Fluoro-olefins. Part III.* Some Rearrangement Reactions of Polyhalogeno-olefins, and Routes to Butadienes.†

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The equilibrium between polyhalogenobutadiene and polyhalogeno-*cyclo*butene obtains at high temperatures; use is made of this to synthesise perfluoro*cyclo*butene in high yield by reaction of perfluoro*cyclo*butene with hydrogen iodide to give $CHF_2 \cdot CHF \cdot CHF \cdot CHF_2$ followed by chlorination and treatment with zinc and ethanol.

Thermal dimerisation of $CFCl \colon CFCl$ yields exclusively $CFCl_2 \cdot CFCl \cdot CF \colon CFCl$, dechlorination of which gives $CFCl \colon CF \cdot CF \colon CFCl$. The diene is converted into 2 : 3-dichlorotetrafluoro*cyclo*butene when heated, and chlorination of the last compound gives 1 : 2 : 3 : 4-tetrachlorotetrafluoro*cyclo*butane; this cannot be obtained by cyclic dimerisation of 1 : 2-dichlorodifluoroethylene. Attempts to prepare perfluoro*cyclo*buta-1 : 3-diene were unsuccessful. Proofs of structure are given involving the preparation of $CFCl_2 \cdot CFCl \cdot CO_2H$ and $(CFCl \cdot CO_2H)_2$.

Reaction schemes are considered for the open-chain dimerisation of poly-halogeno ethylenes and it is concluded that either a non-radical reaction, possibly involving a *cyclo*butane intermediate, or a radical-chain reaction can occur under suitable conditions. Predictions are made for $CF_2 \colon CCl_2$, $CFCl \colon CCl_2$, $CF_2 \colon CHCl$, $CHF \colon CCl_2$, and $CHCl \colon CCl_2$.

Syntheses of polyfluorobutadienes have been described (*J.*, 1952, 4423; 1953, 3371; 1954, 4026). The present communication describes certain rearrangements of polyfluoro-olefins which may be used to synthesise polyhalogeno-butadienes or -*cyclo*butanes.

Miller (in " Preparation, Properties, and Technology of Fluorine and Organic Fluoro-compounds," Slesser and Schramm, McGraw-Hill, New York, 1951; Prober and Miller, *J. Amer. Chem. Soc.*, 1949, **71**, 598) has shown that, when heated at 150—180°, hexafluoro-butadiene is converted into hexafluoro*cyclo*butene and mixed dimers C_8F_{12} and trimers $C_{12}F_{18}$. We have now found that perfluoro*cyclo*butene can be isomerised by heat into perfluorobutadiene, *i.e.*,

$$\begin{array}{c} CF_2\text{—}CF \\ | \quad\quad \| \\ CF_2\text{—}CF \end{array} \rightleftharpoons CF_2 \colon CF \cdot CF \colon CF_2$$
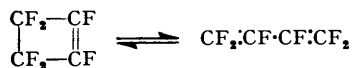
The equilibrium, with its attendant side-reactions, can also be attained from perfluoro-butadiene. Perfluoro*cyclo*hexene does not react analogously; this illustrates the difference in stability between the 4- and 6-membered rings.
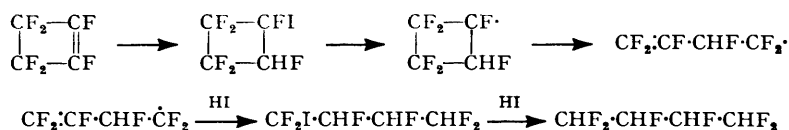
An interesting reaction occurs when perfluoro*cyclo*butene is heated with hydrogen iodide, since $1 : 1 : 2 : 3 : 4 : 4$-hexafluorobutane is produced in excellent yield:

$$\begin{array}{c} \text{CF}_2\text{---CF} \\ | \quad\quad || \\ \text{CF}_2\text{---CF} \end{array} \xrightarrow{\text{HI}} \text{CHF}_2\text{·CHF·CHF·CHF}_2$$

The hexafluorobutane boils at 64° and the marked increase in b. p. on replacement of fluorine by hydrogen is noteworthy (cf. n-C_4F_{10} b. p. $-5°$, $\text{H·[CF}_2]_4\text{·H}$, b. p. 38·5°, $\text{CF}_3\text{·CH}_2\text{·CH}_2\text{·CF}_3$ b. p. 24°). The compound which would be expected by addition of hydrogen to the double bond, *i.e.*, $1 : 2 : 3 : 3 : 4 : 4$-hexafluoro*cyclo*butane (b. p. 27°, Buxton and Tatlow, *J.*, 1954, 1177) was not produced. The structure of the hexafluorobutane was proved by its photochemical chlorination to give $1 : 2 : 3 : 4$-tetrachlorohexafluorobutane, dechlorination of which yields hexafluorobutadiene (*J.*, 1952, 4423).

Two interpretations of this rearrangement reaction are possible. The more probable is that hydrogen iodide reacts more readily with hexafluorobutadiene than with perfluoro*cyclo*butene, and thus converts the diene present in equilibrium with the *cyclo*butene into compounds such as $\text{CF}_2\text{I·CHF·CF:CF}_2$, $\text{CF}_2\text{I·CF:CF·CHF}_2$, $\text{CHF}_2\text{·CHF·CF:CF}_2$, or $\text{CHF}_2\text{·CF:CF·CHF}_2$. These compounds will be reduced further to give $1 : 1 : 2 : 3 : 4 : 4$-hexafluorobutane, and in this way the continuous removal of hexafluorobutadiene from the equilibrium mixture, at a temperature where hexafluoro*cyclo*butene itself is not attacked by hydrogen iodide or by its decomposition products hydrogen and iodine, leads to almost quantitative conversion of hexafluoro*cyclo*butene into the hexafluorobutane.

A second and somewhat less probable scheme is that addition of hydrogen iodide to the double bond is followed, at the elevated reaction temperatures used, by carbon–iodine bond cleavage and rearrangement of the free radical; this is followed by reduction:
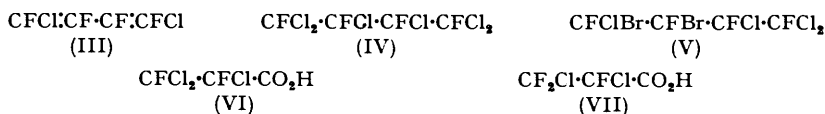
$$\begin{array}{c} \text{CF}_2\text{---CF} \\ | \quad\quad || \\ \text{CF}_2\text{---CF} \end{array} \longrightarrow \begin{array}{c} \text{CF}_2\text{---CFI} \\ | \quad\quad | \\ \text{CF}_2\text{---CHF} \end{array} \longrightarrow \begin{array}{c} \text{CF}_2\text{---CF·} \\ | \quad\quad | \\ \text{CF}_2\text{---CHF} \end{array} \longrightarrow \text{CF}_2\text{:CF·CHF·CF}_2\text{·}$$

$$\text{CF}_2\text{:CF·CHF·ĊF}_2 \xrightarrow{\text{HI}} \text{CF}_2\text{I·CHF·CHF·CHF}_2 \xrightarrow{\text{HI}} \text{CHF}_2\text{·CHF·CHF·CHF}_2$$

Perfluoro*cyclo*butene is readily prepared in high yield from chlorotrifluoroethylene, and its reaction with hydrogen iodide followed by chlorination and then dechlorination thus provides a convenient synthesis of perfluorobutadiene which can be applied on a larger scale than that described earlier [$\text{CF}_2\text{:CFCl} \xrightarrow{\text{ICl}} \text{CF}_2\text{Cl·CFClI} \xrightarrow[\text{or Hg. }h\nu]{\text{Zn, dioxan}} (\text{CF}_2\text{Cl·CFCl})_2 \longrightarrow \text{C}_4\text{F}_6$; *J.*, 1952, 4423]. The rearrangement reaction is clearly capable of extension to the synthesis of other polyfluoro- and polyfluorochloro-dienes and studies in this connection will be reported later.

Scherer (U.S.P. 2,676,193; *Chem. Abs.*, 1953, **47**, 6435) has reported that $1 : 2$-dichloro-difluoroethylene is dimerised by heat to give (I) or (II) or a mixture of the two. *cis-trans-*Isomerism is clearly possible in (I) and (II). The results of our own studies carried out several years ago on this reaction show that (I) is formed predominantly and probably almost exclusively; its stereochemical nature is unknown.
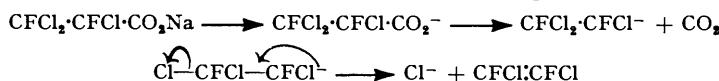
$$\text{(I)} \quad \text{CFCl:CF·CFCl·CFCl}_2 \quad\quad\quad\quad \text{CF}_2\text{Cl·CFCl·CCl:CFCl} \quad \text{(II)}$$

The dimerisation of $1 : 2$-dichlorodifluoroethylene is readily effected in a sealed vessel or by passage of the olefin through a hot tube. Small amounts of what are probably trimers are also produced. The dimer must contain chlorine on adjacent carbon atoms, since when it is treated with zinc and dioxan, a diene $\text{C}_4\text{Cl}_2\text{F}_4$ is produced in good yield by loss of chlorine but not of fluorine; such a diene could arise from (I) or (II). The dimer contains one double bond, since it absorbs chlorine or bromine to give $\text{C}_4\text{Cl}_6\text{F}_4$ or $\text{C}_4\text{Br}_2\text{Cl}_4\text{F}_4$ respectively. Clear proof that the dimer is (I) and not (II), and hence that the diene is (III) and the chlorinated and brominated products are (IV) and (V), comes from alkaline permanganate oxidation of the dimer to give the trichloro-difluoropropionic acid (VI). This oxidation must be carried out at a pH <10 to prevent further breakdown of (VI) into dichlorofluoroacetic acid and oxalic acid; some breakdown

of (VI) occurs even with such pH control, but a 74% yield of $\alpha\beta\beta$-trichlorodifluoropropionic acid was obtained under the best conditions. This shows that the double bond in the dimer is terminal and that (II), which would give the dichlorotrifluoropropionic acid (VII), is not formed. There is no reason to expect that (VII) would be less stable than (VI) and hence preferentially degraded during the oxidation; in fact, the reverse would be the

$$\text{CFCl:CF·CF:CFCl} \qquad \text{CFCl}_2\text{·CFCl·CFCl·CFCl}_2 \qquad \text{CFClBr·CFBr·CFCl·CFCl}_2$$
$$\text{(III)} \qquad\qquad\qquad\qquad \text{(IV)} \qquad\qquad\qquad\qquad\qquad \text{(V)}$$

$$\text{CFCl}_2\text{·CFCl·CO}_2\text{H} \qquad\qquad \text{CF}_2\text{Cl·CFCl·CO}_2\text{H}$$
$$\text{(VI)} \qquad\qquad\qquad\qquad\qquad \text{(VII)}$$

case, since increased fluorine content increases the stability of a polyhalogeno-acid. The presence of polyhalogenobut-2-enes formed either by the initial reaction or by allylic rearrangement [(I) $\rightleftharpoons$ CFCl$_2$·CF:CF·CFCl$_2$] would explain the loss of material during the oxidation, but the ease of chlorination and bromination of the dimer shows that polyhalogenobut-2-enes are not present. Such compounds add chlorine or bromine only with difficulty and without allylic rearrangement, and preferential halogenation of the but-1-ene would thus be expected; the olefin recovered from the reaction of the dimer with less than a molar equivalent of halogen was identical with the original dimer however. All these points suggest that the dichlorodifluoroethylene dimer is very largely, and probably completely, (I).
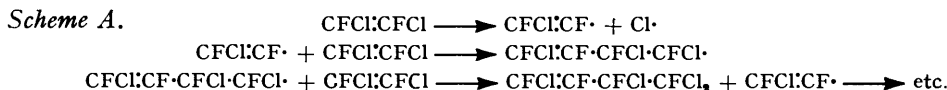
The constitution of (VI) is proved by the formation of 1 : 2-dichlorodifluoroethylene by pyrolysis of its anhydrous sodium salt. This reaction, which has been applied to the salts of perfluoro-mono- and -di-basic acids (*J.*, 1952, 4259; 1954, 4026) and appears to be of general application with polyhalogeno-acids, is believed to proceed *via* a fluoro-carbanion :

$$\text{CFCl}_2\text{·CFCl·CO}_2\text{Na} \longrightarrow \text{CFCl}_2\text{·CFCl·CO}_2^- \longrightarrow \text{CFCl}_2\text{·CFCl}^- + \text{CO}_2$$

$$\text{Cl—CFCl—CFCl}^- \longrightarrow \text{Cl}^- + \text{CFCl:CFCl}$$

The acid (VII) would have given chlorotrifluoroethylene by this procedure. Further proof of structure is given by conversion of the acid into 1 : 1 : 2 : 2-tetrachlorodifluoroethane by reaction of its silver salt with chlorine (cf. *J.*, 1951, 584; 1952, 4259) :

$$\text{CFCl}_2\text{·CFCl·CO}_2\text{Ag} \xrightarrow{\text{Cl}_2} \text{CFCl}_2\text{·CFCl}_2 + \text{CO}_2 + \text{AgCl}$$

The following schemes are possible for the thermal dimerisation of 1 : 2-dichlorodifluoroethylene or 1 : 2-dichloroethylene which similarly yields CHCl$_2$·CHCl·CH:CHCl (Bauer, U.S.P. 2,267,712/1942) :

Scheme A.
$$\text{CFCl:CFCl} \longrightarrow \text{CFCl:CF·} + \text{Cl·}$$
$$\text{CFCl:CF·} + \text{CFCl:CFCl} \longrightarrow \text{CFCl:CF·CFCl·CFCl·}$$
$$\text{CFCl:CF·CFCl·CFCl·} + \text{CFCl:CFCl} \longrightarrow \text{CFCl:CF·CFCl·CFCl}_2 + \text{CFCl:CF·} \longrightarrow \text{etc.}$$
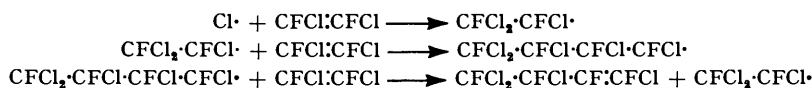
This involves a chain reaction with regeneration of the CFCl:CF radical. The compound (II) would be formed if the CFCl:CCl radical were produced by loss of fluorine instead of chlorine.

Scheme B. A non-chain reaction would be obtained by dimerisation of the CFCl:CF radicals :

$$\text{CFCl:CF·} \longrightarrow \text{CFCl:CF·CF:CFCl} \xrightarrow{\text{Cl}_2} \text{CFCl}_2\text{·CFCl·CF:CFCl}$$

but one would have to assume either that thermal chlorination of the diene gave only 1 : 2-addition, which is unlikely in view of experiments on the halogenation of perfluorobutadiene (*J.*, 1952, 4423), or that allylic rearrangement (CFCl$_2$·CF:CF·CFCl$_2$ $\rightleftharpoons$ CFCl$_2$·CFCl·CF:CFCl) converted the 1 : 4-addition product into the presumedly more stable 1 : 2-addition product.

*Scheme C.* The radical CFCl$_2$·CFCl can be visualised as a chain carrier :

$$\text{Cl·} + \text{CFCl:CFCl} \longrightarrow \text{CFCl}_2\text{·CFCl·}$$
$$\text{CFCl}_2\text{·CFCl·} + \text{CFCl:CFCl} \longrightarrow \text{CFCl}_2\text{·CFCl·CFCl·CFCl·}$$
$$\text{CFCl}_2\text{·CFCl·CFCl·CFCl·} + \text{CFCl:CFCl} \longrightarrow \text{CFCl}_2\text{·CFCl·CF:CFCl} + \text{CFCl}_2\text{·CFCl·}$$

Scheme D. Combination of two radicals, each relatively stable (cf. *J.*, 1953, 1764; *J.*, 1952, 2504 *et seq.*) :

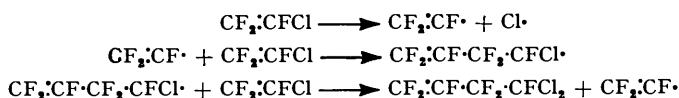$$CFCl:CF\cdot + CFCl_2\cdot CFCl\cdot \longrightarrow CFCl_2\cdot CFCl\cdot CF:CFCl$$
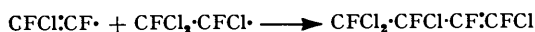
Scheme E. Formation of a *cyclo*butane followed by chlorine migration and C–C cleavage :
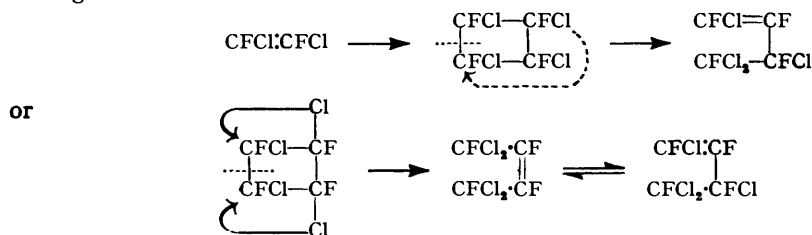
The *cyclo*butane need be formed only as a transition complex in a bimolecular reaction.

Some distinction between these schemes can be made by consideration of the open-chain dimerisation of other polyhalogeno-ethylenes. Miller (*op. cit.*) has shown that pyrolysis of chlorotrifluoroethylene gives 1 : 2-dichlorohexafluoro*cyclo*butane at lower temperatures and 3 : 4-dichlorohexafluorobut-1-ene at higher temperatures. Application of Scheme A to the last reaction would give

$$CF_2:CFCl \longrightarrow CF_2:CF\cdot + Cl\cdot$$
$$CF_2:CF\cdot + CF_2:CFCl \longrightarrow CF_2:CF\cdot CF_2\cdot CFCl\cdot$$
$$CF_2:CF\cdot CF_2\cdot CFCl\cdot + CF_2:CFCl \longrightarrow CF_2:CF\cdot CF_2\cdot CFCl_2 + CF_2:CF\cdot$$

The direction of attack of a free radical on chlorotrifluoroethylene is well established as exclusively on the CF_2 group (*J.*, 1953, 1592). Thus Scheme A would give 4 : 4-dichloro-hexafluorobut-1-ene, and Miller does not find this as a reaction product. Allylic rearrangement of the 4 : 4- into the 3 : 4-dichlorobutene is implausible, and Scheme A is thus unsatisfactory for application to chlorotrifluoroethylene and hence for 1 : 2-dichlorodifluoroethylene. Mechanisms involving homolytic fission of a C–F bond are unlikely and are not considered. Scheme B would give hexafluorobutadiene by combination of two $CF_2:CF$ radicals, and provided that the allylic rearrangement $CF_2Cl\cdot CF:CF\cdot CF_2Cl$ $\rightleftharpoons CF_2:CF\cdot CFCl\cdot CF_2Cl$ gave only the 3 : 4-dichloro-compound at high temperature, would account for the dimerisation product. A chlorination reaction involving free chlorine atoms or molecules of the type postulated in Scheme B is unlikely to give only the butene and no compounds formed by addition of two molecules of chlorine to the diene, however, and is considered less likely than the other possible mechanisms.
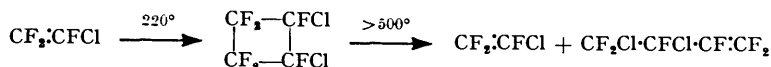
Scheme C can also be rejected, since the chlorine atom would attack the CF_2 group of chlorotrifluoroethylene to give $CF_2Cl\cdot CFCl\cdot$ and this would in turn give $CF_2Cl\cdot CFCl\cdot CF_2\cdot CFCl\cdot$. The conversion of this radical into $CF_2Cl\cdot CFCl\cdot CF:CF_2$ by reaction with chlorotrifluoroethylene is highly improbable.

Complete distinction between Schemes D and E cannot be made on the evidence available. Scheme D applied to chlorotrifluoroethylene would be

$$CF_2:CFCl \longrightarrow CF_2:CF\cdot + Cl\cdot$$
$$Cl\cdot + CF_2:CFCl \longrightarrow CF_2Cl\cdot CFCl\cdot$$
$$CF_2:CF\cdot + CF_2Cl\cdot CFCl\cdot \longrightarrow CF_2:CF\cdot CFCl\cdot CF_2Cl$$
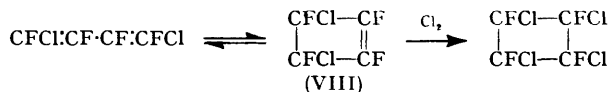
and this would be in accord with the direction of radical addition to chlorotrifluoroethylene and with the stabilities of the combining radicals. Although Scheme D explains the facts, it is not considered highly probable, since other products such as those formed by self-combination of $CF_2:CF$ or $CF_2Cl\cdot CFCl$ radicals would be expected. It is thus concluded that the open-chain dimerisation of chlorotrifluoroethylene is not a free-radical process but a bimolecular reaction possibly involving a *cyclo*butane intermediate as in Scheme E. It seems probable that 1 : 2-dichlorodifluoroethylene dimerisation occurs by a similar
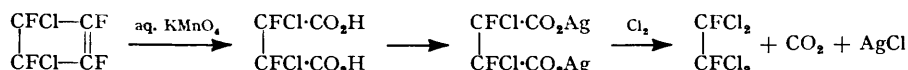
process. Some support for the application of Scheme E to chlorotrifluoroethylene dimerisation is given by the pyrolysis of 1 : 2-dichlorohexafluoro*cyclo*butane, which yields both chlorotrifluoroethylene and 3 : 4-dichlorohexafluorobut-1-ene (Miller, *op. cit.*) :

$$CF_2\text{:}CFCl \xrightarrow{220°} \begin{matrix} CF_2-CFCl \\ | \quad\quad | \\ CF_2-CFCl \end{matrix} \xrightarrow{>500°} CF_2\text{:}CFCl + CF_2Cl\cdot CFCl\cdot CF\text{:}CF_2$$

To throw further light on the possibility of Scheme E for general application to the open-chain dimerisation of polyhalogeno-olefins, 1 : 2 : 3 : 4-tetrachlorotetrafluoro*cyclo*butane was synthesised. Attempts to prepare this compound by cyclic dimerisation of 1 : 2-dichlorodifluoroethylene failed, but the realisation of the hexafluorobutadiene ⇌ hexafluoro*cyclo*butene equilibrium reported above led to the following successful synthesis :
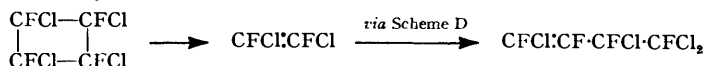
$$CFCl\text{:}CF\cdot CF\text{:}CFCl \rightleftharpoons \begin{matrix} CFCl-CF \\ | \quad\quad \| \\ CFCl-CF \end{matrix} \xrightarrow{Cl_2} \begin{matrix} CFCl-CFCl \\ | \quad\quad | \\ CFCl-CFCl \end{matrix}$$
(VIII)

The interconversion diene ⇌ *cyclo*butene is probably a general reaction for polyhalogeno-compounds. The equilibrium lies in favour of the *cyclo*butene, and can be approached from either compound with the formation of only relatively small amounts of products with a higher b. p. The conversion of the *cyclo*butene into the diene shows that halogen migration has not occurred during rearrangement of the diene into the *cyclo*butene; compounds such as 1 : 4-, 1 : 3-, or 1 : 2-dichlorotetrafluoro*cyclo*butene are not produced. Further proof is given by the aqueous permanganate oxidation of (VIII) to give αβ-dichloro-αβ-difluorosuccinic acid, isolated as its silver salt and thence converted into 1 : 1 : 2 : 2-tetrachlorodifluoroethane :

$$\begin{matrix} CFCl-CF \\ | \quad\quad \| \\ CFCl-CF \end{matrix} \xrightarrow{aq.\ KMnO_4} \begin{matrix} CFCl\cdot CO_2H \\ | \\ CFCl\cdot CO_2H \end{matrix} \rightarrow \begin{matrix} CFCl\cdot CO_2Ag \\ | \\ CFCl\cdot CO_2Ag \end{matrix} \xrightarrow{Cl_2} \begin{matrix} CFCl_2 \\ | \\ CFCl_2 \end{matrix} + CO_2 + AgCl$$
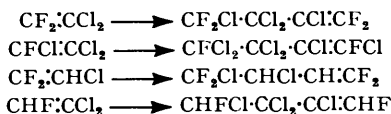
Chlorine adds smoothly to 2 : 3-dichlorotetrafluoro*cyclo*butene to give 1 : 2 : 3 : 4-tetrachlorotetrafluoro*cyclo*butane. Reaction of the last compound with zinc and dioxan gives the *cyclo*butene again, but attempts to remove a second molecule of chlorine to give perfluoro*cyclo*buta-1 : 3-diene failed. Pyrolysis of the tetrachlorotetrafluoro*cyclo*butane gives moderate yields of 1 : 3 : 4 : 4-tetrachlorotetrafluorobut-1-ene (I), and this supports Scheme E as the method of open-chain dimerisation of polyhalogeno-ethylenes by a non-radical mechanism :

$$\begin{matrix} CFCl-CFCl \\ | \quad\quad\ \ \diagdown \\ CFCl-CFCl \end{matrix} \rightarrow CFCl\text{:}CF\cdot CFCl\cdot CFCl_2$$
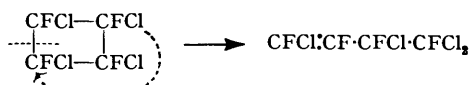
although it should be noted that free-radical Scheme D proceeding with initial formation of 1 : 2-dichlorodifluoroethylene would give the same product :

$$\begin{matrix} CFCl-CFCl \\ | \quad\quad | \\ CFCl-CFCl \end{matrix} \rightarrow CFCl\text{:}CFCl \xrightarrow{via\ Scheme\ D} CFCl\text{:}CF\cdot CFCl\cdot CFCl_2$$
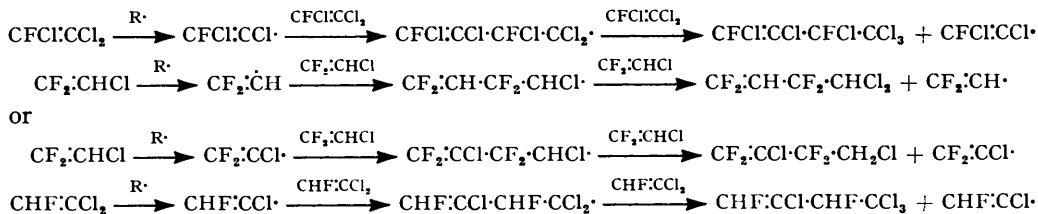
The open-chain dimerisation of other polyhalogeno-ethylenes by a non-radical mechanism can now be predicted with reasonable certainty according to Scheme E provided that (*a*) the olefin contains fluorine and (*b*) peroxides are absent, *e.g.*,

$$CF_2\text{:}CCl_2 \rightarrow CF_2Cl\cdot CCl_2\cdot CCl\text{:}CF_2$$
$$CFCl\text{:}CCl_2 \rightarrow CFCl_2\cdot CCl_2\cdot CCl\text{:}CFCl$$
$$CF_2\text{:}CHCl \rightarrow CF_2Cl\cdot CHCl\cdot CH\text{:}CF_2$$
$$CHF\text{:}CCl_2 \rightarrow CHFCl\cdot CCl_2\cdot CCl\text{:}CHF$$

It cannot be emphasised too strongly that a free-radical dimerisation of polyhalogeno-ethylenes can very probably be achieved also, *e.g.*, by use of a peroxide initiator with olefins which do not give long-chain polymers readily under free-radical conditions. The direction of addition of a free radical to $\overset{*}{C}FCl\text{:}CCl_2$, $\overset{*}{C}F_2\text{:}CHCl$, and $\overset{*}{C}HF\text{:}CCl_2$, which

falls into this category, is known to be at the carbon atom indicated by an asterisk (unpublished results), and a free radical R produced from a peroxide would abstract chlorine and so enable Scheme A to operate :

$$CFCl{:}CCl_2 \xrightarrow{R\cdot} CFCl{:}CCl\cdot \xrightarrow{CFCl{:}CCl_2} CFCl{:}CCl\cdot CFCl\cdot CCl_2\cdot \xrightarrow{CFCl{:}CCl_2} CFCl{:}CCl\cdot CFCl\cdot CCl_3 + CFCl{:}CCl\cdot$$

$$CF_2{:}CHCl \xrightarrow{R\cdot} CF_2{:}\dot{C}H \xrightarrow{CF_2{:}CHCl} CF_2{:}CH\cdot CF_2\cdot CHCl\cdot \xrightarrow{CF_2{:}CHCl} CF_2{:}CH\cdot CF_2\cdot CHCl_2 + CF_2{:}CH\cdot$$

or

$$CF_2{:}CHCl \xrightarrow{R\cdot} CF_2{:}CCl\cdot \xrightarrow{CF_2{:}CHCl} CF_2{:}CCl\cdot CF_2\cdot CHCl\cdot \xrightarrow{CF_2{:}CHCl} CF_2{:}CCl\cdot CF_2\cdot CH_2Cl + CF_2{:}CCl\cdot$$

$$CHF{:}CCl_2 \xrightarrow{R\cdot} CHF{:}CCl\cdot \xrightarrow{CHF{:}CCl_2} CHF{:}CCl\cdot CHF\cdot CCl_2\cdot \xrightarrow{CHF{:}CCl_2} CHF{:}CCl\cdot CHF\cdot CCl_3 + CHF{:}CCl\cdot$$
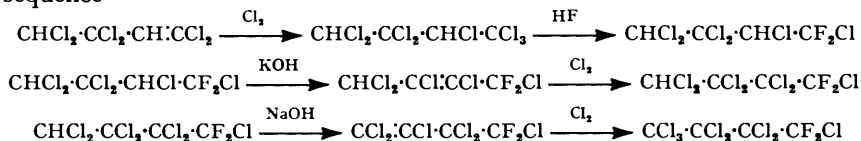
Open-chain dimers different from those obtainable by purely thermal non-radical dimerisation are thus possible.
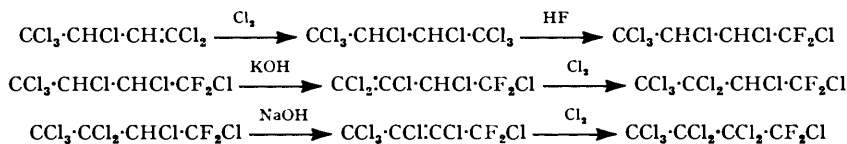
This possibility is being investigated, but there is some indication in the literature that trichloroethylene can give two dimers. When it is heated at 210° under 40 atm. pressure in presence of antioxidants the dimer obtained is believed to be $CCl_3\cdot CHCl\cdot CH{:}CCl_2$ (Rodd, " Chemistry of Carbon Compounds," Elsevier, 1951, Vol. IA, p. 283; French P. 814,423/1937, 51,288/1942; G.P. 721,380/1942; Mugden and Wimmer, G.P. 736,232/1943; U.S.P. 2,338,297/1944), although no precise proof of structure is available. This could be obtained by Scheme E :
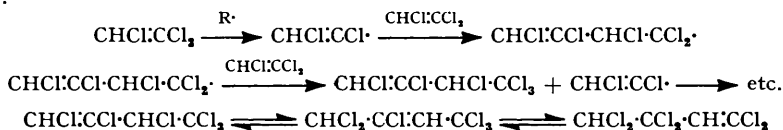
$$CHCl{:}CCl_2 \longrightarrow \begin{array}{c} CCl_2{-}CHCl \\ | \quad\quad | \\ CCl_2{-}CHCl \end{array} \longrightarrow CCl_2{:}CH\cdot CHCl\cdot CCl_3$$

The dimer obtained when trichloroethylene is heated in presence of peroxides such as benzoyl peroxide is probably $CHCl_2\cdot CCl_2\cdot CH{:}CCl_2$ or its allylic rearrangement product ($CHCl_2\cdot CCl_2\cdot CH{:}CCl_2 \rightleftharpoons CHCl_2\cdot CCl{:}CH\cdot CCl_3 \rightleftharpoons CHCl{:}CCl\cdot CHCl\cdot CCl_3$) (G.P. 718,057/1942; French P. 841,728/1939; B.P. 517,213/1940). Henne and Ruh (*J. Amer. Chem. Soc.*, 1947, **69**, 279) have produced evidence in support of this constitution, but it should be noted that their evidence rests upon the formation of $CF_2Cl\cdot CCl_2\cdot CCl_2\cdot CCl_3$ by the sequence

$$CHCl_2\cdot CCl_2\cdot CH{:}CCl_2 \xrightarrow{Cl_2} CHCl_2\cdot CCl_2\cdot CHCl\cdot CCl_3 \xrightarrow{HF} CHCl_2\cdot CCl_2\cdot CHCl\cdot CF_2Cl$$

$$CHCl_2\cdot CCl_2\cdot CHCl\cdot CF_2Cl \xrightarrow{KOH} CHCl_2\cdot CCl{:}CCl\cdot CF_2Cl \xrightarrow{Cl_2} CHCl_2\cdot CCl_2\cdot CCl_2\cdot CF_2Cl$$

$$CHCl_2\cdot CCl_2\cdot CCl_2\cdot CF_2Cl \xrightarrow{NaOH} CCl_2{:}CCl\cdot CCl_2\cdot CF_2Cl \xrightarrow{Cl_2} CCl_3\cdot CCl_2\cdot CCl_2\cdot CF_2Cl$$

but none of the constitutions of the intermediates was proved, and neither yields nor analyses was given. The formation of $CF_2Cl\cdot CCl_2\cdot CCl_2\cdot CCl_3$ could equally well be used as evidence for $CCl_3\cdot CHCl\cdot CH{:}CCl_2$ if the not-impossible replacement of two chlorine atoms on one carbon atom by fluorine occurred :

$$CCl_3\cdot CHCl\cdot CH{:}CCl_2 \xrightarrow{Cl_2} CCl_3\cdot CHCl\cdot CHCl\cdot CCl_3 \xrightarrow{HF} CCl_3\cdot CHCl\cdot CHCl\cdot CF_2Cl$$

$$CCl_3\cdot CHCl\cdot CHCl\cdot CF_2Cl \xrightarrow{KOH} CCl_2{:}CCl\cdot CHCl\cdot CF_2Cl \xrightarrow{Cl_2} CCl_3\cdot CCl_2\cdot CHCl\cdot CF_2Cl$$

$$CCl_3\cdot CCl_2\cdot CHCl\cdot CF_2Cl \xrightarrow{NaOH} CCl_3\cdot CCl{:}CCl\cdot CF_2Cl \xrightarrow{Cl_2} CCl_3\cdot CCl_2\cdot CCl_2\cdot CF_2Cl$$

If Henne and Ruh's conclusions about the constitution of peroxide-produced trichloroethylene dimer are accepted, however, the most probable method of formation is by Scheme A :

$$CHCl{:}CCl_2 \xrightarrow{R\cdot} CHCl{:}CCl\cdot \xrightarrow{CHCl{:}CCl_2} CHCl{:}CCl\cdot CHCl\cdot CCl_2\cdot$$

$$CHCl{:}CCl\cdot CHCl\cdot CCl_2\cdot \xrightarrow{CHCl{:}CCl_2} CHCl{:}CCl\cdot CHCl\cdot CCl_3 + CHCl{:}CCl\cdot \longrightarrow etc.$$

$$CHCl{:}CCl\cdot CHCl\cdot CCl_3 \rightleftharpoons CHCl_2\cdot CCl{:}CH\cdot CCl_3 \rightleftharpoons CHCl_2\cdot CCl_2\cdot CH{:}CCl_2$$

The direction of addition of a free radical to trichloroethylene is known to be to the CHCl group (G. F. Liptrot and B. R. Steele, unpublished results), and the formation of

CHCl:CCl· by attack of R on trichloroethylene rather than the less stable CCl₂:CH· is plausible.

The concept of two reaction schemes, the first non-radical and possibly with a *cyclo*-butane as intermediate, the second free radical, for dimerisation of polyhalogeno-ethylenes must be adopted, since no single mechanism can be put forward to explain all the known dimerisations without unreasonable assumptions. It will clearly not be possible to make any one of the reaction schemes operate at will with every olefin, but it should be possible to demonstrate both mechanisms by careful choice of olefin; experiments along these lines will be reported later.

Experimental

Reactions were carried out in sealed Pyrex or silica tubes unless otherwise stated, with precautions to exclude moisture, air, or materials which might catalyse ionic or free-radical reactions.

Reaction of Hydrogen Iodide with Perfluorocyclobutene.—Perfluorocyclobutene and hydrogen iodide failed to react when heated in a sealed tube at 210° (65 hr.). Perfluorocyclobutene (1·14 g.) and hydrogen iodide (4·99 g.), heated at 275° (24 hr.) in a sealed tube, gave unchanged olefin (0·41 g.) and 1 : 1 : 2 : 3 : 4 : 4-*hexafluorobutane* (90%), b. p. 63—65°, n_D^{20} 1·300 (Found : C, 28·6; H, 2·4%; M, 166. $C_4H_4F_6$ requires C, 28·8; H, 2·4%; M, 166).

In a second experiment, perfluorocyclobutene (2·0 g.) and a 20% excess of hydrogen iodide, heated at 300° (24 hr.), gave 1 : 1 : 2 : 3 : 4 : 4-hexafluorobutane (98%) and unchanged olefin (<2%). Iodine was liberated during the reaction, but no polymerisation or etching of the glass tube was apparent.

The reaction was also carried out successfully in an autoclave. Perfluorocyclobutene (15·0 g.) and hydrogen iodide (100% excess) in a stainless-steel autoclave were heated in an oil-bath at 290—300° (32 hr.) to give 1 : 1 : 2 : 3 : 4 : 4-hexafluorobutane (92%) and perfluoro-cyclobutene (4%). There was no liberation of hydrogen fluoride or carbon.

Further experiments gave yields of 88—93% of the hexafluorobutane from 15—20 g. of perfluorocyclobutene. Careful control of reaction temperature is necessary to prevent formation of hydrogen fluoride.

Conversion of 1 : 1 : 2 : 3 : 4 : 4-Hexafluorobutane into Hexafluorobutadiene.—The hexafluoro-butane (5·3 g.), chlorine (100% excess), and water (4 ml.) in a silica tube were exposed to ultra-violet light (24 hr.) to give 1 : 1 : 2 : 3 : 4-tetrachlorohexafluorobutane (93%), b. p. 134°, n_D^{22} 1·382 (Found : C, 15·8. Calc. for $C_4Cl_4F_6$: C, 15·8%). The infrared spectrum of the chloro-compound was identical with that of a known sample (*J.*, 1952, 4423). Final proof of structure was given by reaction of the tetrachlorohexafluorobutane (6·5 g.) with zinc (30 g.) and refluxing ethanol (80 ml.) (6 hr.) to give perfluorobutadiene (87%), b. p. 5·8° (Found : M, 162. Calc. for C_4F_6 : M, 162). The infrared spectrum of the perfluorobutadiene was identical with that of a known sample (*J.*, 1952, 4423).

Isomerisation of Perfluorocyclobutene and Perfluorobutadiene.—When perfluorocyclobutene (5·6 g.) was passed through a silica tube packed with active carbon flakes, heated to 580° over a 12″ length, examination of the reaction products by infrared spectroscopy revealed the presence of perfluorocyclobutene (89%), perfluorobutadiene (8%), and unidentified material of higher b. p., probably dimers and trimers. Experiments at 550°, 600°, 650°, and 700° gave 3, 10, 12, and 6% yields of perfluorobutadiene, respectively. Final identification of the diene was made by treatment of the combined reaction products with an excess of chlorine with exposure to ultraviolet light (12 hr.) to give 1 : 2-dichlorohexafluorocyclobutane, b. p. 60°, and 1 : 2 : 3 : 4-tetrachlorohexafluorobutane, b. p. 133—134°. The infrared spectrum of the last compound was identical with that of a known specimen; furthermore, the tetrachloro-compound gave perfluorobutadiene (85%) (identified spectroscopically) when treated with zinc and refluxing ethanol.

Hexafluorobutadiene (3·9 g.), passed through the tube used above at 580°, gave perfluoro-cyclobutene (80%) and perfluorobutadiene (10%). Experiments at 600°, 640°, and 690° gave 82, 78, and 84% yields of perfluorocyclobutene, respectively, with perfluorobutadiene as the other major product, though small amounts of dimers and trimers were also detected. The reaction product from the experiment at 580° was photochemically chlorinated (12 hr.) to give 1 : 2-dichlorohexafluorocyclobutane, b. p. 59°, and 1 : 2 : 3 : 4-tetrachlorohexafluorobutane, b. p. 132—134°. The identity of the dichlorohexafluorocyclobutane was confirmed by means of its infrared spectrum.

Dimerisation of 1 : 2-*Dichlorodifluoroethylene.*—(a) *In silica tubes.* The olefin (6·7 g.), heated in a silica tube at 230° (24 hr.), gave unchanged olefin (31%) and its dimer $C_4Cl_4F_4$ (69% based on olefin used), b. p. 140—142°. Similar experiments at 250°, 280°, and 300° gave 73, 66, and 61% yields of dimer, respectively. At the higher temperatures very little original olefin was recovered unchanged but there was an increase in the amount of breakdown products.

(b) *In an autoclave.* Dichlorodifluoroethylene (10·7 g.) was heated at 260° in a 20 ml. autoclave (15 hr.) to give the dimer (71% based on olefin used), unchanged olefin (12%), and intermediate fractions. The combined still residues were distilled to give material believed to contain trimers, but these were not investigated further.

(c) *Properties and reactions of the dimer.* The combined dimer fraction from the above experiments was redistilled to give 1 : 3 : 4 : 4-*tetrachlorotetrafluorobut-1-ene*, b. p. 140·5—141°, n_D^{20} 1·429 (Found : C, 18·0; Cl, 52·9. $C_4Cl_4F_4$ requires C, 18·0; Cl, 53·4%). A sample of the dimer (1·3 g.), treated with an excess of chlorine in a silica tube exposed to ultraviolet light, gave 1 : 1 : 2 : 3 : 4 : 4-hexachlorotetrafluorobutane (97%) (Found : C, 14·2. Calc. for $C_4Cl_6F_4$: C, 14·2%), b. p. 207—208°, n_D^{20} 1·457. Miller (*loc. cit.*) prepared this compound in 32% yield by reaction of hexachlorobutadiene and fluorine, and reports b. p. 133—134°/100 mm., n_D^{20} 1·4568.

A sample of the dimer $C_4Cl_4F_4$ (3·3 g.), mixed with bromine (20% excess), heated to 50°, and exposed to ultraviolet light (8 hr.), gave 1 : 2-dibromo-1 : 3 : 4 : 4-tetrachlorotetrafluoro-butane (83%), b. p. 138—140°/35 mm., n_D^{20} 1·493.

1 : 3 : 4 : 4-Tetrachlorotetrafluorobut-1-ene (6·8 g.), dissolved in dioxan (10 ml.), was added dropwise to zinc (20 g.) and refluxing dioxan (50 ml.) in an apparatus fitted with reflux condenser and take-off so that the reflux liquid could be steadily removed (5 hr.) and dropped into an excess of water. The diene produced by the dehalogenation was thus removed, with dioxan, from the reaction vessel and prevented from being reduced by prolonged contact with the zinc. The lower layer obtained in this way was shaken with water to remove last traces of dioxan and distilled from phosphoric anhydride to give 1 : 4-dichlorotetrafluorobutadiene (78%), b. p. 79°, n_D^{20} 1·403 (Found : C, 20·6; Cl, 30·7%; M, 233. Calc. for $C_4Cl_2F_6$: C, 20·6; Cl, 30·5%; M, 233). Miller (*loc. cit.*) gives b. p. 78° for this diene.

The same diene was produced in 81% yield when 1 : 1 : 2 : 3 : 4 : 4-hexachlorotetrafluoro-butane (4·7 g.) was treated with zinc and dioxan under the same conditions as used above. The dibromo-compound described above (3·9 g.) similarly gave a 75% yield of 1 : 4-dichloro-tetrafluorobutadiene.

αββ-*Trichlorodifluoropropionic Acid.*—1 : 3 : 4 : 4-Tetrachlorotetrafluorobut-1-ene (5·9 g.), potassium permanganate (6·0 g.), and water (50 ml.) were heated at 80° under a reflux condenser (8 hr.). The pH of the solution was kept at 7—8·5 by periodic addition of 5% aqueous sodium hydroxide; this was found necessary to prevent extensive breakdown of the chain when more alkaline solutions were used. The excess of permanganate was destroyed by treatment with sulphur dioxide, and the solution was extracted by ether in the usual way (cf. *J.*, 1950, 3037, 2789; 1952, 4259; 1953, 1548). Distillation of the dried ethereal extracts gave a small amount (0·4 g.) of an acid containing fluorine and chlorine which was possibly dichlorofluoroacetic acid, but was not definitely identified, b. p. 90—95°/25 mm., and αββ-*trichlorodifluoropropionic acid* (74%), b. p. 115—118°/25 mm., 95—96°/5 mm. (Found : C, 16·9; H, 0·6; Cl, 49·5%; equiv., 215. $C_3HO_2Cl_3F_2$ requires C, 16·9; H, 0·5; Cl, 49·9%; equiv., 213·5). The acid is a solid at room temperature.

Sodium αββ-trichlorodifluoropropionate (3·2 g.), prepared by exact neutralisation of the acid followed by freeze-drying, was thoroughly dried *in vacuo* over phosphoric anhydride (7 days), then spread in a thin layer on a platinum sheet which was placed inside a steel tube. The tube was closed at one end, and the other end led to an oil pump *via* a trap cooled in liquid oxygen. The apparatus was evacuated to 10^{-2} mm. and the closed end of the tube was slowly pushed (1 hr.) into a furnace at 300°. In this way pyrolysis of the sodium salt was effected at the lowest possible temperature and the products were immediately removed from the reaction zone. Distillation gave carbon dioxide and 1 : 2-dichlorodifluoroethylene (84%), b. p. 21—22°, identified spectroscopically. The residue on the platinum sheet was sodium chloride containing only a trace of sodium fluoride.

Silver αββ-trichlorodifluoropropionate (2·1 g.), prepared by neutralisation of the acid with silver carbonate followed by filtration and freeze-drying, was dried *in vacuo* then sealed with an excess of chlorine in a Pyrex tube. Reaction occurred at 20°, and was completed at 40°. Distillation of the volatile products gave 1 : 1 : 2 : 2-tetrachlorodifluoroethane (79%), b. p. 92—93°, n_D^{20} 1·413 (Found : M, 205. Calc. for $C_2Cl_4F_2$: M, 204), identified spectroscopically.

Rearrangement of 1 : 4-*Dichlorotetrafluorobutadiene.*—The diene (3·9 g.), heated at 250° in

a sealed tube (12 hr.), gave unchanged diene (12%), 2 : 3-*dichlorotetrafluoro*cyclobutene (56%), b. p. 65·5°, n_D^{20} 1·375 (Found : C, 20·4; Cl, 30·0%; *M*, 233. $C_4Cl_2F_4$ requires C, 20·6; Cl, 30·5%; *M*, 233), and products of higher b. p. believed to be dimers. The presence of a double bond in the *cyclo*butene was shown by its reaction with chlorine (10% excess) on exposure to ultraviolet light to give 1 : 2 : 3 : 4-tetrachlorotetrafluoro*cyclo*butane (95%), b. p. 129°, m. p. 45—46°. The tetrachloro-compound was reconverted into 2 : 3-dichlorotetrafluoro-*cyclo*butene in 83% yield by reaction with zinc and refluxing ethanol with continuous removal of the olefin; this shows that no rearrangement occurred during the photochemical chlorination.

Attempts were made to dechlorinate 2 : 3-dichlorotetrafluoro*cyclo*butene by reaction with zinc and dioxan in a sealed tube at 120°, 150°, and 180°. There was only slight reaction at 120°, and the products from the reactions at the higher temperatures contained hydrogen; none of the products corresponded to a tetrafluoro*cyclo*butadiene.

1 : 4-Dichlorotetrafluorobutadiene was also converted into the dichlorotetrafluoro*cyclo*-butene by passage through a hot tube. The diene (4·7 g.), passed through a platinum tube packed with active carbon at 320° (2 hr.), gave a 74% yield of the *cyclo*butene; unchanged diene and products of higher b. p. were also detected.

2 : 3-Dichlorotetrafluoro*cyclo*butene (3·4 g.), passed through a platinum tube packed with active carbon at 380°, gave unchanged dichlorotetrafluoro*cyclo*butene (70%), 1 : 4-dichlorotetra-fluorobutadiene (14%), and unidentified products of higher b. p. After initial separation by distillation, the *cyclo*butene and the diene were chlorinated to show the presence of one and two double bonds respectively, and to confirm their identity with the compounds previously described.

αβ-Dichloro-αβ-difluorosuccinic Acid.—2 : 3-Dichlorotetrafluoro*cyclo*butene (3·8 g.), water (15 ml.), and potassium permanganate (4 g.) were heated at 70° in a stainless-steel autoclave (10 hr.). There was no unchanged *cyclo*butene. The aqueous solution was treated with sulphur dioxide and extracted with ether in the usual way. Distillation of the material remaining after removal of the ether gave *αβ-dichloro-αβ-difluorosuccinic acid* (62%), b. p. 100—105°/0·1 mm. (Found : equiv., 112·5. $C_4H_2O_4Cl_2F_2$ requires equiv., 111·5). This was neutralised with a slight excess of silver carbonate, and filtration and freeze-drying of the aqueous solution gave *silver αβ-dichloro-αβ-difluorosuccinate* (Found : Ag, 49·0. $C_4O_4Cl_2F_2Ag_2$ requires Ag, 49·4%).

Reaction of the silver salt (0·8 g.) with a 10% excess of chlorine in a sealed tube at 30° gave 1 : 1 : 2 : 2-tetrachlorodifluoroethane (71%), b. p. 92° (isoteniscope) (Found : *M*, 203. Calc. for $C_2Cl_4F_2$: *M*, 204), identified spectroscopically.

Pyrolysis of 1 : 2 : 3 : 4-*Tetrachlorotetrafluoro*cyclobutane.—The *cyclo*butane (5·3 g.), passed through a platinum tube packed with active charcoal and heated to 350°, gave 1 : 3 : 4 : 4-tetra-chlorotetrafluorobut-1-ene (57%), 1 : 2-dichlorodifluoroethylene (11%), and unidentified products, b. p. 50—100°.

The *cyclo*butane (3·1 g.), heated in a silica tube at 290°, gave 1 : 3 : 4 : 4-tetrachlorotetra-fluorobut-1-ene (51%), unchanged 1 : 2 : 3 : 4-tetrachlorotetrafluoro*cyclo*butane (22%), a small amount of 1 : 2-dichlorodifluoroethylene (9%), and unidentified products.