Fluoro-olefins. Part IV. Synthesis of Polyfluoroalkanes containing Functional Groups from Chlorotrifluoroethylene, and the Short-chain Polymerisation of Olefins.†*

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The photochemical reaction of $CF_2Cl·CFClI$ with chlorotrifluoroethylene yields compounds of general formula $Cl·[CF_2·CFCl]_n·I$; those with $n = 1$—11 have been isolated. The iodine can easily be replaced by chlorine to give compounds $Cl·[CF_2·CFCl]_n·Cl$ which show high chemical and thermal stability. The terminal $CF_2Cl·CFCl$ group can be converted into $CF_2{:}CF$, which can then undergo addition reactions such as formation of sulphonic acids $Cl·[CFCl·CF_2]_{n-1}·CHF·CF_2·SO_3H$, and can be oxidised to give long-chain acids $Cl·[CFCl·CF_2]_{n-1}·CO_2H$. Photochemical oxidation of the $-CFClI$ group in $Cl·[CF_2·CFCl]_n·I$ gives $Cl·[CF_2·CFCl]_{n-1}·CF_2·CO_2H$. Reactions of the salts of these acids are described. The factors which affect the short-chain polymerisation of fluoro-olefins are considered.

THE development of a chemistry based upon perfluorocarbons as parent compounds, just as hydrocarbons are regarded as parent compounds in organic chemistry, can follow two main paths, (*a*) conversion of an organic compound containing a functional group into the corresponding perfluoro-compound and (*b*) synthesis of the polyfluoro-compound from smaller molecules. The replacement of hydrogen by fluorine in a compound which already contains the functional group can be achieved only to a limited extent by direct fluorination or by use of cobaltic fluoride, since loss of the functional group usually occurs with formation of the perfluorocarbon from the resulting fragment. Electrolysis of an organic compound in anhydrous hydrogen fluoride leads in certain cases to formation of the perfluoro-compound which still retains the functional group, *e.g.*, the electrolysis of derivatives of carboxylic acids to give perfluoroacyl fluorides (U.S.P. 2,593,737/1951) and the electrolysis of alkanesulphonyl fluorides or chlorides to give perfluoroalkanesulphonyl fluorides almost quantitatively (Gramstad and Haszeldine, *J.*, in the press). Even with this improved technique, replacement of hydrogen by fluorine in a long-chain compound is often accompanied by excessive breakdown and formation of a complex mixture of products. The approach which involves replacement of hydrogen by fluorine is thus best suited for preparation of short-chain compounds.

The second approach is to build up a polyfluorocarbon chain by controlled polymerisation of a suitable relatively cheap polyhalogeno-olefin, yet leaving an atom or group at the end or ends of the chain which can be easily converted into a suitable functional group. This approach, which is potentially the more versatile, has been exemplified by the synthesis of compounds $CF_3·[CF_2·CF_2]_n·I$ from tetrafluoroethylene and trifluoroiodomethane (Haszeldine, *J.*, 1949, 2856; 1953, 3761), since the value of n can be controlled and the C–I bond can be made to undergo a wide variety of reactions, *e.g.*, replacement by $-MgI$, $-CO_2H$, $-PO_3H$, or $-CF{:}CF_2$ as reported earlier (see Haszeldine, *Ann. Reports*, 1954, **51**, 279, for references).

The second approach has now been studied further by use of chlorotrifluoroethylene as the olefin and 1 : 2-dichloro-1 : 2 : 2-trifluoroiodoethane (I) as the source of polyfluoroalkyl radical. The value of the fluoroethane (I) lies in its ease of preparation from chlorotrifluoroethylene and iodine monochloride (Part I, *J.*, 1952, 4423) and in its ready conversion after reaction into a $CF_2{:}CF-$ group which is thus attached at the end of a polyfluoroalkane chain and is available for subsequent reaction, *e.g.*, by oxidation to give $-CO_2H$, or by addition to give $-CHF·CF_2·SO_3H$.

Commercially available chlorotrifluoroethylene can be polymerised to a solid high polymer. Miller, Dittman, Ehrenfeld, and Probe (*Ind. Eng. Chem.*, 1947, **39**, 333)

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* Part III, *J.*, 1955, 3880.

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described the preparation of oils and waxes from chlorotrifluoroethylene by use of benzoyl peroxide in chloroform, but such products contain C_6H_5, $C_6H_5{\cdot}CO{\cdot}O$, $CHCl_2$, or CCl_3 end groups which cause instability and necessitate further treatment to replace hydrogen or chlorine in the end groups by fluorine. During this step appreciable loss of material occurs. Furthermore, the products so obtained cannot be used for further synthesis, since they contain no potential functional group.

1 : 2-Dichloro-1 : 2 : 2-trifluoroiodoethane reacts smoothly with chlorotrifluoroethylene under the influence of ultraviolet light or heat or a combination of the two, to give products $Cl{\cdot}[CF_2{\cdot}CFCl]_n{\cdot}I$ produced by a free-radical chain reaction :

$$\text{(I)}\ CF_2Cl{\cdot}CFClI \xrightarrow{h\nu} CF_2Cl{\cdot}CFCl{\cdot} + I{\cdot}$$

$$CF_2Cl{\cdot}CFCl{\cdot} + CF_2{:}CFCl \longrightarrow CF_2Cl{\cdot}CFCl{\cdot}CF_2{\cdot}CFCl{\cdot} \quad \text{Initiation}$$

$$CF_2Cl{\cdot}CFCl{\cdot}CF_2{\cdot}CFCl{\cdot} + CF_2{:}CFCl \longrightarrow Cl{\cdot}[CF_2{\cdot}CFCl]_3{\cdot}CF_2{\cdot}CFCl{\cdot} \quad \text{Propagation}$$

$$CF_2Cl{\cdot}CFCl{\cdot}CF_2{\cdot}CFCl{\cdot} + CF_2Cl{\cdot}CFClI \longrightarrow CF_2Cl{\cdot}CFCl{\cdot}CF_2{\cdot}CFClI + CF_2Cl{\cdot}CFCl{\cdot} \longrightarrow \text{etc.}$$

Chain Transfer

Peroxide initiators could clearly be used for this reaction on a larger scale. As demonstrated for the reaction of trifluoroiodomethane with tetrafluoroethylene (*J.*, 1953, 3761), the main factors which determine n in $Cl{\cdot}[CF_2{\cdot}CFCl]_n{\cdot}I$ are the relative concentrations of the chain-transfer agent (I), the monomer (*i.e.*, chlorotrifluoroethylene), and the growing polymer radical. A high ratio of the chain-transfer agent to chlorotrifluoroethylene enables the $CF_2Cl{\cdot}CFCl{\cdot}CF_2{\cdot}CFCl{\cdot}$ radical, produced by the initial reaction of the $CF_2Cl{\cdot}CFCl{\cdot}$ radical with the olefin, to react with 1 : 2-dichloro-1 : 2 : 2-trifluoroiodoethane (I) rather than with chlorotrifluoroethylene, and so produce 1 : 2 : 4-trichlorohexafluoro-4-iodobutane (II) with regeneration of a $CF_2Cl{\cdot}CFCl{\cdot}$ radical. This chain transfer is best effected in the liquid phase where the concentration of the fluoroethane (I) is at a maximum. Use of a ratio of 15 : 1 gives a 75% yield of the compound (II).

$$\text{(II)}\ CF_2Cl{\cdot}CFCl{\cdot}CF_2.CFClI \qquad CF_2Cl{\cdot}CFCl{\cdot}CF_2{\cdot}CFCl_2\ \text{(III)}$$

Irradiation of equimolar quantities of 1 : 2-dichloro-1 : 2 : 2-trifluoroiodoethane and the olefin gives compounds $Cl{\cdot}[CF_2{\cdot}CFCl]_n{\cdot}I$ in the following yields : $n = 2$, 18% ; $n = 3$, 14% ; $n = 4$, 17% ; $n > 4$, 39%. Use of an excess of chlorotrifluoroethylene gives a wider spread of products with consequently more difficulty in separation of individual members of the polymer series.

Each member of the series $Cl{\cdot}[CF_2{\cdot}CFCl]_n{\cdot}I$ contains a CFClI group and has properties similar to those of $CF_2Cl{\cdot}CFClI$. The ratio of the amount of the latter to that of polymeric product $Cl{\cdot}[CF_2{\cdot}CFCl]_n{\cdot}I$ at any instant must thus be high, otherwise further reaction of chlorotrifluoroethylene with the polymer already formed will occur :

$$Cl{\cdot}[CF_2{\cdot}CFCl]_n{\cdot}I \xrightarrow[h\nu]{mCF_2{:}CFCl} Cl{\cdot}[CF_2{\cdot}CFCl]_{(m+n)}{\cdot}I$$

and increased spread in the value of n will result. The optimum method for the synthesis of any given longer-chain iodo-compound is thus to proceed stepwise using an excess of the chain-transfer agent, since a compound $Cl{\cdot}[CF_2{\cdot}CFCl]_n{\cdot}I$ can be converted into $Cl{\cdot}[CF_2{\cdot}CFCl]_{(n+1)}{\cdot}I$ in high yield under these conditions, *e.g.*,

$$Cl{\cdot}[CF_2{\cdot}CFCl]_2{\cdot}I \xrightarrow{CF_2{:}CFCl} Cl{\cdot}[CF_2{\cdot}CFCl]_3{\cdot}I \xrightarrow{CF_2{:}CFCl} Cl{\cdot}[CF_2{\cdot}CFCl]_4{\cdot}I \longrightarrow \text{etc.}$$

where the compounds $Cl{\cdot}[CF_2{\cdot}CFCl]_n{\cdot}I$ with $n = 2$, 3, 4, etc., are used successively as chain-transfer agents.

The compounds $Cl{\cdot}[CF_2{\cdot}CFCl]_n{\cdot}I$ remain liquid to a greater value of n than the corresponding compounds $CF_3{\cdot}[CF_2{\cdot}CF_2]_n{\cdot}I$, but when n is greater than 20 waxes and solids are obtained which resemble poly(chlorotrifluoroethylene) and poly(tetrafluoroethylene) in appearance.

The C–I bond in a –CFClI group is appreciably weaker than that in trifluoroiodomethane. This is attributed to steric repulsion caused by the chlorine atom, and is reflected in the ultraviolet spectra of compounds which contain this group (cf. $CF_3\cdot CF_2\cdot CF_2I$, $\lambda_{max.}$ 271 mμ; $CF_3\cdot CF_2\cdot CFClI$, $\lambda_{max.}$ 286 mμ; $CF_2Cl\cdot CF_2I$, $\lambda_{max.}$ 272 mμ; $CF_2Cl\cdot CFClI$, $\lambda_{max.}$ 283 mμ in light petroleum : see Haszeldine, *J.*, 1953, 1764; Haszeldine and Steele, *J.*, 1953, 1592, for interpretation of the spectra). This means that photolysis of the C–I bond in 1 : 2-dichloro-1 : 2 : 2-trifluoroiodoethane is particularly easy and that the chain transfer step is particularly efficient. The reaction of 1 : 2-dichloro-1 : 2 : 2-trifluoroiodoethane with chlorotrifluoroethylene is thus more easily controlled than that between trifluoroiodomethane and tetrafluoroethylene, and the compounds $Cl\cdot[CF_2\cdot CFCl]_n\cdot I$ where $n = 2$—20 are readily produced. These compounds contain a CF_2 group adjacent to the terminal CFClI group, and this makes them appreciably more stable to distillation than the dichlorotrifluoroiodoethane, which has a CF_2Cl group next to the CFClI group and tends to lose iodine monochloride when heated. The compounds are very sensitive to oxygen which must be rigidly excluded during distillation if breakdown is to be avoided. Exposure of the crude polymer to air before distillation appears to cause formation of peroxides, since decomposition during distillation is then much more marked and the higher members of the series cannot be obtained pure.

The possibility of radical combination's occurring during the polymerisation can be excluded for the shorter-chain polymer, but material of this type might be present to a small extent in the polymer of higher molecular weight.

Free radicals were unambiguously shown to add exclusively to the CF_2 group of chlorotrifluoroethylene by earlier studies (Haszeldine and Steele, *J.*, 1953, 1592; 1954, 3747), where it was also shown that poly(chlorotrifluoroethylene) is formed by head-to-tail addition; it is thus highly probable that the $CF_2Cl\cdot CFCl$ radical attacks the CF_2 group of chlorotrifluoroethylene. This was rigidly proved by study of 1 : 2 : 4-trichlorohexafluoro-4-iodobutane (II), photochemical chlorination of which gives 1 : 1 : 3 : 4-tetrachlorohexafluorobutane (III). This product is isomeric with 1 : 2 : 3 : 4-tetrachlorohexafluorobutane (IV) which would be produced if the $CF_2Cl\cdot CFCl$ radical attacked the CFCl group of chlorotrifluoroethylene :

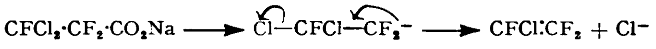
$$CF_2Cl\cdot CFCl\cdot \xrightarrow{CF_2{:}CFCl} CF_2Cl\cdot CFCl\cdot CFCl\cdot CF_2\cdot \xrightarrow{CF_2Cl\cdot CFClI} CF_2Cl\cdot CFCl\cdot CFCl\cdot CF_2I \xrightarrow[h\nu]{Cl_2} \underset{(IV)}{(CF_2Cl\cdot CFCl)_2}$$

The absence of even traces of compound (IV) in the photochemical chlorination product was shown by reaction with zinc and ethanol, which failed to yield hexafluorobutadiene; this conversion is known to occur in high yield under the conditions used (Part I, *loc. cit.*) and the diene is readily detectable even in small amount by means of its infrared spectrum. Attack of the $CF_2Cl\cdot CFCl$ radical is thus exclusively on the CF_2 group of chlorotrifluoroethylene.

1 : 1 : 3 : 4-Tetrachlorohexafluorobutane (III) reacts with zinc and ethanol under mild conditions to give 4 : 4-dichlorohexafluorobut-1-ene (V), which is isomeric with the 1 : 4-dichlorohexafluorobut-2-ene described in Part I (*loc. cit.*). Photochemical chlorination regenerates 1 : 1 : 3 : 4-tetrachlorohexafluorobutane, and bromination similarly gives 1 : 2-dibromo-4 : 4-dichlorohexafluorobutane (VI). Permanganate oxidation of the butene (V) must be carried out with control of pH to prevent complete breakdown. ββ-Dichlorotrifluoropropionic acid (VII) is formed in good yield. Pyrolysis of its anhydrous silver salt causes breakdown to silver chloride, etc., instead of the coupling to give $(CFCl_2\cdot CF_2)_2$ which might have been expected by analogy with silver perfluoropropionate which gives perfluorobutane (*J.*, 1953, 1548). The silver salt reacts smoothly with chlorine, however, and pyrolysis of anhydrous sodium 3 : 3-dichlorotrifluoropropionate also proceeds as expected :

$$\underset{(V)}{CF_2{:}CF\cdot CF_2\cdot CFCl_2} \qquad \underset{(VI)}{CF_2Br\cdot CFBr\cdot CF_2\cdot CFCl_2} \qquad \underset{(VII)}{CFCl_2\cdot CF_2\cdot CO_2H}$$

$$CFCl_2\cdot CF_2\cdot CO_2Ag + Cl_2 \longrightarrow CFCl_2\cdot CF_2Cl + CO_2 + AgCl$$



$$CFCl_2\cdot CF_2\cdot CO_2Na \longrightarrow Cl{-}CFCl{-}CF_2^- \longrightarrow CFCl{:}CF_2 + Cl^-$$

Application of the silver- and sodium-salt degradation reactions to chloropolyfluoro-acids as well as to perfluoro-mono- and -di-basic acids (*J.*, 1951, 584; 1952, 993; 1954, 4026) was demonstrated recently (Part III, *loc. cit.*) and is here illustrated further. It will be noted that olefin formation is accompanied by loss of chlorine rather than fluorine. The formation of 1 : 1 : 2-trichlorotrifluoroethane and chlorotrifluoroethylene in good yield by the above reactions proves the structure of the acid (VII), and hence of the butene (V) and the butanes (III) and (II).

The constitution of the longer-chain members of the $Cl{\cdot}[CF_2{\cdot}CFCl]_n{\cdot}I$ series will clearly follow that of the compound where $n = 2$. This is supported by the ultraviolet spectra shown in Table 1, which reveal the –CFClI chromophore.

TABLE 1. *Ultraviolet spectra of* $Cl{\cdot}[CF_2{\cdot}CFCl]_n{\cdot}I$ *in light petroleum* (b. p. 60—80°).

n	$\lambda_{max.}$	ε	$\lambda_{min.}$	ε	*n*	$\lambda_{max.}$	ε	$\lambda_{min.}$	ε
1	283	315	229	25	7	293·5	350	240	70
2	286·5	320	231	35	8	293·5	345	241	70
3	291	330	238·5	50	9	294	355	242	75
4	291·5	335	237·5	60	10	294	360	242	80
5	292	345	240	65	16—18		$\lambda_{max.}$ 294 mμ		
6	293	345	242	65	20 (average)	$\lambda_{max.}$ 290 mμ in $CHCl_3$			

The –CFClI chromophore shows maximum absorption at 286 mμ, shifting to 294 mμ with increase in chain length (*J.*, 1953, 1592, 1764) whereas the $-CF_2I$ chromophore absorbs at 271—272 mμ (*J.*, 1953, 1764, 3761) for solutions in light petroleum. Increase in chain length in $Cl{\cdot}[CF_2{\cdot}CFCl]_n{\cdot}I$ thus causes a distinct shift toward the red of 10 mμ, and there is little change in the spectrum when $n > 4$. The material which has an average value of $n = 20$ is insufficiently soluble in light petroleum, but chloroform dissolves it readily.

The polymer series $Cl{\cdot}[CF_2{\cdot}CFCl]_n{\cdot}I$ reacts smoothly with chlorine to give $Cl{\cdot}[CF_2{\cdot}CFCl]_n{\cdot}Cl$, particularly if an inert diluent is used with the more viscous compounds. These compounds show great thermal and chemical stability approaching that of poly(chlorotrifluoroethylene). There is no point of weakness for chemical attack, since the end groups are CF_2Cl and $CFCl_2$. The compounds range from liquids through thin oils, viscous oils, and waxes, to solids. Replacement of iodine by chlorine in a polymer fraction which contains a range of values for *n* gives a product which remains an oil despite the fact that individual members of the mixtures are waxes or solids. Such mixtures can be used as lubricants or as thermally stable liquids, and this method of preparation of polyfluoro-oils is better than any so far devised, since end-group stabilisation is achieved simply yet efficiently and without loss of material or use of powerful fluorinating agents. The thermal stability of the compounds $Cl{\cdot}[CF_2{\cdot}CFCl]_n{\cdot}Cl$ makes their separation by distillation easier, and the compounds with $n = 1—8$ have thus been isolated.

The iodine in $Cl{\cdot}[CF_2{\cdot}CFCl]_n{\cdot}I$ can be replaced by fluorine by use of reagents such as bromine or chlorine trifluoride (*e.g.*, $CF_2Cl{\cdot}CFCl{\cdot}CF_2{\cdot}CFClI \longrightarrow CF_2Cl{\cdot}CFCl{\cdot}CF_2{\cdot}CF_2Cl$).

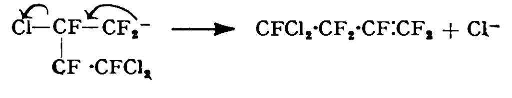
Reaction of $Cl{\cdot}[CF_2{\cdot}CFCl]_3{\cdot}Cl$ with zinc and ethanol under mild conditions gives the olefin (VIII) :

$$CF_2Cl{\cdot}CFCl{\cdot}CF_2{\cdot}CFCl{\cdot}CF_2{\cdot}CFCl_2 \longrightarrow CF_2{:}CF{\cdot}CF_2{\cdot}CFCl{\cdot}CF_2{\cdot}CFCl_2 \quad \text{(VIII)}$$

and this type of reaction can be applied to the longer-chain compounds to give $CF_2{:}CF{\cdot}[CF_2{\cdot}CFCl]_m{\cdot}Cl$. The structure of the olefin (VIII) follows from the reactions of the monocarboxylic acid obtained by permanganate oxidation in presence of sodium hydrogen carbonate. Pyrolysis of the anhydrous sodium salt gives 4 : 4-dichlorohexafluorobut-1-ene (V), identical with the compound described above :

$$\text{(VIII)} \xrightarrow{KMnO_4} CFCl_2{\cdot}CF_2{\cdot}CFCl{\cdot}CF_2{\cdot}CO_2H \longrightarrow CFCl_2{\cdot}CF_2{\cdot}CFCl{\cdot}CF_2{\cdot}CO_2Na$$

$$CFCl_2{\cdot}CF_2{\cdot}CFCl{\cdot}CF_2{\cdot}CO_2Na \longrightarrow CFCl_2{\cdot}CF_2{\cdot}CFCl{\cdot}CF_2^- + CO_2 + Na^+$$



$$\underset{\displaystyle CF{\cdot}CFCl_2}{Cl{-}\overset{|}{CF}}{-}CF_2^- \longrightarrow CFCl_2{\cdot}CF_2{\cdot}CF{:}CF_2 + Cl^-$$

Reaction of the silver salt of the acid similarly gave 1 : 1 : 3 : 4-tetrachlorohexafluorobutane (III) :

$$\mathrm{CFCl_2{\cdot}CF_2{\cdot}CFCl{\cdot}CF_2{\cdot}CO_2Ag + Cl_2 \longrightarrow CFCl_2{\cdot}CF_2{\cdot}CFCl{\cdot}CF_2Cl + AgCl + CO_2}$$

The olefins $\mathrm{CF_2{:}CF{\cdot}[CF_2{\cdot}CFCl]_{\mathit{m}}{\cdot}Cl}$ can be used to give other compounds which contain functional groups. Peroxide-initiated reaction with sodium hydrogen sulphite thus yields sulphonic acids :

$$\mathrm{Cl{\cdot}[CFCl{\cdot}CF_2]_{\mathit{m}}{\cdot}CF{:}CF_2 \xrightarrow{NaHSO_3} Cl{\cdot}[CFCl{\cdot}CF_2]_{\mathit{m}}{\cdot}CHF{\cdot}CF_2{\cdot}SO_3Na}$$

this is illustrated by preparation of the compounds where $m = 1$ or 2. Barrick (U.S.P. 2,403,207/1946) first showed that tetrafluoroethylene reacted with sodium hydrogen sulphite to give tetrafluoroethanesulphonic acid, and Koshar, Trott, and LaZerte (*J. Amer. Chem. Soc.*, 1953, **75**, 4595) have recently extended this to the reactions of longer-chain terminal perfluoro-olefins. The longer-chain polychloropolyfluoroalkanesulphonic acids are strong acids which are readily soluble in water and liberate hydrogen chloride from sodium chloride. They show distinct surface activity in aqueous solution.

Photochemical oxidation of 1-chlorohexafluoro-1-iodopropane in presence of water gives pentafluoropropionic acid in high yield ($\mathrm{C_2F_5{\cdot}CFClI \xrightarrow{O_2,\,\mathit{h\nu}} C_2F_5{\cdot}COF \xrightarrow{H_2O} C_2F_5{\cdot}CO_2H}$; Francis and Haszeldine, *J.*, 1955, 2151). This useful general method for the preparation of polyfluoro-acids has been applied to the compounds $\mathrm{Cl{\cdot}[CF_2{\cdot}CFCl]_{\mathit{n}}{\cdot}CF_2{\cdot}CFClI}$ to give satisfactory yields of long-chain polyfluoro-acids. On a small scale ultraviolet light can be used to cleave the C–I bond to initiate the radical chain reaction leading to the formation of the polyfluoroalkoxy-radical, but on a larger scale thermal cleavage of the C–I bond, or abstraction of iodine by a radical generated from an added peroxide such as benzoyl peroxide can be used in absence of light. This permits use of conventional equipment such as autoclaves :

$$\begin{tikzcd}
\mathrm{Cl{\cdot}[CF_2{\cdot}CFCl]_{\mathit{n}}{\cdot}CF_2{\cdot}CFClI} \arrow[r, "h\nu\ \text{(or Ph}\cdot)"] & \mathrm{Cl{\cdot}[CF_2{\cdot}CFCl]_{\mathit{n}}{\cdot}CF_2{\cdot}CFCl{\cdot}} + \mathrm{I{\cdot}}\ \text{(or PhI)} \arrow[d, "\mathrm{O_2}"] \\
 & \mathrm{Cl{\cdot}[CF_2{\cdot}CFCl]_{\mathit{n}}{\cdot}CF_2{\cdot}CFCl{\cdot}O_2{\cdot}}
\end{tikzcd}$$

$$\mathrm{Cl{\cdot}[CF_2{\cdot}CFCl]_{\mathit{n}}{\cdot}CF_2{\cdot}CFCl{\cdot}O_2{\cdot} + Cl{\cdot}[CF_2{\cdot}CFCl]_{\mathit{n}}{\cdot}CF_2{\cdot}CFClI \longrightarrow Cl{\cdot}[CF_2{\cdot}CFCl]_{\mathit{n}}{\cdot}CF_2{\cdot}CFCl{\cdot}O_2{\cdot}I}$$
$$\mathrm{+\ Cl{\cdot}[CF_2{\cdot}CFCl]_{\mathit{n}}{\cdot}CF_2{\cdot}CFCl{\cdot} \xrightarrow{O_2} etc.}$$

$$\mathrm{Cl{\cdot}[CF_2{\cdot}CFCl]_{\mathit{n}}{\cdot}CF_2{\cdot}CFCl{\cdot}O_2{\cdot}I \longrightarrow Cl{\cdot}[CF_2{\cdot}CFCl]_{\mathit{n}}{\cdot}CF_2{\cdot}CFCl{\cdot}O{\cdot} + {\cdot}OI \longrightarrow etc.}$$

$$\mathrm{Cl{\cdot}[CF_2{\cdot}CFCl]_{\mathit{n}}{\cdot}CF_2{\cdot}CFClO{\cdot} \longrightarrow Cl{\cdot} + Cl{\cdot}[CF_2{\cdot}CFCl]_{\mathit{n}}{\cdot}CF_2{\cdot}COF \longrightarrow Cl{\cdot}[CF_2{\cdot}CFCl]_{\mathit{n}}{\cdot}CF_2{\cdot}CO_2H}$$

The long-chain acids obtained contain a terminal $\mathrm{CF_2{\cdot}CO_2H}$ group and are thus as strong as the perfluoro-carboxylic acids and markedly surface-active. This route to long-chain acids is simpler than that which involves electrochemical fluorination. Polyfluoro-acids can thus be prepared by attack at either end of the $\mathrm{Cl{\cdot}[CF_2{\cdot}CFCl]_{\mathit{n}}{\cdot}I}$ chain, and dicarboxylic acids can be prepared by photochemical oxidation of $\mathrm{I{\cdot}[CFCl{\cdot}CF_2{\cdot}]_{\mathit{n}}{\cdot}CO_2H}$.

The present study thus demonstrates that polyfluoroalkanes with reactive end groups capable of use in further synthesis can be obtained from chlorotrifluoroethylene without use of expensive chemicals, compounds such as trifluoroiodomethane, or electrochemical fluorination. The iodine in the polymer is present only as end group, and makes available the further syntheses of compounds containing such terminal groups as MgI, $\mathrm{SO_3H}$, $\mathrm{PO_3H}$, NO, $\mathrm{NO_2}$, SH by processes described earlier for polyfluoroiodoalkanes.

Factors affecting the Short-chain Polymerisation of Fluoro-olefins.—The studies on the short-chain polymerisation of a fluoro-olefin with a compound R·CFXY to give R·CFX·[fluoro-olefin]$_n$·Y which have been reported above and in earlier papers lead to several general observations and predictions on the factors affecting such reactions. The conclusions reached can be applied to all reactions of this type (sometimes referred to as " telomerisation " reactions).

(*a*) *Initiation step.* Initiation is usually achieved by use of a polyhalogenoalkyl radical (*e.g.*, $CF_3\cdot$, $CF_2Cl\cdot CFCl\cdot$) but is not restricted to this, since a bromine atom (*J.*, 1954, 3747) can also be used. Two distinct stages are involved in the initiation step : generation of the initiating radical, and its reaction with the olefin. The rate of generation of the initiating $R\cdot CFX\cdot$ radical from a compound $R\cdot CFXY$ (in a typical case R = polyhalogenoalkyl, or F; X = halogen or hydrogen; Y = halogen usually different from X and of higher atomic weight) depends on the following three factors :

(i) The strength of the C–Y bond and hence the stability of the $R\cdot CFX\cdot$ free radical; the weaker C–Y, the greater the ease of generation of $R\cdot CFX\cdot$. The nature of both Y and X determines the C–Y bond strength, which decreases in the series $Y = F > Cl > Br > I$ for a given X, and which can be predicted, with reasonable certainty, to decrease in the series $R\cdot CF_2{-}Y$ (Y = F) > $R\cdot CF_2{-}Y$ (Y = Cl) > $R\cdot CHF{-}Y$ (Y = Cl) > $R\cdot CFCl{-}Y$ (Y = Cl) > $R\cdot CF_2{-}Y$ (Y = Br) > $R\cdot CHF{-}Y$ (Y = Br) > $R\cdot CFCl{-}Y$ (Y = Br) > $R\cdot CFBr{-}Y$ (Y = Br) > $R\cdot CF_2{-}Y$ (Y = I) > $R\cdot CHF{-}Y$ (Y = I) > $R\cdot CFCl{-}Y$ (Y = I) > $R\cdot CFBr{-}Y$ (Y = I) > $R\cdot CFI{-}Y$ (Y = I). The reason for the effect of X on the C–Y bond energy has been discussed earlier (Haszeldine, *J.*, 1953, 1764) and is associated with the stability of the $R\cdot CFX\cdot$ free radical and with the increase in steric strain between X and Y as X becomes larger. The change in C–Y bond energy is readily seen when Y = I or Br by use of ultraviolet spectra (*J.*, 1953, 1764; and unpublished data).

(ii) The physical conditions, *e.g.*, the intensity of ultraviolet light and/or the temperature which provide the energy for C–Y fission.

(iii) The concentration of peroxide if a peroxide is used instead of, or in combination with, light or heat to cause C–Y fission.

Generation of the $R\cdot CFX\cdot$ radical must be followed by the second stage of the initiation reaction, *i.e.*, attack on the olefin. The ease of this reaction depends mainly upon the reactivity of the olefin and to a lesser extent on the reactivity of the attacking radical $R\cdot CFX\cdot$. In general, halogen bonded to the doubly-bonded carbon atoms, or to carbon atoms adjacent to the doubly-bonded carbon atoms in an olefin containing more than three carbon atoms, decreases the ease of free-radical attack relative to the corresponding unsubstituted olefin (*J.*, 1952, 2504; 1953, 1199, 1592, 3559, 3565; 1955, 3005). Halogenoethylenes are special cases, since the polyfluoro- and chloropolyfluoro-ethylenes polymerise readily; in general, the greater the atomic weight of the halogen in a halogenoethylene, and the more symmetrically the halogen is distributed (cf. $CF_2{:}CCl_2$ and $CFCl{:}CFCl$), the less readily does the olefin polymerise, and the less readily is it attacked by a free radical.

The reactivity of $R\cdot CFX\cdot$ is seldom of sufficient importance to be decisive in polymerisations of the type under discussion, since the more reactive olefins readily combine with even the least reactive radicals. It is only with olefins heavily or symmetrically substituted by halogen such as chlorine or bromine, or in which steric inhibition of radical attack occurs, that the less reactive radicals fail to add and more reactive radicals (*e.g.*, X in $R\cdot CFX\cdot$ = H, F, or Cl) must be used.

(*b*) *Propagation.* The efficiency of the propagation step

$$R\cdot CFX\cdot[\text{olefin}]\cdot + \text{olefin} \longrightarrow R\cdot CFX\cdot[\text{olefin}]_2\cdot, \text{ etc.}$$

which is always competing with the chain transfer step

$$R\cdot CFX\cdot[\text{olefin}]\cdot + R\cdot CFXY \longrightarrow R\cdot CFX\cdot[\text{olefin}]\cdot Y + R\cdot CFX\cdot$$

depends upon (i) the ease of polymerisation of the olefin, (ii) the reactivity of the intermediate free radical $R\cdot CFX\cdot[\text{olefin}]\cdot$ towards olefin and towards $R\cdot CFXY$, (iii) the stability of the product $R\cdot CFX\cdot[\text{olefin}]_n\cdot Y$, and (iv) the relative ease of the chain-transfer step.

(i) An olefin which reacts readily with fragments from a decomposing peroxide to give a polymer of high molecular weight will, in general, tend to give a longer-chain polymer with $R\cdot CFXY$ than one which does not. This is illustrated by comparison of tetrafluoroethylene, chlorotrifluoroethylene, or trifluoroethylene with, say, ethylene or trichloroethylene. The ease of polymerisation is related to the ease of radical attack as discussed under (*a*).

(ii) This is clearly closely related to (*a*) and to (i), since the reactivity of the radical

R·CFX·[olefin]· produced by attack of R·CFX· on the olefin will determine the ease of attack on a second molecule of the olefin.

Why a radical such as R·CFX·CH_2·CH_2· should attack R·CFXY rather than another molecule of ethylene, whereas a radical such as R·CFX·CF_2·CF_2· should attack another molecule of tetrafluoroethylene rather than R·CFXY is clearly related to the difference between the C–Y and C–C bond energies in R·CFX·CH_2·CH_2Y and R·CFX·CH_2·CH_2–CH_2·CH_2· or in R·CFX·CF_2·CF_2Y and R·CFX·CF_2·CF_2–CF_2·CF_2·. Full discussion of this important factor is deferred, but the conclusions reached empirically by experiment are summarised in (*c*).

In special circumstances the choice of R·CFXY must be governed by the particular olefin to be polymerised. Thus, if trifluoroiodomethane is used as source of the R·CFX· radical (*i.e.*, CF_3) to attack chlorotrifluoroethylene, R·CFX is reactive, whereas the intermediate radical produced during polymerisation is CF_3·[CF_2·CFCl]$_n$·CF_2·CFCl·, which is less reactive. In the special situation where there are comparable concentrations of CF_3· and CF_3·[CF_2·CFCl]$_n$·CF_2·CFCl· radicals, therefore, the chlorotrifluoroethylene present will be attacked by the CF_3· radicals rather than by the CF_3·[CF_2·CFCl]$_n$·CF_2·CFCl· radicals. New reaction chains will thus predominate over propagation, and shorter-chain rather than longer-chain polymer will be produced. Such situations are rare, but the possibility should be considered when deciding upon reactant ratios and reaction conditions.

A case can also arise of the type discussed earlier in this paper where the initiating radical (*e.g.*, CF_2Cl·CFCl·) is of the same type as the intermediate radical (*e.g.*, CF_2Cl·CFCl·[CF_2·CFCl]$_n$·CF_2·CFCl·). Both initiating radical and intermediate radical can attack the olefin with equal facility (provided *n* is small), and if the formation of long-chain polymer is to be avoided, the chain transfer reaction must be made as efficient as possible, *e.g.*, by making Y = I rather than Br, and by increase in the ratio of transfer agent to olefin.

(iii) The stability of the product R·CFX·[olefin]$_n$·Y under the conditions used is important, since if the C–Y bond is weak, subsequent homolytic fission may occur to give the radical R·CFX·[olefin]$_n$· which can then initiate a new reaction chain. This leads to longer-chain polymer and to a wider spread in the value of *n* than is usually desirable. Choice of reaction conditions is important here. Thus if heat is used to cause C–Y fission in R·CFXY, and C–Y in R·CFX·[olefin]$_n$·Y is of approximately the same strength as C–Y in R·CFXY (*e.g.*, in the reaction of CF_2Cl·CFClI with CF_2:CFCl), then the further reaction of R·CFX·[olefin]$_n$·Y with olefin can be avoided only by use of a high ratio of R·CFXY to olefin. Use of ultraviolet light at room temperature is preferable in such a case to obtain maximum yields of short-chain polymer, since the concentration of R·CFX·[olefin]$_n$·Y in the chain-transfer agent R·CFXY is usually such that ultraviolet light entering the reaction vessel preferentially photolyses R·CFXY; the essential difference from use of heat is that only a relatively low percentage of the reaction mixture receives energy at any one instant. Heat is thus best used for those reactions where C–Y in the polymer is relatively strong (*e.g.*, in the reaction of CF_3I with C_2H_4).

(iv) The chain-transfer step can clearly be favoured by use of a high ratio of R·CFXY to olefin, and this often outweighs the factors (i)—(iii). Choice of reaction conditions affects this ratio, particularly when the olefin is gaseous. In this case only the liquid phase should be irradiated in a photochemical reaction, since here the ratio is high, as required, whereas in the gas phase the ratio is usually low (see *J.*, 1953, 3761, for illustrations of this). If heat is used instead of light, the olefin in the gas phase in the vessel used should be reduced to a minimum by use of sufficient transfer agent almost to fill the vessel, by use of sufficient pressure of olefin to cause it to liquefy and dissolve in the chain-transfer agent, or by use of an inert gas to achieve the same effect (cf. *J.*, 1953, 3761). Other aspects of the transfer step are discussed under (*c*).

(*c*) *Chain transfer*. (i) In the type of polymerisation under discussion, R·CFXY acts both as source of the initiating radical and as chain-transfer agent. The C–Y bond strength in R·CFXY is important in both these processes. If the C–Y bond is weak compared with that in the polymer (*e.g.*, the C–I bond in the reaction of trifluoroiodomethane with ethylene to give CF_3·[CH_2·CH_2]$_n$·I), then chain transfer will occur readily and *n* will be mainly 1 or 2, and often exclusively 1. If, on the other hand, the C–Y bond in $R\cdot CFXY$ is strong, *e.g.*, when Y = Cl, then chain transfer is difficult and the propagation reaction will be favoured; coupling of radicals to give $R\cdot CFX\cdot[olefin]_n\cdot[olefin]_n\cdot CFX\cdot R$ can become an import side-reaction in such circumstances. Formation of shorter-chain polymer can be favoured, but not necessarily achieved, by use of a high ratio of transfer agent to olefin.

(ii) If the chain transfer agent is efficient (*i.e.*, C–Y in $R\cdot CFXY$ is weak, yet $R\cdot CFX$ is sufficiently reactive to attack the olefin, *e.g.*, when $R\cdot CFXY = CF_3I$, $CF_2Cl\cdot CFClI$, or $CF_2Br\cdot CFClBr$), a reactive olefin (*i.e.*, one which is readily polymerised by a peroxide) can be made to give polymer where *n* is low by control of the ratio transfer agent : olefin. Such olefins (*e.g.*, C_2F_4 and C_2F_3Cl) will not give exclusively the compound where $n = 1$, however, unless a very high (>10 : 1) ratio is used, and usually *n* will show a spread, *e.g.*, $n = 1$ (60%), 2 (20%), 3 (8%), 4 (3%), etc.

(iii) If the chain-transfer agent is efficient in the sense defined above, and the olefin is not reactive (*i.e.*, is not readily polymerised by a peroxide), then the product is $R\cdot CFX\cdot[olefin]_n\cdot Y$ where $n = 1$, and it becomes difficult to make $n \gg 1$. The C–Y bond in the polymer is not necessarily strong. Examples of such olefins taken from earlier work from these laboratories are C_2H_4, C_2H_2, $CH_2{:}CH\cdot CF_3$, $CH_2{:}C{:}CH_2$, $CH_3\cdot CH{:}CH_2$, $CF_3\cdot CF{:}CF_2$, and $CFCl{:}CFCl$. Olefins which are of intermediate reactivity in this sense are $CH_2{:}CF_2$, $CH_2{:}CHF$, $CH_2{:}CHCl$, and $CH_2{:}CH\cdot CO_2Me$. Attempts to force olefins such as ethylene, propene, 3 : 3 : 3-trifluoropropene, or hexafluoropropene to give a polymer $R\cdot CFX\cdot[olefin]_n\cdot Y$ with $n > 4$ or 5, by cutting down the proportion of chain-transfer agent $R\cdot CFXY$, merely causes the intermediate radical (*e.g.*, $R\cdot CFX\cdot CH_2\cdot\dot{C}H\cdot CF_3$ from 3 : 3 : 3-trifluoropropene) to undergo mainly reactions other than by addition with a second molecule of olefin, *e.g.*, disproportionation, dimerisation, or internal expulsion of halogen to give an olefin.

Consideration of the various factors discussed above for a particular olefin under study makes it possible to achieve maximum yields of short-, medium-, or long-chain polymer with the minimum of experiments.

EXPERIMENTAL

1 : 2-Dichloro-1 : 2 : 2-trifluoroiodoethane was prepared from iodine monochloride and chlorotrifluoroethylene and purified by distillation (Part I, *loc. cit.*). Reactions were carried out in silica or Pyrex tubes unless otherwise stated, with precautions to exclude air and moisture. Distillations were carried out in nitrogen; this is particularly important for the iodo-compounds which are readily oxidised and are liable to form peroxides.

Reaction of 1 : 2-*Dichloro*-1 : 2 : 2-*trifluoroiodoethane with Chlorotrifluoroethylene*.—(a) *With a molar ratio* 15 : 1. In a typical experiment the iodo-compound (420 g., 1·5 mole) was shaken in a silica tube with chlorotrifluoroethylene (11·7 g., 0·1 mole) and the liquid phase was exposed to ultraviolet light (5 days). No chlorotrifluoroethylene remained, and distillation of the liquid products gave 1 : 2-dichloro-1 : 2 : 2-trifluoroiodoethane, b. p. 98—100°, 1 : 2 : 4-*trichlorohexafluoro*-4-*iodobutane* (75% based on olefin), b. p. 80°/25 mm. (Found : C, 12·1; Cl + I, 59·3. $C_4Cl_3IF_6$ requires C, 12·1; Cl + I, 59·1%), and a still residue (20% based on olefin) consisting of longer-chain material.

(b) *With equimolar ratio*. The last experiment was repeated with 0·25 mole of each reactant. The course of the reaction is easily followed by the increase in viscosity, and requires 2—7 days for completion. The shorter time applies to reaction in absence of solvent, the longer time applies when an inert solvent (1 : 1 : 2-trichlorotrifluoroethane) is used to prevent oily polymer from sticking to the sides of the tube and being decomposed by photolysis. No chlorotrifluoroethylene was recovered in either set of conditions, and distillation gave (*a*) unchanged 1 : 2-dichloro-1 : 2 : 2-trifluoroiodoethane, (*b*) 1 : 2 : 4-trichlorohexafluoro-4-iodobutane (18% based on olefin), b. p. 78—80°/20 mm., (*c*) 1 : 2 : 4 : 6-*tetrachlorononafluoro*-6-*iodohexane* (14% based on olefin), b. p. 140—142°/30 mm. (Found : C, 14·1; Cl + I, 52·5. $C_6Cl_4IF_9$ requires C, 14·1; Cl + I, 52·2%), (*d*) 1 : 2 : 4 : 6 : 8-*pentachlorododecafluoro*-8-*iodo-octane* (17% based on olefin), b. p. 135—140°/*ca*. 0·1 mm., n_D^{20} 1·435 (Found : C, 15·5; Cl + I, 48·5. $C_8Cl_5IF_{12}$ requires C, 15·3; Cl + I, 48·3%), and (*e*) a still residue (39% based on olefin) consisting mainly of $Cl\cdot[CF_2\cdot CFCl]_n\cdot I$ with $n = 5$ and 6.

The still residues from several such experiments were combined and distilled to give 1 : 2 : 4 : 6 : 8 : 10-*hexachloropentadecafluoro*-10-*iododecane*, b. p. 185—190°/*ca*. 0·1 mm., n_D^{20} 1·432 (Found : C, 16·3; Cl + I, 45·3. $C_{10}Cl_6IF_{15}$ requires C, 16·1; Cl + I, 45·6%), and

1 : 2 : 4 : 6 : 8 : 10 : 12-*heptachloro-octadecafluoro*-12-*iodododecane*, b. p. 200—208°/*ca.* 0·01 mm., n_D^{20} 1·428 (Found : C, 16·8; Cl + I, 43·0. $C_{12}Cl_7IF_{18}$ requires C, 16·8; Cl + I, 43·6%).

(c) *With an excess of chlorotrifluoroethylene.* In a typical experiment 1 : 2-dichloro-1 : 2 : 2-trifluoroiodoethane (0·05 mole) and chlorotrifluoroethylene (0·25 mole) were shaken and irradiated in a sealed silica tube with the vapour phase shielded from light (3 days). Distillation of the combined products from four such experiments gave the compounds $Cl\cdot[CF_2\cdot CFCl]_n\cdot I$ with $n = 1$ (0%), $n = 2$ (5%), $n = 3$ (7%), $n = 4$ (11%), $n = 5$ (13%), and $n = 6$ (12%). The b. p.s are as reported above, and yields based on $CF_2Cl\cdot CFClI$ are shown in parentheses. Further distillation gave 1 : 2 : 4 : 6 : 8 : 10 : 12 : 14-*octachloroheneicosafluoro*-14-*iodotetradecane* (12%), b. p. 230—240°/*ca.* 0·001 mm. (Found : C, 17·2; Cl + I, 41·9. $C_{14}Cl_8IF_{21}$ requires C, 17·2; Cl + I, 42·0%). At this point the high temperature caused liberation of iodine, particularly if traces of oxygen were present. The still residue was therefore transferred to a " molecular-distillation " unit and arbitrary fractions were taken. Control of bath-temperature was used to effect separation, and each fraction took approx. 4 hr. to distil. A series of fractions of the average composition shown in Table 2 were thus obtained.

TABLE 2.

n in $Cl\cdot[CF_2\cdot CFCl]_n\cdot I$	8	9	10	11
Yield (%)	7	4	5	4
C (found); Calc. in parentheses (%)	17·5(17·5)	17·7(17·8)	18·0(18·1)	18·4(18·3)

The colourless residue (16% based on $CF_2Cl\cdot CFClI$) became pink on exposure to ultraviolet light, and a qualitative test for iodine was strongly positive. When cold the residue was a hard wax but it was quite mobile when hot. It had the average composition $Cl\cdot[CF_2\cdot CFCl]_{20}\cdot I$ (Found : C, 19·4; Cl + I, 34·0. Calc. for $C_{40}Cl_{21}IF_{60}$: C, 19·2; Cl + I, 35·0%). Attempts to separate it further by molecular distillation gave solids which could not be purified by recrystallisation to give analytically pure compounds. The solids were mixtures of homologues, and resembled poly(tetrafluoroethylene) in appearance and feel.

Each of the above compounds was redistilled to obtain clean separation from its homologues before analysis. The compounds are thermally stable and decompose rapidly at room temperature only if kept in presence of air or moisture, particularly when exposed to light.

Reaction of the Compounds $Cl\cdot[CF_2\cdot CFCl]_n\cdot I$ *with Chlorine.*—(a) 1 : 2 : 4-*Trichlorohexafluoro*-4-*iodobutane.* This compound (12·6 g.) and chlorine (20% excess) were exposed to ultraviolet light in a silica tube (2 days). The products were shaken with 10% aqueous sodium hydroxide to remove iodine trichloride, dried (P_4O_{10}), and distilled to give 1 : 1 : 3 : 4-*tetrachlorohexafluorobutane* (96%), b. p. 133—134° (Found : C, 15·5; Cl, 46·6. $C_4Cl_4F_6$ requires C, 15·8; Cl, 46·7%).

(b) *Polymer* $Cl\cdot[CF_2\cdot CFCl]_n\cdot I$. The crude iodine-containing polymer (40·7 g.), obtained by use of an excess of chlorotrifluoroethylene as described above, was sealed in a silica tube with 1 : 1 : 2-trichlorotrifluoroethane (50 ml.) as inert diluent, and dry chlorine (10% excess). The tube was shaken vigorously and exposed to ultraviolet light (7 days). The deposited iodine trichloride was removed by treatment with aqueous sodium hydroxide, and the dried organic layer was distilled to give diluent and the *compounds* shown in Table 3.

TABLE 3. *Compounds* $Cl\cdot[CF_2\cdot CFCl]_n\cdot Cl$.

				Found		Reqd.	
n	B. p./mm.	n_D	Yield (%)	C	Cl	C	Cl
2	78°/100	—	7	15·5	46·6	15·8	46·7
3	96—98/20 (*ca.* 205/760)	1·397 *	7	17·0	42·4	17·1	42·2
4	145—147/20	1·408 †	9	17·8	39·8	17·9	39·7
5	135—139/*ca.* 0·1	1·413 †	8	18·5	37·5	18·4	38·0
6	190—195/*ca.* 0·1	—	12	18·7	36·3	18·7	36·9
7	235—240/0·1—0·01	—	14	19·0	36·1	19·0	36·7

* At 20°. † At 22°.

The still residue was transferred to a " molecular " still where slow distillation gave $Cl\cdot[CF_2\cdot CFCl]_7\cdot Cl$ (*ca.* 1%), then a fraction (probably 1 : 1 : 3 : 5 : 7 : 9 : 11 : 13 : 15 : 16-*decachlorotetracosafluorohexadecane*) of average composition $Cl\cdot[CF_2\cdot CFCl]_8\cdot Cl$ (10%) (Found : C, 19·1. $C_{16}Cl_{10}F_{24}$ requires C, 19·2%). The residue had average composition $Cl\cdot[CF_2\cdot CFCl]_{18}\cdot Cl$ [Found : C, 20·0. Calc. for $C_{36}Cl_{20}F_{54}$: C, 20·0, cf. $(CF_2\cdot CFCl)_n$: C, 20·6%].

1 : 2 : 4-*Trichloroheptafluorobutane.*—To 1 : 2 : 4-trichlorohexafluoro-4-iodobutane (2·7 g.)

and carbon tetrachloride (5 ml.) in a silica flask was added a solution of chlorine trifluoride (*ca.* 2 g.) in carbon tetrachloride (5 ml.), at such a rate that the vigorous reaction did not get out of control (1 hr.). After being kept (3 hr.), water (5 ml.) was added followed by an excess of 5% aqueous sodium hydroxide. Distillation of the dried (P_4O_{10}) organic liquid gave 1 : 2 : 4-*trichloroheptafluorobutane* (84%), b. p. 99—100° (Found : C, 16·8%; *M*, 286. $C_4Cl_3F_7$ requires C, 16·7%; *M*, 287·5).

Synthesis and Reactions of 4 : 4-*Dichlorohexafluorobut*-1-*ene and* 3 : 3-*Dichlorotrifluoropropionic Acid.*—(a) 1 : 1 : 3 : 4-Tetrachlorohexafluorobutane (8·3 g.) was dissolved in ethanol (20 ml.) and added dropwise at 60° to a stirred suspension of zinc dust (25 g.) in ethanol (30 ml.). After 1 hr. the volatile components were slowly distilled off and collected in a flask containing water; ethanol was added to the reaction flask during this process at a rate sufficient to keep the volume in it constant. The liquid obtained as the lower layer in the receiver was washed with water, dried, and distilled to give 4 : 4-*dichlorohexafluorobut*-1-*ene* (78%), b. p. 70—71° (Found : C, 20·7; Cl, 30·2%; *M*, 232. $C_4Cl_2F_6$ requires C, 20·6; Cl, 30·5%; *M*, 233).

The absence of 1 : 2 : 3 : 4-tetrachlorohexafluorobutane in the 1 : 1 : 3 : 4-isomer was shown by the fact that vigorous refluxing of the last compound (5·7 g.) or of 4 : 4-dichlorohexafluorobut-1-ene (4·8 g.) with zinc and ethanol failed to give hexafluorobutadiene (cf. Part I, *loc. cit.*). Under these more vigorous conditions compounds containing hydrogen, probably $CF_2{:}CF{\cdot}CF_2{\cdot}CHFCl$, $CF_2{:}CF{\cdot}CF_2{\cdot}CH_2F$, etc., are formed by reduction of the $CFCl_2$ group.

Reaction of 4 : 4-dichlorohexafluorobut-1-ene (2·6 g.) with a slight excess of chlorine was rapid on exposure to ultraviolet light (8 hr.) and gave an almost quantitative yield of the parent 1 : 1 : 3 : 4-tetrachlorohexafluorobutane. The olefin (1·7 g.) similarly reacted with an excess of bromine (4 hr.) to give 1 : 2-*dibromo*-4 : 4-*dichlorohexafluorobutane* (91%), b. p. 65°/5 mm. n_D^{20} 1·427 (Found : C, 12·4; Br + Cl, 58·4. $C_4Br_2Cl_2F_6$ requires C, 12·2; Br + Cl, 58·8%). The dibromo-compound reverted to the olefin when treated with zinc and ethanol at 40° (1 hr.).

(b) 4 : 4-Dichlorohexafluorobut-1-ene (10·2 g.) was oxidised with aqueous potassium permanganate by the method developed for the oxidation of compounds which contain the $CF{:}CF_2$ group (*J.*, 1952, 4259) as modified for the oxidation of compounds which also contain chlorine (Part III, *loc. cit.*). Control of pH was essential to prevent extensive breakdown, and this was achieved either by intermittent addition of aqueous sodium hydroxide as before, or by use of sodium hydrogen carbonate as a buffer. The reaction mixture was worked up in the usual manner (sulphur dioxide, sulphuric acid, ether-extraction), and the dried ($MgSO_4$) ethereal extracts were distilled from 0·1 g. of phosphoric oxide to give ββ-*dichlorotrifluoropropionic acid* (62%), b. p. 83—85°/20 mm. (Found : C, 18·2; H, 0·8%; equiv., 196·7. $C_3HO_2Cl_2F_3$ requires C, 18·3; H, 0·5%; equiv., 197·0).

Reaction of the acid with silver carbonate followed by freeze-drying gave the silver salt which was thoroughly dried over phosphoric oxide *in vacuo*. The silver salt (3·2 g.) was pyrolysed at 10 mm. in a platinum tube heated rapidly from 150° to 400°. The volatile products, collected in a trap cooled by liquid oxygen, contained carbon dioxide and unidentified material of b. p. <100°, but 1 : 1 : 4 : 4-tetrachlorohexafluorobutane was not detected. The residue in the pyrolysis tube contained silver, silver chloride, and carbon.

A second sample of the silver salt (2·6 g.) was sealed with an excess of dry chlorine and heated stepwise to 120° (2 hr.). Fractionation gave 1 : 1 : 2-trichlorotrifluoroethane (78%), b. p. 47°, identified spectroscopically.

Sodium ββ-dichlorotrifluoropropionate was prepared by neutralisation of the acid followed by freeze-drying. The dried (P_4O_{10}) salt (3·8 g.) was placed in a platinum tube closed at one end and connected *via* a trap cooled in liquid oxygen to a pump. The pressure in the platinum tube was maintained at <1 mm., and the tube was slowly pushed into a furnace heated to 320°, and finally to 420°. Sodium chloride with only a trace of sodium fluoride remained as residue. The volatile products which had collected in the trap were carbon dioxide and chlorotrifluoroethylene (83%), identified spectroscopically.

Synthesis and Reactions of 4 : 6 : 6-*Trichlorononafluorohex*-1-*ene and* 3 : 5 : 5-*Trichlorohexafluoropentanoic Acid.*—1 : 1 : 3 : 5 : 6-Pentachlorononafluorohexane (15·7 g.) was dissolved in ethanol (35 ml.) and added dropwise to zinc (30 g.) and ethanol (30 ml.), stirred vigorously, and heated to 50°. After 1 hr. the mixture was filtered and added to an excess of water. The organic layer was dried and distilled, to give 4 : 6 : 6-*trichlorononafluorohex*-1-*ene* (59%), b. p. 80—82°/105 mm. (Found : C, 20·7; Cl, 30·1. $C_6Cl_3F_9$ requires C, 20·6; Cl, 30·5%), and unidentified more volatile products which contained hydrogen and were formed in increased yield if a higher temperature was used for the dechlorination. This dechlorination is very sensitive to conditions. Reaction of the olefin with zinc and refluxing ethanol did not give a diene, but only a mixture of mono-olefins containing hydrogen which could not be resolved into pure compounds.

4 : 6 : 6-Trichlorononafluorohex-1-ene (7·7 g.) was oxidised by potassium permanganate (4·2 g.), water (35 ml.), and sodium hydrogen carbonate (5 g.) at 70° (8 hr.) and the acid produced was extracted by ether in the usual way. Distillation of the dried ethereal extracts from 0·1 g. of phosphoric oxide gave 3 : 5 : *5-trichlorohexafluoropentanoic acid* (57%), b. p. 135°/18 mm. (Found: C, 19·2; H, 0·3; Cl, 33·7%; equiv., 313. $C_5HO_2Cl_3F_6$ requires C, 19·1; H, 0·3; Cl, 34·0%; equiv., 313·5).

The sodium salt (2·3 g.) was prepared by neutralisation of the acid, isolated by freeze-drying, and dried *in vacuo*. It was then pyrolysed as described for sodium ββ-dichlorotrifluoropropionate at 320—400°/1—5 mm. The products which condensed in the trap cooled by liquid oxygen were 4 : 4-dichlorohexafluorobut-1-ene (63%), b. p. 70—71° (Found: C, 20·6. Calc. for $C_4Cl_2F_6$: C, 20·7%), identical with the olefin described earlier.

The silver salt (2·8 g.) was thoroughly dried *in vacuo*, then heated with chlorine (15% excess) at 130° (3 hr.). The products were removed by pumping through a cooled trap, and the excess of chlorine and the carbon dioxide allowed to escape. The residual liquid was washed with aqueous sodium hydroxide, then distilled to give an initial fraction (0·15 g.), b. p. 79—82°, followed by 1 : 1 : 3 : 4-tetrachlorohexafluorobutane (55%), b. p. 132—134° (Found: C, 15·8. $C_4Cl_4F_6$ requires C, 15·8%), identical with the compound described earlier.

Polyfluoroalkanesulphonic Acids.—(a) *From* 4 : *4-dichlorohexafluorobut-*1-*ene*. The olefin (4·6 g., 0·020 mole) was shaken with sodium sulphite (2·5 g., 0·021 mole), borax (2 g.), water (12 ml.), and benzoyl peroxide (0·5 g.) and heated at 80° (2 hr.), 100° (1 hr.) and 110° (8 hr.). No olefin was recovered. The filtered aqueous solution was freeze-dried to give a white solid. An attempt to generate the free sulphonic acid by heating half of the solid with concentrated sulphuric acid was unsuccessful, since hydrogen fluoride was liberated and caused extensive etching. The second half of the solid was therefore extracted with boiling absolute alcohol (3 times), and evaporation of the ethanol *in vacuo* gave the pure sodium salt of the sulphonic acid. This was dried over phosphoric oxide, then heated *in vacuo* with fuming sulphuric acid to give 4 : *4-dichloro-*1 : 1 : 2 : 3 : 3 : *4-hexafluorobutanesulphonic acid* (69% total yield), which when redistilled had b. p. 118—120°/3·5 mm. (Found: C, 15·0; H, 0·4; Cl, 21·7%; equiv., 317. $C_4H_2O_3Cl_2F_6S$ requires C, 15·2; H, 0·6; Cl. 22·5%; equiv., 315).

(b) 4 : 6 : 6 *Trichlorononafluorohex-*1-*ene*. This olefin (0·022 mole) was treated with a similar mixture to that in (a) for the same time. The product was isolated by freeze-drying and extraction with ethanol, then distilled from sulphuric acid to give 4 : 6 : *6-trichloro-*1 : 1 : 2 : 3 : 3 : 4 : 5 : 5 : *6-nonafluorohexanesulphonic acid* (57%), and when redistilled had b. p. 130—133°/*ca.* 0·1 mm. (Found: C, 16·5; H, 0·5; Cl, 24·4%; equiv., 428. $C_6H_2O_3Cl_3F_9S$ requires C, 16·7; H, 0·5; Cl, 24·8%; equiv., 431·5).

Photochemical Oxidation of Compounds $Cl{\cdot}[CF_2{\cdot}CFCl]_n{\cdot}I$.—(*a*) The compound $Cl{\cdot}[CF_2{\cdot}CFCl]_2{\cdot}I$ (4·3 g.) was sealed in a 200 ml. silica tube with oxygen (7 atm.) and 10% aqueous sodium hydroxide (20 ml.) and shaken vigorously in a horizontal position so that the organic liquid was distributed over the sides of the tube. After exposure to an ultraviolet lamp 5 cm. from the tube for 12 hr., the tube was opened and recharged with oxygen. After further irradiation (12 hr.) the excess of oxygen was pumped away. There was no residual organic layer after acidification with hydrochloric acid and allowing the emulsion to separate. The aqueous solution was extracted with ether (10 × 20 ml.) and distillation of the dried ethereal extracts gave 3 : *4-dichloropentafluorobutanoic acid* (63%), b. p. 105—107°/25 mm. (Found: C, 19·5%; equiv., 250. $C_4HO_2Cl_2F_5$ requires C, 19·4%; equiv., 247).

(*b*) The compound $Cl{\cdot}[CF_2{\cdot}CFCl]_5{\cdot}I$ (5·7 g.) was sealed in a silica tube with oxygen (8 atm.) and 1 : 2-dichlorotetrafluoroethane (20 ml.) as diluent, shaken vigorously, and exposed to ultraviolet light (8 hr.). Distillation of the product gave unchanged iodo-compound (2·1 g.) and a more volatile fraction which showed acyl fluoride absorption in the infrared (5·3 μ). When the last fraction was treated with aqueous sodium hydroxide, fluoride but not chloride was liberated. Acidification (hydrochloric acid) gave an organic layer which solidified when separated; infrared spectroscopic examination showed it to contain a CO_2H group. The aqueous solution was extracted with ether, evaporation of which left a colourless oil which spectroscopic examination showed also contained a CO_2H group. The combined yield of the acid $Cl{\cdot}[CF_2{\cdot}CFCl]_4{\cdot}CF_2{\cdot}CO_2H$ was 57%. Its equivalent was determined by titration of its solution in aqueous dioxan with aqueous sodium hydroxide (Found: equiv., 605. $C_{10}HO_2Cl_5F_{14}$ requires equiv., 596·5).

(*c*) A mixture (5 g.) of compounds $Cl\cdot[CF_2\cdot CFCl]_n\cdot I$ where *n* had an average value of 6 was heated stepwise to 150° during 5 hr. in a sealed shaken tube containing water (20 ml.), benzoyl peroxide (0·1 g.), ammonium persulphate (0·1 g.), and oxygen (3 atm.). A further amount of oxygen and benzoyl peroxide was added, and the tube heated as before. The acidic aqueous solution was made alkaline with aqueous sodium hydroxide, filtered to remove decomposition products arising from the benzoyl peroxide, acidified (hydrochloric acid), then extracted with ether. Distillation of the dried ethereal extracts gave a mixture of polyfluoro-carboxylic acids (42%), b. p. 65—130°/0·01 mm., and a residue (26%) of a clear wax which was free from iodine and carboxyl groups. The mixed polyfluoro-acids had equiv. 680, revealing an average composition $Cl\cdot[CF_2\cdot CFCl]_5\cdot CF_2\cdot CO_2H$ (equiv., 713).

(*d*) The compound $Cl\cdot[CF_2\cdot CFCl]_2\cdot I$ (6·1 g.), oxygen (5 atm.), and water (10 ml.) were shaken vigorously and exposed to ultraviolet light (2 days). The tube was recharged with oxygen and again irradiated (2 days). The acidic solution was extracted with ether (10 + 15 ml.) and the dried ethereal extracts were distilled, to give 3 : 4-dichloropentafluorobutanoic acid (57%), b. p. 98—100°/23 mm.

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