_3$ are presented. The polarisation of certain of these during reactions involving ionic intermediates can be represented as $CH_3\cdot\overset{\delta-}{C}H{=}\overset{\delta+}{C}F_2$, $CF_3\cdot\overset{\delta-}{C}Me{=}\overset{\delta+}{C}F_2$, $(CF_3)_2\overset{\delta-}{C}{=}\overset{\delta+}{C}H_2$, and $(CF_3)(CClF_2)\overset{\delta-}{C}{=}\overset{\delta+}{C}H_2$. New syntheses for the ketones $CF_3\cdot CO\cdot CH_3$, $CF_3\cdot CO\cdot CF_3$, and $CF_3\cdot CH_2\cdot CO\cdot CF_3$ are described.

In previous papers the direction of addition of a trifluoromethyl radical to the olefins $R\cdot CH:CH_2$ ($R = Me$, Cl, F, CO_2Me, CF_3, or CN), $CF_2:CClF$, and $CF_3\cdot CF:CF_2$ has been unambiguously shown to be exclusively to the $:CH_2$ or $:CF_2$ groups. A full discussion of these results has been deferred until later in this series, but as pointed out (Part III, *J.*, 1953, 1592), one explanation of the marked specificity of radical attack is that the carbon atom attacked is the one most favoured on steric grounds, *i.e.*, the terminal $:CX_2$ ($X = H$ or F) group. There is no doubt that the steric factor is of importance, but evidence is now presented to show that radical addition can occur contrary to that predicted on steric grounds alone.

Trifluoroiodomethane reacts smoothly with 1 : 1-difluoroprop-1-ene on exposure to ultra-violet light, to give only the addition product, which might be (I) or (II). It is noteworthy that, as found with propylene (*J.*, 1953, 1199), no, or only very slight, abstraction of allylic hydrogen atoms occurs despite the possibility for resonance stabilisation of the resultant radical ($\cdot CH_2\cdot CH:CF_2 \longleftrightarrow CH_2:CH\cdot CF_2\cdot$). That the constitution of the product is exclusively (I) follows from its ready dehydro-iodination by powdered potassium hydroxide to 1 : 1 : 3 : 3 : 3-pentafluoro-2-methylpropene (III) (83%); (II) where the iodine atom is adjacent to the pentafluoroethyl group and consequently would be difficult to remove (cf. *J.*, 1951, 2495), would have given (IV) by this procedure. The presence of the $C:CF_2$ group in (III) is shown by the characteristic $C:C$ stretching absorption at 5·64 μ, and by oxidation of the olefin to trifluoroacetone. The $CH:CH_2$ group (cf. IV) is characterised by its $C:C$ stretching vibration at 6·0 μ as in 3 : 3 : 3-trifluoropropene; furthermore, oxidation of (IV) is known to yield pentafluoropropionic acid and not trifluoroacetone. Examination of infra-red spectra and of the oxidation products showed that a mixture of (III) and (IV) was not present.

$CF_3\cdot CHMe\cdot CF_2I$	$CF_3\cdot CF_2\cdot CHI\cdot CH_3$	$CF_3\cdot CMe:CF_2$	$C_2F_5\cdot CH:CH_2$
(I)	(II)	(III)	(IV)

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* Part IV, preceding paper.

Thus, with a chain mechanism of the type outlined earlier :

$$CF_3I \xrightarrow{h\nu} CF_3\cdot + I\cdot$$

$$\text{Initiation:} \quad CF_3\cdot + CH_3{\cdot}CH{:}CF_2 \longrightarrow CF_3{\cdot}CHMe{\cdot}CF_2\cdot$$

$$\text{Transfer:} \quad CF_3{\cdot}CHMe{\cdot}CF_2\cdot + CF_3I \longrightarrow CF_3{\cdot}CHMe{\cdot}CF_2I + CF_3\cdot \longrightarrow \text{etc.}$$

it follows that attack of the trifluoromethyl radical is exclusively on the $:CH\cdot$ group of 1 : 1-difluoroprop-1-ene.

The reaction of bromotrichloromethane with 1 : 1-difluoroprop-1-ene is more difficult to effect than for trifluoroiodomethane, but with acetyl peroxide as initiator a 1 : 1 addition product was isolated. This was shown to be 1-bromo-3 : 3 : 3-trichloro-1 : 1-difluoro-2-methylpropane (V) by dehydrohalogenation to a mixture of (VI) and (VII), which were not separated but whose presence may be inferred since treatment of the mixture with antimony trifluorodichloride gave the known 1 : 1 : 3 : 3 : 3-pentafluoro-2-methylpropene and 1 : 1-dichloro-3 : 3 : 3-trifluoro-2-methylpropene :

$$CH_3{\cdot}CH{:}CF_2 \xrightarrow{CCl_3Br} \underset{(V)}{CCl_3{\cdot}CHMe{\cdot}CF_2Br} \xrightarrow{KOH-EtOH} \underset{(VI)}{CCl_3{\cdot}CMe{:}CF_2} + \underset{(VII)}{CCl_2{:}CMe{\cdot}CF_2Br}$$

$$CCl_3{\cdot}CMe{:}CF_2 \xrightarrow{SbF_3Cl_2} CF_3{\cdot}CMe{:}CF_2 \qquad CCl_2{:}CMe{\cdot}CF_2Br \xrightarrow{SbF_3Cl_2} CF_3{\cdot}CMe{:}CCl_2$$

It is also possible that (VI) might undergo allylic rearrangement to give 1 : 1 : 3-trichloro-3 : 3-difluoro-2-methylpropene in presence of antimony fluoride, and thence 1 : 1-dichloro-3 : 3 : 3-trifluoro-2-methylpropene. The ease of replacement of chlorine or bromine by fluorine shows that the halogen atoms replaced must have been allylic (cf. Haszeldine, *J.*, 1953, 3371). If the reaction of bromotrichloromethane with 1 : 1-difluoropropene had given the compound $CCl_3{\cdot}CF_2{\cdot}CHBr{\cdot}CH_3$, subsequent reaction with ethanolic potassium hydroxide could have removed only hydrogen bromide, to give $CCl_3{\cdot}CF_2{\cdot}CH{:}CH_2$ which, since the chlorine atoms are not allylic, could not readily yield a pentafluorobutene; nor could it yield a 1 : 1-dihalogenotrifluoro*iso*butene.

If it is assumed that the acetyl peroxide removes a bromine atom from bromotrichloromethane so that the trichloromethyl radical initiates the attack on 1 : 1-difluoropropene, the above results show that the trichloromethyl radical, like the trifluoromethyl radical, attacks the $:CH\cdot$ group.

The aluminium chloride-catalysed reaction of hydrogen chloride with 1 : 1-difluoroprop-1-ene yields only 1-chloro-1 : 1-difluoropropane, whose constitution follows from the boiling point (25°) (cf. $CHF_2{\cdot}CHCl{\cdot}CH_3$ 52°, $CH_3{\cdot}CF_2{\cdot}CH_2Cl$ 55°) and from the formation of only 1 : 1 : 1-trifluoropropane on treatment with antimony trifluoride. Hydrogen bromide does not react with 1 : 1-difluoropropene in the dark, and the aluminium bromide-catalysed reaction gives only 1-bromo-1 : 1-difluoropropane (b. p. 46°; cf. $CHF_2{\cdot}CHBr{\cdot}CH_3$ b. p. 72·5°, $CHF_2{\cdot}CH_2{\cdot}CH_2Br$, b. p. 93°), converted by antimony trifluoride into 1 : 1 : 1-trifluoropropane. The polarisation of 1 : 1-difluoropropene during reactions involving ionic intermediates is thus $CH_3{\cdot}\overset{\delta-}{CH}{=}\overset{\delta+}{CF_2}$.

The photochemical reaction of hydrogen bromide with 1 : 1-difluoropropene yields only 2-bromo-1 : 1-difluoropropane (93%). The free-radical and ionic reactions are thus very distinct and, as regards the direction of addition, the bromine atom acts like the trihalogenomethyl radicals :

$$HBr \xrightarrow{h\nu} H\cdot + Br\cdot$$

$$Br\cdot + CH_3{\cdot}CH{:}CF_2 \longrightarrow CH_3{\cdot}CHBr{\cdot}CF_2\cdot \xrightarrow{HBr} CH_3{\cdot}CHBr{\cdot}CHF_2 + Br\cdot \longrightarrow \text{etc.}$$

The reaction of 1 : 1 : 3 : 3 : 3-pentafluoro-2-methylpropene with hydrogen chloride is more difficult to effect than that of 1 : 1-difluoropropene, but again only one product (VIII) is formed; its constitution follows from its conversion into the known 1 : 1 : 1 : 3 : 3 : 3-hexafluoro-2-methylpropane :

$$CF_3{\cdot}CMe{:}CF_2 \xrightarrow{HCl} \underset{(VIII)}{CF_3{\cdot}CHMe{\cdot}CF_2Cl} \xrightarrow{SbF_3Cl_2} (CF_3)_2CHMe$$

The aluminium bromide-catalysed reaction of hydrogen bromide with pentafluoro-2-methylpropene similarly gave 1-bromo-1 : 1-difluoro-2-trifluoromethylpropane. The decreased ease of reaction with electrophilic reagents of pentafluoro-2-methylpropene relative to 1 : 1-difluoropropene is attributed to the deactivating influence of the electron-withdrawing trifluoromethyl group on the unsaturation electrons: the inductive ($F_3C \multimap CMe{:}CF_2$) and hyperconjugative ($F^-CF_2{:}CMe{\cdot}CF_2^+$) effects of the fluoroalkyl group, and the inductive effect of the vinylic fluorine atoms act in the same direction to give the overall polarisation $CF_3{\cdot}\overset{\delta-}{C}Me{=}\overset{\delta+}{C}F_2$ [cf. $CH_3{\cdot}CH{:}CF_2$ where the inductive and hyperconjugative effects of the CH_3 group ($CH_3 \rightarrowtail CH{:}CF_2$; $H^+ CH_2{:}CH{\cdot}CF_2^-$) oppose the inductive effect of the fluorine atoms].

3 : 3 : 3-Trifluoro-2-trifluoromethylprop-1-ene (IX) was synthesised as follows:

$$CF_3{\cdot}CMe{:}CF_2 \xrightarrow{Cl_2} CF_3{\cdot}CMeCl{\cdot}CF_2Cl \xrightarrow{KOH} \underset{(X)}{(CF_3)(CF_2Cl)C{:}CH_2} \xrightarrow{SbF_3Cl_2} \underset{(IX)}{(CF_3)_2C{:}CH_2}$$

Dehydrochlorination of the dichloro-compound is difficult, since the chlorine atom to be removed is adjacent to a polyfluoroalkyl group and is consequently unreactive (cf. Haszeldine, *J.*, 1951, 2459), and is best effected by solid potassium hydroxide. The product, 3-chloro-3 : 3-difluoro-2-trifluoromethyl-prop-1-ene (X) contains an allylic chlorine atom which is readily converted into a trifluoromethyl group. The hexafluoro*iso*butene (IX) was oxidised to hexafluoroacetone in neutral or acid solution, but the yield was low, since there are no halogen atoms attached directly to an olefinic carbon atom (cf. $CF_3{\cdot}CMe{:}CF_2 \longrightarrow CF_3{\cdot}CO{\cdot}CH_3$, above); the yield of hexafluoroacetone was improved by use of the sequence:

$$(CF_3)_2C{:}CH_2 \xrightarrow{Br_2} (CF_3)_2CBr{\cdot}CH_2Br \xrightarrow{KOH} (CF_3)_2C{:}CHBr \xrightarrow{KMnO_4} CF_3{\cdot}CO{\cdot}CF_3$$

The direction of ionic addition to (IX) was shown by reaction with hydrogen chloride or by aluminium bromide-catalysed reaction with hydrogen bromide:

$$(CF_3)_2\overset{\delta-}{C}{=}\overset{\delta+}{C}H_2 + HX \longrightarrow (CF_3)_2CH{\cdot}CH_2X \quad (X = Br \text{ or } Cl)$$

The constitution of the chloro-compound follows from its synthesis by mild chlorination of 1 : 1 : 1 : 3 : 3 : 3-hexafluoro-2-methylpropane [$(CF_3)_2CH{\cdot}CH_3 \longrightarrow (CF_3)_2CH{\cdot}CH_2Cl$]; the chlorination is thus markedly directed, as for 1 : 1 : 1-trifluoropropane and similar compounds (*J.*, 1951, 2495). The constitution of the synthetic chloro-compound follows from the ease with which it is dehydrochlorinated by cold ethanolic potassium hydroxide to 3 : 3 : 3-trifluoro-2-trifluoromethylpropene: this shows that there is an acidic hydrogen atom adjacent to the perfluoroalkyl groups:

$$OH^- \quad H{-}C(CF_3)_2{-}CH_2{-}Cl \longrightarrow H_2O + (CF_3)_2C{:}CH_2 + Cl^-$$

Photochemical reaction of hydrogen bromide with (IX) at −60° (since there was a slow dark reaction at 20°) gave the same product (93%) as from the ionic reaction. 1 : 1 : 1-Trifluoropropene also gives the same product from the ionic or radical addition of hydrogen bromide (Haszeldine, *J.*, 1952, 2504).

The reaction of trifluoroiodomethane with hexafluoro*iso*butene (IX) could give (XI) or (XII). That only (XI) is formed follows from the reaction with powdered or ethanolic

$$\underset{(XI)}{(CF_3)_2CI{\cdot}CH_2{\cdot}CF_3} \qquad \underset{(XII)}{(CF_3)_3C{\cdot}CH_2I} \qquad \underset{(XIII)}{(CF_3)_2C{:}CH{\cdot}CF_3}$$

potassium hydroxide, since the known olefin 1 : 1 : 1 : 4 : 4 : 4-hexafluoro-2-trifluoromethyl-but-2-ene (XIII) was produced (81%); (XII) cannot undergo intramolecular dehydroiodination. The trifluoromethyl radical, like the bromine atom, thus attacks the $:CH_2$ group of an olefin $RR'C{:}CH_2$. This conclusion is supported by the photochemical reaction of 3-chloro-3 : 3-difluoro-2-trifluoromethylprop-1-ene (X) (*i.e.*, $R = CF_3$, $R' = CF_2Cl$) with trifluoroiodomethane to give 1-chloro-1 : 1 : 4 : 4 : 4-pentafluoro-2-iodo-2-trifluoromethylbutane (XIV), the constitution of which followed from two reactions : (*a*) Zinc and ethanol yielded 1 : 1 : 4 : 4 : 4-pentafluoro-2-trifluoromethylbut-1-ene (XV), which on oxidation gave the known hexafluorobutan-2-one (XVI) :

$$(CF_3)(CF_2Cl)C{:}CH_2 \xrightarrow[h\nu]{CF_3I} \underset{\text{(XIV)}}{(CF_3)(CF_2Cl)CI{\cdot}CH_2{\cdot}CF_3} \xrightarrow{\text{Zn-EtOH}}$$

$$\underset{\text{(XV)}}{(CF_3{\cdot}CH_2)(CF_3)C{:}CF_2} \xrightarrow{KMnO_4} \underset{\text{(XVI)}}{CF_3{\cdot}CH_2{\cdot}CO{\cdot}CF_3}$$

(*b*) Dehydroiodination of (XIV) yielded (XVII) which, since it contains an allylic chlorine atom, was readily converted by antimony trifluoride into (XIII) :

$$\text{(XIV)} \xrightarrow{KOH} \underset{\text{(XVII)}}{(CF_3)(CF_2Cl)C{:}CHCF_3} \xrightarrow{SbF_3Cl_2} \underset{\text{(XIII)}}{(CF_3)_2C{:}CHCF_3}$$

Discussion.—The direction of addition of a trifluoromethyl radical or of a bromine atom to olefins $R{\cdot}CH{:}CH_2$ was established earlier (Part II, *J.*, 1953, 1199), and the present work shows that for $CRR'{:}CH_2$ ($R = CF_3$, $R' = CF_3$ or CF_2Cl) attack is again on the methylene group (to an extent of at least 80—90% and probably exclusively). Of the three theories considered earlier, the first, that a radical may be considered as an electrophilic reagent and thus adds to the more electronegative carbon atom of the olefin, may be discarded (see also Parts I—III, *locc. cit.*), if it is assumed that the polarisation of the olefin during radical attack is the same as that shown during attack by ionic reagents, *e.g.*, $RR'\overset{\delta-}{C}{=}\overset{\delta+}{C}H_2$, as above, although this theory would predict correctly for $CH_3{\cdot}\overset{\delta-}{C}H{=}\overset{\delta+}{C}F_2$.

The second theory, that radical attack is on the carbon atom most susceptible to attack on steric grounds, could explain all the results obtained hitherto, although, since fluorine is only slightly larger than hydrogen, it it difficult to account for the marked specificity of attack on an olefin such as vinyl fluoride. The results with 1 : 1-difluoroprop-1-ene reveal for the first time that addition can occur (to an extent of at least 85—95% and probably exclusively) to other than the terminal carbon atom in a system containing a terminal double bond.

The third theory—that the stability of the intermediate free radical determines the orientation in radical addition reactions—will be discussed in detail later. It may be noted at this stage, however, that the results given above show that the tertiary radicals $(CF_3)_2\dot{C}{\cdot}CH_2{\cdot}CF_3$, $(CF_3)(CF_2Cl)\dot{C}{\cdot}CH_2{\cdot}CF_3$, and $(CF_3)_2\dot{C}{\cdot}CH_2Br$ are more stable than the corresponding primary radicals $(CF_3)_3C{\cdot}CH_2{\cdot}$, $(CF_3)_2(CF_2Cl)C{\cdot}CH_2{\cdot}$, and $(CF_3)(CF_2Cl)CBr{\cdot}CH_2{\cdot}$. The results also show that the order of radical stability is not always tertiary > secondary > primary, since the primary (by carbon skeleton) radicals $CF_3{\cdot}CHMe{\cdot}CF_2{\cdot}$, $CCl_3{\cdot}CHMe{\cdot}CF_2{\cdot}$, and $CHMeBr{\cdot}CF_2{\cdot}$ are more stable than the secondary (by carbon skeleton) radicals $CH_3{\cdot}\dot{C}H{\cdot}CF_2{\cdot}CF_3$, $CH_3{\cdot}\dot{C}H{\cdot}CF_2{\cdot}CCl_3$, and $CH_3{\cdot}\dot{C}H{\cdot}CF_2Br$ (see also below).

One may regard an increase in radical stability as caused (*a*) by replacement of hydrogen attached to the carbon atom formally carrying the lone electron by *any other* atom or group, or (*b*) by the hyperconjugative stabilisation which becomes possible when hydrogen is on the carbon atom *adjacent* to that carrying the lone electron. Both effects operate in the same direction in many examples : thus the radical $(CF_3)_2\dot{C}{\cdot}CH_2{\cdot}CF_3$ could be regarded as more stable than $(CF_3)_3C{\cdot}CH_2{\cdot}$, since by (*a*) it has no hydrogen atoms attached to the carbon atoms carrying the lone electron and, by (*b*), it is stabilised by resonance forms of the type $(CF_3)_2C{:}\underset{H\cdot}{C}H{\cdot}CF_3$ which the second radical cannot show. For the radicals which might be formed by addition of the trifluoromethyl radical to 1 : 1-difluoropropene, however, (*a*) and (*b*) do not operate in the same sense. If (*a*) were all-important the radical $CF_3{\cdot}CHMe{\cdot}CF_2{\cdot}$ would be more stable than the radical $CH_3{\cdot}\dot{C}H{\cdot}CF_2{\cdot}CF_3$; whereas, if (*b*) were all-important, radical $CH_3{\cdot}\dot{C}H{\cdot}CF_2{\cdot}CF_3$, which has three hydrogen atoms available for resonance stabilisation of the type H· $CH_2{:}\dot{C}H{\cdot}CF_2{\cdot}CF_3$, would be the more stable. The experimental result indicates that $CF_3{\cdot}CHMe{\cdot}CF_2{\cdot}$ is more stable than $CH_3{\cdot}\dot{C}H{\cdot}CF_2{\cdot}CF_3$, *i.e.*, in this example at least, (*a*) is more important than (*b*). If this important postulate is adopted, *viz.*, that radical stability decreases as the number of hydrogen atoms attached directly to the carbon atom carrying the lone electron is increased, then we have, for decreasing radical stability, tertiary (*i.e.*, $\geqslant$C·) > secondary (*i.e.*, >CH·) > primary (*i.e.*, $-CH_2\cdot$), where the terms primary, secondary, and tertiary indicate not the carbon skeleton, but the ***number of atoms or groups other than hydrogen*** which are attached to the carbon atom formally carrying the lone electron. Into this classification fall all free radicals so far studied. There is clearly the possibility, however, that, by suitable choice of groups R and R′ in a secondary radical RR′CH·, the stability of a secondary radical can be made greater than that of a tertiary radical. Evidence that this can actually occur, and a discussion of other examples of relative radical stability, will be presented later.

EXPERIMENTAL

Experiments were carried out in Pyrex (30 ml.) or silica (100 ml.) tubes with stringent precautions to exclude air, moisture, etc., which might catalyse ionic or free-radical reactions. The tubes were filled from a vacuum system and sealed whilst evacuated. 1 : 1-Difluoroprop-1-ene was prepared as described earlier (Haszeldine, *J.*, 1953, 3371).

Reactions of 1 : 1-*Difluoroprop*-1-*ene*.—(a) *With trifluoroiodomethane*. A silica tube containing the olefin (4·2 g.) and trifluoroiodomethane (16·1 g.) was irradiated by a Hanovia lamp at a distance of 10 cm. for 2 weeks with the liquid phase shielded from light. Distillation then gave unchanged reactants and 1 : 1 : 1 : 3 : 3-*pentafluoro*-3-*iodo*-2-*methylpropane* (I) (77%), b. p., 95°/760 mm., 57°/200 mm., n_D^{20} 1·394 (Found : C, 17·5; H, 1·6%; *M*, 271. $C_4H_4F_5I$ requires C, 17·5; H, 1·4%; *M*, 274); fluoroform was not a reaction product, and only a small amount of iodine was liberated.

The reaction between 1 : 1-difluoroprop-1-ene (1·2 g.) and trifluoroiodomethane (4·0 g.) in a Pyrex vessel was much slower and after 2 weeks' irradiation the yield of (I) was 30%; its identity with the product obtained above was shown by comparison of infra-red spectra. It showed ultra-violet spectrum in light petroleum : $\lambda_{max.}$ 270 mμ, ε 330; $\lambda_{min.}$ 238, ε 120.

The iodo*iso*butane (3·1 g.) was dissolved in ethanol (5 ml.), cooled to 0°, and stirred; to it was added dropwise ice-cold 10% ethanolic potassium hydroxide (10% excess). Air was passed through the apparatus to sweep out evolved gases, and the reaction mixture was heated to boiling and allowed to cool. An excess of water was then added. The gaseous product was fractionated, to give 1 : 1 : 3 : 3 : 3-pentafluoro-2-methylpropene (69%), b. p. 13·8° (isoteniscope) (Found : C, 32·6; H, 1·9%; *M*, 146. Calc. for $C_4H_3F_5$: C, 32·9; H, 2·1%; *M*, 146). Henne, Shepard, and Young (*J. Amer. Chem. Soc.*, 1950, **72**, 3577) report b. p. 12·8—13·5°/745 mm. for this compound. The pentafluoro-2-methylpropene was obtained in 83% yield by addition of the iodo*iso*butane dropwise to thoroughly dried, powdered potassium hydroxide heated at 30° and later at 80°.

The decrease in b. p. of 4—5° caused by chain branching in the fluorobutenes is shown by comparison of $CF_3{\cdot}CMe{:}CF_2$ (13·8°, this paper) and $CF_3{\cdot}CH_2{\cdot}CH{:}CF_2$ (18·6°, unpublished results), and of $CF_3{\cdot}CMe{:}CH_2$ (6·3°; Swarts, *Bull. Soc. chim. Belg.*, 1927, **36**, 191) and of $CF_3{\cdot}CH_2{\cdot}CH{:}CH_2$ (10·6°; Leedham and Steele, unpublished).

(b) *With hydrogen bromide*. The olefin (1·9 g.) and anhydrous hydrogen bromide (10% excess) were sealed in a silica tube and irradiated for 4 days, with the lower half of the tube shielded from light. This irradiation time is probably longer than that necessary for complete reaction. Distillation gave 2-bromo-1 : 1-difluoropropane (93%), b. p. 72—73° (Found : *M*, 159. Calc. for $C_3H_5BrF_2$: *M*, 159). McBee, Hass, Thomas, Toland, and Truchan (*J. Amer. Chem. Soc.*, 1947, **69**, 944) report b. p. 72·6° for this compound.

Hydrogen bromide did not react with 1 : 1-difluoroprop-1-ene in the dark. When hydrogen bromide and the olefin (weights as above) were sealed with aluminium bromide (0·2 g.) and kept at 20° for 2 days the product was 1-*bromo*-1 : 1-*difluoropropane* (53%), b. p. 46—46·5° (Found : C, 22·3; H, 3·1%; *M*, 158. $C_3H_5BrF_2$ requires C, 22·6; H, 3·1%; *M*, 159), and unchanged reactants, but no material with b. p. >50°. The bromofluoropropane, sealed with antimony trifluoride (5 g.) and antimony trifluorodichloride (3 g.), and heated to 120°, gave

1 : 1 : 1-trifluoropropane (63%), b. p. −13° (Found: *M*, 98. Calc. for $C_3H_5F_3$: *M*, 98), identified spectroscopically.

(c) *With hydrogen chloride.* 1 : 1-Difluoroprop-1-ene (1·1 g.), anhydrous hydrogen chloride (30% excess), and aluminium chloride (0·01 g.) were heated to 150° for 12 hr. Distillation gave 1-chloro-1 : 1-difluoropropane (68%), b. p. 25° (isoteniscope) (Found: *M*, 113. Calc. for $C_3H_5ClF_2$: *M*, 114·5). Henne and Whaley (*ibid.*, 1942, **64**, 1157) report b. p. 25·8°. Reaction of the chlorofluoro-compound with antimony fluorides as described above gave 1 : 1 : 1-trifluoropropane, identified spectroscopically.

(d) *With bromotrichloromethane.* 1 : 1-Difluoroprop-1-ene (4·6 g.), bromotrichloromethane (20 ml.), and acetyl peroxide (0·9 g.) were shaken in a small autoclave for 18 hr. at 100°, to give unchanged fluoropropene (10%), bromotrichloromethane, and a fraction of higher b. p. which was distilled through a short column to give 1-*bromo*-3 : 3 : 3-*trichloro*-1 : 1-*difluoro*-2-*methylpropane* (65%), b. p. 60—65°/*ca.* 0·1 mm. (Found: C, 20·8; H, 1·8. $C_4H_4BrCl_3F_2$ requires C, 20·7; H, 1·7%). To the last compound, dissolved in ethanol (20 ml.), was added with stirring a 10% excess of 10% ethanolic potassium hydroxide; the reaction was completed by heating at 40° for 10 min. The lower layer obtained by addition of an excess of hydrochloric acid was dried (P_2O_5), sealed immediately with antimony trifluorodichloride (30 g.), and, after being set aside at 20° for 12 hr., was heated to 80° for 1 hr. Distillation gave 1 : 1 : 3 : 3 : 3-pentafluoro-2-methylpropene (31%), identical with the material described above, and 1 : 1-dichloro-3 : 3 : 3-trifluoro-2-methylpropene (42%), b. p. 88—88·5° (Found: C, 26·4; H, 1·5%; *M*, 180. Calc. for $C_4H_3Cl_2F_3$: C, 26·8; H, 1·7%; *M*, 179). Henne *et al.* (*loc. cit.*) report b. p. 88·4° for the last compound.

Reactions of 1 : 1 : 3 : 3 : 3-*Pentafluoro*-2-*methylpropene*.—(a) *Oxidation.* The olefin (0·8 g.) was shaken with an excess of acidified potassium permanganate for 24 hr., and the mixture was then heated to 80° for 2 hr. The volatile product contained no pentafluoro-2-methylpropene. The material obtained by treatment of the aqueous phase in the usual way with sulphur dioxide, followed by ether-extraction, removal of the ether, and treatment of the residual ketone hydrate with phosphoric oxide, was combined with the volatile reaction product. Treatment with 2 : 4-dinitrophenylhydrazine gave 1 : 1 : 1-trifluoroacetone 2 : 4-dinitrophenylhydrazone (40% based on pentafluoro-2-methylpropene), m. p. 138°, identified by comparison of its spectrum with that of a known sample (Haszeldine and Leedham, *J.*, 1952, 3483); in a later experiment a specimen of the trifluoroacetone was identified by its b. p. (21°) and its infra-red spectrum.

(b) *With hydrogen chloride.* The olefin (2·1 g.) and anhydrous hydrogen chloride (50% excess) were heated stepwise during 48 hr. to 210°, to give 1-*chloro*-1 : 1 : 3 : 3 : 3-*pentafluoro*-2-*methylpropane* (56%), b. p. 58—59° (Found: C, 26·2; H, 2·5%; *M*, 181. $C_4H_4ClF_5$ requires C, 26·3; H, 2·2%; *M*, 182·5), and unchanged reactants. Treatment of the product with antimony trifluorodichloride (5 g.) at 140° for 2 hr. gave 1 : 1 : 1 : 3 : 3 : 3-hexafluoro-2-methylpropane (*ca.* 70%), b. p. 20° (isoteniscope) (Found: *M*, 166. Calc. for $C_4H_4F_6$: *M*, 166). Henne *et al.* (*loc. cit.*) report b. p. 21·5°.

(c) *With hydrogen bromide.* There was no reaction when the pentafluoro*iso*butene (2·2 g.) and anhydrous hydrogen bromide (20% excess) were sealed in a silica tube and kept in the dark. Aluminium bromide (0·2 g.) was added and the resealed tube was heated to 60° for 3 hr., to give 1-*bromo*-1 : 1 : 3 : 3 : 3-*pentafluoro*-2-*methylpropane* (45%), b. p. 78° (Found: C, 21·1; H, 2·0%; *M*, 225. $C_4H_4BrF_5$ requires C, 21·1; H, 1·8%; *M*, 227), and unchanged reactants. The bromo-compound (0·9 g.) gave a 69% yield of 1 : 1 : 1 : 3 : 3 : 3-hexafluoro-2-methylpropane (*M*, 166) when heated with antimony trifluorodichloride at 120°.

(d) *With chlorine.* Pentafluoro*iso*butene (2·7 g.) and a slight excess of chlorine, exposed to sunlight for 20 min., gave 1 : 2-dichloro-1 : 1 : 3 : 3 : 3-pentafluoro-2-methylpropane (100%), b. p. 75—76°, n_D^{23} 1·345 (Found: C, 22·2; H, 1·7%; *M*, 217. Calc. for $C_4H_3Cl_2F_5$: C, 22·1; H, 1·4%; *M*, 217).

The dichloro-compound (6·1 g., prepared as above) was dripped slowly on to a mass of finely powdered, anhydrous potassium hydroxide (200 g.) heated at 50° in a flask fitted with a short column and a still-head. The still-head was operated under total reflux initially, but as the temperature of the potassium hydroxide was slowly raised to 120°, the material of b. p. $<60°$ was removed through the still-head. The total reaction time was 2 days. Redistillation gave 3-*chloro*-3 : 3-*difluoro*-2-*trifluoromethylprop*-1-*ene* (28%), b. p. 52—55° (Found: C, 26·3; H, 1·5%; *M*, 178. $C_4H_2ClF_5$ requires C, 26·6; H, 1·1%; *M*, 180·5), which was immediately treated with antimony trifluorodichloride (20 g.) at 20° (5 hr.), then 50° (3 hr.), to give 3 : 3 : 3-*trifluoro*-2-*trifluoromethylprop*-1-*ene* (93% based on the monochloro-compound), b. p. 11—13°

(isoteniscope) (Found: C, 29·5; H, 1·6%; *M*, 161. $C_4H_2F_6$ requires C, 29·3; H, 1·2%; *M*, 164). The molecular weight of this compound and vapour-pressure measurements suggest that a small amount of impurity may have been present.

Reactions of 3 : 3 : 3-*Trifluoro*-2-*trifluoromethylprop*-1-*ene*.—(a) *Oxidation*. The olefin (2·3 g.) was sealed with acidified aqueous potassium permanganate and heated stepwise to 100° (25 hr.). Treatment with sulphur dioxide, followed by ether-extraction, gave, on removal of the ether, hexafluoroacetone hydrate. This was sealed with an excess of phosphoric oxide and heated to 30° (3 hr.). Fractionation *in vacuo* gave hexafluoroacetone (16%), b. p. −28°, identified by comparison of the spectra of its semicarbazone and 2 : 4-dinitrophenylhydrazone with those of known specimens. The yield of the ketone was improved (55%) when the olefin was treated with bromine and then potassium hydroxide, to give 1-bromo-3 : 3 : 3-trifluoro-2-trifluoromethylprop-1-ene, before the oxidation step.

(b) *With hydrogen bromide*. There was no reaction when the hexafluoro*iso*butene (1·5 g.) and hydrogen bromide (30% excess) were sealed in a silica tube and kept for 48 hr. at −60°, but on exposure to ultra-violet light at this temperature for 10 hr. the formation of a liquid of higher b. p. was observed, and distillation gave 2-*bromomethyl*-1 : 1 : 1 : 3 : 3 : 3-*hexafluoropropane*, (93%), b. p. 78° (Found: C, 19·5; H, 0·9. $C_4H_3BrF_6$ requires C, 19·6; H, 1·2%).

The olefin (1·5 g.), hydrogen bromide (10% excess), and aluminium bromide (0·05 g.), kept in the dark at room temperature for 8 hr., gave the same bromo-compound (81%) (Found: *M*, 240). There was a slow reaction with hydrogen bromide in the absence of the aluminium halide.

(c) *With hydrogen chloride*. The olefin (1·3 g.) and a 20% excess of hydrogen chloride were heated to 180° for 6 hr., to give 2-*chloromethyl*-1 : 1 : 1 : 3 : 3 : 3-*hexafluoropropane* (67%), b. p. 58° (Found: C, 23·7; H, 1·4%; *M*, 200. $C_4H_3ClF_6$ requires C, 23·9; H, 1·5%; *M*, 200·5).

The same chloro-compound (60%) was obtained by irradiation (2 hr.) of 1 : 1 : 1 : 3 : 3 : 3-hexafluoro-2-methylpropane (1·1 g.) and chlorine (0·5 mol.) in a silica tube, the lower portion of which was shielded and cooled to 25°. A small amount of the 1 : 1-dichloro-compound was also isolated.

(d) *With trifluoroiodomethane*. 3 : 3 : 3-Trifluoro-2-trifluoromethylprop-1-ene (2·7 g.) and trifluoroiodomethane (5·3 g.) were sealed in a silica tube and exposed to ultra-violet light for 7 days, to give unchanged reactants and 1 : 1 : 1 : 4 : 4 : 4-*hexafluoro*-2-*iodo*-2-*trifluoromethylbutane* (71%) (Found: C, 16·8; H, 0·5. $C_5H_2F_9I$ requires C, 16·7; H, 0·5%), distilled at low pressure to prevent possible decomposition (b. p. 20—21°/*ca.* 20 mm.). It was divided into two portions (i) and (ii). To (i) was added the theoretical amount of 10% ethanolic potassium hydroxide at 20° and the mixture was heated at 40° (1 hr.). The gas evolved during the reaction was collected, with the gas evolved on acidification (HCl) of the reaction medium, in a trap cooled by liquid oxygen. Portion (ii) was added dropwise to finely powdered anhydrous potassium hydroxide in a flask fitted with reflux condenser at 40°, connected to a liquid-oxygen trap. The reaction temperature was 85°. The same olefin was obtained from (i) (61%) and (ii) (81%). The two fractions were combined and redistilled, to give 1 : 1 : 1 : 4 : 4 : 4-*hexafluoro*-2-*trifluoromethylbut*-2-*ene*, b. p. 33° (Found: C, 26·1; H, 0·4%; *M*, 232. C_5HF_9 requires C, 25·9; H, 0·4%; *M*, 232), shown by its infra-red spectrum to be identical with a specimen prepared by an unambiguous route (unpublished results).

Reaction of 3-*Chloro*-3 : 3-*difluoro*-2-*trifluoromethylprop*-1-*ene with Trifluoroiodomethane*.—The olefin (4·7 g.) was sealed with trifluoroiodomethane (8·0 g.) in a silica tube and exposed to light from a Hanovia lamp at 4 cm. distance for 7 days. The unchanged trifluoroiodomethane and olefin (27%) were removed by distillation, and the residual 1-chloro-1 : 1 : 4 : 4 : 4-pentafluoro-2-iodo-2-trifluoromethylbutane (69%) was divided into two parts.

One part was added dropwise to powdered zinc (5 g.) and refluxing ethanol (10 ml.). After 1 hr. an excess of water was added and the apparatus was swept out with nitrogen. The combined volatile product was purified in a vacuum system, to give 1 : 1 : 4 : 4 : 4-pentafluoro-2-trifluoromethylbut-1-ene (91%) (Found: *M*, 215), and this was sealed with slightly acidified (H_2SO_4) potassium permanganate solution and heated stepwise to 50° during 10 hr. The ketone was isolated as described for hexafluoroacetone and 1 : 1 : 1-trifluoroacetone above, and when treated with semicarbazide yielded 1 : 1 : 1 : 4 : 4 : 4-hexafluorobutan-2-one semicarbazone, m. p. 123° (65%) (cf. Haszeldine, *J.*, 1952, 3490).

The second portion of 1-chloro-1 : 1 : 4 : 4 : 4-pentafluoro-2-iodo-2-trifluoromethylbutane was dehydroiodinated by solid potassium hydroxide by the technique described above, but with a pressure of 400 mm. in the apparatus so that the 1-chloro-1 : 1 : 4 : 4 : 4-pentafluoro-2-trifluoromethylbut-2-ene was removed as soon as formed. The product was sealed immediately with antimony trifluoride (10 g.) which had been activated with chlorine (20% Sb^V salts), and the mixture was heated to 40° for 1 hr. Purification of the gaseous product in a vacuum system gave 1 : 1 : 1 : 4 : 4 : 4-hexafluoro-1-trifluoromethylbut-2-ene (45%), b. p. 32—33° (Found: *M*, 230. Calc. for C_5HF_9: *M*, 232), shown by spectroscopic examination to be identical with the compound described above.

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