769. *Reactions of Fluorocarbon Radicals. Part XII.* The Synthesis of Fluorocarbons and of Fully Fluorinated Iodo-, Bromo-, and Chloro-alkanes.*

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The reaction of trifluoroiodomethane or of pentafluoroiodoethane with tetrafluoroethylene yields only $CF_3\cdot[CF_2\cdot CF_2]_n\cdot I$ or $CF_3\cdot CF_2\cdot[CF_2\cdot CF_2]_n\cdot I$. Isolation of the individual members of each series thus gives $CF_3\cdot[CF_2]_m\cdot I$ (m = 2—15). The mechanism and control of the polymerisation reaction are considered. The fluoroiodoalkanes have been converted into the compounds $CF_3\cdot[CF_2]_m\cdot X$ where X = H, Cl, Br, or F, and these compounds are compared with their unsubstituted (by fluorine) analogues. Perfluoro*cyclo*butane and perfluoro*cyclo*propane are by-products from the photochemical reactions of tetrafluoroethylene; the infra-red spectrum of the perfluoro*cyclo*propane readily distinguishes it from the isomeric hexafluoropropene.

The first paper of this series (Haszeldine, *J.*, 1949, 2856) described the reaction of trifluoroiodomethane with tetrafluoroethylene to give a polymer of the general formula $CF_3\cdot[CF_2\cdot CF_2]_n\cdot I$ from which small amounts of compounds with n = 1, 2, etc., were isolated. This reaction has been investigated in detail, and as reported earlier (*Nature*, 1951, **167**, 139; **168**, 1028) can now be controlled to give good yields of the compounds with n = 1—10. The present paper gives details of the similar reaction with pentafluoroiodoethane and of the conversion of the fully fluorinated iodoalkanes into the 1*H*-fluorocarbons † and into the corresponding fully fluorinated chloro- and bromo-alkanes.

The reaction of trifluoroiodomethane with tetrafluoroethylene involves a radical chain:

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

Initiation: $$CF_3\cdot + C_2F_4 \longrightarrow CF_3\cdot CF_2\cdot CF_2\cdot$$

Propagation: $$CF_3\cdot CF_2\cdot CF_2\cdot + (n-1)C_2F_4 \longrightarrow CF_3\cdot[CF_2\cdot CF_2]_n\cdot$$

Transfer: $$CF_3\cdot CF_2\cdot CF_2\cdot + CF_3I \longrightarrow CF_3\cdot CF_2\cdot CF_2I + CF_3\cdot$$

$$CF_3\cdot[CF_2\cdot CF_2]_n\cdot + CF_3I \longrightarrow CF_3\cdot[CF_2\cdot CF_2]_n\cdot I + CF_3\cdot, \text{ etc.}$$

The main factors which determine the value of n in $CF_3\cdot[CF_2\cdot CF_2]_n\cdot I$ are the relative concentrations of the chain transfer agent (*i.e.*, trifluoroiodomethane), the monomer (*i.e.*, tetrafluoroethylene), and the growing polymer radical. When the ratio of trifluoroiodomethane to tetrafluoroethylene is high, the C_3F_7 radical produced by addition of a CF_3 radical to tetrafluoroethylene reacts preferentially with the fluoro-iodide to give heptafluoroiodopropane and regenerate a trifluoromethyl radical. This chain transfer is best effected in the liquid phase where the concentration of trifluoroiodomethane is at a maximum. The reaction of trifluoroiodomethane with tetrafluoroethylene in the vapour phase gives substantially more of the polymer with $n > 2$, since the relative concentration of trifluoroiodomethane is lower, and the chance is high that the heptafluoroiodopropane formed in the vapour phase can undergo subsequent homolytic fission to generate a C_3F_7 radical which then combines with tetrafluoroethylene. Thus, when the molar ratio of trifluoroiodomethane to tetrafluoroethylene is 10 : 1 and only the liquid reactants are exposed to

* Part XI, *J.*, 1953, 3219. † 1*H* denotes a single H atom at position 1 (cf. *J.*, 1952, 5059).

light, the yield of heptafluoroiodopropane is much higher (94%) than when a molar ratio of 5 : 1 is used (81%), or when the vapour phase is irradiated (12%).

When the conditions are such that the trifluoromethyl radical can combine with a molecule of tetrafluoroethylene and then with a second molecule of the olefin to give a C_5F_{11} radical, the conditions are also such that the C_5F_{11} radical will tend to continue the polymerisation, and a spread of products with $n = 3$—10 is obtained. Equimolar amounts of trifluoroiodomethane and tetrafluoroethylene thus give the compounds with $n = 1, 2, 3,$ and >3 in 16, 10, 5, and 63% yield respectively, and when the molar ratio of trifluoroiodomethane to tetrafluoroethylene is 1 : 10 only small amounts of liquid products are obtained, and n has a value 10—20.

The wave-length of the light used to generate the trifluoromethyl radical which initiates the chain also affects n: light of shorter wave-length generates a more energetic radical, and in turn leads to a C_3F_7 radical which tends to propagate. This is apparent from comparison of results where Pyrex or silica reaction vessels are used, *i.e.*, where the initiating radiation is of $\lambda >3000$ or >2200 Å, respectively.

Each member of the polymer series $CF_3{\cdot}[CF_2{\cdot}CF_2]_n{\cdot}I$ is a fluoro-iodide with properties very similar to those of trifluoroiodomethane. The ratio of trifluoroiodomethane to the polymeric product must thus also be high, otherwise towards the end of the reaction the polymer already formed undergoes further reaction with tetrafluoroethylene:

$$CF_3{\cdot}[CF_2{\cdot}CF_2]_n{\cdot}I \xrightarrow{h\nu} CF_3{\cdot}[CF_2{\cdot}CF_2]_n{\cdot} \xrightarrow{mC_2F_4} CF_3{\cdot}[CF_2{\cdot}CF_2]_{m+n}{\cdot} \xrightarrow{CF_3{\cdot}[CF_2{\cdot}CF_2]_n{\cdot}I} CF_3{\cdot}[CF_2{\cdot}CF_2]_{m+n}{\cdot}I$$

Since a fluoro-iodide $CF_3{\cdot}[CF_2]_x{\cdot}I$ can be converted into the fluoro-iodide $CF_3{\cdot}[CF_2]_{x+2}{\cdot}I$ in high yield by reaction with a small amount of tetrafluoroethylene, the optimum method for the synthesis of the longer-chain perfluoroalkyl iodides is to proceed stepwise (*i.e.*, $C_3F_7I \longrightarrow C_5F_{11}I$; $C_5F_{11}I \longrightarrow C_7F_{15}I$; etc.).

The thermal reaction of trifluoroiodomethane with tetrafluoroethylene in glass vessels is more difficult to control, since the reactants are mainly in the vapour phase and a large excess of trifluoroiodomethane cannot be maintained. Reaction in an autoclave of a large excess of trifluoroiodomethane with tetrafluoroethylene, added portionwise, gives good yields of the 1 : 1 (50%), 1 : 2 (20%), and 1 : 3 (8%) addition products, and this method is convenient for the large-scale preparation of the fluoro-iodides containing up to fifteen carbon atoms.

The boiling points of the fluoro-iodides $CF_3{\cdot}[CF_2{\cdot}CF_2]_n{\cdot}I$ increase by *ca.* 40° per $CF_2{\cdot}CF_2$ unit, so that separation of individual members of the polymer series is not difficult. The compounds with $n = 5$—10 are readily soluble in ether and can thus be separated from compounds with $n >20$ which resemble polytetrafluoroethylene in appearance and properties. The marked increase in solubility of the fully fluorinated iodoalkanes in electron-donor solvents relative to the solubility of the corresponding fluorocarbons is ascribed to molecular-compound formation of the type recently described for heptafluoroiodopropane (Haszeldine, *J.*, 1953, 2662).

Pentafluoroiodoethane reacts with tetrafluoroethylene under conditions similar to those described for trifluoroiodomethane to give a polymer $CF_3{\cdot}CF_2{\cdot}[CF_2{\cdot}CF_2]_n{\cdot}I$. The compound with $n = 1$ can be prepared in 91% yield, and fluoro-iodides containing up to sixteen carbon atoms have been isolated. By taking alternate members of the series $CF_3{\cdot}[CF_2{\cdot}CF_2]_n{\cdot}I$ and $CF_3{\cdot}CF_2{\cdot}[CF_2{\cdot}CF_2]_n{\cdot}I$ the complete range of fluoro-iodides $CF_3{\cdot}[CF_2]_m{\cdot}I$ can be obtained. They are key compounds for the synthesis of fluorocarbon derivatives of the type RX (see *J.*, 1951, 2495). The fluoro-iodides were first prepared by this route, but an alternative synthesis has been described recently (*J.*, 1951, 584; 1952, 4259). Their ultra-violet spectra in light petroleum are given in the following Table. The $\cdot CF_2{\cdot}CF_2I$ chromophore is

Compound	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$	Compound	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$
CF_3I *	267·5	155	—	—	$C_6F_{13}I$	271	290	214	18
C_2F_5I *	268·5	165	224	105	$C_7F_{15}I$	270·5	270	218	22
C_3F_7I *	271	195	229	22	$C_8F_{17}I$	271	310	221	27
C_4F_9I	271	270	215	11	$C_9F_{19}I$	270·5	320	220	30
$C_5H_{11}I$	271	275	213	18	$C_{10}F_{21}I$	271	310	222	22

* Vapour spectra.

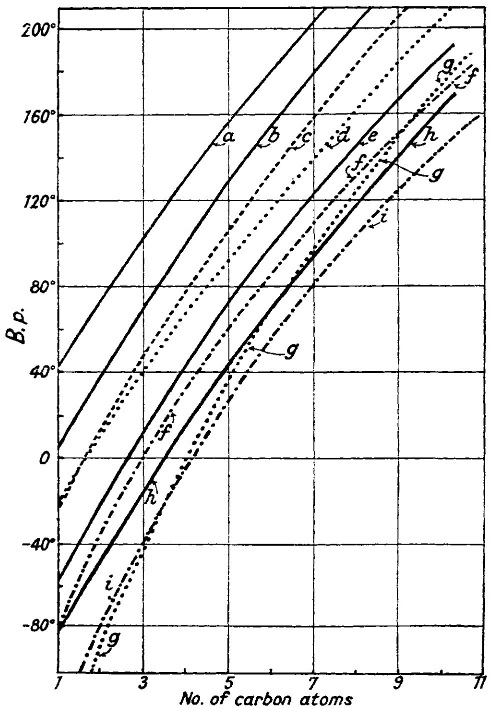
characterised by a band *ca.* 271 mμ, whereas the $\cdot CF_2\cdot CFI\cdot CF_2\cdot$ chromophore shows a band *ca.* 280 mμ (Haszeldine, *J.*, 1953, 3559).

Compounds of the type $CF_3\cdot[CF_2]_n\cdot CF{:}CF\cdot[CF_2]_m\cdot CF_3$, $CF_3\cdot[CF_2]_n\cdot CF{:}CF_2$, or $CF_3\cdot[CF_2]_n\cdot CF_3$ are not products from the reaction of trifluoroiodomethane with tetrafluoroethylene, *i.e.*, radical combination or disproportionation does not occur to any extent.

The fully fluorinated iodoalkanes are converted into the corresponding 1*H*-compounds by reaction with alcoholic potassium hydroxide at *ca.* 100° (cf. Banus, Emeléus, and Haszeldine, *J.*, 1951, 60), or with hydrogen at 350°. The hydrogen atom in the 1*H*-compounds is less reactive than in a hydrocarbon, but by photochemical halogenation it can be replaced by chlorine or bromine.

Irradiation of the fully fluorinated iodoalkanes and chlorine or bromine gives high yields (>90%) of the fully fluorinated chloro- or bromo-alkanes. These compounds, some of which have also been prepared from the corresponding carboxylic acids (*J.*, 1952, 4259), are almost as inert as the fluorocarbons.

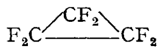
a, $CH_3\cdot[CH_2]_n\cdot I$ *d*, $CF_3\cdot[CF_2]_n\cdot I$ *g*, $CH_3\cdot[CH_2]_n\cdot H$
b, $CH_3\cdot[CH_2]_n\cdot Br$ *e*, $CF_3\cdot[CF_2]_n\cdot Br$ *h*, $CF_3\cdot[CF_2]_n\cdot H$
c, $CH_3\cdot[CH_2]_n\cdot Cl$ *f*, $CF_3\cdot[CF_2]_n\cdot Cl$ *i*, $CF_3\cdot[CF_2]_n\cdot F$



Although perfluorohexadecane has been prepared from cetane by the cobalt fluoride or the elementary-fluorine method (Haszeldine and Smith, *J.*, 1950, 2689, 2787, 3617), there is appreciable decomposition when compounds with more than nine carbon atoms are fluorinated. More important is the isomerisation which occurs: *n*-heptane, for example, gives perfluorodimethyl*cyclo*pentane (3%) and perfluoroethyl*cyclo*pentane (8%) (Burford *et al.*, *Ind. Eng. Chem.*, 1947, **39**, 319). Since the isomeric fluorocarbons have very similar boiling points, it is difficult to obtain a pure fluorocarbon by direct fluorination. Pure fluorocarbons can now be synthesised in 70—90% yield from the fluorinated iodoalkanes $CF_3\cdot[CF_2]_n\cdot I$: iodine is replaced by fluorine by use of cobalt trifluoride, fluorine, bromine trifluoride, chlorine trifluoride, or antimony pentafluoride. The infra-red spectra of the synthetic fluorocarbons $CF_3\cdot[CF_2]_n\cdot F$ will be discussed in another paper.

The boiling points of the fluorocarbons, the 1*H*-fluorocarbons and the fully fluorinated 1-chloro-, 1-bromo-, and 1-iodo-alkanes are compared with those of the corresponding hydrocarbons, and chloro-, bromo-, and iodo-alkanes in the Figure. The compounds $CF_3\cdot[CF_2]_n\cdot X$ boil about 60° below the unsubstituted compounds $CH_3\cdot[CH_2]_n\cdot X$ (X = Cl, Br, I) despite the much higher molecular weight, but the boiling-point difference is less marked for $CF_3{\cdot}[CF_2]_n{\cdot}H$ and $CH_3{\cdot}[CH_2]_n{\cdot}H$. The boiling-point curve for the hydrocarbons cuts across the curves for the fluorocarbons, for the 1*H*-fluorocarbons, and for the fully fluorinated chloroalkanes at C_4, C_6, and C_9 respectively.

The volatile by-products from the photochemical reactions of tetrafluoroethylene are perfluoro*cyclo*butane (1%) and perfluoro*cyclo*propane (3%). They are transparent to light of the wave-length used, and, once formed, do not react further. Perfluoro*cyclo*propane was originally considered to be a product from the pyrolysis of chlorodifluoromethane (Benning, Downing, and Park, U.S.P. 2,394,581/1946), but the C_3F_6 so obtained was later shown to be hexafluoropropene by infra-red, Raman, and electron-diffraction studies [(*a*) Young and Murray, (*b*) Edgell, and (*c*) Buck and Livingston, *J. Amer. Chem. Soc.*, 1948, **70**, 2814, 2816, 2817]. Atkinson (*J.*, 1952, 2684) recently reported a compound C_3F_6 produced by the mercury-sensitised photochemical polymerisation of tetrafluoroethylene, and showed that it had a melting point (−80°) much higher than that of hexafluoropropene (−156°); it was concluded that the compound was perfluoro*cyclo*propane. The constitution of the C_3F_6 isolated during the present work follows from its boiling point (−31·5°, cf. hexafluoropropene, b. p. −29·8°) and from its infra-red spectrum. This readily distinguishes it from hexafluoropropene as shown in the following Table :

$CF_3{\cdot}CF{:}CF_2$	
C:C stretching vibration 5·56 μ	No major band below 7 μ
C–F stretching vibration 8·29, 8·50 μ	C–F stretching vibration 7·85 μ
No major band 11—12 μ	Extremely strong band at 11·60 μ
Strong band at 9·67 μ	No major band 9·1—10·0 μ
Strong band at 13·05 μ	No major band 12·5—13·5 μ

Furthermore, comparison of the infra-red spectrum with that of a specimen of the C_3F_6 first isolated by Dr. Atkinson shows that the two are identical. There is thus no doubt but that both compounds C_3F_6 exist. The perfluoro*cyclo*propane is probably formed by reaction of a CF_2 radical with tetrafluoroethylene :

$$CF_3{\cdot} + C_2F_4 \longrightarrow CF_3{\cdot}CF_2{\cdot} + {\cdot}CF_2{\cdot}$$
$$C_2F_4 \longrightarrow 2CF_2{\cdot}$$
$$C_2F_4 + {\cdot}CF_2{\cdot} \longrightarrow cyclo\text{-}C_3F_6$$

(see also Atkinson, *loc. cit.*).

Experimental

Trifluoroiodomethane and pentafluoroiodoethane were prepared as described earlier (*J.*, 1948, 2188; 1949, 2953). Tetrafluoroethylene was purified by distillation in a vacuum system. Molecular weights were determined by Regnault's method. Unless otherwise stated, the fluoroiodides described below were identical with the compounds prepared by an alternative route (Haszeldine, *J.*, 1952, 4259) where analytical data are given. The use of reaction tubes of 20—50-ml. capacity means that most of the trifluoroiodomethane or pentafluoroiodomethane is in the liquid phase.

Photochemical Reaction of Trifluoroiodomethane with Tetrafluoroethylene.—Yields are based on tetrafluoroethylene; when the yield was low the experiment was done in duplicate and the products were combined for distillation.

(a) *Excess of trifluoroiodomethane.* Trifluoroiodomethane (19·6 g., 0·1 mole) was sealed in a 50-ml. Pyrex tube with tetrafluoroethylene (1·00 g., 0·01 mole) and the *liquid* phase was exposed to ultra-violet radiation from a Hanovia lamp at a distance of 10 cm.; the vapour phase was shielded and the tube was shaken in a vertical position. After 3 hr. a further quantity of tetrafluoroethylene (1·00 g.) was added and the process was repeated. Distillation then gave trifluoroiodomethane (15·5 g.), heptafluoro-1-iodopropane (5·2 g., 94%), b. p. 39—40°, undecafluoro-1-iodopentane (0·3 g., 4%), b. p. 94—96°, and traces of material with a higher b. p. A similar experiment with a silica vessel gave trifluoroiodomethane (15·3 g.), heptafluoroiodopropane (76%), undecafluoro-1-iodopentane (15%), pentadecafluoro-1-iodoheptane (5%), b. p. 134—138°, and a small residue.

The above experiments, repeated with the tetrafluoroethylene added in one portion (2·0 g.), gave (Pyrex vessel) heptafluoroiodopropane (81%), undecafluoroiodopentane (8%), and pentadecafluoroiodoheptane (3%), and (silica vessel) 62, 21, and 12% of the same compounds.

The first experiment was repeated and the *vapour* phase was irradiated. A very rapid reaction could be observed, and small particles of solid were formed as a mist inside the tube and finally deposited on the side. The products were heptafluoroiodopropane (12%), undecafluoroiodopentane (9%), pentadecafluoroiodoheptane (5%), and solid products (70%) (see below).

(b) *Equimolar amounts of trifluoroiodomethane and tetrafluoroethylene.* The conditions of the first experiment of (a) above were applied to trifluoroiodomethane (3·95 g., 0·02 mole) and tetrafluoroethylene (1·00 g., 0·01 mole). The liquid-phase reaction was rapid and solid was deposited after 10 min. The tube was opened, a second 1·00-g. portion of tetrafluoroethylene was added, and irradiation was continued for 30 min. Distillation gave heptafluoroiodopropane (16%), undecafluoroiodopentane (10%), pentadecafluoroiodoheptane (5%), and solid products (63%). The corresponding yields if the 2·00 g. of tetrafluoroethylene were added initially were 4, <0·5, and 90% respectively.

The products when a silica vessel was used were mainly solid, although traces of liquid (*ca.* 2%) were isolated.

(c) *Excess of tetrafluoroethylene.* Trifluoroiodomethane (0·4 g., 0·002 mole) and tetrafluoroethylene (2·0 g., 0·02 mole), sealed in a Pyrex tube the lower portion of which was shielded from light, were exposed to ultra-violet light for 1 hr. Rapid growth of the polymer could be observed in the vapour phase, and the small nuclei which initially appeared as a mist grew and formed amorphous particles *ca.* 1 mm. in diameter. These moved rapidly round the tube before becoming attached to the walls or sinking to the bottom of the vessel. The motion of the polymer particles ceased when the light was removed. The product was solid polymer (95%), but small yields of heptafluoroiodopropane, undecafluoroiodopentane, and pentadecafluoroiodoheptane (2—5%) collected in the shielded portion of the tube. Prolonged irradiation gave only solid products.

Thermal Reaction of Trifluoroiodomethane with Tetrafluoroethylene.—(a) *Excess of trifluoroiodomethane.* Trifluoroiodomethane (5·50 g., 0·027 mole) and tetrafluoroethylene (1·00 g., 0·01 mole) were sealed in a 50-ml. tube which was heated slowly to 200° during 8 hr. Fractionation gave heptafluoroiodopropane (23%), undecafluoroiodopentane (8%), pentadecafluoroiodoheptane (5%), and solid products (60%).

(b) *Excess of tetrafluoroethylene.* Trifluoroiodomethane (2·0 g., 0·01 mole) and tetrafluoroethylene (2·0 g., 0·02 mole) were similarly treated and yielded heptafluoroiodopropane (9%), undecafluoroiodopentane and pentadecafluoroiodoheptane (3%), and solid products (87%).

(c) *In an autoclave.* Trifluoroiodomethane (40·3 g.) and tetrafluoroethylene (5·0 g.) were heated to 220° during 8 hr. in a 50-ml. autoclave; 5·0 g. of tetrafluoroethylene were added and the cycle was repeated. A total of 20·0 g. of tetrafluoroethylene were added in this way. Distillation gave heptafluoroiodopropane (51%), undecafluoroiodopentane (21%), pentadecafluoroiodoheptane (8%), and solid products (15%). The yield of the lower members of the polymer series is increased if only one addition of tetrafluoroethylene is made and the product is then distilled, but the process is tedious.

Solid Products from Trifluoroiodomethane and Tetrafluoroethylene.—The products from the photochemical reactions when the yield of heptafluoroiodopropane was <10% were combined and distilled through a short heated column the take-off of which was heated to prevent blockage. The new *compounds* are shown in the following Table. Yields are expressed as % by wt. of the crude solid product. Compounds of higher b. p. can be isolated from the still residue when required.

Compound	B. p./mm.	Yield (%)	Found (%) C	Found (%) I	Reqd. (%) C	Reqd. (%) I
$C_9F_{19}I$	83—87°/45 (180—182°/760 micro-b. p.)	31	18·3	21·1	18·1	21·3
$C_{11}F_{23}I$	115—120/43	26	19·1	18·3	19·0	18·2
$C_{13}F_{27}I$	102—104 /10	19	19·5	16·1	19·6	16·0
$C_{15}F_{31}I$	99—105/3	9	20·1	14·0	20·1	14·2
Residue, average composition, $C_{23}F_{47}I$		15	21·3	9·6	21·3	9·8

The solid products from autoclave experiments on the scale shown above were distilled to give :

Compound	$C_9F_{19}I$	$C_{11}F_{23}I$	$C_{13}F_{27}I$	$C_{15}F_{31}I$	Residue
Yield (% of crude)	57	21	11	4	7

Fluorocarbons were not detected in the intermediate fractions in the above distillations.

Volatile Products from Photochemical Reactions involving Tetrafluoroethylene.—The volatile products from the photochemical experiments in which an excess of tetrafluoroethylene had been used were exhaustively fractionated *in vacuo*. The most volatile fraction was treated with bromine to remove tetrafluoroethylene; there was no residue, *i.e.*, hexafluoroethane is not a product. Spectroscopic examination of the other products revealed perfluoro*cyclo*butane (1%) and perfluoro*cyclo*propane (3% based on tetrafluoroethylene), b. p. −31·5° (isoteniscope) (Found: C, 24·0; F, 75·6%; *M*, 150. Calc. for C_3F_6: C, 24·0; F, 76·0%; *M*, 150). The infra-red spectrum of this compound distinguishes it from hexafluoropropene.

Photochemical Reaction of Pentafluoroiodoethane with Tetrafluoroethylene.—(i) *Excess of pentafluoroiodoethane*. Under conditions identical with those for the photochemical reaction of trifluoroiodomethane (a) above, pentafluoroiodoethane (25 g., 0·1 mole) and tetrafluoroethylene (two portions of 1·0 g.; 0·02 mole total) irradiated in the liquid phase in a Pyrex vessel gave nonafluoro-1-iodobutane (6·3 g., 91%), b. p. 66—68°, tridecafluoro-1-iodohexane (0·4 g., 4%), b. p. 116—119°, and solid products (*ca.* 1 g.).

The products in a silica vessel were nonafluoroiodobutane (61%), tridecafluoroiodohexane (17%), *heptadecafluoro-1-iodo-octane* (7%), b. p. 95°/103 mm., 160—161°/760 mm. (micro) (Found: C, 17·7; I, 23·0. C_8IF_{17} requires C, 17·6; I, 23·3%), and solid products (6%).

(ii) *Excess of tetrafluoroethylene*. The results were similar to those described above for trifluoroiodomethane, and solid polymer was the main product (see below).

Solid Products from Pentafluoroiodoethane and Tetrafluoroethylene.—The solid products from the photochemical and autoclave experiments were distilled, to give the new *iodo*-compounds shown in the Table. Yields are as % by wt. of the crude solid:

Compound	B. p./mm.	Yield (%)	Found (%) C	Found (%) I	Reqd. (%) C	Reqd. (%) I
$C_{10}F_{21}I$	102—106°/45 195—200°/760 (micro b. p.)	34	18·7	19·5	18·6	19·7
$C_{12}F_{25}I$	108—110/18	20	19·2	16·9	19·3	17·0
$C_{14}F_{29}I$	93—97/5	11	20·0	14·7	19·9	15·0
$C_{16}F_{33}I$	87—94/0·5	4	20·2	13·5	20·3	13·4
Residue, average composition, $C_{26}F_{53}I$		31	21·5	8·5	21·6	8·8

The fluoro-iodides $CF_3\cdot[CF_2]_n\cdot I$ with $n > 8$ are white waxy solids which sublime as plates *in vacuo*, and closely resemble the perfluoroalkanes. The crystals become pink on exposure to ultra-violet light.

Reaction of Heptafluoroiodopropane, Nonafluoroiodobutane, or Undecafluoroiodopentane with Tetrafluoroethylene.—The fluoro-iodides were sealed with tetrafluoroethylene (3 × 1 g.) in a silica tube, and the liquid phase was irradiated for 3 hr. after the addition of each portion of tetrafluoroethylene. Distillation gave the following results:

Starting compound	Product (%) $C_5F_{11}I$	$C_6F_{13}I$	$C_7F_{15}I$	$C_8F_{17}I$	Solid
C_3F_7I (21 g.)	57	—	21	—	22
C_4F_9I (22 g.)	—	51	—	17	32
$C_5F_{11}I$ (25 g.)	—	—	44	—	59

Replacement of Iodine in fully Fluorinated Iodoalkanes by Hydrogen, Chlorine, Bromine, or Fluorine.—(a) *By hydrogen*. Alcoholic potassium hydroxide (400% of 10%) was heated with the fluoro-iodide (3 g.) at 100—130° for 10 hr. to give the corresponding 1*H-fluorocarbons* shown in the Table:

Compound	B. p.	Yield (%)	Found: C (%)	Found: *M*	Required: C (%)	Required: *M*
C_3F_7H [a]	−16°	51	21·2	170	21·2	170
C_4F_9H	14	47	21·7	220	21·8	220
$C_5F_{11}H$	44	41	22·3	270	22·2	270
$C_6F_{13}H$	69—70	32	22·5	320	22·5	320
$C_7F_{15}H$	96	36	23·0	367	22·7	370
$C_8F_{17}H$	69—70°/149 mm. (micro-b. p. 118°/760 mm.)	27	22·8	—	22·9	—

[a] Haszeldine, *J.*, 1952, 3423, reports b. p. −14°.

The compounds C_3F_7H, C_4F_9H, and $C_5F_{11}H$ were also obtained (>80%) by reaction of the corresponding fluoro-iodides with hydrogen (60 atm.) at 350° in presence of Raney nickel catalyst. The C–H stretching vibration in the infra-red is at 3·35 μ.

(b) *By bromine*. The fluoro-iodide (1—2 g.) was sealed in a silica tube with a 10% excess of bromine and the mixture was irradiated by ultra-violet light for 7 days. The procucts were washed with aqueous sodium hydroxide and fractionated *in vacuo*, to give the bromo-compounds shown in the annexed Table. The compounds were first obtained by this route and are identical with those prepared from the silver salts of the corresponding acids (Haszeldine, *J.*, 1952, 4259).

$CF_3\cdot[CF_2]_n\cdot Br$	B. p.	Yield (%)	*M* (found)	*M* (calc.)
C_2F_5Br	−20°	92	200	199
C_3F_7Br	12	98	249	249
C_4F_9Br	43—44	95	298	299
$C_5F_{11}Br$	74—75	90	348	349
$C_6F_{13}Br$	100—101	91	395	399

(c) *By chlorine.* Reaction of the fluoro-iodide (1—2·5 g.) with a 30% excess of chlorine as in (b) above gave the products $CF_3\cdot[CF_2]_n\cdot Cl$ shown in the annexed Table.

$CF_3\cdot[CF_2]_n\cdot Cl$	B. p.	Yield (%)	*M* (found)	*M* (calc.)
C_2F_5Cl	−36°	98	154	154·5
C_3F_7Cl	−1	97	204	204·5
C_4F_9Cl	29—30	98	255	254·5
$C_5F_{11}Cl$	60	96	304	304·5
$C_6F_{13}Cl$	85—86	95	353	354·5
$C_7F_{15}Cl$	109—110	93	402	404·5

(d) *By fluorine, by means of cobalt trifluoride or fluorine.* The fluoro-iodide (2·5—3·5 g.) was added dropwise to a horizontal cobalt fluoride reaction vessel heated at 350—400° and charged with 100 g. of cobalt trifluoride. The products were condensed in a trap cooled by liquid oxygen, and were washed with dilute aqueous sodium hydroxide and distilled, to give the fluorocarbons shown in the annexed Table. See Haszeldine and Smith, *J.*, 1951, 603, for the physical properties of fluorocarbons prepared from the corresponding hydrocarbons.

$CF_3\cdot[CF_2]_n\cdot CF_3$	B. p.	Yield (%)	Found	Calc.
C_3F_8	−38°	89 (77)	*M*, 190	*M*, 188
C_4F_{10}	− 1	87 (81)	*M*, 238	*M*, 238
C_5F_{12}	26	84 (72)	*M*, 286	*M*, 288
C_6F_{14}	56	78 (—)	*M*, 335	*M*, 338
C_7F_{16}	82—83	79 (67)	*M*, 386	*M*, 388
C_8F_{18}	103—104	78 (69)	*M*, 440	*M*, 438
C_9F_{20}	124	80 (—)	C, 22·0%	C, 22·1%
$C_{10}F_{22}$	145—146	74 (—)	C, 22·2%	C, 22·3%
$C_{11}F_{24}$	160—162	73 (—)	C, 22·1%	C, 22·4%
$C_{12}F_{26}$	177—179	77 (65)	C, 22·3%	C, 22·6%

In an alternative method, the fluoro-iodide (2·5—3·0 g.) was vaporised by addition dropwise to a heated steel vessel whence it was carried by a stream of oxygen-free nitrogen into a reaction chamber, 12″ long, packed with gold-plated copper turnings in the way described by Haszeldine and Smith (*J.*, 1950, 2689 *et seq.*) and heated to 150°. A slight excess of fluorine diluted by nitrogen (1 : 10) was passed into the reactor simultaneously. The reaction products, treated as described above, gave the yields shown in parentheses in the Table.

(e) *By fluorine, by means of bromine or chlorine trifluoride or antimony pentafluoride.* To the fluoro-iodide (2 g.) in a small cylindrical nickel trap cooled by liquid nitrogen was added dropwise a 200% excess of bromine trifluoride. The gaseous products were collected in a silica trap cooled by liquid nitrogen. After the addition of 5 drops of the halogen fluoride, the temperature was allowed to rise to *ca.* −20°, to complete the vigorous reaction and prevent accumulation of an excess of bromine trifluoride in presence of unchanged fluoro-iodide. The vessel was then cooled and further halogen fluoride added. It is important to control the reaction in this way to prevent small explosions. The gaseous products were treated as in (b) above. Only traces of bromofluorocarbons were detected. The yields are shown in the Table below.

The reaction of chlorine trifluoride and the more volatile fluoro-iodides (C_2—C_4) was carried out in the vapour phase at 50—100°, in the apparatus described for fluorine [(c) above]. Chlorine trifluoride was diluted by nitrogen (1 : 10) and passed slowly through the less-volatile fluoro-iodides in a silica vessel cooled to 10—20°. The products were washed with aqueous alkali and purified by distillation. The chloro-fluorocarbon (up to 15%) was obtained as by-product in each case. The yields are shown in the Table.

The fluoro-iodide under investigation (2 g.) was sealed with an excess of antimony pentafluoride in a small autoclave which was then heated at 250° for 8 hr., then stepwise to 320° during 24 hr. Distillation gave the results shown in the Table.

Fluorocarbon		C_3F_8			C_4F_{10}			C_5F_{12}			C_6F_{14}	
Reagent	BrF_3	ClF_3	SbF_5	BrF_3	ClF_3	SbF_5	BrF_3	ClF_3	SbF_5	BrF_3	ClF_3	SbF_5
Yield (%)	89	70	67	88	61	70	85	67	65	80	71	68
Fluorocarbon		C_7F_{16}			C_8F_{18}			C_9F_{20}			$C_{10}F_{22}$	
Reagent	BrF_3	ClF_3	SbF_5	BrF_3	ClF_3	—	BrF_3	—	—	BrF_3	—	SbF_5
Yield (%)	84	73	66	81	64	—	75	—	—	76	—	60

Conversion of 1*H-Fluoroalkanes into Chloro- or Bromo-fluoroalkanes.*—In the general procedure, the 1*H*-fluoroalkane (1—2 g.) was sealed in a silica tube with a 250% excess of chlorine or bromine. Oxygen was excluded. The tube was then fitted with a heater wound on an open frame which fitted over the tube so that the contents of the tube could be heated (100—150°) and irradiated. A Hanovia lamp was used without the Woods filter, and was placed as close as possible to the reaction vessel. Irradiation was continued for 3—4 weeks (this period may be excessive), and the products were then distilled to give the results shown below. The % of reaction is shown in the Table; the yield was quantitative.

Compound	C_3F_7H	C_4F_9H	$C_5F_{11}H$	$C_6F_{13}H$	$C_7F_{15}H$	$C_8F_{17}H$
Chloro-compound (%)	89	81	77	79	65	73
Bromo-compound (%)	62	68	69	70	58	66

Ultra-violet Spectra.—A Beckman DU instrument was used. The light petroleum used as solvent had b. p. 60—70°.

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