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POLYFLUORINATED LINEAR BIFUNCTIONAL COMPOUNDS (CONTAINING LIKE FUNCTIONS) AS POTENTIAL MONOMERS

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INTRODUCTION

An effective method of increasing the stability of polymeric materials is to introduce fluorine atoms into the "framework" of their chains. However, the chemistry of fluorine-containing polymers has developed relatively one-sidedly owing to the poor availability of polyfluorinated bifunctional compounds.

Fluorine-containing polymers have been obtained mainly by the polymerisation of unsaturated fluoro-monomers (mainly fluorine-containing derivatives of ethylene and propene). Nevertheless, during the past two or three years a great deal of experimental information has accumulated on the preparation of perfluorinated and polyfluorinated bifunctional derivatives, such as various perfluorodicarboxylic acids, their esters, nitriles, amides, and amidines, $\alpha H, \alpha H, \omega H, \omega H$-perfluoro-diamines and -glycols, perfluoro-$\alpha\omega$-dienes, perfluoroolefin oxides, and several others.

At the present time a versatile method for the preparation of stable new polymers (by polycondensation) has become available to chemists working in the polymer field. The authors of the present review have endeavoured to survey the methods of preparation and the properties of those polyfluorinated bifunctional compounds, containing two like groups, which may be potential monomers for the preparation of new fluorine-containing polycondensation polymers.

1. FLUORINE-CONTAINING ALKADIENES

The known fluorine-containing alkadienes comprise mainly compounds in which only a proportion of the hydrogen atoms have been replaced by fluorine atoms. Butadienes of various degrees of fluorination have been prepared in many ways and have been relatively well studied. Several perfluoro-$\alpha\omega$-dienes of the type $CF_2:CF[CF_2CF_2]_nCF:CF_2$, where $n = 1, 2, 3$, etc., are also known, as well as some fluorine-containing allenes.

Fluorine-containing alkadienes can polymerise by themselves, or copolymerise with other olefins. The polymerisation of perfluorobutadiene and of fluoroprene and their copolymerisation with other olefins have been studied in some detail. Perfluorobutadiene polymerises only under high pressures, forming a solid polymer. Higher analogues of perfluorodienes condense only on irradiation[1-12].

Fluorine-containing olefins exhibit electron-acceptor properties, and react very easily with nucleophilic reagents, which has enabled fluorine-containing alkadienes to be used to obtain various sulphur-, nitrogen-, and oxygen-containing polymers[13]. Furthermore, fluorine-containing alkadienes present wide opportunities for obtaining other bifunctional compounds, such as acids, esters, amines, diols, etc.

The principal methods of obtaining fluorine-containing alkadienes are examined below.

(*a*) Fluorination of Halogenated Hydrocarbons with Subsequent Dehalogenation or Dehydrohalogenation of the Products

The usual method for obtaining compounds of low molecular weight containing fluorine is the fluorination of halogenated hydrocarbons. Fluorine-containing halogenoalkanes on dehalogenation or dehydrohalogenation are readily converted into olefins in good yields. For example, fluorination of 1,2-dichlorodifluoroethylene gives in one stage 1,2,3,4-tetrachlorohexafluorobutane, from which perfluorobutadiene has been prepared[14] by the action of zinc in alcohol:

$$2CFCl{=}CFCl + F_2 \rightarrow CF_2ClCFClCFClCF_2Cl \xrightarrow[C_2H_5OH]{Zn} CF_2{=}CFCF{=}CF_2.$$

1,2-Dichlorodifluoroethylene on heating forms 1,3,4,4-tetrachlorotetrafluorobut-1-ene, which on chlorination gives hexachlorotetrafluorobutane. Fluorination of the latter with antimony trifluoride, followed by dechlorination of the product, yields perfluorobutadiene[15]:

$$2CFCl{=}CFCl \rightarrow CFCl_2CFClCF{=}CFCl \rightarrow CFCl_2CFClCFClCFCl_2 \rightarrow$$
$$\rightarrow CF_2ClCFClCFClCF_2Cl \rightarrow CF_2{=}CFCF{=}CF_2.$$

Similarly, trichlorofluoroethylene gives 2,3-dichlorotetrafluorobuta-1,3-diene:

$$2CFCl{=}CCl_2 + F_2 \rightarrow CF_2ClCCl_2CCl_2CF_2Cl \rightarrow CF_2{=}CClCCl{=}CF_2.$$

However, by no means all alkadienes containing fluorine can be obtained in this way, since, firstly, the fluorination of hydrocarbons and their halogeno-derivatives usually gives a mixture of products which are difficult to separate, and, secondly, not all halogenoalkanes can be converted into the desired alkadienes. Therefore this method is of very limited application.

Reaction of 3-chloropent-2-ene with hydrogen fluoride and antimony trifluoride gives 3,3-difluoropentane, which on partial chlorination yields 1,5-dichloro-3,3-difluoropentane in one stage, from which 3,3-difluoropenta-1,4-diene can be obtained[16] by the action of alkali:

$$CH_3CH_2CCl{=}CHCH_3 + HF \xrightarrow{SbF_3} CH_3CH_2CF_2CH_2CH_3 \xrightarrow{Cl_2}$$
$$\longrightarrow CH_2ClCH_2CF_2CH_2CH_2Cl \xrightarrow{KOH} CH_2{=}CHCF_2CH{=}CH_2.$$

Further chlorination of 1,5-dichloro-3,3-difluoropentane in the presence of light forms decachloro-3,3-difluoropentane, which on treatment with zinc in alcohol gives a good yield of hexachloro-3,3-difluoropenta-1,4-diene[16]:

$$CH_2ClCH_2CF_2CH_2CH_2Cl \xrightarrow{Cl_2} CCl_3CCl_2CF_2CCl_2CCl_3 \longrightarrow CCl_2{=}CClCF_2CCl{=}CCl_2$$

In order to obtain 1,1-difluoro-3-methylbutadiene, 1-chloro-1,1-difluoro-3-methylbutane was synthesised from 1,1-dichloro-3-methylbut-1-ene and hydrogen fluoride. Chlorination of 1-chloro-1,1-difluoro-3-methylbutane gives two isomers:

$$CF_2ClCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2Cl \quad (I) \quad \text{and} \quad CF_2ClCH_2CCl(CH_3)_2. \quad (II)$$

The former gives 4-chloro-1,1-difluoro-3-methylbut-1-ene on treatment with caustic potash, while the latter yields 1,1-difluoro-3-methylbutadiene[17] under the action of tributylamine at 180°:[17]

$$CCl_2{=}CHCH(CH_3)_2 + HF \longrightarrow CF_2ClCH_2CH(CH_3)_2 + HCl,$$

$$CF_2ClCH_2CH(CH_3)_2 + Cl_2 \rightarrow \begin{cases} CF_2ClCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2Cl \xrightarrow{KOH} CF_2{=}CH\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2Cl \\ CF_2ClCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}ClCH_3 \xrightarrow{(C_4H_9)_3N} CF_2{=}CH\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 \end{cases}$$

(*b*) Free-Radical Addition of Halogenoalkanes to Olefins with Subsequent Dehalogenation or Dehydrohalogenation of the Products

Reactions involving free-radical addition at a multiple bond have been finding increasing application during recent years in the preparation of fluorine-containing alkadienes. Thus, for example, 1,2-dibromochlorotrifluoroethane when heated in the presence of benzoyl peroxide readily adds on to fluoroethylene to form 1,4-dibromo-2-chloro-1,1,2,4-tetrafluorobutane, which on subsequent treatment with alkali and zinc in alcohol is converted into 1,1,2,4-tetrafluorobutadiene in good yield[18-20]:

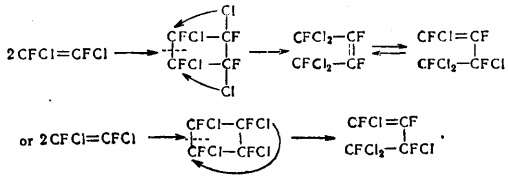
$$CF_2BrCFClBr + CH_2{=}CHF \rightarrow CF_2BrCFClCH_2CHFBr \rightarrow$$
$$\rightarrow CF_2BrCFClCH{=}CHF \rightarrow CF_2{=}CF{-}CH{=}CHF.$$

Thus by using different olefins and halogenoalkanes it is possible to obtain a series of fluorine-containing derivatives of butadiene. Several of them polymerise to form rubber-like resins, insoluble in the usual organic solvents.

Halogenoolefins can be used instead of halogenoalkanes in these additions. An example is the addition of trifluoroiodoethylene to ethylene. The resulting addition product is converted, on treatment with alkali in mineral oil, into 1,1,2-trifluorobutadiene[21]:

$$CF_2{=}CFI + CH_2{=}CH_2 \rightarrow CF_2{=}CFCH_2CH_2I \rightarrow CF_2{=}CFCH{=}CH_2.$$

Another example of the addition of halogenoolefins to unsaturated compounds is the thermal dimerisation of 1,2-dichlorodifluoroethylene into 1,3,4,4-tetrachlorotetrafluorobut-1-ene, which on dechlorination with zinc is converted into 1,4-dichlorotetrafluorobutadiene. Haszeldine[22] regards the dimerisation as a bimolecular reaction taking place according to one of the following mechanisms:



Under the same experimental conditions Ruh *et al.*[23,24] isolated, together with the dimer, a trimer, 1,3,4,5,6,6-hexachlorohexafluorohex-1-ene, from which 1,6-dichlorohexafluorohexa-1,3,5-triene was obtained by the action of zinc in alcohol. Formation of the trimer cannot be explained by the mechanism suggested by Haszeldine for

this reaction, and we regard a radical reaction mechanism as more probable:

$$CFCl{=}CFCl \rightarrow CFCl{=}CF + Cl^{\cdot},$$
$$CFCl{=}CF^{\cdot} + n\,CFCl{=}CFCl \rightarrow CFCl{=}CF(CFClCFCl)_n^{\cdot},$$
$$CFCl{=}CF(CFClCFCl)_n^{\cdot} + CFCl{=}CFCl \rightarrow CFCl{=}CF(CFClCFCl)_n Cl + CFCl{=}CF^{\cdot},$$

where n = 1 or 2.

$$CFCl{=}CFCFClCFClCFClCFCl_2 \xrightarrow{Zn} CFCl{=}CFCF{=}CFCF{=}CFCl.$$

1,2,3,4,5,6-Hexachlorooctafluorohexane, which reacts with zinc to give perfluorohexa-1,3,5-triene, was obtained from 1,3,4,5,6,6-hexachlorohexafluorohex-1-ene on chlorination followed by fluorination. In this way numerous fluorine-containing derivatives of butadiene and several higher analogues of fluorine-containing alkadienes have been synthesised. Addition of 1,2-dichlorotrifluoroiodoethane to perfluorocyclobutene and subsequent dechlorination of the product with zinc in alcohol result in two isomeric perfluorovinylcyclobutenes[13]:

$$CF_2ClCFClI + \begin{matrix}CF{=}CF\\ |\quad |\\ CF_2{-}CF_2\end{matrix} \rightarrow \begin{matrix}CFClCFClCF - CFI\\ |\qquad\quad |\\ F_2C - CF_2\end{matrix} \longrightarrow$$
$$\longrightarrow CF_2{=}CF{-}\begin{matrix}C = CF\\ |\quad |\\ F_2C - CF_2\end{matrix}; \quad CF_2{=}CFCF{-}\begin{matrix}CF\\ |\\ F_2C - CF\end{matrix}{=}.$$

These olefins can be not only polymerised but also migration-copolymerised with nucleophilic bifunctional compounds to form oxygen-, sulphur-, or nitrogen-containing polymers[13].

(c) Telomerisation of Fluorinated Compounds and Subsequent Reactions of the Resulting Telomers

The methods described above permit the synthesis of fluorine-containing alkadienes of low molecular weight only, mainly butadiene derivatives. Telomerisation is of fundamental importance for the synthesis of the higher analogues of fluorine-containing alkadienes, especially perfluorodienes.

Telomers with alternating double bonds are obtained by the telomerisation of acetylenic compounds with fluorocarbons containing another halogen. However, acetylene itself, on interaction with pentafluoroiodoethane in the presence of ultraviolet radiation, gives mainly an addition product and only 0.5% of the telomerisation product, 5,5,6,6,6-pentafluoro-1-iodohexa-1,3-diene[25]:

$$CF_3CF_2I + CH{\equiv}CH \rightarrow CF_3CF_2CH{=}CHI + CF_3CF_2(CH{=}CH)_2I \quad (0.5\%).$$

Fluorine-containing acetylenes, such as 3,3,3-trifluoropropyne, easily undergo telomerisation, irradiation of a mixture of this compound and trifluoroiodomethane yielding 1,1,1,6,6,6-hexafluoro-2-iodo-4-trifluoromethylhexa-2,4-diene[26]:

$$CF_3I + 2\,CH{\equiv}CCF_3 \rightarrow CF_3CH{=}\begin{matrix}C\\ |\\ CF_3\end{matrix}{-}CH{=}CICF_3.$$

In a similar manner 2*H*,4*H*-octafluoro-5-iodo-3-pentafluoroethylhepta-2,4-diene, 3*H*,5*H*-decafluoro-2-iodo-4-trifluoromethylocta-2,4-diene, etc. have been obtained.

Since acetylenic compounds undergo telomerisation with difficulty, their use in the preparation of higher telomers is limited.

The telomerisation of chlorotrifluoroethylene with 1,2-dichlorotrifluoroiodoethane yields the telomers $CF_2ClCFCl[CF_2CFCl]_nI$ (n = 1 or 2), which in the presence of mercury or radiation form the dimeric products $[CF_2ClCFCl[CF_2CFCl]_n]_2$. The latter on treatment with zinc in alcohol are converted at 50° into the corresponding chlorofluoro-$\alpha\omega$-dienes, and at 75° into trienes[23,27]:

$$CF_2ClCFClI + n\,CF_2{=}CFCl \rightarrow CF_2ClCFCl(CF_2CFCl)_nI \rightarrow [CF_2ClCFCl(CF_2CFCl)_{n-1}CF_2CFCl]$$
$$\xrightarrow[75^\circ]{50^\circ} \begin{matrix}[CF_2{=}CF(CF_2CFCl)_{n-1}CF_2CFCl]_2\\ [CF_2{=}CF(CF_2CFCl)_{n-1}CF_2CF{=}]_2,\end{matrix}$$

where n = 1, 2.

In a recently developed method for obtaining perfluoro-$\alpha\omega$-dienes, tetrafluoroethylene is telomerised with 1,2-dichlorotrifluoroiodoethane in the presence of benzoyl peroxide with the formation of $\alpha\beta$-dichloroperfluoro-ω-iodoalkanes:

$$CF_2ClCFClI + n\,CF_2{=}CF_2 \longrightarrow CF_2ClCFCl(CF_2CF_2)_nI,$$

where n = 1–4. Dimerisation of the latter with zinc in the presence of acetic anhydride in methylene dichloride yields $\alpha\beta\psi\omega$-tetrachloroperfluoroalkanes, which on dechlorination with zinc in a mixture of glacial acetic acid and anhydride give perfluoro-$\alpha\omega$-dienes[28–31]:

$$2CF_2ClCFCl(CF_2)_nI \rightarrow CF_2ClCFCl(CF_2CF_2)_nCFClCF_2Cl \rightarrow CF_2{=}CF(CF_2CF_2)_nCF{=}CF_2,$$

where n = 2, 3, 4, and 6.

(d) Other Methods

Several fluorine-containing alkadienes have been obtained by the dehydration of fluorine-containing diols[32–34]. However, the diols themselves are not readily available, and owing to their acid properties they split off water with difficulty, so that the alkadienes are obtained in low yields. Better results are obtained by the pyrolysis of diacetates of fluorine-containing diols. Thus, for example, the diacetate of 5,5,5-trifluoropentane-2,4-diol at 470° gives a 75% yield of 5,5,5-trifluoropenta-1,3-diene[32]:

$$CF_3\underset{|}{C}H{-}CH_2{-}\underset{|}{C}HCH_3 \xrightarrow{470^\circ} CF_3CH{=}CHCH{=}CH_2.$$
$$OCOCH_3 \quad OCOCH_3$$

1,1,1,6,6,6-Hexafluorohexa-2,4-diene and 3,3,4,4-tetrafluorohexa-1,5-diene have been obtained in a similar manner[35].

Pyrolysis of sodium perfluoroadipate yields a mixture of perfluorobutadiene and the sodium salt of the unsaturated acid $CF_2{=}CFCF_2CF_2COONa$, which suggests the following mechanism[36,37]:

$$NaOOC(CF_2)_4COONa \rightarrow {}^-OOC(CF_2)_4COONa \xrightarrow{-CO_2}$$
$$\longrightarrow {}^-CF_2{-}CF_2CF_2CF_2COONa \xrightarrow{-F^-} CF_2{=}CFCF_2CF_2COONa \rightarrow CF_2{=}CFCF{=}CF_2.$$

Although this reaction has been proposed as a general method for obtaining perfluorodienes, it has been accomplished in only one case, and owing to the inaccessibility of perfluorodicarboxylic acids this method has no practical value.

Fluorine-containing alkadienes are readily obtained by the dimerisation of olefins containing both iodine and fluorine. Thus the action of zinc in dioxan on pentafluoro-3-iodopropene and 2-chlorotetrafluoro-3-iodopropene gave

respectively perfluorohexa-1,5-diene and 2,5-dichloroocta-fluorohexa-1,5-diene[38]:

$$2\,CF_2{=}CXCF_2I \rightarrow CF_2{=}CXCF_2CF_2CX{=}CF_2,$$

where X = F or Cl.

It might be expected that 2,2,3,3-tetrafluorocyclobutene could be obtained by the reaction of tetrafluoroethylene with acetylene. But it has been found that at 600° the only products are 1,1,4,4-tetrafluorobutadiene and perfluorocyclobutane[39].

The latter is obviously a product of the dimerisation of tetrafluoroethylene. Formation of 1,1,4,4-tetrafluorobutadiene is probably preceded by that of difluorocarbene ($:CF_2$):

$$CF_2CF_2 \xrightarrow{600^\circ} 2{:}CF_2,$$

$$2CF_2{=}CF_2{+}CH{\equiv}CH \longrightarrow CH_2{=}CH{-}CH{=}CF_2.$$

It is known that substitution takes place when a lithium alkyl or a Grignard reagent reacts with a fluoroolefin. Tetrafluoroethylene reacts with sodium butyl- or phenyl-acetylide to give compounds of the type RC:C.CF:CF.C:CR [40]:

$$RC{\equiv}CNa{+}CF_2{=}CF_2 \longrightarrow RC{\equiv}C{-}CF{=}CF{-}C{\equiv}CR,$$

where R = C_4H_9, C_6H_5.

Heating perfluorobut-2-yne with trifluoromethylsulphur pentafluoride CF_3SF_5 at 525° yields perfluoro-(2,3,4-trimethylhexa-2,4-diene) and perfluoro-(2,3,4,5-tetramethylhexa-2,4-diene) in the proportions 2 : 1. The following mechanism has been suggested for the formation of these hexadienes[41], based on their structure established by nuclear magnetic resonance:

$$2CF_3C{\equiv}C{-}CF_3 \longrightarrow \begin{matrix} CF_3{-}C{=}C{-}CF_3 \\ | \quad | \\ CF_3{-}C{=}C{-}CF_3 \end{matrix},$$

$$\begin{matrix} CF_3{-}C{=}C{-}CF_3 \\ | \quad | \\ CF_3{-}C{=}C{-}CF_3 \end{matrix} + CF_3^{\cdot} + F^{\cdot} \longrightarrow \begin{matrix} CF_3C{=}C{-}C{=}CF{-}CF_3 \\ \quad\quad | \quad\quad | \\ \quad\quad F_3C \quad CF_3 \end{matrix},$$

$$\begin{matrix} CF_3{-}C{=}C{-}CF_3 \\ | \quad | \\ CF_3{-}C{=}C{-}CF_3 \end{matrix} + 2CF_3^{\cdot} \longrightarrow CF_3{-}C{=}C{-}C{=}C{-}CF_3.$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \begin{matrix} \diagup & | & | & \diagdown \\ CF_3 & CF_3 & CF_3 & CF_3 \end{matrix}$$

2. FLUORINE-CONTAINING ALLENES

The first representative of the fluorinated allenes is perfluoroallene, which has been obtained by the action of alkali on 1,3-dibromo-1,1,3,3-tetrafluoropropane[33,42,43]:

$$CF_2BrCH_2CF_2Br + 2\,KOH \rightarrow CF_2{=}C{=}CF_2 + 2\,KBr.$$

Similarly, elimination of hydrogen bromide from 1,3-dibromo-1,1-difluoropropane gives a good yield of 1,1-difluoroallene[44]:

$$CF_2BrCH_2CH_2Br + 2\,KOH \rightarrow CF_2{=}C{=}CH_2 + 2\,KBr.$$

1,1-Difluoroallene is formed also by the pyrolysis (at 800°–950°) of 2,2,3,3-tetrafluorocyclobutylmethyl acetate, 1,1,2,2-tetrafluoro-3-methylenecyclobutane being obtained as an intermediate product, which suggests the following mechanism for the reaction[45–47]:

$$CH_3COOCH_2\underset{\displaystyle CF_2{-}CF_2}{\overset{\displaystyle |}{CH}}{-}CH_2 \longrightarrow CH_2{=}\underset{\displaystyle CF_2{-}CF_2}{\overset{\displaystyle |}{C}}{-}CH_2 \longrightarrow CF_2{=}C{=}CH_2 + CH_2{=}CF_2.$$

Another representative of the fluorine-containing allenes is 4,4,4-trifluorobuta-1,2-diene, obtained by elimination of hydrogen iodide from 4,4,4-trifluoro-2-iodobut-1-ene, which is formed on addition of trifluoroiodomethane to allene.

The formation of 4,4,4-trifluorobuta-1,2-diene is accompanied by that of 4,4,4-trifluorobut-1-yne[48]:

$$CF_3I + CH_2{=}C{=}CH_2 \rightarrow CF_3CH_2CI{=}CH_2 \rightarrow CF_3CH{=}C{=}CH_2 + CF_3CH_2C{\equiv}CH.$$

Great interest has been shown in the preparation of 1,1,4,4-tetrafluorobuta-1,2,3-triene. Addition of bromine to 1,1,4,4-tetrafluorobutadiene gives 1,4-dibromo-1,1,4,4-tetrafluorobut-2-ene, which is converted by the action of alkali into perfluorobuta-1,2,3-triene:

$$CF_2{=}CH{-}CH{=}CF_2 + Br_2 \rightarrow CF_2BrCH{=}CH{-}CF_2Br \rightarrow CF_2{=}C{=}C{=}CF_2.$$

This product is very unstable, and decomposes violently in air at room temperature[49,50].

3. FLUORINE-CONTAINING DIOLS

Fluorine-containing diols are of great interest as monomers for the synthesis of polyesters[51–53] and polyurethanes[54]. The fluorine-containing polyesters which have been obtained up to the present are heat-resistant rubberlike or glasslike substances. After vulcanisation, the polyester from adipic acid and 2,2,3,3,4,4-hexafluoropentane-1,5-diol, for example, greatly resembles natural rubber in properties and possesses high thermal stability[55]. Several of the known fluorine-containing polyurethanes are successfully applied as coatings. However, the use of both these and others is restricted by the lack of a practicable method for obtaining fluorine-containing diols.

Up to the present there have been no data on the existence of perfluoro-diols, probably owing to the instability of the group CF_2OH, since, at the instant of formation, it splits off hydrogen fluoride to form an acid fluoride. Only $\alpha\omega$-bis(hydroxymethyl)perfluoroalkanes $HOCH_2[CF_2]_nCH_2OH$, where n = 1, 2, 3, 4, and 8, are known.

Fluorine-containing diols are usually obtained by the reduction of esters, anhydrides of dicarboxylic acids, or diketones, and also by the hydrolysis of epoxides. Diols are also formed by the reaction of Grignard reagents with diesters and diketones.

(*a*) Reduction of Fluorine-Containing Diesters, Anhydrides of Dicarboxylic Acids, and Diketones

A practicable method of obtaining fluorine-containing diols, which is widely employed under laboratory conditions, is reduction of esters of fluorine-containing dicarboxylic acids with lithium aluminium hydride or sodium borohydride[56–62]:

$$C_2H_5OOC(CF_2)_nCOOC_2H_5 \rightarrow HOCH_2(CF_2)_nCH_2OH,$$

where n = 2, 3, 4, and 8.

Anhydrides[63] or chlorides[64] of dicarboxylic acids can be used instead of esters. Reaction of difluoromalonyl dichloride with lithium aluminium hydride yields 2,2-difluoropropane-1,3-diol, which is obtained also by the action of the same reducing agent on ethyl $\alpha\alpha$-difluoro-β-hydroxypropionate, obtained by the Prins reaction[65]:

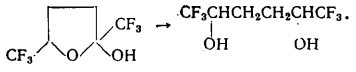
$$CF_2{=}CF_2 + CH_2O + H_2O \xrightarrow{C_2H_5OH} HOCH_2CF_2COOC_2H_5 \xrightarrow{LiAlH_4} HOCH_2CF_2CH_2OH.$$

The reduction of fluorine-containing diketones also results in the formation of diols in good yields. Thus the

action of lithium aluminium hydride on 3,3,4,4-tetrafluorohexane-2,5-dione gives the corresponding diol[35]:

$$CH_3COCF_2CF_2COCH_3 \rightarrow CH_3\underset{\underset{OH}{|}}{C}HCF_2CF_2\underset{\underset{OH}{|}}{C}HCH_3.$$

Reduction of tetrahydro-2,5-bistrifluoromethylfuran-2-ol has given 1,1,1,6,6,6-hexafluorohexane-2,5-diol, which is regarded[35] as a mixture of optical isomers (*dextro*, *laevo*, and *meso* configurations):



When ethyl perfluorosuccinate, perfluoroglutarate, and perfluoroadipate are reduced with hydrogen in the presence of a catalyst (a mixture of the oxides of copper, chromium, and calcium or barium) in an autoclave at 130°–250°, the corresponding diols are formed in yields of about 50%.[66] Hydrogenation of the diperfluorobutyrate of perfluorooct--4-ene-4,5-diol (see Section 9) results in the formation of 4*H*,5*H*-perfluorooctane-4,5-diol[67]:

$$C_3F_7COOC{=}COOCC_3F_7 \xrightarrow[Pd/C]{H_2} C_3F_7\underset{\underset{OH}{|}}{C}H{-}\underset{\underset{OH}{|}}{C}HC_3F_7.$$

Reduction of trifluoroacetylacetone with hydrogen under pressure in the presence of nickel has given 1,1,1-trifluoropentane-2,4-diol[32]:

$$CF_3COCH_2COCH_3 \rightarrow CF_3\underset{\underset{OH}{|}}{C}HCH_2\underset{\underset{OH}{|}}{C}HCH_3$$

The action of aluminium isopropoxide on 3-hydroxy-3-trifluoromethylbutan-2-one forms 2-trifluoromethylbutane--2,3-diol[23]:

$$CH_3\underset{\underset{OH}{|}}{\overset{\overset{CF_3}{|}}{C}}{-}COCH_3 \rightarrow CH_3\underset{\underset{OH}{|}}{\overset{\overset{CF_3}{|}}{C}}{-}\underset{\underset{OH}{|}}{C}HCH_3$$

(*b*) Addition of Grignard Reagents to Diesters and Diketones

Secondary and tertiary diols are often prepared by a procedure based on the reaction of carbonyl compounds (esters or ketones) with Grignard reagents. Several fluorine-containing glycols have been obtained by the reaction of ethyl perfluoroglutarate with CH_3MgI, C_2H_5MgI, and C_3H_7MgI. It is interesting that methylmagnesium iodide forms the tertiary diol, 3,3,4,4,5,5-hexafluoro-2,6-dimethylheptane-2,6-diol, in 85% yield, whereas ethylmagnesium and isopropylmagnesium iodides form mainly the corresponding secondary diols, with only a small quantity of the tertiary diols as side-products[33]:

$$CH_3MgI + CF_2(CF_2COOC_2H_5)_2 \longrightarrow CF_2\left(CF_2\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_3\right)_2, \quad (85\%)$$

$$C_2H_5MgI + CF_2(CF_2COOC_2H_5)_2 \longrightarrow CF_2(CF_2\underset{\underset{OH}{|}}{C}HC_2H_5)_2 + CF_2\left(CF_2\underset{\underset{OH}{|}}{\overset{\overset{C_2H_5}{|}}{C}}{-}C_2H_5\right)_2, \quad (23\%) \quad (5\%)$$

$$C_3H_7MgI + CF_2(CF_2COOC_2H_5)_2 \longrightarrow CF_2\left(CF_2\underset{\underset{OH}{|}}{C}H\overset{CH_3}{\underset{CH_3}{<}}\right)_2. \quad (77\%)$$

An interesting reaction between perfluoroacetone and ethynylenedimagnesium dibromide yields perfluoro-2,5--dimethylhex-3-yne-2,5-diol[68]:

$$2CF_3COCF_3 + BrMgC{\equiv}CMgBr \longrightarrow CF_3{-}\underset{\underset{OH}{|}}{\overset{\overset{CF_3}{|}}{C}}{-}C{\equiv}C{-}\underset{\underset{OH}{|}}{\overset{\overset{CF_3}{|}}{C}}{-}CF_3.$$

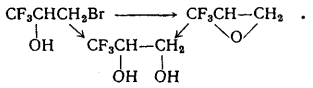
Reaction of ethynylmagnesium bromide with perfluoroacetone gave 4*H*-perfluoro-2-methylbut-3-yn-2-ol, which on oxidation with oxygen in the presence of cuprous chloride gave perfluoro-2,7-dimethylocta-3,5-diyne-2,7-diol[68]:

$$CF_3COCF_3 + CH{\equiv}CMgBr \rightarrow CF_3{-}\underset{\underset{OH}{|}}{\overset{\overset{CF_3}{|}}{C}}{-}C{\equiv}CH \rightarrow CF_3{-}\underset{\underset{OH}{|}}{\overset{\overset{CF_3}{|}}{C}}{-}C{\equiv}C{-}C{\equiv}C{-}\underset{\underset{OH}{|}}{\overset{\overset{CF_3}{|}}{C}}{-}CF_3.$$

1,1,4,4-Tetrakis(chlorodifluoromethyl)butyne-1,4-diol and 1,1,6,6-tetrakis(chlorodifluoromethyl)hexa-2,4-diyne-1,6--diol[69] have been obtained in a similar manner.

(*c*) Hydrolysis of Fluorine-Containing Epoxides and Other Methods

Owing to the influence of the fluoroalkyl group, fluorine--containing epoxides are more stable to hydrolysis than are the unfluorinated epoxides. However, when they are heated with acids, fluorine-containing diols are readily formed. Thus, for example, 1,2-epoxy-3,3,3-trifluoropropane on boiling with 1% sulphuric acid is converted into 3,3,3-trifluoropropane-1,2-diol, which has also been obtained by heating 1-bromo-3,3,3-trifluoropropan-2-ol with alkali and then with dilute sulphuric acid[70]:



Similarly, 4,4,5,5,6,6,6-heptafluorohexane-2,3-diol, 5,5,6,6,7,7,7-heptafluorooctane-3,4-diol, and other diols containing fluorine[71] have been obtained from the corresponding epoxides. Fluorine-containing diols can be obtained also by the oxidation of fluorine-containing olefins. Thus oxidation of 1,4-dibromo-1,1,4,4-tetrafluorobut-2-ene with potassium permanganate at 5°–10° gives 1,4-dibromo--1,1,4,4-tetrafluorobutane-2,3-diol in good yield[50]:

$$CF_2BrCH{=}CHCF_2Br \rightarrow CF_2Br\underset{\underset{OH}{|}}{C}H{-}\underset{\underset{OH}{|}}{C}HCF_2Br.$$

4. FLUORINE-CONTAINING DIETHERS

Monoethers containing fluorine have been widely studied, since they are very easily prepared by addition of alcohols to fluorine-containing olefins, but the corresponding diethers have been little studied up to the present. Although, as mentioned above, perfluorinated diols do not exist, perfluorinated diethers have proved to be very stable.

The present review does not cover diethers such as $R_FO[CH_2]_nOR_F$, which can be regarded as derivatives of unfluorinated diols. Some perfluorodiethers have been obtained by electrochemical fluorination of the corresponding unfluorinated diethers. In this way, for example, the

diethyl ether of diethylene glycol has been perfluorinated, the resulting ether being recommended for use as a lubricant[72]:

$$C_2H_5OCH_2CH_2OCH_2CH_2OC_2H_5 \rightarrow C_2F_5OCF_2CF_2OCF_2CF_2OC_2F_5.$$

It is interesting that electrochemical fluorination of dioxan yielded, instead of perfluorodioxan, the perfluorinated dimethyl ether of ethylene glycol[72]:



$\rightarrow CF_3OCF_2CF_2OCF_3.$

The chief method of preparing fluorine-containing monoethers is the reaction of fluorinated olefins with alcohols. However, the reaction of fluorine-containing dienes with alcohols has remained almost unstudied. The only example is the reaction of perfluorobutadiene with sodium ethoxide, yielding 1,4-diethoxyperfluorobuta-1,3-diene[73]:

$$CF_2{=}CFCF{=}CF_2 + 2\,C_2H_5ONa \rightarrow C_2H_5OCF{=}CFCF{=}CFOC_2H_5 + 2\,NaF.$$

Diethers are also obtained by alkylating fluorine-containing diols. Thus dimethyl sulphate acts on 1,1,4,4-tetrakis(chlorodifluoromethyl)but-2-yne-1,4-diol to give 1,1,4,4-tetrakis(chlorodifluoromethyl)-1,4-dimethoxybut-2-yne[69]:

$$(CF_2Cl)_2C(OH)-C\equiv C-C(OH)(CF_2Cl)_2 + (CH_3)_2SO_4 \rightarrow (CF_2Cl)_2C(OCH_3)-C\equiv C-C(OCH_3)(CF_2Cl)_2.$$

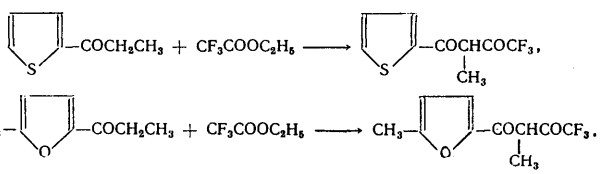
5. FLUORINE-CONTAINING DIKETONES

Fluorine-containing monoketones have been widely studied. They can be synthesised by all the classical methods other than pyrolysis of salts of fluorine-containing carboxylic acids. Perfluorinated diketones and dialdehydes are altogether unknown. Most of the known diketones containing fluorine are β-diketones, the chief method of synthesis being the Claisen reaction.

The action of fluorine-containing esters on ketones or fluorinated ketones of the type R_FCOCH_2R in the presence of sodium ethoxide gives β-diketones in good yield[74-78]:

$$R'_FCOOR + RCH_2COR_F \longrightarrow R'_FCOCH(R)COR_F.$$

Not only aliphatic but also cyclic, aromatic, and heterocyclic ketones undergo the Claisen reaction. Thus ethyl 2-thienyl ketone and ethyl 5-methylfur-2-yl ketone react with ethyl trifluoroacetate to form the corresponding β-diketones[78]:



It is noteworthy that propiophenone reacts smoothly with ethyl trifluoroacetate forming the β-diketone, whereas butyrophenone and pentyl phenyl ketone yield only insignificant quantities of the β-diketones, the main products being alkyl trifluoromethyl ketones[78]:

$$C_6H_5COCH_2R + CF_3COOC_2H_5 \longrightarrow CF_3COCH_2R + C_6H_5COOCH_3,$$

where R = C_4H_9 and C_5H_{11}.

The Friedel–Crafts reaction has also been used to obtain β-diketones. Thus reaction of difluoromalonyl chloride with benzene in the presence of aluminium chloride gives a good yield of dibenzoyldifluoromethane[64]:

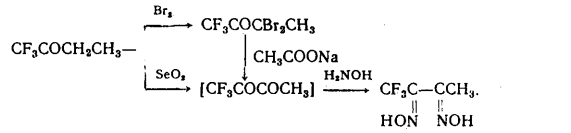
$$CF_2(COCl)_2 + 2C_6H_6 \longrightarrow CF_2(COC_6H_5)_2 + 2HCl.$$

Owing to the influence of the fluoroalkyl group, fluorine-containing β-diketones tend to pass into enolic forms and stable chelate complexes, which can be used to synthesise polymeric chelate complexes.

The only fluorine-containing α-diketone which has been isolated is perfluorooctane-4,5-dione, which is formed on pyrolysis of perfluoro(dipropylvinylene dibutyrate)[67]:

$$C_3F_7COOC(F_7C_3)=C(C_3F_7)OOCC_3F_7 \xrightarrow{600^\circ} C_3F_7COCOC_3F_7.$$

Other α-diketones have been obtained only in the form of dioximes. Thus bromination of 1,1,1-trifluorobutan-2-one gives the 3,3-dibromo-derivative, which on treatment with hydroxylamine in the presence of sodium acetate yields the dioxime of 1,1,1-trifluorobutane-2,3-dione. This last compound has been obtained also by oxidation of 1,1,1-trifluorobutan-2-one with selenium dioxide in aqueous medium, and isolation as the dioxime:



The dioxime of 3,3,3-trifluoropropane-1,2-dione has been obtained similarly[79].

The only representative of the γ-diketones is 3,3,4,4-tetrafluorohexane-2,5-dione, which has been obtained by treating perfluorosuccinic acid with methylmagnesium bromide:

$$(CF_2COOH)_2 + 2CH_3MgBr \rightarrow CH_3COCF_2CF_2COCH_3 + 2MgBrOH.$$

Under the same conditions perfluoroglutaric acid gives a mixture of

$$CH_2{=}C(CH_3)-(CF_2)_3COCH_3 \text{ and } CH_3CO(CF_2)_3COCH_3,$$

which could not be separated[35].

6. FLUORINE-CONTAINING DICARBOXYLIC ACIDS

The great interest in fluorine-containing dicarboxylic acids is due to the possibility of using them in polycondensations and in the preparation of other fluorine-containing bifunctional compounds.

The polycondensation of fluorine-containing dicarboxylic acids (perfluoroadipic, perfluorosebacic, etc.) or their chlorides with diols, thiols, or diamines has been used to prepare polyesters, polythioesters, polyamides, and polyurethanes[30,31,51,61,62,80-85], but the number of polymeric compounds obtained from fluorine-containing dicarboxylic acids is small owing to the poor availability of these acids.

Perfluorinated succinic, glutaric, and adipic acids have been more thoroughly studied. Perfluorosuberic and perfluorosebacic acids have also been synthesised, as well as several of their higher homologues. Fluorine-containing dicarboxylic acids containing an odd number of carbon atoms have been little studied. Several fluorine-containing unsaturated dicarboxylic acids are also known, such as difluorofumaric, difluoromaleic, etc.

Fluorine-containing dicarboxylic acids have been synthesised by the electrochemical fluorination of dicarboxylic acids, the oxidation of fluorine-containing hydrocarbons, and other methods.

(*a*) Electrochemical Fluorination of Dicarboxylic Acids

Electrochemical fluorination is now applied not only in the laboratory but also on an industrial scale, for example in the production of trifluoroacetic acid. With increasing number of carbon atoms in the initial carboxylic acids, however, the yields of the fluorinated acids drop sharply, which limits the usefulness of this method for the preparation of the higher perfluorodicarboxylic acids. On electrochemical fluorination of succinic anhydride, perfluorosuccinic acid is obtained together with perfluoropropionic acid[58]:

$$(CH_2CO)_2O \rightarrow \underset{(33\%)}{CF_3CF_2COOH} + \underset{(23\%)}{(CF_2COOH)_2}.$$

Fluorination of adipic anhydride yields only a minute quantity of perfluoroadipic acid[58,85].

The electrochemical fluorination of sebacic acid produces a mixture of fluorocarbons, perfluorononanoyl fluoride, and perfluorosebacoyl fluoride[82,86]:

$$HOOC(CH_2)_8COOH \rightarrow FOC(CF_2)_8COF + CF_3(CF_2)_8COF.$$

(*b*) Oxidation of Fluorine-Containing Olefins

The chief method of preparing fluorine-containing dicarboxylic acids is oxidation of fluorine-containing dienes and olefins, among which the more readily available cycloalkenes are most often employed. Oxidation of 3,3-difluoropenta-1,4-diene — see Section 1 (*a*) — with potassium permanganate at 60° gives difluoromalonic acid[16]:

$$CF_2(CH{=}CH_2)_2 \xrightarrow{KMnO_4} CF_2(COOH)_2.$$

When perfluoro-$\alpha\omega$-dienes — see Section 1 (*c*) — are oxidised with potassium permanganate in aqueous acetone medium, the corresponding perfluoro-$\alpha\omega$-dicarboxylic acids are obtained in good yields[30,87]:

$$CF_2{=}CF(CF_2)_n\dot{C}F{=}\dot{C}F_2 \rightarrow HOOC(CF_2)_nCOOH,$$

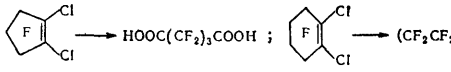
where n = 4, 6, 8, and 12.

A more practicable method for obtaining some fluorine-containing dicarboxylic acids is oxidation of fluorine-containing cycloalkenes. Thus perfluorosuccinic acid has been obtained by the oxidation of perfluoro- or 1,2-dichlorotetrafluorocyclobutene[88]:

$$\begin{array}{l} CF_2{-}CX \\ | \quad\quad \| \\ CF_2{-}CX \end{array} \xrightarrow{KMnO_4} (CF_2COOH)_2,$$

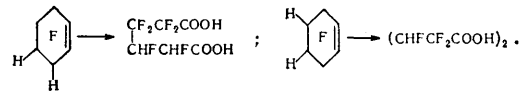
where X = Cl, F.

Similarly, oxidation of 1,2-dichlorohexafluorocyclopentene yields perfluoroglutaric acid[89,91], and 1,2-dichlorooctafluorocyclohexene gives perfluoroadipic acid[90,92-94]:

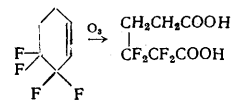


In this way adipic acids having different degrees of fluorination have been obtained.

It is interesting that among the products of the fluorination of benzene 3*H*,4*H*- and 4*H*,5*H*-perfluorocyclohexenes have been isolated, oxidation of the former giving (±)-*erythro*-2*H*,3*H*-perfluoroadipic acids, and of the latter *DL*-3*H*,4*H*-perfluoroadipic acids[95,96]:

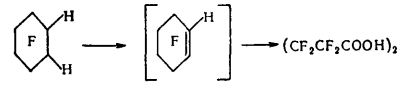


On further oxidation, 2*H*,3*H*-perfluoroadipic acid yields perfluorosuccinic acid, and the 3*H*,4*H* acid gives perfluoromalonic acid. Oxidation goes far more readily and in better yields in acetone or aqueous acetone medium than in water, fluorine-containing olefins being oxidised more readily than are unfluorinated olefins, probably because they are more electrophilic[93]. Ozone can replace potassium permanganate as oxidising agent. Thus ozonolysis of 3,3,4,4-tetrafluorocyclohexene in methylene chloride yields 2,2,3,3-tetrafluoroadipic acid[97]:



3,3,4,4-Tetrafluoroadipic acid has been obtained similarly.

Several fluorine-containing alkanes can also be oxidised by potassium permanganate in neutral medium to form dicarboxylic acids. In this way perfluoroadipic acid has been obtained from 1*H*,2*H*-perfluorocyclohexane. It is obvious that during the reaction hydrogen fluoride is split off from the decafluorocyclohexane forming 1*H*-perfluorocyclohexene, which is then further oxidised:



Similarly, perfluorosuccinic acid has been obtained from 1*H*,2*H*-hexafluorocyclobutane[98].

A new type of oxidation is the reaction with oleum of substituted fluorocarbons possessing $CFCl_2$, CFClH, and CFClBr terminal groups, yielding fluorides of fluorine-containing carboxylic acids. The groups CCl_3 and CF_2Cl are more stable, and therefore when fluorocarbons of the types $CCl_3[CF_2CFCl]_nBr$ and $Cl[CF_2CFCl]_nCl$ were heated with oleum in an autoclave, the main reaction products were monocarboxylic acids and only insignificant quantities of dicarboxylic acids[99-101]:

$$CCl_3(CF_2CFCl)_nBr \rightarrow CCl_3(CF_2CFCl)_{n-1}CF_2COOH + HOOC(CF_2CFCl)_{n-1}CF_2COOH$$

and

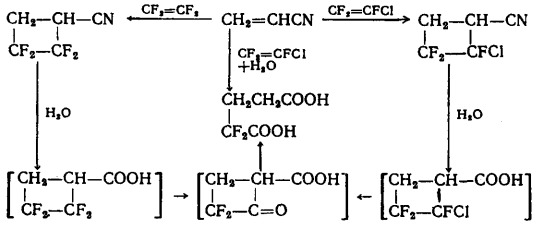
$$Cl(CF_2CFCl)_nCl \rightarrow ClCF_2(CFClCF_2)_{n-1}COOH + HOOC(CFClCF_2)_{n-1}COOH.$$

where n = 2–4. The resulting acids were not isolated in a pure form. As the length of the alkyl chain increases, the reaction requires more forcing conditions.

(*c*) Other Methods

When acrylonitrile reacts with tetrafluoroethylene in the presence of "terpene B" in an autoclave at 150°, 2,2,3,3-tetrafluorocyclobutanecarbonitrile is formed[47],

which on hydrolysis with caustic soda is converted into 2,2-difluoroglutaric acid in 30% yield. This last acid has been synthesised also by the hydrolysis of 2-chloro-2,3,3-trifluorocyclobutanecarbonitrile, obtained from acrylonitrile and chlorotrifluoroethylene in the presence of water and hydroquinone in an autoclave at 150°:[102]



When an attempt is made to obtain perfluoroacrylic acid by the alkaline hydrolysis of perfluoroacrylonitrile, fluoromalonic acid is obtained instead[103]:

$$CF_2{=}CFCN \xrightarrow{H_2O} CHF(COOH)_2.$$

Several fluorine-containing dicarboxylic acids have been obtained by the hydrolysis of fluorine-containing esters, for whose preparation other, more practicable methods have been found. Thus in the presence of sodium ethoxide, ethyl malonate readily adds on to ethyl 3-(perfluoroalkyl)acrylate to form the ethyl 2-(perfluoroalkyl)-propane-1,1,3-tricarboxylate, which on hydrolysis gives the 2-(perfluoroalkyl)glutaric acid[60]:

$$R_FCH{=}CHCOOC_2H_5 + CH_2(COOC_2H_5)_2 \rightarrow R_FCHCH_2COOC_2H_5 \rightarrow R_FCH(CH_2COOH)_2,$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad CH(COOC_2H_5)_2$$

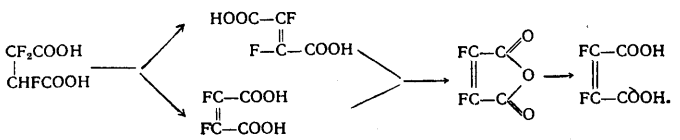
where $R_F = C_3F_7$, C_7F_{15}.

An interesting reaction is the dimerisation of radicals generated from fluorine-containing monocarboxylic acids. Thus the action of acetyl peroxide on fluoroacetic acid yields 2,3-difluorosuccinic acid[104]:

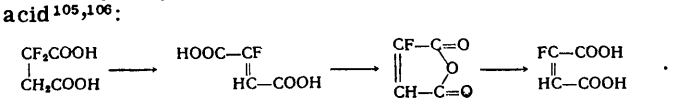
$$(CH_3COO)_2 \longrightarrow 2CH_3COO^{\cdot} \longrightarrow 2CH_3^{\cdot} + 2CO_2,$$
$$CH_3^{\cdot} + CH_2FCOOH \longrightarrow {}^{\cdot}CHFCOOH,$$
$$2{}^{\cdot}CHFCOOH \longrightarrow (CHFCOOH)_2.$$

In a similar manner perfluorosuccinic acid has been obtained from difluoroacetic acid.

A few fluorine-containing unsaturated acids (difluorofumaric, difluoromaleic, etc.) have been synthesised. Elimination of hydrogen fluoride from trifluorosuccinic acid gives a mixture of the two isomers, difluorofumaric and difluoromaleic acids. Both acids give difluoromaleic anhydride on treatment with phosphorus pentoxide, and this is converted into difluoromaleic acid on hydrolysis:



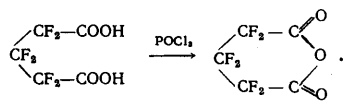
Elimination of hydrogen fluoride from 2,2-difluorosuccinic acid produces only fluorofumaric acid, which with phosphorus pentoxide gives fluoromaleic anhydride, and this on hydrolysis is readily converted into fluoromaleic acid[105,106]:



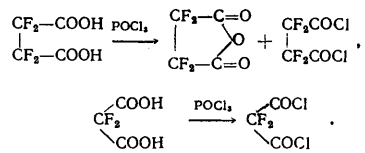
7. ANHYDRIDES AND CHLORIDES OF FLUORINE-CONTAINING DICARBOXYLIC ACIDS

Only those fluorine-containing dicarboxylic acids which can form five- or six-membered rings are able to form anhydrides. Those of perfluorinated malonic, adipic, and sebacic acids are unknown.

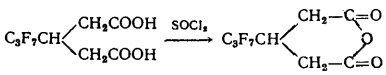
The anhydrides are formed when the fluorine-containing dicarboxylic acids are heated with phosphorus pentoxide[105,106]. In contrast to the unfluorinated dicarboxylic acids, those containing fluorine more often form the anhydrides, not the chlorides, on treatment with phosphoryl or thionyl chloride. Thus phosphoryl chloride gives the anhydride with perfluoroglutaric acid[83]:



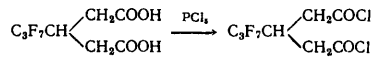
Under these conditions perfluorosuccinic acid yields a mixture of the anhydride and chloride, but perfluoromalonic acid forms only its chloride[64]:



Reaction of thionyl chloride with 3-(perfluoropropyl)-glutaric acid gives the anhydride instead of the chloride[60]:



With phosphorus pentachloride perfluoroglutaric acid gives a very low yield of its chloride, the acid decomposing with the evolution of carbon dioxide[83]. Nevertheless, phosphorus pentachloride reacts with 3-(perfluoropropyl)-glutaric acid to give the chloride[60]:



Perfluoroadipic and perfluorosebacic acids give acid chlorides on treatment with phosphorus pentachloride. Since, however, this reagent sublimes readily, it is difficult to purify the acid chlorides thus obtained. Thionyl chloride reacts with perfluorinated dicarboxylic acids only in the presence of catalytic amounts of potassium chloride, good yields of the acid chlorides then being obtained[30,31]:

$$HOOC(CF_2CF_2)_nCOOH + 2KCl \rightleftarrows KOOC(CF_2CF_2)_nCOOK + 2HCl,$$
$$KOOC(CF_2CF_2)_nCOOK + 2SOCl_2 \rightarrow ClSO_2OC(CF_2CF_2)_nCOSO_2Cl + 2KCl,$$
$$ClSO_2OC(CF_2CF_2)_nCOSO_2Cl \rightarrow ClOC(CF_2CF_2)_nCOCl + 2SO_2,$$

where $n = 2, 4$.

Potassium chloride can be replaced by pyridine, when reaction takes place instantaneously (probably owing to the better solubility of pyridine salts of perfluorodicarboxylic acids in thionyl chloride), but the pyridine hydrochloride formed in the reaction sublimes on being heated, which also impedes purification of the acid chlorides obtained.

Perfluoroadipoyl fluoride has been obtained by the electrochemical fluorination of adipic acid, but neither the yield nor its constants were given[85].

By heating silver perfluoroglutarate with iodine, Hauptschein *et al.* obtained perfluoro-γ-butyrolactone[107], together with hexafluoro-1,3-diiodopropane:

$$AgOOC(CF_2)_3COOAg + I_2 \rightarrow I(CF_2)_3I + CF_2(O)CF_2(CO)CF_2 .$$

According to Tiers[108], however, the lactone was actually perfluorosuccinyl fluoride.

8. ESTERS OF FLUORINE-CONTAINING DICARBOXYLIC ACIDS

Esters of fluorine-containing dicarboxylic acids are of great value for identifying the acids, and in several cases also for their preparation. Moreover, it is mostly from them that fluorine-containing diols and diamides are obtained.

Such esters are prepared mainly by esterifying dicarboxylic acids with alcohols, but there exist also many other methods for obtaining them.

(*a*) Esterification of Fluorine-Containing Dicarboxylic Acids

The esterification of fluorine-containing dicarboxylic acids has been accomplished by the classical methods involving reaction of the acids with alcohols in the presence of catalysts such as gaseous hydrogen chloride, concentrated sulphuric acid, toluene-*p*-sulphonic acid, fluorosulphuric acid, etc.[58,61,62,82,88,109]

Diazomethane is often used to obtain the methyl esters of dicarboxylic acids; thus with difluoromalonic acid it gives a good yield of dimethyl difluoromalonate[16,27].

Fluorine-containing dicarboxylic acids can be esterified also with olefins. In the presence of catalytic quantities of concentrated sulphuric acid or toluene-*p*-sulphonic acid, propene adds on to perfluorosuccinic acid to form the diisopropyl ester[110]:

$$(CF_2COOH)_2 + 2\,CH_2{=}CHCH_3 \rightarrow \left(CF_2COOCH\langle{}^{CH_3}_{CH_3}\rangle\right)_2 .$$

The diethyl ester has been obtained similarly.

Esters are prepared also by reaction of the acid chlorides or fluorides with alcohols.

(*b*) Addition of Ethyl Malonate to Unsaturated Compounds and to Ketones

Ethyl malonate, which contains active hydrogen atoms, can add on to fluorine-containing unsaturated compounds and ketones to form fluorine-containing derivatives of malonic ester, which on hydrolysis give fluorine-containing mono- or di-carboxylic acids, depending on the structure of the starting materials.

In the presence of sodium ethoxide, ethyl malonate easily adds on to 3,3,4,4,5,5,5-heptafluoro-1-nitropentene forming ethyl 3,3,4,4,5,5,5-heptafluoro-2-nitromethylpentane-1,1-dicarboxylate[111]:

$$C_3F_7CH{=}CHNO_2 + CH_2(COOC_2H_5)_2 \rightarrow C_3F_7CH(CH_2NO_2)CH(COOC_2H_5)_2 .$$

Ethyl 2-(perfluoroalkyl)propane-1,1,3-tricarboxylates — see Section 6 (*c*) — have been obtained similarly. In the presence of sodium, malonic ester reacts with tetrafluoroethylene to form ethyl 2,3-difluorobut-2-ene-1,1,4,4-tetracarboxylate[40]:

$$2NaCH(COOC_2H_5)_2 + CF_2{=}CF_2 \longrightarrow (C_2H_5OOC)_2CHCF{=}CFCH(COOC_2H_5)_2 .$$

Perfluoroacetone reacts with malonic ester in the presence of pyridine to form ethyl 3,3,3-trifluoro-2-hydroxy-2-trifluoromethylpropane-1,1-dicarboxylate[112]:

$$(CF_3)_2C{=}O + CH_2(COOC_2H_5)_2 \longrightarrow (CF_3)_2C(OH)CH(COOC_2H_5)_2 ,$$

but in the presence of acetic anhydride and zinc chloride, the corresponding 2-acetoxy ester is formed, and this on low-temperature pyrolysis in the presence of a catalytic quantity of potassium carbonate, eliminates acetic acid to give ethyl perfluoroisopropylidenemalonate[107,113]:

$$(CF_3)_2C{=}O + CH_2(COOC_2H_5)_2 \xrightarrow{(CH_3CO)_2O} (CF_3)_2C(OCOCH_3)CH(COOC_2H_5)_2 \xrightarrow{130^\circ-140^\circ} (CF_3)_2C{=}C(COOC_2H_5)_2 .$$

Addition of ammonia to this ester yields ethyl 1-amino-3,3,3-trifluoro-2-trifluoromethylpropane-1,1-dicarboxylate[113]:

$$(CF_3)_2C{=}C(COOC_2H_5)_2 + NH_3 \longrightarrow (CF_3)_2CHC(NH_2)(COOC_2H_5)_2 .$$

(*c*) Other Methods

The action of potassium fluoride on ethyl bromomalonate yields, instead of the expected fluoromalonic ester, a small quantity of ethyl difluoromalonate[114]:

$$CHBr(COOC_2H_5)_2 \xrightarrow{KF} CF_2(COOC_2H_5)_2 .$$

Ethyl fluoromalonate has been obtained only by the pyrolysis of ethyl 2-fluoro-3-oxosuccinate, which in turn is obtained by the interaction of ethyl oxalate and ethyl fluoroacetate in the presence of sodium ethoxide[114-116]:

$$(COOC_2H_5)_2 + CH_2FCOOC_2H_5 \longrightarrow COCHF(COOC_2H_5)COOC_2H_5 \longrightarrow CHF(COOC_2H_5)_2 .$$

Sulphur tetrafluoride acts on ethyl acetonedicarboxylate to give a good yield of ethyl 3,3-difluoroglutarate[117]:

$$CO(CH_2COOC_2H_5)_2 \xrightarrow{SF_4} CF_2(CH_2COOC_2H_5)_2 .$$

Esters of fluorine-containing dicarboxylic acids should be obtainable also by the hydrolysis of diethers of the type $ROCF_2XCF_2OR$, but such compounds are not yet known. Ethyl monofluoroethylene 1,2-dicarboxylate has been synthesised by the hydrolysis of 1,4-diethoxytetrafluorobuta-1,3-diene[73] (see Section 4):

$$C_2H_5OCF{=}CFCF{=}CFOC_2H_5 \longrightarrow (C_2H_5OOCCHFCHFCOOC_2H_5) \longrightarrow C_2H_5OOC{-}CH{=}CF{-}COOC_2H_5 .$$

When acetyl peroxide decomposes in methyl fluoroacetate, the fluorine-containing radicals recombine to form methyl 2,3-difluorosuccinate[118]:

$$(CH_3COO)_2 \longrightarrow CH_3COO^{\cdot} \longrightarrow CH_3^{\cdot} + CO_2 ,$$

$$CH_3^{\cdot} + CH_2FCOOCH_3 \longrightarrow CH_4 + {}^{\cdot}CHFCOOCH_3 ,$$

$$2\,{}^{\cdot}CHFCOOCH_3 \longrightarrow (CHFCOOCH_3)_2 .$$

9. ESTERS OF FLUORINE-CONTAINING DIOLS

Fluorine-containing diols react with monocarboxylic acids or their chlorides to form esters of the diols.

It is interesting that, when acted upon by tetracarbonylnickel in benzonitrile, chlorides of perfluorocarboxylic acids form esters of the type $R_FCOOCR_F=CR_FOCOR_F$.[67]

$$R_FCOCl \xrightarrow[C_6H_5CN]{Ni(CO)_4} [R_F\dot{C}O] \rightarrow [R_FCOCOR_F] \xrightarrow{R_F\dot{C}O} R_F-C(=O)-O-C(R_F)=C(R_F)-O-C(=O)-R_F,$$

where $R_F = C_3F_7$, $H[CF_2]_4$.

10. FLUORINE-CONTAINING DIAMIDES AND IMIDES

The diamides are important derivatives of fluorine-containing dicarboxylic acids. Most of them are obtained by interaction of the chlorides or the esters with ammonia or with amines in ether or in aqueous medium. Interaction of the anhydrides of fluorine-containing dicarboxylic acids with ammonia yields only monoamides[105,119].

A specific method for obtaining fluorine-containing amides is the addition of ammonia and amines to fluoroolefins with subsequent hydrolysis of the addition products. Thus hydrolysis of the addition product from ethylamine and perfluorobutadiene results in formation of *NN'*-diethylfluoroethylene-1,2-dicarboxyamide, together with the corresponding monoamide[73]:

$$CF_2=CFCF=CF_2 \xrightarrow{C_2H_5NH_2} \begin{cases} (CF_2=CFCF=CFNHC_2H_5) \rightarrow CF_2=CFCHFCONHC_2H_5, \\ (C_2H_5NHCF=CFCF=CFNHC_2H_5) \rightarrow \\ \rightarrow C_2H_5NHCOCF=CHCONHC_2H_5. \end{cases}$$

Fluorine-containing imides have been obtained by heating fluorine-containing diamides with concentrated sulphuric acid; perfluorosuccinimide, perfluoroglutarimide, etc. have been obtained in this way[73,120].

Heating of the monoanilide of difluoromaleic acid affords *N*-phenyldifluoromaleimide[105]:

$$HOOC-CF=CFCONHC_6H_5 \longrightarrow \begin{matrix} CF-C(=O) \\ \| \quad \quad N-C_6H_5 \\ CF-C(=O) \end{matrix}.$$

N-*p*-Chlorophenyldifluoromaleimide has been obtained similarly.

With diazomethane difluoromaleimide gives the *N*-methylimide[120]:

$$\begin{matrix} CF-C(=O) \\ \| \quad \quad NH \\ CF-C(=O) \end{matrix} + CH_2N_2 \longrightarrow \begin{matrix} CF-C(=O) \\ \| \quad \quad NCH_3 \\ CF-C(=O) \end{matrix}.$$

11. FLUORINE-CONTAINING DINITRILES AND DIAMIDINES

Fluorine-containing dinitriles have been little studied. Perfluoroglutaronitrile and perfluoroadiponitrile have been obtained from the corresponding diamides by removing water with phosphorus pentoxide[90,121]:

$$H_2NOC(CF_2)_nCONH_2 \xrightarrow{P_2O_5} NC(CF_2)_nCN,$$

where $n = 3, 4$.

Perfluoroacrylonitrile when heated dimerises to form a dinitrile[103]:

$$2CF_2=CFCN \longrightarrow \begin{matrix} CF_2-CF-CN \\ | \quad \quad | \\ CF_2-CF-CN \end{matrix}.$$

Reaction of the sodium derivative of diphenylacetonitrile with tetrafluoroethylene gives 1,1,4,4-tetraphenyldifluorobut-2-ene-1,4-dicarbonitrile[40]:

$$2(C_6H_5)_2CNaCN + CF_2=CF_2 \longrightarrow \begin{matrix} (C_6H_5)_2CCF=CFC(C_6H_5)_2 \\ | \quad \quad | \\ CN \quad \quad CN \end{matrix}.$$

On reacting with liquid ammonia, perfluoroadiponitrile gives the diamidine, and perfluoroglutaronitrile forms the imidine:

$$(CF_2CF_2CN)_2 + 2NH_3 \longrightarrow \left(CF_2CF_2C(=NH)NH_2 \right)_2;$$

$$\begin{matrix} CF_2CN \\ CF_2 \\ CF_2CN \end{matrix} + NH_3 \longrightarrow \begin{matrix} CF_2C=NH \\ CF_2 \quad N \\ CF_2C-NH_2 \end{matrix}.$$

When heated with monoamidines above their melting points, both diamidines and imidines form polytriazines:

$$\left[\begin{matrix} R \\ N \quad N \\ \quad \quad \diagdown \\ \quad \quad \quad N \end{matrix} -(CF_2)_n- \right]_x,$$

where $n = 3, 4$. The resulting polytriazines resemble agate in appearance, and possess great thermal stability. Only a slight loss in weight is observed when they are heated to 350°.[122]

12. FLUORINE-CONTAINING DIAMINES

Fluorine-containing diamines are practically unknown. The production of fluorine-containing polyamides in the form of filaments is mentioned in the patent literature[80], but no other information is available on the synthesis or application of the polyamides.

Perfluorodiamines of the type $NH_2[CF_2]_nNH_2$ do not exist, since immediately on formation they split off hydrogen fluoride and form perfluorodinitriles.

2,2,3,3,4,4-Hexafluoropentamethylenediamine and 2,2,3,3,4,4,5,5-octafluorohexamethylenediamine have been synthesised by reduction of the corresponding dinitriles with hydrogen in the presence of platinum dioxide[90,121]:

$$NC-(CF_2)_nCN \xrightarrow[Pt]{H_2} H_2NCH_2(CF_2)_nCH_2NH_2,$$

where $n = 3, 4$.

Several secondary diamines have been synthesised by reducing *N*-substituted diamides of perfluoroglutaric acid with lithium aluminium hydride[123]:

$$RNHCO(CF_2)_3CONHR \xrightarrow{LiAlH_4} RNHCH_2(CF_2)_3CH_2NHR,$$

where R = CH_3, C_2H_5, iso-C_3H_7, n-C_4H_9, t-C_4H_9, iso-C_4H_9. An attempt to reduce *N*-substituted perfluorosuccinamides was unsuccessful, since the reaction was accompanied by an explosion.

13. FLUORINE-CONTAINING DINITRO-COMPOUNDS

Fluorine-containing dinitro-compounds have not been extensively studied. Most of the known ones have been obtained by the addition of nitrogen dioxide to fluorine--containing olefins.

Hass[124], Coffman[65], and Haszeldine[125] reported that reaction of nitrogen dioxide with tetrafluoroethylene and chlorotrifluoroethylene yields tetrafluoro-1,2-dinitroethane and chlorotrifluoro-1,2-dinitroethane respectively. Probably lack of care in the experiment or of precision in the reaction conditions prevented these workers from noticing several other most interesting products which are also formed, and from studying these reactions.

In a study of the nitration of perfluoroolefins with nitrogen dioxide, Knunyants and his coworkers established[126] that the process is more complicated, that it depends to a considerable extent on the characteristics of the fluoroolefin involved, and that it results in the formation of interesting substances. Thus in the reaction of tetrafluoroethylene with nitrogen dioxide in non-polar solvents, formation of small quantities of telomers of tetrafluoroethylene is accompanied by that of a mixture of tetrafluoro--1,2-dinitroethane and tetrafluoro-2-nitroethyl nitrite in the proportions 1 : 1.

$$CF_2=CF_2 \xrightarrow{N_2O_4} \begin{cases} O_2N-CF_2CF_2-ONO \\ O_2N-CF_2CF_2NO_2 \\ O_2N(CF_2CF_2)_nNO_2 \end{cases}.$$

When tetrafluoroethylene is nitrated in polar solvents, the yield of the dinitro-compound is lower. In the absence of solvents, perfluoropropene and perfluoroisobutene react with nitrogen dioxide under more severe conditions.

It is interesting that, when perfluoropropene is nitrated under these conditions, almost the sole reaction product is hexafluoro-2-nitropropyl nitrite, with only an insignificant quantity of hexafluoro-1,2-dinitropropane. In the case of perfluoroisobutene, pentafluoro-1,2-dinitro-2-trifluoromethylpropane and pentafluoro-2-nitro-2-trifluoromethylpropyl nitrite are formed in equal proportions.

From the experimental results, fluoroolefins can be arranged in the following sequence according to their reactivity towards nitrogen dioxide:

$$CF_2=CF_2 > CF_3CF=CF_2 > \begin{matrix} CF=CF \\ | \quad | \\ CF_2-CF_2 \end{matrix} < \begin{matrix} CF_3 \\ \diagdown \\ CF_3 \end{matrix}\!\!>C=CF_2.$$

The conditions under which nitration of fluoroolefins is accomplished, the nature of the products, and several other facts indicate that this reaction proceeds by a free radical mechanism:

$$CF_2=CF_2 + {}^{\bullet}NO_2 \longrightarrow O_2NCF_2\dot{C}F_2 \begin{cases} \xrightarrow{\dot{O}NO} O_2NCF_2CF_2NO_2 \\ \xrightarrow{ONO^{\bullet}} O_2NCF_2CF_2ONO \end{cases}.$$

Tetrafluoroethylene reacts with nitric oxide to form tetrafluoro-1,2-dinitroethane, but the main reaction product is tetrafluoro-1-nitro-2-nitrosoethane[127]. It is interesting that this last product reacts smoothly with tetrafluoroethylene to give an oxazetidine or a polymer thereof:

$$O_2NCF_2CF_2NO + CF_2=CF_2 \longrightarrow O_2NCF_2CF_2N \begin{matrix} - O \\ | \quad | \\ CF_2-CF_2 \end{matrix} \longrightarrow \left(\begin{matrix} -N-O-CF_2-CF_2- \\ | \\ CF_2-CF_2NO_2 \end{matrix} \right)_x.$$

The reaction is carried out at 0°–20°, and results in a 60–65% yield of polymer. The polymers obtained are viscous oils or elastomers, depending on their molecular weight, and possess high frost-resistance.

Dinitro-compounds are obtained also by the addition of nitromethane to fluorine-containing nitroolefins. Thus in the presence of sodium methoxide nitromethane adds on to 3,3,4,4,5,5,5-heptafluoro-1-nitropentene to form 1,1,1,2,2,3,3-heptafluoro-5-nitro-4-nitromethylpentane in good yield[111]:

$$C_3F_7CH=CHNO_2 + CH_3NO_2 \longrightarrow C_3F_7CH(CH_2NO_2)_2.$$

14. FLUORINATED BIFUNCTIONAL COMPOUNDS CONTAINING HETEROATOMS

Fluorinated bifunctional compounds containing heteroatoms have been little studied. A few fluorine-containing thia-, oxa-, and aza-compounds and fluoroalkadienes containing heteroatoms have been synthesised. The first group includes aza-, oxa-, and thia-dicarboxylic acids and their derivatives, and the second group compounds of the type $(CF_2{:}CF)_nM$ and their derivatives, where M = Hg, P, As, Sb, Si, and Sn. These compounds have not yet found any application.

(*a*) Fluorine-Containing Thia-, Oxa-, and Aza-Compounds

Most of the thia- and aza-compounds have been obtained by the addition of mercapto- or amino-esters to fluorine--containing unsaturated esters, which enables long-chain fluorine-containing bifunctional compounds to be prepared. In the presence of a quaternary base, mercaptoacetic ester adds on to ethyl 3-(perfluoropropyl)acrylate, forming ethyl 3-perfluoropropyl-4-thiaadipate, which is converted into the acid on hydrolysis with formic acid[60,128,129]:

$$C_3F_7CH=CHCOOC_2H_5 + HSCH_2COOC_2H_5 \rightarrow \begin{matrix} C_3F_7CHCH_2COOC_2H_5 \\ | \\ SCH_2COOC_2H_5 \end{matrix} \longrightarrow \begin{matrix} C_3F_7CHCH_2COOH \\ | \\ S-CH_2COOH \end{matrix}.$$

This ester has been obtained also by the reaction of bromoacetic ester with ethyl 4,4,5,5,6,6,6-heptafluoro-3--sodiothiohexanoate, itself obtained by the action of sodium hydride on the corresponding mercapto-ester[128]:

$$C_3F_7CHCH_2COOC_2H_5 + NaH \longrightarrow \begin{matrix} C_3F_7CHCH_2COOC_2H_5 \\ | \\ SNa \end{matrix} \xrightarrow{BrCH_2COOC_2H_5} \begin{matrix} C_3F_7CHCH_2COOC_2H_5 \\ | \\ SCH_2COOC_2H_5 \end{matrix}.$$

Aza-compounds have been obtained similarly. However, oxa-compounds cannot be prepared by these methods.

Reaction of ethyl 3-(perfluoropropyl)acrylate with hydrogen sulphide in the presence of a quaternary base in pyridine forms ethyl 3,5-bis(perfluoropropyl)-4-thiapimelate, which has been converted into the acid, the acid chloride, and the corresponding diol[60]:

$$2C_3F_7CH=CHCOOC_2H_5 + H_2S \longrightarrow \begin{matrix} S(CHCH_2COOC_2H_5)_2 \\ | \\ C_3F_7 \end{matrix} \longrightarrow \begin{matrix} S(CHCH_2COOH)_2 \\ | \\ C_3F_7 \end{matrix} \longrightarrow \begin{matrix} S(CHCH_2COCl)_2 \\ | \\ C_3F_7 \end{matrix} \longrightarrow \begin{matrix} S(CHCH_2CH_2OH)_2 \\ | \\ C_3F_7 \end{matrix}.$$

Oxa-compounds have been prepared by the addition of fluorine-containing diols to unsaturated compounds. Thus addition of 2,2,3,3,4,4-hexafluoropentanediol to acrylonitrile yields 5,5,6,6,7,7-hexafluoro-3,9-dioxaundecane--1,11-dicarbonitrile, which is converted into the ethyl

TABLE. Fluorine-containing bifunctional compounds.

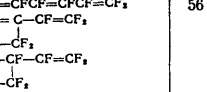
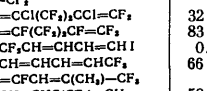
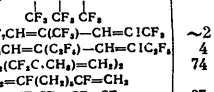
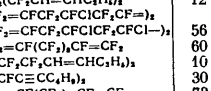
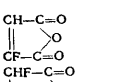
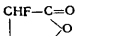
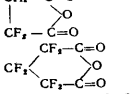
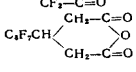
Compound	Yield, %	B.p., °C/mm	M.p., °C	n_D^{20}	d_4^{20}	References
1	2	3	4	5	6	7
Alkadienes						
$CF_2=C=CF_2$		—38				42, 43, 135, 136
$CF_2=C=CH_2$	56	—27				44—47, 137
$CF_2=CClCCl=CFCl$		104/740				135
$CF_2=C=C=CF_2$		—5				49, 50
$CF_2=CFCCl=CFCl$		72				135
$CF_2=CClCCl=CF_2$		69		1.3832		135, 138
$CFCl=CFCF=CFCl$	78	79		1.403		22, 135, 139
$CF_2=CFCF=CFCl$		35			1.471 (25)	140
$CF_2=CFCCl=CF_2$		37				135, 139, 141
$CF_2=CF-CF=CF_2$	3—98	7.4	—132	1.378	1.553 (—20)	14, 15, 18, 21, 22, 27, 36, 37, 135, 138, 139, 142—145
$CF_2CF=C=CF_2$	~1	6				146
$CF_2=CFCH=CFCl$	64	53		1.3804	1.431 (24)	18
$CF_2=CFCH=CF_2$	80	15.5				18, 21
$CF_2=CH-C\equiv CH$	85	0±2°				147
$CF_2=CFCF=CH_2$	54	—12				13, 148
$CF_2=CHCH=CF_2$	80	5				39, 141, 149
$CF_2=CFCH=CHF$	80	16.5		1.3427	1.342 (0)	18, 21
$CF_2=CClCH=CH_2$						141
$CF_2CH=C=CH_2$	44	16				48
$CF_2=CFCH=CH_2$	65—88	8.0				18, 19, 21
$CF_2=CHCF=CH_2$	42	16.9				19
$CFCl=CHCH=CH_2$		53.4		1.4267	1.066 (25)	150
$CH_2=CFCCl=CH_2$						151
$CF_2=CHCH=CH_2$	50	3.5—5		1.338	1.0 (2)	20, 141, 150, 152
$CH_2=CFCF=CH_2$		5—8	—92	1.373	1.001 (0)	9, 153
$CH_2=CHCF=CH_2$		12.0		1.400	0.843 (4)	154—156
$CF_2(CCl=CCl_2)_2$	91	101/13	—40.8	1.5171	1.748	16
$CF_2=CFC(CF_3)=CF_2$		37		1.3250	1.289	18, 135, 157
$CF_2=C(CF_3)Cl-CCl=CHCl$	54	43/38		1.4125(25)		69
$CF_2=C(CF_3)-CH=CF_2$	78	32.8		1.3087	1.494 (0)	157
$CF_2=CF-CH=CHCF_3$		50.5		1.3322	1.389 (22)	18
$CF_2=CHCF_2CH=CF_2$		45		1.3583	1.3935	158
$CF_2=C(CF_3)-CH=CH_2$	78	32		1.3372	1.310 (0)	157
$CF_2=CFCH=CHCH_3$	60	44		1.3689	0.9974 (+24)	159
$CF_2CH=CHCH=CH_2$	75	45		1.3751	1.027	32
$CF_2=CFCH_2CH=CH_2$	65	38/870		1.3435	1.0324 (27)	159
$CF_2=C(CH_3)-CF=CH_2$	60	50		1.3631	1.095 (25)	19, 39
$CH_2=C(CF_3)-CH=CH_2$	20	41		1.3485	1.064	32, 34, 160, 161
$CF_2(CH=CH_2)_2$	83	47	—135	1.3552	0.9368	16
$CF_2=CHC(CH_3)=CH_2$	61	35		1.3705	0.946 (25)	17, 20, 39, 150
$CF_2=C(CH_3)-CH=CH_2$	23	39		1.3760	0.9582 (25)	20, 39, 150 152
$CH_2=C(CH_3)-CF=CH_2$		47		1.397	0.847 (25)	155, 156
$CFCl=CFCF=CFCF=CFCl$	46	132		1.4324	1.6116 (25)	23, 24
$CF_2=CFCF=CFCF=CF_2$	56	65/748			1.537 (25)	23
						13
						13
$CF_2=CCl(CF_2)_2CCl=CF_2$	32	113.9	—34.1	1.3613	1.6789	38, 136
$CF_2=CF(CF_2)_2CF=CF_2$	83	59.6	—70.0	1.296	1.609	31, 38
$CF_2CF_2CH=CHCH=CHI$	0.5	104/46				25
$CF_2CH=CHCH=CHCF_3$	66	85.5		1.3403	1.286 (25)	35
$CF_2=CFCH=C(CH_3)-CF_3$		71		1.3531	1.350 (22)	18
$CF_2CH=CHC(CF_3)=CH_2$	58	74		1.3780	1.052	32
$CH_2=C(C_2F_5)-CH=CH_2$		54		1.3328(24)		161
$CH_2=CH(CF_2)_2CH=CH_2$	67	75.5		1.3415	1.135	35
$CF_2=CFCH=C(CH_3)_2$	42	52		1.3606	0.8538 (24)	159
$CF_3-CH=C(CF_3)-CH=CICF_3$	9	60/77				26
$CH_2=C(C_2F_5)-CH=CH_2$		68		1.3260		161
$CF_2CH=C(CH_3)-CH=CICH_3$		54/7		1.3260		26
$(CF_2=CFCF_2CF_2-)_2$	72.5	106		1.3020	1.695	28—31
$(CF_2=CFCF_2CF=)_2$	78	99				27
$(CF_2=CFCF_2CFCl-)_2$	51	58/20				27
$(CF_3)_2C=CClCCl=C(CF_3)_2$		123		1.3462	1.6838	162
		92		1.2886	1.6998 (25)	41
$C_2F_5CH=C(CF_3)-CH=CICF_3$	~2	83/56				26
$CF_3CH=C(C_2F_5)-CH=CIC_2F_5$	4	86/100				26
$CF_2(CF_2C\cdot CH_3)=CH_2)_2$	74	140		1.3682	1.110	33
$CH_2=CF(CH_2)_2CF=CH_2$		87/4		1.4036	0.9978	163
$CF_2=CF(CF_2)_4CF=CF_2$	67.8	148		1.3100	1.796	30, 31
		111.5		1.2994	1.7359 (25)	41
$(CH_2=C(CH_3)-CF_2CF_2)_2$	85	31/4		1.3620	1.228	33
$CF_2=CFCH=CH(CH_3)_2CH_3$	72	25/35		1.3810	0.838 (24)	159
$CF_2(CF_2CH=CHC_2H_5)_2$	12	86/19		1.3884	1.214	33
$(CF_2=CFCF_2CFClCF_2CF=)_2$		115/20				27
$(CF_2=CFCF_2CFClCF_2CFCl-)_2$	56	150/0.1				27
$CF_2=CF(CF_2)_6CF=CF_2$	60	181		1.3115	1.826	28—31
$(-CF_2CF_2CH=CHC_2H_5)_2$	10	92/14		1.3800	1.250	33
$(=CFC\equiv CC_4H_9)_2$	30	91/1		1.4842(25)		40
$CF_2=CF(CF_2)_{12}CF=CF_2$	72.9	147/33	73			30, 31
$(=CFC\equiv CC_6H_5)_2$	9		82			40
Diols						
$CF_3CHOHCH_2OH$	30	69.5/10	25.3	1.3617	1.505	70
$HOCH_2CF_2CH_2OH$	93		52.5			56, 64
$CF_2BrCHOHCHOHCF_2Br$		80/1	74.5			50
$HOCH_2(CF_2)_2CH_2OH$	90		85			56, 58, 63, 66
$CF_3CHOHCHOHCH_3$		77/23	66.5			164
$CF_3CHOHCH_2CH_2OH$	83	104/20				165
$HOCH_2(CF_2)_3CH_2OH$	93		77.5			56, 63, 66
$CH_3C(CF_3)OHCHOHCH_3$		58/5.5		1.3866	1.3282 (25)	34

TABLE (contd.)

1	2	3	4	5	6	7
$CF_3CHOHCH_2CHOHCH_3$	85	78/3		1.3798	1.294	32
$HOCH_2(CF_2)_4CH_2OH$	88		68			56, 57, 66, 166
$C_3F_7CHOHCH_2CH_2OH$			90			167
$C_3F_7CHOHCF_2OHCH_3$						71
$HOCH_2(C_4HF_7)CH_2OH$		139/15	20—30			59
$CF_3CHOHCH_2CH_2CHOHCF_3$	75		75-120**			35
$CH_3CHOHCF_2CF_2CHOHCH_3$	64	201		1.3865	1.359 (25)	35
$C_3F_7CHOHCHOHC_2H_5$			88			71
$C_3F_7CHOHC(CH_3)_2OH$						71
$[\equiv C-C(CF_2Cl)_2OH]_2$	71		51			69
$[\equiv C-C(CF_3)_2OH]_2$	57.3		59			68
$C_2F_7CH(OH)CHOHC_2F_7$	50		71			67
$HO-C(CF_3)_2C\equiv CC(CH_3)_2OH$	63		77			68
$C_3F_7CH(CH_2CH_2OH)_2$	62	82/0.1		1.3752		60
$CF_3(CF_2CHOHC_2H_5)_2$	23		94			33
$CF_3[CF_2C(CH_3)_2OH]_2$	82		78			33
$[C\equiv C-C(CF_2Cl)_2OH]_2$	79		79			69
$[C\equiv C-C(CF_3)_2OH]_2$	83.3		70***			68
$HOCH_2(CF_2)_4CH_2OH$	85		136			166
$[CF_2CF_2C(CH_3)_2OH]_2$	98		81			33
$CF_3(CF_2CHOHC_2H_5)_2$	77		80			33
$CF_2[CF_2C(C_2H_5)_2OH]_2$	5		68			33
Diethers						
$CF_2OCF_2CF_2OCF_2$		13				72
$C_2F_5O(CF_2CF_2O)_2C_2F_5$		96.6/737		1.250	1.617 (30)	72
$(CF=CFOC_2H_5)_2$	41.8	83—5/17		1.3871	1.1883	73
$[=CFOCH(CH_3)_2]_2$		58—65/40				168
$[\equiv CC(CF_2Cl)_2OCH_3]_2$	46	67/0.2		1.4061(25)		69
$(CH_3)_2COCF=CFOC(CH_3)_2$						168
Diketones						
$CF_2COCH_2COCF_2$	72	63				74, 75
$CF_2COCH_2COCH_3$	62—80	107		1.3892		74—77
$C_2F_5COCH_2COCH_3$	84.5	111/631		1.3729		76
$CH_3COCF_2CF_2COCH_3$	45	128—130				35
$CF_2COCH_2COC_2H_5$	84	124/755		1.3951	1.22	77
$CF_2COCH(CH_3)COCH_3$	4.9	123/755		1.356	1.22	77
$C_3F_7COCH_2COCH_3$	78.5	56/38		1.3646		76
$CF_2COCH(CH_3)COC_2H_5$	66	148/735		1.3921	1.22	77, 78
$C_3F_7COCOC_2F_7$		95				67
$C_4F_9COCH_2COCH_3$	80	68/33		1.3589		76
$CF_2COCH_2COCH_2CH(CH_3)_2$	87	88/64		1.4103	1.13	77
$CF_2COCH(C_2H_5)COC_2H_7$	34	113/98				78
$CF_2COCH_2COC_6H_{13}$	55	65/6		1.4196	1.09(23)	77
Dicarboxylic acids						
$CF_2(COOH)_2$	63		117			16, 27, 169
$CHF(COOH)_2$			135			103, 114
HOOCCF=CFCOOH (*trans-*)	34		268—270			105, 106
HOOCCF=CFCOOH (*cis-*)			219—220			105, 106
$HOOCCF_2COCOOH$	81		116—118			170
$(CFClCOOH)_2$	62	100—105/0.1				22
$HOOCCF_2CFClCOOH$	85		55			105, 106
$(CF_2COOH)_2$	96	150/15	115—116			38,88,98,104,119
HOOCCH=CFCOOH (*trans-*)	77		236—237			105
HOOCCH=CFCOOH (*cis-*)	78		132—133			105
$HOOCCHFCF_2COOH$	83		111—112			105, 106
$HOOCCH_2CF_2COOH$	79		154—155			105, 170
$(CHFCOOH)_2$						104
$HOOCCF_2CH(OH)COOH$	57		139—140			170
$CFCl(CF_2COOH)_2$		130—145/0.1				99
$CF_2(CF_2COOH)_2$	90	134/3	78—88			89—91, 93
$HOOCCF_2CH_2COCOOH$						170
$HOOCCH_2CH_2CF_2COOH$	30		103			102
$(CFClCF_2COOH)_2$	51					27, 90
$(CF_3CF_2COOH)_2$	86		134			30, 31, 57, 90, 92—94, 171
$HOOCCF_2CHFCF_2CF_2COOH$	54		128			59, 95, 172, 173
$HOOCCHF(CF_2)_3COOH$			116			172—174
$HOOCCF_2CHCOCOOH$						170
$HOOCCHFCHFCF_2CF_2COOH$			126			93, 95, 96
$(CHFCF_2COOH)_2$			163			95, 174
$HOOCCH_2CH_2CF_2CF_2COOH$						97
$(CF_3CH_2COOH)_2$			247			97
$HOOC(CF_2CFCl)_3CF_2COOH$		145—165/0.2				99
$HOOCCF_2C(CF_3)FCF_2CF_2COOH$			60			109, 175
$CF_2C_4H_7(COOH)_2$						176
$HOOC(CF_2CFCl)_3COOH$	75	140—160/1				100
$HOOC(CF_2)_4COOH$	95		143			30, 31
$C_3F_7CH(CH_2COOH)_2$	94		121			60
$HOOC(CF_2CFCl)_3CF_2COOH$			105			99
$HOOC(CF_2CFCl)_4COOH$		155/0.6				100
$HOOC(CF_2)_6COOH$	92	160				30, 31, 80, 82, 87
$HOOC(CF_2CFCl)_4CF_2COOH$						99
$HOOC(CF_2CFCl)_4COOH$		140/0.08				100
$C_9F_{17}CH(CH_2COOH)_2$	53		125			60
$HOOC(CF_2)_{12}COOH$	71.8		191			30, 31
Anhydrides of dicarboxylic acids						
	89	128	20	1.4179 (25)		105, 106, 177
	81	78		1.3661 (25)		105
	62	54		1.3240	1.6209	63, 64, 119

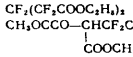
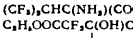
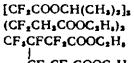
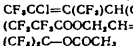
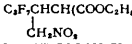
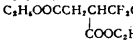
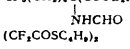
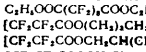
TABLE (contd.)

1	2	3	4	5	6	7
	76	162		1.4452 (25)		105, 178
		122				105
	76.5	72		1.3190	1.6541(25)	83
	86	93/0.2	48.5			60

Chlorides and fluorides of dicarboxylic acids

$CF_2(COCl)_2$		66.8				64
$(CF_2COCl)_2$		86				64
$(CF_2COF)_2$	44—56	18	—59			107, 108
$(CF_2CF_2COCl)_2$	78.3	131		1.3488	1.679	30, 31
$(CF_2CF_2COF)_2$						85
$(C_4HF_7)(COCl)_2$		138				59
$C_2F_5CH(CH_2COCl)_2$	88	65/1.6		1.3926		60
$ClOC(CF_2)_3COCl$	80	101/23	29	1.3336	1.771 (37)	30, 31
$C_7F_{15}CH(CH_2COCl)_2$	73	80/0.7		1.3699		60

Esters of dicarboxylic acids

$CF_2(COOCH_3)_2$	81	60/12	—35	1.3721	1.3059	16, 27, 114
$CH_3OOCCF_2CFClCOOCH_3$	61	192		1.3908 (25)		105
$(CF_2COOCH_3)_2$		173		1.3555 (25)		120
$(CHFCOOCH_3)_2$	53	68/0.7				118
$CF_2(COOCH_2CF_3)_2$	57	157		1.326	1.525	64
$CF_2(CF_2COOCH_3)_2$	80	100/34	—31	1.3518	1.4856	89
$CH_3OOCCF_2CH_2COCOOCH_3$		89/3		1.4064 (25)		170
$CH_3OOCCF_2CH_2CH_2COOCH$	70	65/12				102
$(CFClCF_2COOCH_3)_2$		155/2				27
$(=CFCOOC_2H_5)_2$ (*cis-*)		55/1.1		1.4121 (25)		105
$(=CFCOOC_2H_5)_2$ (*trans-*)		72/1.1		1.4273 (25)		105
$C_2H_5OOCCF_2COCOOC_2H_5$	38	63/1		1.3972 (25)		170
$C_2H_5OOCCF_2CFClCOOC_2H_5$		219		1.3945 (25)		105
$(CF_2COOC_2H_5)_2$	60	89/15		1.3690	1.2640	58,88,107,110,119
$(CF_2COSC_2H_5)_2$		108/8				107
$C_2H_5OOC—CH=CFCOOC_2H_5$	83.6	74/1.5		1.4330	1.1456	73
$C_2H_5OOC—COCHFCOOC_2H_5$	67	95/1.5		1.42	1.261	114—116
$C_2H_5OOC—CHFCF_2COOC_2H_5$		75/2				105
$C_2H_5OOC—CH_2CF_2COOC_2H_5$	81	205/749		1.3912 (25)		105, 170
$C_2H_5OOCCH(OH)CF_2COOC_2H_5$	74	69/0.5		1.4078 (25)		170
$CF_2(CF_2COOC_2H_5)_2$	81—95	76/3—5		1.3585	1.3444	90, 120, 121
						170
$CF_2(CF_2COSC_2H_5)_2$	90	122/8		1.4351	1.3858(25)	83
$CF_2(CH_2COOC_2H_5)_2$	29	63/2		1.4038 (25)		117
$C_2H_5OOCCF_2CH_2CH_2COOC_2H_5$		127/28				102
$(CF_3)_2C=C(COOC_2H_5)_2$	87.6	59/6		1.3720	1.3025	113
$(CF_3CF_2COOC_2H_5)_2$	71	70/2—3		1.3541	1.4026	90,94,166,179,18
$(CF_2)_2C(OH)—CH(COOC_2H_5)_2$	78.5	58/1		1.3700	1,3730	112
$(CF_3)_2CHC(NH_2)(COOC_2H_5)_2$	53	60/1		1.3840	1.4534	113
	92		113			170
$[CF_2COOCH(CH_3)_2]_2$	88	83/5		1.3728		110
$(CF_2CH_2COOC_2H_5)_2$				1.3920 (25)		106
		112/14		1.361 (12)		109
$CF_2CCl=C(CF_2)CH(COOC_2H_5)_2$		80/1		1.4018	1.3659 (29)	181
$(CF_2CF_2COOCH_2CH=CH_2)_2$		150—160/30				179
	41.7	112/10		1.3842	1.3608	68
	49	145/9		1.3904		111
$[CF_2CF_2COOCH(CH_3)_2]_2$		232/745				179
$C_2F_5CH(CH_2COOC_2H_5)_2$	92	79/1.5		1.3738	1.320	60
	25	125/1		1.4215 (25)		170
	59		87			182
$(CF_2COSC_2H_5)_2$		85—105/ <0.01		1.4719	(25)	183
$(CF_2)_3(COOCH_2C_2F_7)_2$	59	129/30		1.3142	1.7090 (24)	184
$C_2H_5OOC(CF_2)_4COOC_2H_5$		156/27		1.341	1.592 (25)	82, 166
$[CF_2CF_2COO(CH_2)_2CH_3]_2$	86	126/8.5		1.3725	1.2711 (25)	180
$[CF_2CF_2COOCH_2CH(CH_3)_2]_2$	57	118/8		1.3697	1.2671 (25)	180
$[CF_2CF_2COOCH(CH_3)C_2H_5]_2$	87	111/5		1.3680	1.2643 (25)	180
$[CF_2CF_2COOC(CH_3)_3]_2$		100—110/8				180
	90	104/0.7		1.3900	1.306	60
$[=CFCH(COOC_2H_5)_2]_2$	48.5	150/1		1.4452		40
$CF_2(CF_2COOC_4H_{13})_2$	74	158/5		1.3938	1.1447 (25)	180
$(CF_2CF_2COOC_4H_{13})_2$	58	155/3.5		1.3888	1.2038 (25)	180
$(CF_2COSC_{10}H_7)_2$			130			184

Esters from fluorine-containing diols

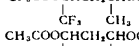
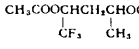
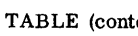
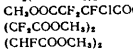
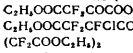
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	88	188		1.3809		32

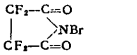
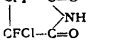
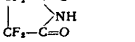
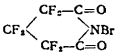
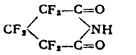
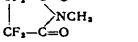
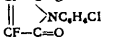
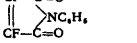
TABLE (contd.)

1	2	3	4	5	6	7
$[CH_3COOCH(CF_3)CH_2]_2$	100	133/75		1.3630	1.310 (26)	35
$[CH_3COOCH(CH_3)CF_2]_2$	87	205		1.3870	1.246 (25)	35
$(C_2F_5COOCH_2CF_2)_2CF_2$	62	131/30		1.3140	1.7085 (23)	184
$(C_4F_9COOCH_2CF_2CF_2)_2$	72	85/1.5		1.360	1.734 (25)	184
$(C_3H_7COOCH_2CF_2CF_2)_2$	77	112/1		1.3793	1.3181 (25)	185
	5	89/19				67
$(NO_2C_6H_4COOCH_2)_2CF_2$			107			64
$(CH_2C_6H_4SO_2CH_2CF_2)_2CF_2$	79	92				123
	19	167/20		1.3255		64
$(NO_2C_6H_4COOCH_2CF_2CF_2)_2$			105			57
$(C_6H_5COOCH_2)_2(C_4HF_7)$	66		74			59
$[\equiv C—C(CF_2Cl)_2SO_2C_6H_4CH_3]_2$	75		189			69
$[(CF_2)_4COOCH_2(CF_2)_4H]_2$	quant.		58			31
$[(CF_2)_4COOCH_2(CF_2)_6H]_2$	quant.		110			31

Diamides of dicarboxylic acids

$CF_2(CONH_2)_2$			206			16, 27, 169
$CHF(CONH_2)_2$			198			128
$H_2NCOCF=CFCONH_2$ (*trans-*)	84		>280			105
$H_2NCOCHFCF_2CONH_2$	78		195			105
$H_2NCOCF_2CFClCONH_2$	83		250			105
$(CF_2CONH_2)_2$			261			79, 119, 169
$(CHFCONH_2)_2$						133
						121
$H_2NCO(CF_2)_2CONH_2$	96		208			90, 121
$(CF_2CF_2CONH_2)_2$			237			90, 94, 121
$H_2NCOCF_2CF_2CHFCF_2CONH_2$			205			59, 172
$H_2NCOCHF(CF_2)_2CONH_2$			180			172
$(CHFCF_2CONH_2)_2$			206			96
	70		168			109
$CF_2(CF_2CONHCH_3)_2$	87.5		144			123
$(CF_2CONHCH_2CH_2OH)_2$			142			119
$C_6H_5NHCOCH=CFCONHC_6H_5$			55			73
$CF_2(CF_2CONHC_6H_5)_2$	91.3		120			123
$H_2NCO(CF_2)_4CONH_2$			239			30, 31, 82, 123
$CF_2[CF_2CONHCH(CH_3)_2]_2$	62		139			123
$(CF_2CONHC_6H_5)_2$			130			119
$CF_2(CF_2CONHCH_2C_3F_7)_2$	45		135			123
$CF_2(CF_2CONHC_6H_5)_2$	88		117			123
$CF_2[CF_2CONHC(CH_3)_3]_2$	66		120			123
$(CF_2CONHC_6H_5)_2$			227			64
						119
$(CF_2CF_2CONHC_6H_5)_2$	quant.		196			30, 31
$(C_4HF_7)(CONHC_6H_5)_2$			164			59
$(C_4HF_7)(CONHC_{11}H_5)$			196			59
$[(CF_2)_4CONHC_6H_5]_2$	quant.		199			30, 31
$(CF_2CONHC_{18}H_{37})_2$			105			119

Imides of dicarboxylic acids

	87					120
	39	48/2		1.4333(25)		105
	80	178	66			120
						120
	89	159	27			120
			97			120
	90		74			105
	46		88			105

Dinitriles and diamidines of dicarboxylic acids

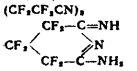
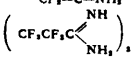
$CN(CF_2)_3CN$		38/745				90, 121
$(CF_2CF_2CN)_2$	64	63		1.2770	1.4303	90, 121
						122
			125			122
$(C_6H_4)_2CCF=CFC(C_6H_4)_2$	46	166				40

TABLE (contd.)

1	2	3	4	5	6	7
Diamines						
$CF_2(CF_2CH_2NH_2)_2$						90, 121
$(CF_2CF_2CH_2NH_2)_2$	40	65/5—6	44			90, 121
$CF_2(CF_2CH_2NHCH_3)_2$	43.8	55/10.5		1.3771(26.5)		123
$CF_2(CF_2CH_2NHC_2H_5)_2$	44	46/0.05		1.3864 (27)		123
$CF_2[CF_2CH_2NHCH(CH_3)_2]_2$	41.4	70/0.55		1.3917 (25)		123
$CF_2(CF_2CH_2NHCH_2C_3F_7)_2$	52.5	72/0.04		1.3278 (28)		123
$CF_2(CF_2CH_2NHC_4H_9)_2$	39.8	70/0.5		1.4038 (25)		123
$CF_2[CF_2CH_2NHC(CH_3)_3]_2$	39.2	67/0.37		1.4020 (26)		123
Dinitro-compounds						
$NO_2CFClCFClNO_2$	47	55/35	12—18	1.4116(25)	1.646	124
$NO_2CF_2CCl_2NO_2$	47	81/103				125
$NO_2CF_2CFClNO_2$	51	98		1.3748	1.674 (25)	124, 125
$NO_2CF_2CF_2NO_2$	53	59	—41.5	1.3249	1.622	65, 124—126
$CF_2CF(NO_2)CF_2NO_2$		76		1.3141	1.6313	126
$(CF_2)_2C(NO_2)CF_2NO_2$		92		1.3212	1.660	126
$C_3F_7CH(CH_2NO_2)_2$	68		62			111
Thia-, oxa-, and aza-compounds						
$C_3F_7CHCH_2COOH$ SCH_2COOH	82		72.5			128, 129
$C_3F_7CHCH_2COOH$ $NHCH_2COOH$	89		156			128, 129
$CF_2(CF_2CH_2OCH_2COCl)_2$	93	110/0.1	49—52			129, 130
$CF_2(CF_2CH_2OCH_2COOH)_2$	76		82			129, 130
$CF_2(CF_2CH_2OCH_2CONH_2)_2$			147			129, 130
$CF_2(CF_2CH_2OCH_2CH_2CN)_2$	28	180/0.08		1.4040	1.381	130
$S[CH(C_2F_7)CH_2COCl]_2$	85	86/0.7		1.3892		60
$S[CH(C_2F_7)CH_2COOH]_2$	78		156			60
$S[CH(C_2F_7)CH_2CH_2OH]_2$	86	109/0.2	47			60
$C_3F_7CHCH_2COOC_2H_5$ $SCH_2COOC_2H_5$	85	85/0.4		1.4028	1.363	128, 129
$S[CH(CF_3)CH_2COOC_2H_5]_2$	57	114/3	3	1.3737		60
$C_3F_7CHCH_2COOC_2H_5$ $NHCH_2COOC_2H_5$	75	80/0.11		1.3831	1.326	129
$CF_2(CF_2CH_2OCH_2CH_2COOCH_3)_2$	22	125/0.06		1.4028	1.348	129, 130
$CF_2(CF_2CH_2OCH_2COOC_2H_5)_2$	77	134/0.1		1.4010	1.345	129, 130
$C_3F_7CHCH_2COOC_2H_5$ $CH_3NCH_2COOC_2H_5$	58	95/1.9		1.3860	1.298	128, 129
$CF_2(CF_2CH_2OCH_2CH_2COOC_2H_5)_2$	70	131/0.07		1.4041	1.287	129, 130
$S(CHCH_2COOC_2H_5)_2$ C_3F_7	74	100/0.6		1.3763	1.475	60
Fluoroalkadienes containing heteroatoms						
$(CF_2{=}CF)_2Hg$		65/17				131
$(CF_2{=}CF)_2PCl$	60	94		1.4095	1.550 (28)	132, 186
$(CF_2{=}CF)_2PF$	50	63				132, 186
$(CF_3C{\equiv}C)_2Hg$			42			134
$(CF_2{=}CF)_3P$	35.4	99		1.3909	1.6150 (23.5)	132, 186
$(CF_2{=}CF)_3As$	40	110/746		1.3838	1.8400 (18)	133, 186
$(CF_2{=}CF)_3Sb$	41	75/74		1.4190	2.06 (24)	133, 186
$(CH_3)_2Sn(CF{=}CF_2)_2$	65	58/38				187
$CF_2{=}CFCH{=}CHSi(CH_3)_3$	78	36/40		1.4151	1.4159 (24)	188
$(CF_2{=}CF)_4Si$	42	119		1.3621	1.6182	189
$(CF_2{=}CF)_2PN(C_2H_5)_2$	37.5	60/25		1.4098	1.291 (25)	132, 186
$[CF_2CH{=}CHSi(CH_3)_3]_2$	23.6	60/60		1.4348	0.9009 (22)	188

* Where the specific gravity or refractive index is not given for 20°, the corresponding temperature is indicated in parentheses.

** Mixture of *D*, *L*, and *meso*-forms.

*** Hydrate.

ester on hydrolysis with alcoholic hydrogen chloride; this ester has been obtained also by the direct addition of 2,2,3,3,4,4-hexafluoropentane-1,5-diol to ethyl acrylate[129,130]:

$$CF_2(CF_2CH_2OH)_2 \xrightarrow{CH_2{=}CHCN} CF_2(CF_2CH_2OCH_2CH_2CN)_2 \xrightarrow{HCl-C_2H_5OH}$$
$$\xrightarrow{CH_2{=}CHCOOC_2H_5} CF_2(CF_2CH_2OCH_2CH_2COOC_2H_5)_2 .$$

The C—O—C bond in compounds of this type is comparatively unstable, and on hydrolysis with alkali or mineral acids it undergoes cleavage with the formation of a diol.

However, on cautious hydrolysis of the above ester with formic acid, a good yield of the corresponding acid is obtained, and this has been converted into the chloride and the diamide[129,130].

(*b*) Fluoroalkadienes Containing Heteroatoms

These compounds are obtained by the action of fluorine-containing Grignard reagents on the chlorides of certain elements. Trifluorovinylmagnesium iodide reacts with mercuric chloride at -10° to form bis(trifluorovinyl)mercury[131]:

$$2CF_2{=}CFMgI + HgCl_2 \longrightarrow Hg(CF{=}CF_2)_2 + MgCl_2 + MgI_2 .$$

The compounds $Si(CF{:}CF_2)_4$ and $M(CF{:}CF_2)_3$, where M = P, As, Sb, have been prepared in a similar manner[132,133].

Reaction of trifluorovinylmagnesium iodide with diethylphosphoramidous dichloride forms *NN*-diethylbis(trifluorovinyl)phosphinous amide, which on treatment with hydrogen chloride followed by fluorination with antimony trifluoride is converted into bis(trifluorovinyl)phosphinous fluoride[132]:

$$CF_2{=}CFMgI + Cl_2PN(C_2H_5)_2 \longrightarrow (CF_2{=}CF)_2PN(C_2H_5)_2 \xrightarrow{HCl}$$
$$\longrightarrow (CF_2{=}CF)_2PCl \xrightarrow{SbF_3} (CF_2{=}CF)_2PF .$$

Trifluorovinylmagnesium iodide reacts with dimethyltin dichloride to give dimethylbis(trifluorovinyl)tin[12]:

$$(CH_3)_2SnCl_2 + 2CF_2{=}CFMgI \longrightarrow (CH_3)_2Sn(CF{=}CF_2)_2 .$$

Bis(trifluoroprop-1-ynyl)mercury has also been described[134]:

$$CF_3C{\equiv}CH \longrightarrow (CF_3C{\equiv}C)_2Hg.$$

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CHROMATOGRAPHY OF PROTEINS ON CELLULOSE ION EXCHANGERS

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