715. *The Addition of Free Radicals to Unsaturated Systems. Part IV.*† *The Direction of Radical Addition to Hexafluoropropene.*‡

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The photochemical reaction of trifluoroiodomethane or of hydrogen bromide with hexafluoropropene yields only $CF_3\cdot[CF_2\cdot CF(CF_3)]_n\cdot CF_2\cdot CFI\cdot CF_3$ or $CF_3\cdot CHF\cdot CF_2Br$, respectively, and radical attack is thus exclusively on the CF_2 group of hexafluoropropene. Aluminium halide-catalysed addition of hydrogen bromide also yields $CF_3\cdot CHF\cdot CF_2Br$. Photochemical polymerisation of hexafluoropropene gives a trimer (a perfluorononene), a tetramer, and a pentamer.

Oxidation of the product obtained by interaction of nonafluoro-2-iodobutane and acetylene yields the acid, $C_2F_5(CF_3)CF\cdot CO_2H$, derivatives of which are described.

RADICAL attack on olefins of the type $R\cdot CH\colon CH_2$ (R = Me, Cl, F, CO_2Me, CF_3, or CN) is exclusively on the terminal methylene group, and trifluoroiodomethane, for example, yields only $CHIR\cdot CH_2\cdot CF_3$ (*J.*, 1952, 2504; 1953, 1199). The results of experiments with a perfluoro-olefin of the type $R\cdot CF\colon CF_2$ are now reported. Trifluoroiodomethane and hydrogen bromide were used as sources of trifluoromethyl radicals and bromine atoms, respectively, and the assumptions made have been outlined earlier (*J.*, 1952, 2504).

Attack by a Trifluoromethyl Radical.—Trifluoroiodomethane and hexafluoropropene react only slowly when exposed to light of wave-length >3000 Å, which only the fluoro-iodide can absorb, and yield a compound $CF_3\cdot[C_3F_6]\cdot I$ whose constitution is described below. The reaction is faster in silica vessels, *i.e.*, with light of wave-length >2200 Å, and yields $CF_3\cdot[C_3F_6]_n\cdot I$ where $n = 1$ and 2. Spectroscopic examination shows that the nonafluoroiodobutanes are identical, *i.e.*, the direction of addition of trifluoroiodomethane is independent of the wave-length of the light used to initiate reaction.

The compound when $n = 1$ might be (I) or (II) but the following evidence shows that only (I) is formed (probably exclusively, but at least to an extent of 85%). The compound

(I) $CF_3\cdot CFI\cdot CF_2\cdot CF_3$ $(CF_3)_2CF\cdot CF_2I$ (II)

fails to react with iodine pentafluoride at 220°, but with bromine trifluoride at <0° yields perfluoro-*n*-butane (78%) which can be derived only from (I). Perfluoro-*n*-butane was synthesised from butane, perfluorobut-1-ene, and perfluorobut-2-ene by reaction with cobalt trifluoride, and from trispentafluoroethylarsine by pyrolysis, for comparison with the

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* Catchpole and Hughes (*loc. cit.*) record for ethyl 1-methylallyl and but-2-enyl ethyl ether respectively n_D^{25} 1·3872 and 1·4020.

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product from (I). Cobalt trifluoride also reacts with (I) to give perfluoro-*n*-butane (84%); a control experiment to determine manipulation losses with the known nonafluoro-1-iodobutane [an isomer of (I)] also gave perfluoro-*n*-butane (87%). Since the yields are comparable, it is thus very probable that the compound with $n = 1$ is exclusively (I), *i.e.*, attack of the trifluoromethyl radical is entirely on the CF_2 group of hexafluoropropene with a chain mechanism of the type proposed earlier (*J.*, 1949, 2856):

$$\begin{array}{lrcl} & CF_3I & \xrightarrow{h\nu} & CF_3\cdot + I\cdot \\ \text{Initiation:} & CF_3\cdot + CF_3\cdot CF{:}CF_2 & \longrightarrow & CF_3\cdot\dot{C}F\cdot CF_2\cdot CF_3 \\ \text{Propagation:} & CF_3\cdot\dot{C}F\cdot CF_2\cdot CF_3 + CF_3\cdot CF{:}CF_2 & \longrightarrow & CF_3\cdot\dot{C}F\cdot CF_2\cdot CF(CF_3)\cdot CF_2\cdot CF_3, \text{ etc.} \\ \text{Transfer:} & CF_3\cdot\dot{C}F\cdot CF_2\cdot CF_3 + CF_3I & \longrightarrow & CF_3\cdot CFI\cdot CF_2\cdot CF_3 + CF_3\cdot \longrightarrow \text{etc.} \end{array}$$

In support of the above constitution, the ultra-violet spectrum of the compound where $n = 1$ shows a maximum at 280 mμ, *i.e.*, 10 mμ further to the red than would be expected for (II), which is a completely fluorinated primary iodoalkane (*J.*, 1953, 1764; see below).

Only the compound with $n = 1$ is formed in Pyrex vessels, and this is (I). The now unlikely possibility that the compound where $n = 2$ obtained in silica vessels is (IV)

$$\text{(III)}\quad CF_3\cdot CFI\cdot CF_2\cdot CF(CF_3)\cdot CF_2\cdot CF_3 \qquad\qquad CF_3\cdot CF_2\cdot CF(CF_3)\cdot CF(CF_3)\cdot CF_2I\quad \text{(IV)}$$

(formed by attack on the CF group of the second molecule of hexafluoropropene) can be discarded, since (I) reacts with hexafluoropropene on irradiation to give only (III), which is identical with the compound where $n = 2$:

$$\text{(I)} \xrightarrow{h\nu} (C_2F_5)(CF_3)CF\cdot \xrightarrow{C_3F_6} (C_2F_5)(CF_3)CF\cdot CF_2\cdot\dot{C}F\cdot CF_3 \xrightarrow{(C_2F_5)(CF_3)CFI} \text{(III)}$$

The compound (III) reacts with cobalt trifluoride to give perfluoro-3-methylhexane.

Since nonafluoro-2-iodobutane is the first acyclic fully fluorinated secondary iodoalkane to be reported, two free-radical reactions (with nitric oxide and acetylene) have been investigated to show its similarity to the corresponding primary iodoalkanes. Nonafluoro-2-iodobutane readily combines with nitric oxide when the mixture is irradiated in the presence of mercury (to remove any nitrogen dioxide formed) and yields the monomeric deep blue nitroso-compound (cf. *J.*, 1953, 2075). The perfluorobutyl radical also combines

$$(C_2F_5)(CF_3)CFI \xrightarrow{h\nu} (C_2F_5)(CF_3)\cdot CF\cdot \xrightarrow{NO} (C_2F_5)(CF_3)CF\cdot NO$$

with acetylene, and oxidation of the fluoroiodohexene so obtained yields hexafluoro-2-trifluoromethylbutanoic acid (cf. *J.*, 1950, 3037, 2789):

$$(C_2F_5)(CF_3)CFI \xrightarrow{h\nu} (C_2F_5)(CF_3)CF\cdot \xrightarrow{C_2H_2} (C_2F_5)(CF_3)CF\cdot CH{:}CH\cdot$$

$$(C_2F_5)(CF_3)CF\cdot CH{:}CH\cdot \xrightarrow{(C_2F_5)(CF_3)CFI} (C_2F_5)(CF_3)CF\cdot CH{:}CHI \xrightarrow{KMnO_4} (C_2F_5)(CF_3)CF\cdot CO_2H$$

This acid resembles the perfluoro-acids described in another series, and gives a methyl ester and amide in the usual way.

The photochemical polymerisation of pure hexafluoropropene is slow, and yields only products of short chain length. The main product is a trimer, C_9F_{18}, the infra-red spectrum of which reveals a strong C:C stretching vibration at 5·77 μ characteristic of the $\cdot CF{:}CF\cdot$ group (Haszeldine, *J.*, 1952, 4423). A $\cdot CF{:}CF_2$ group, which is characterised by a band at 5·56 μ (cf. $CF_3\cdot CF{:}CF_2$ 5·56, $C_2F_5\cdot CF{:}CF_2$ 5·56, $CHF{:}CF_2$ 5·56) cannot be present, but a $>C{:}CF_2$ group, which is characterised by a band at 5·71 μ [*e.g.*, $(CF_3)_2C{:}CF_2$] could be present, since replacement of a trifluoromethyl group by a perfluoroalkyl group of higher molecular weight shifts the C:C stretching vibration to slightly longer wave-length (Haszeldine and Steele, *J.*, 1953, 1592). Perfluorononenes such as $CF_3\cdot CF{:}CF\cdot CF_2\cdot CF(CF_3)\cdot CF_2\cdot CF_2\cdot CF_3$ or $CF_2{:}C(CF_3)\cdot CF_2\cdot CF(CF_3)\cdot CF_2\cdot CF_2\cdot CF_3$, produced by diradical formation from hexafluoropropene, polymerisation, and disproportionation, thus seem probable. That trimerisation did not yield perfluoro-1 : 3 : 5-trimethyl*cyclo*hexane is shown by the spectra. The polymeric material of higher molecular weight contains a tetramer and pentamer, probably with end groups similar to those postulated above for the trimer.

Attack by a Bromine Atom.—Hexafluoropropene and hydrogen bromide react in the dark only in presence of an aluminium halide, and give a product identical with that from the photochemical reaction. The latter reaction is slow at room temperature; bromine is liberated and dibromohexafluoropropane (2%) is formed as well as the bromohexafluoropropane. The last compound could be (V) or (VI), and that it is actually (V) (to the extent

$$\underset{\text{(V)}}{CF_3\cdot CHF\cdot CF_2Br} \qquad \underset{\text{(VI)}}{CF_3\cdot CFBr\cdot CHF_2} \qquad \underset{\text{(VII)}}{CF_3\cdot CF_2\cdot CHFBr}$$

of the least 90%) is shown by its reaction with cobalt trifluoride, since 1-bromoheptafluoropropane (80%), perfluoropropane (5%), 1 : 1 : 1 : 2 : 3 : 3 : 3-heptafluoropropane (4%), and unchanged (V) were obtained. The recovered bromohexafluoropropane was identical with the starting product, so that preferential fluorination of (V) compared with (VI) is not involved. It is noteworthy that the hydrogen atom in (V) can be replaced by fluorine without appreciable replacement of bromine by fluorine.

B. R. Steele has prepared a mixture containing (V) (85%) and (VII) (15%) by an alternative unpublished route, and comparison of the infra-red spectrum with that of the product from hexafluoropropene shows that the only common bands are those of (V); (VII) cannot be a product of the reaction of hexafluoropropene with hydrogen bromide. Furthermore, since independent evidence (see below) shows that the polarisation of hexafluoropropene is to $CF_3\cdot\overset{\delta-}{CF}{=\!\!=}\overset{\delta+}{CF_2}$, the product formed from the aluminium halide-catalysed reaction is almost certainly (V).

These three lines of evidence, particularly the first, show that the product is (V), and that attack of the bromine atom, like that of the trifluoromethyl radical, is on the CF_2 group of hexafluoropropene :

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

$$Br\cdot + CF_3\cdot CF{:}CF_2 \longrightarrow CF_3\cdot\dot{C}F\cdot CF_2Br \xrightarrow{HBr} CF_3\cdot CHF\cdot CF_2Br + Br\cdot$$

Discussion.—The polarisation of hexafluoropropene during reactions involving ionic intermediates is to $CF_3\cdot\overset{\delta-}{CF}{=\!\!=}\overset{\delta+}{CF_2}$, since base-catalysed reaction with, say, ethyl alcohol proceeds as follows :

$$EtO^- + CF_2{:}CF\cdot CF_3 \longrightarrow EtO\cdot CF_2\cdot\overset{-}{C}F\cdot CF_3 \xrightarrow{EtOH} EtO\cdot CF_2\cdot CHF\cdot CF_3 + EtO^- \longrightarrow \text{etc.}$$

and ammonia yields αβββ-tetrafluoropropionitrile (personal communication, Minnesota Mining and Manufacturing Co.) :

$$CF_3\cdot CF{:}CF_2 \xrightarrow{NH_3} [CF_3\cdot CHF\cdot CF_2\cdot NH_2] \xrightarrow{-2HF} CF_3\cdot CHF\cdot CN$$

This polarisation is the resultant of the inductive and hyperconjugative ($CF_3\cdot CF{:}CF_2 \longleftrightarrow F\ CF_2{:}CF\cdot\overset{+}{C}F_2$) effects of the trifluoromethyl group, and of the additional effect (not found with $CH_3\cdot CH{:}CH_2$ and $CF_3\cdot CH{:}CH_2$ studied earlier) of back-co-ordination (*e.g.*, $\overset{+}{F}{:}CF\cdot\overset{-}{C}F\cdot CF_3$). If it is again assumed (see Parts I—III) that the polarisation of the double bond when the neutral trifluoromethyl radical or bromine atom approaches is the same as in ionic reactions, it follows that radical attack takes place on the more positive carbon atom of the olefin, not the less positive as would be required if the radical were to be regarded as an electrophilic reagent. It is difficult to justify this assumption for a molecule like hexafluoropropene where various effects are operating but, since the compounds $CH_3\cdot CH{:}CH_2$ and $CF_3\cdot CH{:}CH_2$ both undergo radical attack at the terminal methylene group, it is unlikely that polar effects in the molecule play a major part in determining orientation of attack. The substituents on the carbon atoms of the double bond have a major effect on the *rate* of addition, however, and if it is assumed that the chain-transfer step is equally efficient for the reaction of trifluoroiodomethane or of hydrogen bromide with propene, 3 : 3 : 3-trifluoropropene, and hexafluoropropene, then the ease of addition decreases in the order $CH_3{\cdot}CH{:}CH_2 \gg CF_3{\cdot}CH{:}CH_2 > CF_3{\cdot}CF{:}CF_2$.

If steric factors are neglected, and the relative stability of the possible intermediate radicals governs the orientation of attack, it follows that the secondary radicals $CF_3{\cdot}\dot{C}F{\cdot}CF_2{\cdot}CF_3$ and $CF_3{\cdot}\dot{C}F{\cdot}CF_2Br$ are more stable than the corresponding primary radicals $(CF_3)_2{\cdot}CF{\cdot}CF_2{\cdot}$ and $CF_3{\cdot}CFBr{\cdot}CF_2{\cdot}$ (cf. Part II, *loc. cit.*). A full discussion is deferred, but consideration of the ultra-violet spectra in the following Table is relevant.

Absorption spectra in light petroleum.

	$\lambda_{max.}$	ε	$\lambda_{min.}$	ε
$CH_3{\cdot}CH_2{\cdot}CHI{\cdot}CH_3$	261	555	219	24
$CF_3{\cdot}CH_2{\cdot}CHI{\cdot}CH_3$	267	430	218	25
$CF_3{\cdot}CH_2{\cdot}CHI{\cdot}CF_3$	270	290	224·5	26
$CF_3{\cdot}CF_2{\cdot}CFI{\cdot}CF_3$	280	220	236	50
$CF_3{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2I$	271	270	215	11

The unsubstituted alkyl iodide corresponding to nonafluoro-2-iodobutane has absorption maximum at 261 mμ, and, as fluorine is introduced into the molecule, the maximum moves to longer wave-length and ε decreases. The spectrum of nonafluoro-1-iodobutane, which is typical of the fully fluorinated *n*-iodoalkanes (Haszeldine, *J.*, 1953, 1764) is included for comparison, and shows that the primary and secondary iodides can be readily distinguished by a difference in $\lambda_{max.}$ of *ca.* 10 mμ. If the interpretation of the spectra proposed earlier (*J.*, 1953, 1764) is accepted, it follows (*a*) that the radical derived from the fluoro-iodo-compounds by carbon–iodine bond fission increases in stability with fluorine content, and (*b*) that the $C_2F_5{\cdot}\dot{C}F{\cdot}CF_3$ radical is more stable than the $CF_3{\cdot}[CF_2]_2{\cdot}CF_2{\cdot}$ radical; or, conversely, that the carbon–iodine bond dissociation energy is greater for fully fluorinated *n*-iodoalkanes than for the corresponding secondary iodoalkanes.

EXPERIMENTAL

Trifluoroiodomethane and hexafluoropropene were prepared as described earlier (*J.*, 1951, 584; 1952, 4259) and were purified in a vacuum system; their purity was checked by infra-red spectroscopic examination. Hydrogen bromide was purified and stored *in vacuo*. Precautions were taken to exclude oxygen, moisture, peroxides, etc., which might promote ionic or free-radical reactions. The reaction vessels were of Pyrex (30 ml. capacity) or silica (50-ml. capacity), and were placed 10 cm. from a Hanovia ultra-violet lamp used without the Woods filter; the reaction tubes were sealed *in vacuo*.

Reaction of Trifluoroiodomethane with Hexafluoropropene.—There was no reaction when trifluoroiodomethane (10·0 g.) and hexafluoropropene (3·0 g.) were sealed in Pyrex vessels and kept in the dark for 5 weeks. A slow reaction occurred on exposure to ultra-violet light, and after 2 weeks distillation gave unchanged reactants (90%) and a liquid, b. p. >20°, shown by infra-red spectroscopic examination to be identical with the nonafluoro-2-iodobutane described below.

A similar mixture was sealed in a silica tube, and the liquid phase was shielded from light. Exposure of the vapour to ultra-violet light for 14 days caused liberation of sufficient iodine to colour the liquid red. Distillation gave unchanged hexafluoropropene (15%, separated from trifluoroiodomethane by formation of the dibromide), trifluoroiodomethane, *nonafluoro*-2-*iodobutane* (94% based on C_3F_6 used), b. p. 65·5°, n_D^{20} 1·340 (Found: C, 13·9%; *M*, 346. C_4IF_9 requires C, 13·9%; *M*, 346), and material of b. p. >80° (0·1 g.). The yield of material of b. p. >80° when hexafluoropropene (3·0 g.) and trifluoroiodomethane (4·0 g.) were irradiated as above was 0·7 g. The combined material of b. p. >80° was distilled in a semi-micro apparatus, to give *dodecafluoro-2-iodo-4-trifluoromethylhexane* (0·5 g.), b. p. 136—138° (Found: C, 16·8; $C_7F_{15}I$ requires C, 16·9%), and an intermediate fraction (0·1 g.), b. p. *ca.* 120°, which is possibly 1 : 1 : 1 : 2 : 3 : 3-hexafluorodi-iodopropane (Found: C, 9·4. Calc. for $C_3F_6I_2$: C, 8·9%).

Reactions of Nonafluoro-2-iodobutane.—(a) *With hexafluoropropene.* The fluoroiodobutane (1·9 g., prepared as above) was sealed with hexafluoropropene (0·5 g.) in a 10-ml. silica tube, and irradiated for 14 days, to give dodecafluoro-2-iodo-4-trifluoromethylhexane (51%), b. p. 135—139°, shown by spectroscopic examination to be identical with the compound prepared above.

(b) *With iodine pentafluoride or bromine trifluoride.* The fluoroiodobutane (1·0 g.) was substantially unchanged after being heated with iodine pentafluoride (3 ml.) in a small autoclave at 220° for 12 hr.

To the fluoroiodobutane (1·1 g.) in a nickel tube (5 ml. capacity) cooled to −78°, was added dropwise an excess of bromine trifluoride. The volatile products were condensed, washed with 10% sodium hydroxide solution, and distilled in a vacuum system to give perfluoro-*n*-butane (78%), b. p. 1° (Found : *M*, 238. Calc. for C_4F_{10} : *M*, 238), shown by infra-red spectroscopic examination to be identical with perfluoro-*n*-butane prepared by independent routes using the cobalt fluoride method (Haszeldine and Smith, *J.*, 1950, 3617), or from trispentafluoroethylarsine by pyrolysis.

(c) *With cobalt trifluoride.* Cobalt trifluoride (100 g.) was prepared *in situ* in a 2′ horizontal copper furnace at 250—300°, and the excess of fluorine was displaced by nitrogen. Nonafluoro-2-iodobutane (3·2 g.) was added dropwise from a small dropping funnel which extended into the furnace so that the possible reaction of the fluoroiodobutane vapour with hot copper was kept to a minimum. The exit gases were condensed, washed with aqueous alkali, and distilled in a vacuum system, to give perfluoro-*n*-butane (84%) (*M*, 237), shown by its infra-red spectrum to be identical with the material prepared as above.

*Reaction of Nonafluoro-*1*-iodobutane and of Dodecafluoro-*2*-iodo-*4*-trifluoromethylhexane with Cobalt Trifluoride.*—Nonafluoro-1-iodobutane (3·0 g.), prepared from pentafluoroiodoethane and tetrafluoroethylene (*Nature*, 1950, **166**, 192), was passed over cobalt trifluoride under conditions identical with those described for nonafluoro-2-iodobutane above, to give perfluoro-*n*-butane (87%) (*M*, 238), spectroscopic examination of which showed that no rearranged product was formed.

Dodecafluoro-2-iodo-4-trifluoromethylhexane (0·9 g.) was passed over cobalt trifluoride (20 g.) in a small steel reaction vessel at 350° and gave *perfluoro-*3*-methylhexane* (0·2 g.), b. p. 81—82° (Found : C, 21·6% ; *M*, 390. C_7F_{16} requires C, 21·7% ; *M*, 388).

*Hexafluoro-*2*-trifluoromethylbutanoic Acid.*—Nonafluoro-2-iodobutane (3·2 g.) was sealed with acetylene (10% excess) and heated to 250° for 24 hr. The combined products from three such tubes were distilled, to give 3 : 4 : 4 : 5 : 5 : 5-*hexafluoro-*1*-iodo-*3*-trifluoromethylpent-*1*-ene* (83%), b. p. 74—76°/148 mm., 118—119°/760 mm. (micro) (Found : C, 19·2; H, 0·3. $C_6H_2IF_9$ requires C, 19·4; H, 0·8%). Oxidation of this compound (5·8 g.) by alkaline potassium permanganate and working up as described earlier (*J.*, 1950, 2789) gave, after distillation through a short column, *hexafluoro-*2*-trifluoromethylbutanoic acid* (51%), b. p. 135—136° (Found : C, 22·7; H, 0·3% ; equiv., 265. $C_5HO_2F_9$ requires C, 22·7 ; H, 0·4% ; equiv., 264), as a colourless, fuming liquid with an odour resembling that of heptafluorobutyric acid (*J.*, 1950, 2789). It is a strong acid, soluble in water, ethanol, acetone, and ether, and shows marked similarity in properties to heptafluorobutyric acid and to its isomer perfluoropentanoic acid.

The *methyl ester* (80% yield), b. p. 101—102° (Found : C, 26·1; H, 0·9. $C_6H_3O_2F_9$ requires C, 25·9; H, 1·1%), was converted into the *amide* (92% yield), m. p. 106—107° (Found : C, 23·0; H, 0·5; N, 5·2. $C_5H_2NOF_9$ requires C, 22·8; H, 0·8; N, 5·3%), by the methods outlined earlier (Haszeldine, *J.*, 1950, 2789; Haszeldine and Leedham, *J.*, 1953, 1548).

*Nonafluoro-*2*-nitrosobutane.*—Nonafluoro-2-iodobutane (2·1 g.) was sealed with nitric oxide (80% excess) and mercury (3 g.), and the silica tube was shaken vigorously and exposed to ultra-violet light for 8 days. Fractionation *in vacuo* gave unchanged fluoroiodobutane and *nonafluoro-*2*-nitrosobutane* (86% based on the fluoroiodide used, 23% on fluoroiodide taken) (Found : C, 19·0; N, 5·8% ; *M*, 249. C_4NOF_9 requires C, 19·3; N, 5·6% ; *M*, 249), a deep blue liquid, b. p. 23—25°.

Photochemical Polymerisation of Hexafluoropropene.—Hexafluoropropene (5·1 g.), sealed in a small silica tube so that it was mainly liquid, was exposed to ultra-violet light at a distance of 2 cm. The reaction temperature was thus *ca.* 70°. After 6 weeks, fractionation gave (*a*) unchanged hexafluoropropene (20%), (*b*) a *perfluorononene* (41%), b. p. 121—123°, n_D^{20} 1·296 (Found : C, 23·9; H, 0% ; *M*, 449. C_9F_{18} requires C, 24·0; H, 0% ; *M*, 450), (*c*) a fraction (*ca.* 10%), b. p. 176—180° [Found : C, 23·8. Calc. for $(C_3F_6)_4$: C, 24·0%], and (*d*) a fraction (*ca.* 10%), b. p. 215—220° [Found : C, 24·0. Calc. for $(C_3F_6)_5$: C, 24·0%]. Haszeldine and Smith (*J.*, 1950, 2689) report b. p. 124·6, n_D^{25} 1·294, for perfluoro-1 : 3 : 5-trimethyl*cyclo*hexane. The infra-red spectrum of fraction (*b*) is reported below. The spectra of fractions (*c*) and (*d*) were very similar to that of (*b*). If the hexafluoropropene is inadequately purified, or if traces of air are present during irradiation, the polymerisation is much more rapid and products are obtained which cannot be separated into clear-cut fractions.

Reaction of Hexafluoropropene with Hydrogen Bromide.—(a) *In the dark.* There was no reaction when hexafluoropropene and hydrogen bromide were sealed in Pyrex and kept in the dark for 3 weeks.

(b) *In presence of aluminium halides.* Hexafluoropropene (2·1 g.), hydrogen bromide (10% excess) and aluminium bromide (0·1 g.), sealed and stored at 20° for 7 days, gave 1-bromo-1 : 1 : 2 : 3 : 3 : 3-hexafluoropropane (64%), b. p. 35·5° (Found : C, 15·5; H, 0·2%; *M*, 230. Calc. for C_3HBrF_6 : C, 15·6; H, 0·4%; *M*, 231), and unchanged reactants. The yield after 3 days at 60° was 81%. Aluminium chloride gave a 70% yield after 7 days at room temperature. Park, Sharrah, and Lacher (*J. Amer. Chem. Soc.*, 1949, **71**, 2339) report b. p. 29·8—30·3°/624 mm. for the product from the catalysed vapour-phase reaction of hydrogen bromide with hexafluoropropene; the constitution of the C_3HBrF_6 was not proved by them, but was correctly inferred.

(c) *On exposure to ultra-violet light.* Hexafluoropropene (2·0 g.) and hydrogen bromide (5% excess) were sealed in a Pyrex tube and irradiated for 5 days, to give 1-bromo-1 : 1 : 2 : 3 : 3 : 3-hexafluoropropane (53%) (*M*, 230), identical with the material described above, and unchanged reactants.

A similar mixture sealed in a silica vessel was unchanged after 7 days in the dark, but after irradiation for 7 days, gave a product coloured pale-brown by bromine. The product was washed with water and distilled, to give unchanged hexafluoropropene (10%) (*M*, 150), 1-bromo-1 : 1 : 2 : 3 : 3 : 3-hexafluoropropane (88% based on hexafluoropropene taken) (*M*, 231), b. p. 35·5°, and 1 : 2-dibromohexafluoropropane (*ca.* 2%), b. p. 70—72° (*M*, 310). The identity of the products was confirmed by their infra-red spectra. Haszeldine (*J.*, 1952, 3423) reported b. p. 71° for dibromohexafluoropropane.

Reaction of Bromohexafluoropropane with Cobalt Trifluoride.—1-Bromo-1 : 1 : 2 : 3 : 3 : 3-hexafluoropropane (3·2 g.) was passed (2 hr.) over cobalt trifluoride (100 g.) at 200°, to give (*a*) 1-bromoheptafluoropropane (80%), b. p. 12° (Found: *M*, 248. Calc. for C_3BrF_7: *M*, 249), identified, and shown to be free from its isomer, by its infra-red spectrum, (*b*) unchanged bromohexafluoropropane (5%), (*c*) 1 : 1 : 1 : 2 : 3 : 3 : 3-heptafluoropropane (*ca.* 4%), b. p. −18° (Found : *M*, 170. Calc. for C_3HF_7 : *M*, 170), and (*d*) perfluoropropane (*ca.* 5%), b. p. −39° (Found : *M*, 190. Calc. for C_3F_8 : *M*, 188). The infra-red spectra of (*a*), (*b*), and (*c*) showed that isomers were absent. 1-Bromoheptafluoropropane has b. p. 12° (Haszeldine, *J.*, 1952, 4259), 1 : 1 : 1 : 2 : 3 : 3 : 3-heptafluoropropane has b. p. −19° (cf. *J.*, 1952, 3423), and perfluoropropane has b. p. −35° (Simons and Block, *J. Amer. Chem. Soc.*, 1937, **59**, 1407; 1939, **61**, 2962).

Spectra.—The infra-red spectra given in the annexed Table were recorded by a Perkin–Elmer Model 21 instrument with sodium chloride optics.

$(C_2F_5)(CF_3)\cdot CFI$		$CF_3\cdot CHF\cdot CF_2Br$		$CF_3\cdot CFBr\cdot CF_2Br$	
4·12 (w)	9·0 (m)	3·34 (w)	8·95 (m)	4·12 (w)	8·85 } (s)
4·51 (w)	9·36 (m)	4·43 (w)	9·46 (m)	4·37 (w)	8·95 }
5·28 (w)	9·81 (m)	7·26 (m)	10·18 (s)	4·57 (w)	9·57 (s)
5·60 (w)	10·14 (m)	7·75 (s)	11·40 (m)	5·58 (w)	9·77 (s)
5·80 (w)	10·70 (s)	8·25 (vs)	11·73 (m)	6·15 (w)	9·85 (s)
6·47 (w)	11·23 (m)	8·40 (w)	11·96 (m)	6·55 (w)	10·70 (s)
6·78 (w)	11·45 (w)	8·56 (w)	12·26 (s)	6·82 (w)	10·84 (s)
7·15 (w)	11·63 (m)	8·77 (s)	14·6 (s)	7·17 (w)	11·55 (s)
7·55 (s)	12·25 (s)			7·36 (w)	12·23 (s)
7·85 (s)	13·37 } (s)			7·90 (s)	12·94 (s)
8·15 (b.v.s.)	13·46 }			8·2 (b.v.s.)	13·6 (m)
8·5 (m)	13·86 (s)			8·44 (m)	14·14 (s)
8·67 (m)	14·20 (m)			8·68 (s)	

n-C_4F_{10}		C_3F_6 trimer	
6·94 (w)	10·40 (m)	5·77 (s)	11·30 (w)
7·41 (m)	11·0 (s)	7·27 (s)	11·60 (w)
7·65 (s)	11·54 (w)	8·0 (b.v.s.)	12·05 (w)
7·97 (vs)	13·03 } (w)	8·6 (s)	12·40 (w)
8·10 (s)	13·12 }	9·67 (m)	13·5 (m)
8·35 (w)	13·62 }	9·97 (m)	13·7 (m)
8·70 (s)	13·67 } (s)	10·20 (m)	14·27 (w)
9·35 (m)	13·74 }	11·10 (w)	

b = broad, m = medium, s = strong, v = very, w = weak.

The ultra-violet spectra were measured by a Unicam Spectrophotometer.

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