Fluoro-olefins. Part V. Fluoro-dienes and -trienes and Perfluoromalonic Acid.*

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The compounds $Cl\cdot[CF_2\cdot CFCl]_n\cdot I$ can be coupled to give $Cl\cdot[CF_2\cdot CFCl]_n\cdot[CFCl\cdot CF_2]_n\cdot Cl$. Dienes, trienes (*e.g.*, $CF_2{:}CF\cdot CF_2\cdot CF{:}CF\cdot CF_2\cdot CF{:}CF_2$), and polyfluoro-acids [*e.g.*, $CF_2(CO_2H)_2$ and $(CFCl\cdot CF_2\cdot CO_2H)_2$] have been synthesised from the coupled products, and reactions of the salts of the acids are described.

THE coupling of polyfluoroalkyl chains was originally demonstrated with heptafluoroiodopropane, 1-chlorohexafluoro-1-iodopropane and 1 : 2-dichlorotrifluoro-1-iodoethane :

$$C_3F_7I \longrightarrow C_6F_{14};\quad C_2F_5\cdot CFClI \longrightarrow (C_2F_5\cdot CFCl)_2;\quad CF_2Cl\cdot CFClI \longrightarrow (CF_2Cl\cdot CFCl)_2$$

and is achieved by use of mercury and ultraviolet light or by zinc in an inert solvent, preferably free from active hydrogen, such as dioxan (Haszeldine, *J.*, 1952, 4423; Haszeldine and Steele, *J.*, 1953, 1592; Haszeldine and Walaschewski, *J.*, 1953, 3607). Henne, and Henne and Postelneck (*J. Amer. Chem. Soc.*, 1953, **75**, 5750; 1955, **77**, 2334), have confirmed the reaction with 1 : 2-dichlorotrifluoro-1-iodoethane and heptafluoroiodopropane.

The synthesis of compounds of general formula $Cl\cdot[CF_2\cdot CFCl]_n\cdot I$ by interaction of 1 : 2-dichlorotrifluoro-1-iodoethane and chlorotrifluoroethylene was described in Part IV (*loc. cit.*). These compounds contain a terminal –CFClI group and can thus be coupled readily either by use of mercury and ultraviolet light, or by use of zinc in an inert solvent as outlined above :

$$Cl\cdot[CF_2\cdot CFCl]_n\cdot I \xrightarrow{Hg,h\nu} Cl\cdot[CF_2\cdot CFCl]_n\cdot \longrightarrow Cl\cdot[CF_2\cdot CFCl]_n\cdot[CFCl\cdot CF_2]_n\cdot Cl \quad (I)$$

Such coupled compounds (I) contain a poly(chlorotrifluoroethylene) chain of a new type. They are isomers of the compounds $Cl\cdot[CF_2\cdot CFCl]_m\cdot Cl$ described in Part IV, but are capable of more extensive use in synthesis, since they contain a central $-CFCl\cdot CFCl-$ group which

$$CF_2{:}CF\cdot[CF_2\cdot CFCl]_n\cdot[CFCl\cdot CF_2]_m\cdot CF{:}CF_2 \quad (A)$$

$$CF_2{:}CF\cdot[CF_2\cdot CFCl]_m\cdot CF_2\cdot CF{:}CF\cdot CF_2\cdot[CFCl\cdot CF_2]_x\cdot CF{:}CF_2 \quad (B)$$

can be converted into $-CF{:}CF-$, as well as the terminal $CF_2Cl\cdot CFCl-$ groups which give $CF_2{:}CF-$ groups. Dechlorination of $CF_2Cl\cdot CFCl-$ is easier than dechlorination of

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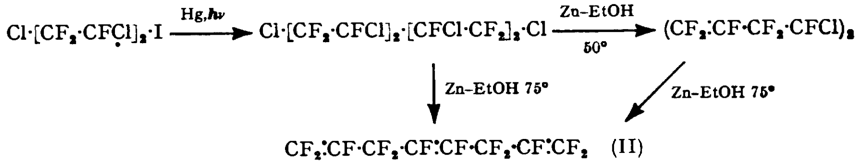
* Part IV, preceding paper.

–CFCl·CFCl– so terminal diolefins (A) or triolefins (B) can be obtained by control of conditions. This is illustrated by the synthesis of perfluoro-octa-1 : 4 : 7-triene (II) :



$$\begin{tikzcd} Cl\cdot[CF_2\cdot CFCl]_2\cdot I \arrow[r, "\text{Hg}, h\nu"] & Cl\cdot[CF_2\cdot CFCl]_2\cdot[CFCl\cdot CF_2]_2\cdot Cl \arrow[r, "\text{Zn-EtOH}", "60^\circ"'] \arrow[d, "\text{Zn-EtOH } 75^\circ"] & (CF_2{:}CF\cdot CF_2\cdot CFCl)_2 \arrow[dl, "\text{Zn-EtOH } 75^\circ"] \\ & CF_2{:}CF\cdot CF_2\cdot CF{:}CF\cdot CF_2\cdot CF{:}CF_2 \quad (II) & \end{tikzcd}$$

The di- and tri-olefins (III) and (IV) are similarly formed from $Cl\cdot[CF_2\cdot CFCl]_3\cdot I$:

$$(CF_2{:}CF\cdot CF_2\cdot CFCl\cdot CF_2\cdot CFCl)_2 \quad (III) \qquad CF_2{:}CF\cdot CF_2\cdot CFCl\cdot CF_2\cdot CF{:}CF\cdot CF_2\cdot CFCl\cdot CF_2\cdot CF{:}CF_2 \quad (IV)$$

These are the first polyfluorotrienes to be described. The double bonds are not conjugated so that the trienes behave as a terminal olefin such as $C_2F_5\cdot CF{:}CF_2$ and a symmetrical olefin such as $CF_3\cdot CF{:}CF\cdot CF_3$; the terminal double bonds are attacked more rapidly by electrophilic reagents or free radicals than the central double bond (Haszeldine and Osborne, in the press).

The dienes and trienes are oxidised at controlled pH to give dicarboxylic acids. For example, perfluoromalonic acid is obtained in good yield, thus proving the structure of (II) :

$$CF_2{:}CF\cdot CF_2\cdot CF{:}CF\cdot CF_2\cdot CF{:}CF_2 \xrightarrow{\text{Aq. KMnO}_4} CF_2(CO_2H)_2$$

Henne and De Witt (*J. Amer. Chem. Soc.*, 1948, **70**, 1548) reported that perfluoromalonic acid was unstable and was readily decarboxylated to difluoroacetic acid. This has not been our experience, and isolation and purification of the acid offered no difficulties. Evans and Tatlow's experience (*J.*, 1954, 3779) with perfluoromalonic acid prepared by oxidation of perfluoro*cyclo*hexa-1 : 4-diene was similar to ours.

Permanganate oxidation of 4 : 5-dichlorododecafluoro-octa-1 : 7-diene affords 3 : 4-dichlorohexafluoroadipic acid (V), the anhydrous disilver salt of which with chlorine gives the known 1 : 2 : 3 : 4-tetrachlorohexafluorobutane, and this in turn yields hexafluorobutadiene:

$$(CF_2{:}CF\cdot CF_2\cdot CFCl)_2 \xrightarrow{\text{KMnO}_4} \underset{(V)}{(CFCl\cdot CF_2\cdot CO_2H)_2} \longrightarrow (CFCl\cdot CF_2\cdot CO_2Ag)_2$$

$$(CFCl\cdot CF_2\cdot CO_2Ag)_2 \xrightarrow{Cl_2} (CFCl\cdot CF_2Cl)_2 \xrightarrow{\text{Zn-EtOH}} CF_2{:}CF\cdot CF{:}CF_2$$

The application of the silver-salt degradation to polyfluoro-acids containing chlorine was demonstrated recently (Haszeldine and Osborne, Part III, *J.*, 1955, 3880; Haszeldine, Part IV). The above reactions prove the structure of (V), and hence of the parent diene and the original coupled product.

Pyrolysis of anhydrous disodium 3 : 4-dichlorohexafluoroadipate gives a high yield of hexafluorobutadiene by loss of chloride from a polyhalogenocarbanion (cf. *J.*, 1951, 5844, 1952, 993, 4259; 1954, 4026; Parts III and IV, *locc. cit.*). The loss of chloride rather than fluoride is noteworthy, since it leads to a higher yield of hexafluorobutadiene than that obtained by pyrolysis of disodium octafluoroadipate (*J.*, 1954, 4026) :

$$(CFCl\cdot CF_2\cdot CO_2Na)_2 \longrightarrow {}^-CF_2\cdot CFCl\cdot CFCl\cdot CF_2{}^- + 2CO_2 + 2Na^+$$

$$\overset{-}{C}F_2-\underset{Cl}{CF}-\underset{Cl}{CF}-\overset{-}{C}F_2 \longrightarrow CF_2{:}CF\cdot CF{:}CF_2 + 2Cl^-$$

Further reactions of the dienes and trienes are under investigation.

EXPERIMENTAL

Coupling of compounds which contain the $-$CFClI group is most conveniently brought about in a silica tube by use of mercury and ultraviolet light. Vigorous shaking is essential with sufficient excess of mercury to keep the contents mobile. Addition of an inert diluent prevents the caking of mercury iodides on the walls of the tube which cuts out the light. Photochemical coupling gives a product uncontaminated by the olefinic or hydrogen-containing materials which are obtained as by-products when zinc is used to effect coupling. This only becomes important when compounds which contain more than 6—8 carbon atoms are coupled, and the shorter-chain compounds can conveniently be coupled by use of zinc–dioxan, etc.

Coupling of Compounds $Cl{\cdot}[CF_2{\cdot}CFCl]_n{\cdot}I$.—(*a*) The compound $Cl{\cdot}[CF_2{\cdot}CFCl]_2{\cdot}I$ (5·1 g.) was diluted with 1 : 1 : 2-trichlorotrifluoroethane (5 ml.) and shaken vigorously with mercury (20 ml.) in a silica tube exposed to ultraviolet light (8 days). Ether-extraction of the organic material followed by distillation gave 1 : 2 : 4 : 5 : 7 : 8-*hexachlorododecafluoro-octane* (81%), b. p. 142—144°/20 mm., n_D^{22} 1·408 (Found : C, 17·9; Cl, 39·7. $C_8Cl_6F_{12}$ requires C, 17·9; Cl, 39·7%).

(*b*) The compound $Cl{\cdot}[CF_2{\cdot}CFCl]_3{\cdot}I$ (4·9 g.), treated as in (*a*), gave 1 : 2 : 4 : 6 : 7 : 9 : 11 : 12-*octachloro-octadecafluorododecane* (74%), b. p. 195—200°/*ca.* 0·1 mm. (Found : C, 18·7; Cl, 36·8. $C_{12}Cl_8F_{18}$ requires C, 18·7; Cl, 36·9%).

Dechlorination of Compounds $Cl{\cdot}[CF_2{\cdot}CFCl]_n{\cdot}[CFCl{\cdot}CF_2]_n{\cdot}Cl$.—(*c*) The compound $Cl{\cdot}[CF_2{\cdot}CFCl]_2{\cdot}[CFCl{\cdot}CF_2]_2{\cdot}Cl$ (6·7 g.), prepared as described above, was diluted with ethanol (20 ml.) and added dropwise to zinc and refluxing ethanol. After 1 hr. the product was filtered and added to an excess of water. Distillation of the lower layer from phosphoric oxide gave *perfluoro-octa*-1 : 4 : 7-*triene* (78%), b. p. 99—100° (Found : C, 29·8; H, 0; F, 70·0%; *M*, 325. C_8F_{12} requires C, 29·6; H, 0; F, 70·4%; *M*, 324), and an unidentified fraction of higher b. p.

The triene was reconverted into the parent chloro-compound by photochemical reaction with a 100% excess of chlorine (6 hr.), thus proving that the triene was not contaminated by compounds containing hydrogen.

(*d*) When reaction (*c*) with zinc was repeated at 50—55° (10 hr.) only a small amount of triene was obtained, and the major product was 4 : 5-*dichlorododecafluoro-octa*-1 : 7-*diene* (51%), b. p. 58°/20 mm. (Found : C, 24·2; H, 0; Cl, 17·7. $C_8Cl_2F_{12}$ requires C, 24·3; H, 0; Cl, 18·0%). Unchanged material (30%) was also present.

(*e*) The compound $Cl{\cdot}[CF_2{\cdot}CFCl]_3{\cdot}[CFCl{\cdot}CF_2]_3{\cdot}Cl$ (8·0 g.) was treated as in (*c*), to give 4 : 9-*dichloro-octadecafluorododeca*-1 : 6 : 11-*triene*, b. p. 115—120°/20 mm. (Found : C, 25·6; H, 0; Cl, 12·6. $C_{12}Cl_2F_{18}$ requires C, 25·8; H, 0; Cl, 12·8%). This triene (2·0 g.) absorbed 3 mols. of chlorine when treated with an excess and exposed to ultraviolet light (24 hr.).

(*f*) Mild treatment of the compound $Cl{\cdot}[CF_2{\cdot}CFCl]_3{\cdot}[CFCl{\cdot}CF_2]_3{\cdot}Cl$ (7·3 g.) with zinc and ethanol as in (*d*) gave 4 : 6 : 7 : 9-*tetrachloro-octadecafluorododeca*-1 : 11-*diene* (56%), b. p. 150—152°/0·1 mm. (Found : C, 22·8; H, 0; Cl, 22·2. $C_{12}Cl_4F_{18}$ requires C, 22·9; H, 0; Cl, 22·6%).

Perfluoromalonic Acid.—Perfluoro-octa-1 : 4 : 7-triene (5·7 g.) was oxidised by aqueous potassium permanganate in presence of sodium hydrogen carbonate (Part III, *loc. cit.*) at 35° (1 hr.) then at 60° (1 hr.). The products were worked up as usual (*J.*, 1950, 2789; Part III) to give an ethereal solution of an acid. Evaporation of the ether left crude perfluoromalonic acid (63%) which, after distillation at 10^{-3} mm. or recrystallisation from benzene, had m. p. 118° (Found : C, 25·7%; equiv., 70. Calc. for $C_3H_2O_4F_2$: C, 25·7%; equiv., 70). This acid can be heated to 160° without decarboxylation. Evans and Tatlow report m. p. 117—118°.

Treatment of an ethereal solution of difluoromalonic acid prepared as above with diazomethane (cf. Henne and De Witt, *loc. cit.*), rather than isolation of the free acid, gave dimethyl perfluoromalonate (81%), b. p. 60—62°/12 mm. (Found : C, 35·6; H, 3·5. Calc. for $C_5H_6O_4F_2$: C, 35·7; H, 3·6%). The absence of methyl difluoroacetate suggests that the difluoroacetic acid obtained by Henne and De Witt was a primary product of their oxidation reaction. For final characterisation an ethereal solution of the dimethyl ester (0·1 g.) was treated with anhydrous ammonia to give perfluoromalonamide, m. p. 207° (Henne and De Witt report m. p. 206·4°) (Found : C, 26·0; H, 2·8; N, 20·3. Calc. for $C_3H_4O_2N_2F_2$: C, 26·1; H, 2·9; N, 20·3%). The infrared spectrum of the amide was identical with that of a specimen prepared by an alternative route.

3 : 4-*Dichlorohexafluoroadipic Acid.*—4 : 5-Dichlorododecafluoro-octa-1 : 7-diene (8·7 g.) was oxidised as described for the preparation of perfluoromalonic acid. Evaporation of the dried ethereal extracts gave 3 : 4-*dichlorohexafluoroadipic acid* as a wax (51%) which was sublimed at 10^{-3} mm., then analysed without further purification (Found : C, 22·6; H, 0·6; Cl, 22·2%;

equiv., 161·5. $C_6H_2O_4Cl_2F_6$ requires C, 22·3; H, 0·6; Cl, 22·0%; equiv., 162·5). A portion (0·8 g.) was redissolved in ether and treated with diazomethane, to give *dimethyl* 3 : 4-*dichlorohexafluoroadipate* (0·5 g.), b. p. 155—158°/2—4 mm. (Found: C, 27·4; H, 1·6; Cl, 20·0. $C_8H_6O_4Cl_2F_6$ requires C, 27·4; H, 1·7; Cl, 20·2%).

The rest of the acid was divided equally and converted into the silver and sodium salts which were thoroughly dried *in vacuo*. Reaction of the disilver salt (1·0 g.) with chlorine (10% excess) at 120° in a sealed tube gave 1 : 2 : 3 : 4-tetrachlorohexafluorobutane (69%), b. p. 130—133°; this was heated (80°) with zinc (1·0 g.) and ethanol (5 ml.) in a sealed tube (3 hr.) to give hexafluorobutadiene (67%), identical with a known sample (*J.*, 1952, 4423).

The *disodium salt* (2·1 g.) (Found: Na, 12·5. $C_6O_4Cl_2F_6Na_2$ requires Na, 12·7%) was pyrolysed *in vacuo* in a platinum tube at 150° rising to 420° (2 hr.). The gaseous product was washed with 5% aqueous sodium hydroxide to remove carbon dioxide, then distilled *in vacuo* to give hexafluorobutadiene (71%), identified by its infrared spectrum.

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