Addition of Free Radicals to Unsaturated Systems. Part XI. The Direction of Radical Addition to 1 : 1 : 3 : 3 : 3-Pentafluoropropene, and the Synthesis of Perfluoro-olefins, -ketones, and -acids.*

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A trifluoromethyl radical attacks the CH group of $CF_3{\cdot}CH{:}CF_2$ to give $(CF_3)_2CH{\cdot}CF_2{\cdot}$, thus showing in a second example that free-radical addition can occur to other than the terminal carbon atom in a system containing a terminal double bond. The photochemical reaction of hydrogen bromide with 1 : 1 : 3 : 3 : 3-pentafluoropropene has also been studied.

New convenient routes to perfluoro-olefins $R_FR_F'C{:}CF_2$ (*e.g.*, perfluoro*iso*butene), -ketones $R_F{\cdot}CO{\cdot}R'_F$ (*e.g.*, $C_3F_7{\cdot}CO{\cdot}CF_3$), and -acids $R_F{\cdot}CO_2H$ (*e.g.*, $C_2F_5{\cdot}CO_2H$), where R_F and $R_F' = CF_3{\cdot}[CF_2]_n{\cdot}CF_2$ and n is not necessarily the same in R_F and R_F', are described.

The attack of a trifluoromethyl radical or of a bromine atom is on the CF_2 group in the olefins $CF_2{:}CFCl$ and $CF_3{\cdot}CF{:}CF_2$, and on the CH_2 or CH group in $CH_2{:}CF_2$ and $CH_3{\cdot}CH{:}CF_2$ (Parts III, IV, V, VII, and X, *J.*, 1953, 1592, 3559, 3565; *J.*, 1954, 923, 3747). The direction of free-radical addition to 1 : 1 : 3 : 3 : 3-pentafluoropropene (I) is now reported, with trifluoroiodomethane and hydrogen bromide again used as sources of a trifluoromethyl radical and a bromine atom respectively.

Trifluoroiodomethane and 1 : 1 : 3 : 3 : 3-pentafluoropropene react only very slowly at room temperature when exposed to light of wavelength >2200 Å, but considerably faster at 100° where a compound of formula $CF_3{\cdot}[C_3HF_5]{\cdot}I$ is obtained in 80% yield. The adduct could be (II) or (III), but the following evidence shows that only the former is formed, probably exclusively but at least to an extent of 90%.

$$\underset{\text{(I)}}{CF_3{\cdot}CH{:}CF_2} \qquad \underset{\text{(II)}}{(CF_3)_2CH{\cdot}CF_2I} \qquad \underset{\text{(III)}}{CF_3{\cdot}CHI{\cdot}CF_2{\cdot}CF_3}$$

Photochemical chlorination of $CF_3{\cdot}[C_3HF_5]{\cdot}I$ gives a dichloride, $C_4F_8Cl_2$, which on treatment with zinc and ethanol gives a high yield (81%) of an olefin C_4F_8. Only $(CF_3)_2CCl{\cdot}CF_2Cl$ derived from (II) could undergo dehalogenation in this way; the compound $CF_3{\cdot}CCl_2{\cdot}CF_2{\cdot}CF_3$ derived from (III) would either not react or would be reduced to compounds such as $CF_3{\cdot}CHCl{\cdot}CF_2{\cdot}CF_3$ and thence $CF_3{\cdot}CH{:}CF{\cdot}CF_3$, and these were not detected. The absence of even a small percentage of the compound $CF_3{\cdot}CCl_2{\cdot}CF_2{\cdot}CF_3$ in the dichloride $C_4F_8Cl_2$ is shown by a comparison of the infrared spectrum of the last compound (C.S. No. 227 †) with that of an authentic sample of 2 : 2-dichloro-octafluorobutane (C.S. 228) prepared by the following route :

$$C_2F_5I + CH_2{:}CF_2 \xrightarrow{h\nu} C_2F_5{\cdot}CH_2{\cdot}CF_2I \xrightarrow{Hg_2F_2} C_2F_5{\cdot}CH_2{\cdot}CF_3 \xrightarrow{Cl_2} C_2F_5{\cdot}CCl_2{\cdot}CF_3$$

The direction of addition of a perfluoroalkyl radical to 1 : 1-difluoroethylene is known to be to the CH_2 group (Part VII, *loc. cit.*). 2 : 2-Dichloro-octafluorobutane has also been synthesised by an independent route (G. F. Liptrot, unpublished results).

Final proof of structure for the compound $(CF_3)_2CCl{\cdot}CF_2Cl$ is the identity of its infrared spectrum with that of the 1 : 2-dichloropentafluoro-2-trifluoromethylpropane obtained by reaction of chlorine with perfluoro*iso*butene. The C_4F_8 olefin obtained by dechlorination of $(CF_3)_2CCl{\cdot}CF_2Cl$ was also shown to be perfluoro*iso*butene by comparison of properties and spectrum with a known sample. A further proof of structure is that octafluorobutane $C_2F_5{\cdot}CH_2{\cdot}CF_3$ prepared as above differs in its infrared spectrum from the compound $CF_3{\cdot}[C_3HF_5]{\cdot}H$ obtained by treatment of $CF_3{\cdot}[C_3HF_5]{\cdot}I$ with zinc and acid; by this

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* Part X, *J.*, 1954, 3747.

† Spectra thus specified have been deposited with the Society. Photocopies, price 3*s.* 0*d.* each per spectrum, may be obtained on application, quoting the C.S. number, to the General Secretary, The Chemical Society, Burlington House, Piccadilly, London, W.1.

treatment the compound (II) would yield $(CF_3)_2CH{\cdot}CHF_2$ whereas the isomer (III) yields $CF_3{\cdot}CH_2{\cdot}C_2F_5$.

The compound (II) is thus the product from the photochemical chain reaction of trifluoroiodomethane with the olefin (I):

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

$$CF_3{\cdot} + CF_3{\cdot}CH{:}CF_2 \longrightarrow (CF_3)_2CH{\cdot}CF_2{\cdot} \qquad \text{Initiation}$$

$$(CF_3)_2CH{\cdot}CF_2{\cdot} + CF_3I \longrightarrow (CF_3)_2CH{\cdot}CF_2I + CF_3{\cdot} \longrightarrow \text{etc.} \qquad \text{Chain transfer}$$

Under the conditions used there was no indication of chain propagation to give products $CF_3{\cdot}[CH(CF_3){\cdot}CF_2]_n{\cdot}I$ with $n > 1$.

The ultraviolet spectra shown in the Table on p. 3007 do not enable clear-cut distinction to be made between the structures (II) and (III), but are of interest in revealing the extent of stabilisation of a radical $CH_3{\cdot}CF_2{\cdot}$ by replacement of the hydrogen by alkyl or perfluoroalkyl groups.

On the assumption that the position of the absorption maximum of an iodo-compound RI can be correlated with the radical stability of R· (*J.*, 1953, 1764), replacement of one hydrogen in $CH_3{\cdot}CF_2{\cdot}$ by a CF_3 group to give $CF_3{\cdot}CH_2{\cdot}CF_2{\cdot}$ causes distinct increase in stability, as indicated by the appearance of the maximum for $CF_3{\cdot}CH_2{\cdot}CF_2I$ at longer wavelength (4 mμ shift). Further replacement of hydrogen by a CF_3 group to give $(CF_3)_2CH{\cdot}CF_2{\cdot}$ further increases the stability (shift for the iodo-compound of 6 mμ). Replacement of the hydrogen in $CF_3{\cdot}CH_2{\cdot}CF_2{\cdot}$ by methyl instead of trifluoromethyl produces no shift in the absorption maximum of the iodide, however, and hence, qualitatively, there is little difference in stability between $CF_3{\cdot}CH_2{\cdot}CF_2{\cdot}$ and $CF_3{\cdot}CHMe{\cdot}CF_2{\cdot}$, but an appreciable difference between $CF_3{\cdot}CHMe{\cdot}CF_2{\cdot}$ or $CF_3{\cdot}CH_2{\cdot}CF_2{\cdot}$ and $(CF_3)_2CH{\cdot}CF_2{\cdot}$.

The ultraviolet spectrum of $C_2F_5{\cdot}CH_2{\cdot}CF_2I$ agrees well with that of $CF_3{\cdot}CH_2{\cdot}CF_2I$. Since the spectrum of $CF_3{\cdot}CH_2{\cdot}CHI{\cdot}CF_3$ shows a maximum at 270 mμ, the maximum for the compound (III) would be predicted to be *ca.* 274 mμ and although this is sufficiently different from 277 mμ to favour the isomer (II), the absence of ultraviolet data on compounds containing the system $-CF_2{\cdot}CHI{\cdot}CF_2-$ makes decisive distinction impossible on spectroscopic grounds.

The formation of the compound (II) and its ready conversion into perfluoro*iso*butene opens up a new route to perfluoro-olefins $R_FR_F'C{:}CF_2$ and ketones $R_F{\cdot}CO{\cdot}R_F'$, where R_F and $R_F' = CF_3{\cdot}[CF_2]_n{\cdot}CF_2$ etc., and n need not be the same in R_F and R_F'. The olefins $R_F{\cdot}CH{:}CF_2$ can be obtained by reaction of a perfluoroalkyl iodide R_FI with 1 : 1-difluoroethylene followed by dehydroiodination (Part VII, *loc. cit.*), and their reaction with a perfluoroalkyl iodide $R_F'I$, followed by chlorination and then dechlorination, yields $R_FR_F'C{:}CF_2$, oxidation of which with aqueous potassium permanganate (cf. the ready oxidation of perfluoro*iso*butene; Brice, LaZerte, Hals, and Pearlson, *J. Amer. Chem. Soc.*, 1953, **75**, 2698) produces the ketone. This route to perfluoro-ketones such as $C_2F_5{\cdot}CO{\cdot}C_3F_7$, $(C_3F_7)_2CO$, and $C_6F_{11}{\cdot}CO{\cdot}CF_3$ (C_6F_{11} = perfluoro*cyclo*hexyl) is sometimes preferable to the route *via* perfluoroalkyl Grignard reagents (*J.*, 1952, 3423; 1953, 1748; 1954, 1273) and is illustrated by the synthesis of perfluoropentan-2-one:

$$C_3F_7I + CF_3{\cdot}CH{:}CF_2 \xrightarrow{h\nu} (C_3F_7)(CF_3)CH{\cdot}CF_2I \xrightarrow{Cl_2,\ h\nu} (C_3F_7)(CF_3)CCl{\cdot}CF_2Cl$$

$$(C_3F_7)(CF_3)CCl{\cdot}CF_2Cl \xrightarrow[\text{dioxan}]{Zn} (C_3F_7)(CF_3)C{:}CF_2 \xrightarrow{\text{aq. KMnO}_4} C_3F_7{\cdot}CO{\cdot}CF_3$$

Oxidation of the olefins $CF_3{\cdot}[CF_2]_n{\cdot}CH{:}CF_2$ to the fluoro-acids is particularly easy, since fluorine is present on the olefinic carbon, and provides a better method of converting a perfluoroalkyl iodide into the corresponding acid than does the oxidation of $CF_3{\cdot}[CF_2]_n{\cdot}CH{:}CHI$ outlined earlier (*J.*, 1950, 3037, 2789; 1953, 1548), *e.g.*:

$$C_2F_5I \xrightarrow{CH_2{:}CF_2} C_2F_5{\cdot}CH_2{\cdot}CF_2I \xrightarrow{KOH} C_2F_5{\cdot}CH{:}CF_2 \xrightarrow{\text{Alk. KMnO}_4} C_2F_5{\cdot}CO_2H$$

1 : 1 : 3 : 3 : 3-Pentafluoropropene and hydrogen bromide do not react in the dark, even when heated for a long period. The photochemical reaction of hydrogen bromide with the pentafluoropropene yields hydrogen, unchanged olefin, 1-bromo-1 : 1 : 3 : 3 : 3-penta-

fluoropropane (IV), and 1 : 2-dibromo-1 : 1 : 3 : 3 : 3-pentafluoropropane. The formation of (IV) was unexpected in view of the results of the direction of addition of the trifluoromethyl radical reported above, since if it is formed by a reaction involving radical intermediates, the chain reaction

$$\text{Br}\cdot + \text{CF}_3\cdot\text{CH}{:}\text{CF}_2 \longrightarrow \text{CF}_3\cdot\dot{\text{C}}\text{H}\cdot\text{CF}_2\text{Br} \xrightarrow{\text{HBr}} \text{CF}_3\cdot\text{CH}_2\cdot\text{CF}_2\text{Br (IV)} + \text{Br}\cdot$$

must occur, with radical attack on the CF_2 group rather than on the CH group. This would be the first instance of a bromine atom and a free radical showing different directions of addition to an unsaturated system.

Ultraviolet spectra in light petroleum.

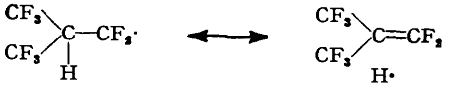
	$\lambda_{max.}$	ε	$\lambda_{min.}$	ε		$\lambda_{max.}$	ε	$\lambda_{min.}$	ε
$CH_3{\cdot}CF_2I$	267	340	207	10	$CF_3{\cdot}CHMe{\cdot}CF_2I$ ...	270	330	238	120
$CF_3{\cdot}CH_2{\cdot}CF_2I$ ...	271	290	219	24	$C_2F_5{\cdot}CH_2{\cdot}CF_2I$ ...	271	300	237	70
$(CF_3)_2CH{\cdot}CF_2I$ ...	277	245	232	45	$CF_3{\cdot}CH_2{\cdot}CHI{\cdot}CF_3$	270	288	224	25

Proof of structure (IV) is given by unambiguous synthesis of this substance from 1 : 1 : 1 : 3 : 3-pentafluoro-3-iodopropane (Part VII, *loc. cit.*) by reaction with bromine in the dark ($CF_3{\cdot}CH_2{\cdot}CF_2I \longrightarrow CF_3{\cdot}CH_2{\cdot}CF_2Br$), and infrared spectroscopic examination shows that the compound (IV) (C.S. No. 229) is free from isomers or contaminants.

Addition of hydrogen bromide to the olefin *via* ionic intermediates would give the compound (IV), since the fluoropropene is polarised as $CF_3{\cdot}\overset{\delta-}{CH}{:}\overset{\delta+}{CF_2}$, and at first sight this seems the most probable explanation of the formation of (IV). Separate experiments show that hydrogen bromide does not react with 1 : 1 : 3 : 3 : 3-pentafluoropropene in the dark at the temperatures used for the photochemical experiments, however, even when bromine, which is liberated during the photochemical experiments and might catalyse the ionic reaction of hydrogen bromide, is added; under these conditions only 1 : 2-dibromo-1 : 1 : 3 : 3 : 3-pentafluoropropane is formed by addition to the olefin, and this explains why the dibromide is a product of the photochemical experiments. Moisture, etc., which might act as catalyst for ionic reactions was, as always, eliminated from reaction mixtures used for photochemical experiments.

Although the available experimental evidence suggests that the compound (IV) is formed by free-radical reaction of hydrogen bromide with the olefin, we are reluctant to accept the conclusions that an ionic reaction is not involved and that a bromine atom behaves differently from a trifluoromethyl radical in this instance. Until a similar effect is observed with a different olefin therefore, we prefer to record the experimental observations but not to attempt to interpret them.

Discussion.—The results for the photochemical reaction of trifluoroiodomethane with pentafluoropropene are interpreted on the basis of stability of intermediate free radicals as outlined in earlier Parts, although full discussion is again deferred to a paper summarising and interpreting the results of this series. On this basis the radical $(CF_3)_2CH{\cdot}CF_2{\cdot}$ is more stable than $CF_3{\cdot}\dot{C}H{\cdot}CF_2{\cdot}CF_3$, and this is in accord with the results on 1 : 1-difluoropropene, and with the concept that a tertiary radical $\geqslant C\cdot$ is more stable than a secondary radical $>CH\cdot$, where the terms tertiary and secondary 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 (Part V, *loc. cit.*). Stabilisation of $(CF_3)_2CH{\cdot}CF_2{\cdot}$ by hyperconjugation involving ***hydrogen*** on the carbon atom adjacent to the carbon formally carrying the lone electron



is also possible and cannot occur with $CF_3{\cdot}\dot{C}H{\cdot}CF_2{\cdot}CF_3$. Radical attack is thus not on the carbon atom of the CF_2 group, which is the most susceptible to attack on steric grounds, and this provides a second example (cf. 1 : 1-difluoropropene, Part V, *loc. cit.*) that free-radical addition can occur to other than the terminal carbon atom in a system containing a terminal double bond.

It should perhaps be noted that if attack of the bromine atom is on the CF_2 group of pentafluoropropene, it would mean that the secondary radical $CF_3\cdot\dot{C}H\cdot CF_2Br$ is more stable than the tertiary radical $CF_3\cdot CHBr\cdot CF_2\cdot$, in which hydrogen hyperconjugation is also possible. It was pointed in Part V that although all free radicals so far studied fall into the stability classification there given, there remains the possibility that by suitable choice of groups R and R′ in a secondary radical $RR'CH\cdot$, the stability of the secondary radical can be made greater than that of a tertiary radical. The formation of the $CF_3\cdot\dot{C}H\cdot CF_2Br$ radical could thus be ascribed to the greater stabilisation by the CF_2Br group, with hyperconjugation of type $CF_3\cdot\dot{C}H\cdot CF_2Br \longleftrightarrow CF_3\cdot CH{:}CF_2\ Br\cdot$, than by analogous hyperconjugation involving the CHBr group in $CF_3\cdot CHBr\cdot CF_2\cdot$. The double bond in $CF_3\cdot CH{:}CF_2$ is not one where such second-order effects are likely to play such a deciding rôle in determining direction of addition, however, and we prefer to leave the issue open.

EXPERIMENTAL

Earlier Parts should be consulted for details of experimental techniques.

1 : 1 : 3 : 3 : 3-*Pentafluoropropene*.—The olefin, prepared in 85% yield by the dehydroiodination of 1 : 1 : 1 : 3 : 3-pentafluoro-3-iodopropane (Part VII, *loc. cit.*), had b. p. −20·7° (Found : *M*, 132. Calc. for C_3HF_5 : *M*, 132), and was spectroscopically pure.

Reaction of Pentafluoropropene with Trifluoroiodomethane.—The olefin (3·80 g., 0·029 mole) and trifluoroiodomethane (8·90 g., 0·045 mole) in a 150-ml. silica tube were exposed to intense ultraviolet radiation (4 days) with the liquid phase shielded. The reaction temperature under these conditions was *ca.* 100°. Distillation *in vacuo* gave unchanged reactants (8·15 g., 64%) (Found : *M*, 174), a mixture of hexafluoroethane (mainly) and fluoroform (0·05 g., *ca.* 5%), identified by means of their infrared spectra, and 1 : 1 : 1 : 3 : 3-*pentafluoro*-3-*iodo*-2-*trifluoromethylpropane* (3·65 g., 80%), b. p. 80°, n_D^{20} 1·347 (Found : C, 14·5; H, 0·3%; *M*, 330. C_4HIF_8 requires C, 14·6; H, 0·3%; *M*, 328).

Reaction of 1 : 1 : 1 : 3 : 3-*Pentafluoro*-3-*iodo*-2-*trifluoromethylpropane with Chlorine*.—The iodo-compound (2·37 g., 0·0072 mole), chlorine (1·02 g., 0·0144 mole), and water (1·0 g.) were exposed to ultraviolet light for 7 days in a silica tube, to give 1 : 2-*dichloro*-1 : 1 : 3 : 3 : 3-*pentafluoro*-2-*trifluoromethylpropane* (1·72 g., 88%), b. p. 63° (micro), n_D^{20} 1·306 (Found : C, 18·0%; *M*, 270. $C_4Cl_2F_8$ requires C, 17·7%; *M*, 271).

Preparation of 2 : 2-*Dichloro-octafluorobutane*.—Chlorine (0·49 g., 0·0069 mole) and 1 : 1 : 1 : 2 : 2 : 4 : 4 : 4-octafluorobutane (0·388 g., 0·00192 mole), sealed in a silica tube (50 ml.) and irradiated (7 days), gave 2 : 2-dichloro-octafluorobutane (0·465 g., 90%), b. p. 64° (micro), n_D^{20} 1·316 (Found : C, 17·6%; *M*, 271. $C_4Cl_2F_8$ requires C, 17·7%; *M*, 271).

Perfluoroisobutene.—1 : 2-Dichloro-1 : 1 : 3 : 3 : 3-pentafluoro-2-trifluoromethylpropane (0·355 g.) was sealed in a Pyrex tube (20 ml.) with zinc dust (4 g.) and dioxan (4 ml.) and heated to 70° in a rotating furnace (4 hr.). Distillation of the volatile products gave perfluoro*iso*butene (0·234 g., 88%), b. p. 7·0° (Found : C, 23·8%; *M*, 202. Calc. for C_4F_8 : C, 24·0%; *M*, 200). Brice *et al.* (*loc. cit.*) reported b. p. 6·5°. The constitution of the perfluoro*iso*butene was proved by comparison of its infrared spectrum with that of a known sample.

Reaction of Pentafluoroiodoethane with 1 : 1-*Difluoroethylene*.—The olefin (1·79 g., 0·028 mole), sealed with pentafluoroiodoethane (6·90 g., 0·028 mole) in a 200-ml. silica tube and irradiated for 5 days with the liquid phase shielded, gave unchanged reactants (1·40 g., 16%) and liquid products. These were distilled, to give 1 : 1 : 1 : 2 : 2 : 4 : 4-*heptafluoro*-4-*iodobutane* (6·70 g., 91%), b. p. 88° n_D^{20} 1·354 (Found : C, 15·8; H, 0·9. $C_4H_2IF_7$ requires C, 15·5; H, 0·6%), and a fraction (*ca.* 0·4 g.), b. p. 140° (micro), n_D^{20} 1·440, probably $C_2F_5\cdot[CH_2\cdot CF_2]_2\cdot I$.

Treatment of 1 : 1 : 1 : 2 : 2 : 4 : 4-*Heptafluoro*-4-*iodobutane with Mercurous Fluoride*.—The iodo-compound (2·0 g.) was heated step-wise to 140° with mercurous fluoride (10 g.) in a Pyrex flask fitted with a reflux condenser. After 4 hr. the volatile products which had passed through the condenser and been collected in a trap cooled in liquid air were distilled to give 1 : 1 : 1 : 2 : 2 : 4 : 4 : 4-*octafluorobutane* (0·63 g., 48%), b. p. 18° (Found : C, 23·3; H, 1·2%; *M*, 200. $C_4H_2F_8$ requires C, 23·8; H, 1·0%; *M*, 202).

Reaction of 1 : 1 : 1 : 3 : 3-*Pentafluoro*-3-*iodo*-2-*trifluoromethylpropane with Zinc and Dilute Acid*.—Sulphuric acid (20 ml. of 5N) was added to zinc dust (10 g.) and the iodo-compound (1·50 g.), and the mixture was warmed until steady evolution of hydrogen was observed. The volatile products passed through a reflux water condenser, were collected in a trap cooled by liquid oxygen, and then distilled, to give 1 : 1 : 1 : 3 : 3-pentafluoro-2-trifluoromethylpropane

(0·59 g., 63%), b. p. 17° (Found : C, 25·1; H, 1·9. Calc. for $C_4H_2F_8$: C, 23·8; H, 1·0%), shown by infrared spectroscopy to be contaminated by an olefin.

Synthesis of Perfluoropentan-2-one.—1 : 1 : 3 : 3 : 3-Pentafluoropropene (3·98 g., 0·030 mole) and heptafluoroiodopropane (10·0 g., 0·032 mole) in a 150-ml. silica tube were exposed to intense ultraviolet light (8 days) at 100° with the liquid phase shielded. The unchanged reactants (37%) were removed *in vacuo*, water (5 ml.) and an excess of chlorine were added to the residual 1 : 1 : 1 : 2 : 2 : 3 : 3 : 5 : 5-nonafluoro-5-iodo-4-trifluoromethylpentane, and the tube was resealed and shaken. After exposure to ultraviolet light (7 days) the crude reaction product was washed with 5% aqueous sodium hydroxide, then added dropwise (5 hr.) to stirred zinc (20 g.) and refluxing dioxan (100 ml.), in a flask fitted with reflux condenser, at 65—70°. The olefin produced, and the entrained dioxan, were collected in a tube containing water. The lower layer was removed, washed with water, and distilled from phosphoric anhydride, to give 1 : 1 : 3 : 3 : 4 : 4 : 5 : 5 : 5-*nonafluoro-2-trifluoromethylpentene* (53% overall), b. p. 60° (Found : C, 24·1%; *M*, 298. C_6F_{12} requires C, 24·0%; *M*, 300).

The olefin was heated (120°) and shaken in a 100-ml. autoclave with potassium permanganate (14 g.) and water (60 ml.) for 12 hr., and the excess of permanganate was decomposed by treatment with sulphur dioxide. Ether-extraction followed by removal of the ether and distillation of the residue from an excess of phosphoric anhydride to decompose the ketone hydrate gave a volatile fraction which was combined with a smaller amount of volatile product obtained on opening the autoclave. Distillation *in vacuo* gave carbon dioxide, unchanged perfluorohexene (8%), and perfluoropentan-2-one (52% based on perfluorohexene used), b. p. 30° (Found : C, 22·6%; *M*, 265. C_5OF_{10} requires C, 22·6%; *M*, 266). Haszeldine (*J.*, 1953, 1748) reports b. p. 29·5° for this ketone.

Preparation of Pentafluoropropionic Acid from Pentafluoroiodoethane.—Pentafluoroiodoethane (4·40 g., 0·03 mole) and 1 : 1-difluoroethylene (1·90 g., 0·03 mole) were heated at 220° in a 20-ml. autoclave for 10 hr. to give 1 : 1 : 1 : 2 : 2 : 4 : 4-heptafluoro-4-iodobutane (95%) and no unchanged reactants. The crude product was treated with alcoholic potassium hydroxide at 30° (cf. Part VII, *loc. cit.*), and the volatile 1 : 1 : 3 : 3 : 4 : 4 : 4-heptafluorobutene evolved (72% yield) was sealed in a 35-ml. autoclave with potassium permanganate (8 g.), water (20 ml.), and potassium hydroxide (4 g.). After 6 hours' shaking and heating (80°) there was no unchanged olefin. The aqueous solution was acidified, treated with sulphur dioxide, filtered, and extracted with ether, as described for similar oxidations (*J.*, 1950, 3037, 2789; 1952, 4259). Addition of water and silver carbonate (10% excess) to the ethereal extracts, removal of the ether by evaporation, and freeze-drying of the aqueous solution gave silver pentafluoropropionate (55% yield based on pentafluoroiodoethane); its identity was confirmed by means of its infrared spectrum.

Reaction of 1 : 1 : 3 : 3 : 3-*Pentafluoropropene with Hydrogen Bromide.*—The olefin (1·23 g., 0·0093 mole) and hydrogen bromide (0·80 g., 0·0099 mole), sealed in a Pyrex tube (50 ml.) and heated at 60° (14 days), underwent no reaction.

The pentafluoropropene (0·767 g., 0·0058 mole), hydrogen bromide (0·49 g., 0·0060 mole), and bromine (1·0 g., 0·0062 mole) were sealed in a 50-ml. Pyrex tube and heated at 60° (6 days) to give unchanged olefin (0·52 g., 68%), unchanged hydrogen bromide (0·485 g., 99%), and 1 : 2-dibromo-1 : 1 : 3 : 3 : 3-pentafluoropropane.

In a typical experiment, 1 : 1 : 3 : 3 : 3-pentafluoropropene (1·11 g., 0·0084 mole) and hydrogen bromide (0·70 g., 0·0086 mole) in a 50-ml. silica tube were irradiated for 6 days, to give non-condensable products (hydrogen) (*ca.* 0·003 g.), unchanged pentafluoropropene (0·40 g., 36%; identified by infrared spectroscopy), 1-*bromo*-1 : 1 : 3 : 3 : 3-*pentafluoropropane* (*ca.* 0·5 g., 40%), b. p. 44°, n_D^{20} 1·319 (Found : C, 17·1; H, 1·3. $C_3H_2BrF_5$ requires C, 16·9; H, 0·9%), and 1 : 2-dibromo-1 : 1 : 3 : 3 : 3-pentafluoropropane (*ca.* 0·8 g., 50%), b. p. 87°, n_D^{20} 1·379. McBee, Truchan, and Bolt (*J. Amer. Chem. Soc.*, 1948, **70**, 2023) report b. p. 88°, n_D^{25} 1·378, for the last compound.

1-Bromo-1 : 1 : 3 : 3 : 3-pentafluoropropane was synthesised by reaction of 1 : 1 : 1 : 3 : 3-pentafluoro-3-iodopropane (2·8 g., 0·011 mole) with bromine (1·8 g., 0·011 mole) in a Pyrex tube (20 ml.). The liquid phase was irradiated for 5 days, and distillation of the products gave 1-bromo-1 : 1 : 3 : 3 : 3-pentafluoropropane (1·3 g., 55%), b. p. 44° (micro), n_D^{18} 1·320. The infrared spectra of the two specimens of bromopentafluoropropane were identical.

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