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Iodoperfluoroalkanes

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ABSTRACT. **In this review the methods for preparing iodoperfluoroalkanes and their chemical properties, namely, radical addition to the carbon–carbon multiple bonds of unsaturated compounds with functional groups, reactions with elements of groups IV–VI and their compounds, cleavage of single bonds by an R_f radical, oxidation of iodoperfluoroalkanes with degradation of the perfluoroalkyl chain or formation of iodonium derivatives, the formation of charge-transfer complexes, and α-halodefluorination reactions are examined. The uses of iodoperfluoroalkanes are described.**

The bibliography includes 285 references.

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I. Introduction

The iodoperfluoroalkanes (IPFAs) CF_3I and C_2F_5I were first prepared at the end of the 1940s for use in the synthesis of organomercury compounds.[1] This marked the beginning of extensive research into perfluoroalkyl derivatives. The use of IPFAs in the syntheses of organic and organoelemental compounds demonstrated their potential as perfluoroalkylating agents[2–6] and reagents for telomerisation.[7] Separate applications for IPFAs in laser,[8–15] electronics,[16] and other fields of engineering[17–19] were progressively established, stimulating further research into preparative methods and a study of their reactivity. At the present time IPFAs are key products in a number of countries for the industrial synthesis of organofluorine compounds and for preparing the initial compounds in the production of drugs and surfactants and the components of artificial blood.[16]

Prominent amongst IPFAs are tertiary iodoperfluoroalkanes,[20,21] which have future potential as working solids for gas lasers.[11]

However, the monographs that are currently available on the chemistry of organofluorine compounds[6,7,16,22–24] do not give a sufficiently clear idea of the methods of synthesis, reactivity, or application of iodoperfluoroalkanes.

In this review an attempt is made to provide a correlated report on the preparative and synthetic methods for obtaining IPFAs and their chemical properties and applications.

With the exception of alkenes with functional groups, reactions of IPFAs with alkenes, which are described in sufficient detail in one monograph,[7] are not covered by the present review. We have made perfluoroalkylation reactions, which are of very considerable synthetic importance and involve extensive literature material, the subject of a separate review.

II. Preparation of iodoperfluoroalkanes

1. Exchange or addition of halogens

Iodoperfluoroalkanes, in particular CF_3I, were first obtained by fluorination of tetraiodomethane.[1] Because of the difficulty in obtaining periodides, this method has more historic significance than preparative value.

$$CI_4 \xrightarrow[20-100^\circ C]{IF_5} CF_3I. \quad 95\%$$

Some considerable time later 2-iodoperfluoro-2-methylpropane was successfully obtained by trifluoromethylation of CI_4 in a glow discharge:[25]

$$CI_4 + CF_3{-}CF_3 \xrightarrow[30\ mm\ Hg]{glow\ discharge} (CF_3)_3CI. \quad 55\%$$

$(CF_3)_3CI$ was synthesised in low yield from 2-bromo-perfluoro-2-methylpropane.[27]

$$(CF_3)_3CBr + NaI \xrightarrow[refluxing]{CH_3CN} (CF_3)_3CI. \quad 5.5\%$$

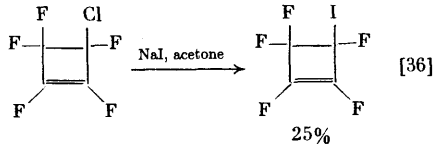
The replacement of iodine in diiodopolyfluoroalkanes is of somewhat greater importance. Usually the reaction consists of the formation of an α,β-diiodoperfluorocarbon by iodination of the corresponding perfluoroalkene followed by replacement of one of the iodine atoms by fluorine. For the substitution reaction use is made of iodine pentafluoride,[1] mixed halofluorides of pentavalent antimony or sulphur tetrafluoride,[28,29] electrochemical fluorination in anhydrous HF,[30,31] and fluorination with hydrogen fluoride in the presence of the catalysts $HF-H_2SO_4$, I_2-HNO_3, $I_2-SO_2Cl_2$ [32] or metal oxides.[33,34]

$$CF_2{=}CF_2 \xrightarrow{I_2} ICF_2CF_2I \longrightarrow \underset{75-100\%}{CF_3CF_2I}.$$

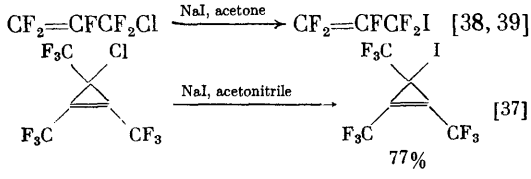
Iodotrifluoromethane labelled with ^{18}F isotope was obtained in 3% yield on treatment of tetrafluoromethane with a mixture of I_2 and $^{18}F_2$:[35]

$$CF_4 \xrightarrow{^{18}F_2+I_2} CF_2{}^{18}FI.$$

Replacement of chlorine at an allylic position by iodine in cyclic and aliphatic chloroperfluoroalkenes is achieved by treatment with sodium iodide in solution at room temperature. Replacement of fluorine on sp^2-hybridised carbon does not occur in this case.[36–39]



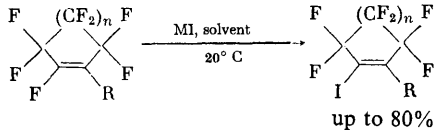
[36]



[38, 39]

[37]

At the same time substitution of a fluorine atom at a vinyl position mainly occurs for perfluorinated cycloalkenes.[40–42] This forms the basis of the preparation of iodoperfluorocycloalkenes by treatment of the respective perfluorocycloalkenes with potassium iodide[40] or sodium iodide[41–43] in a polar solvent. At an elevated temperature the formation of diiodoperfluorocycloalkenes along with the monosubstituted derivative is possible.[43]



,

n = 1, 2; R = CF_3, F; M = Na, K.

At the same time when a fluorine and chlorine atom occur on an sp^2-hybridised carbon it is the chlorine atom which is replaced,[44,56] which corresponds to the order of replacement at an allylic position.

$$(CF_3)_2C{=}CFCl \xrightarrow[\text{refluxing}]{\text{NaI, acetone}} (CF_3)_2C{=}CFI.$$

60%

On treatment of tetraiodoethylene with iodine pentafluoride, addition of fluorine to the double bond takes place together with the replacement of three iodine atoms leading to the formation of iodopentafluoroethane.[1] This method has no preparative value.

$$CI_2{=}CI_2 \xrightarrow[0-130^\circ C]{IF_5} CF_3{-}CF_2I.$$

26%

An interesting case of the formation of iodopentafluoroethane on treatment of iodotrifluoroethylene with an $F_3NO.BF_3$ complex at low temperatures has been reported in a patent.[46]

$$CF_2{=}CFI \xrightarrow[-196^\circ C]{F_3NO\cdot BF_3} CF_3CF_2I.$$

2. Preparation from derivatives of perfluorocarboxylic acids

The slow heating of anhydrous silver perfluoroalkanecarboxylates with a slight excess of iodine (the Borodin–Hunsdiecker reaction) affords the corresponding iodoperfluoroalkanes in high yield.[47,48] The reaction is versatile and can be used to synthesise not only aliphatic[47] but also cyclic[22] and perfluoroalkoxyl iodides[49] as well as diiodoperfluorocarbons (in the case of dibasic acids).[22] This method is important industrially—for the production of CF_3I, for example.

It is assumed[50] that the Borodin–Hunsdiecker reaction occurs via the formation of acyl hypoiodites.

$$R_fCOOAg \xrightarrow{I_2} [R_fCOOI + AgI] \longrightarrow R_fI + AgI + CO_2$$

$R_f{=}C_nF_{2n+1}$ [47], $CF_3OCF_2CF_2$ [49],

$I(CF_2)_n$, cyclo-C_8F_{11} [22].

Iodoperfluoroalkanes can also be obtained from salts of alkali metals[51] or mercury,[52] but in lower yield. The reaction is usually carried out in an aprotic polar solvent. When iodine is replaced by the more polar iodine monochloride in this reaction, the yield of IPFAs does not increase.[53] The two-stage nature of the process and the length of time needed for evaporation and drying of the intermediate salts have impeded the application of this method in industry.

Iodoperfluoroalkanes are also formed by the decomposition of perfluorocarboxylic acid derivatives. Thus, electrolysis of trifluoroacetyl hypoiodite[54] or the decomposition of trifluoroacetyl iodide at room temperature in the presence of hexamethyldistannane[55] gives iodotrifluoromethane in low yield.

$$CF_3COOI \xrightarrow{\text{electrolysis}} CF_3I \xleftarrow{(CH_3)_3Sn-Sn(CH_3)_3} CF_3COI.$$

A method for the synthesis of higher iodoperfluoroalkanes by reaction of the corresponding acids with iodine and benzoyl peroxide has been developed.[56–59] The reaction is radical in nature and takes place in a nonpolar solvent (dibromo- or dichloro-ethane, dibromopropane). The method of preparing IPFAs as described in a patent[56] has industrial value.

$$F(CF_2)_7COOH \xrightarrow[BrCH_2CH_2Br;\ 110^\circ C]{I_2 + (C_4H_3COO)_2} F(CF_2)_7I \quad .$$

60%

3. Preparation from perfluoroalkenes

Because of the ready availability of lower perfluoroalkenes, iodotrifluoromethane, and iodofluorinating agents at the present time, the synthesis of IPFAs from perfluoroalkenes has assumed increasing importance and has been developed in three areas: electrophilic iodofluorination, nucleophilic iodofluorination, and telomerisation of perfluoroalkenes with iodotrifluoromethane and iodopentafluoroethane.

Electrophilic iodofluorination. This was first reported in the case of tetrafluoroethylene (TFE) when a mixture of iodine and iodine pentafluoride was used.[60–62] The reaction takes place via the formation of a carbocation on addition of iodine to the alkene. The reaction is suitable for alkenes with different structures,[63,64] including

perfluoroisobutene[65,66] and perfluoromethylvinyl ether.[67] High yields of the products were obtained (Table 1).

$$R^1R^2C{=}CF_2 + [I{-}F] \xrightarrow{(IF_5+2I_2)} [R^1R^2C\overset{+}{C}F_2] \xrightarrow{F^-} R^1R^2ClCF_3.$$

Iodopentafluoroethane was obtained at 60–80 °C and atmospheric pressure in 90% yield. The conversion of tetrafluoroethylene was 40%.[68] The latter increases on introducing catalysts such as metals[73] or their salts[69–72] into the iodofluorinating mixture. Metal fluorides[69–71] are recognised as the most effective catalysts of the electrophilic iodofluorination of TFE. The methods reported in two Japanese patents[70,71] have been used in the industrial production of iodopentafluoroethane.

Table 1. Yields of products of the iodofluorination of $R^1R^2C{=}CF_2$

R^1	R^2	Yield, %	R^1	R^2	Yield, %
H	F	76 *	F	CF_3O	94
Cl	F	95 *	F	CF_3	69
F	F	99	F	F	90
F	CF_3	69	F	F	70

*Total yield of isomers is given.

Electrophilic iodofluorination of excess TFE with a mixture of iodine and iodine pentafluoride in the presence of antimony fluorides gives a mixture of telomeric IPFAs[74–77] with a small quantity of C_2F_6:

$$CF_2{=}CF_2 \xrightarrow[[SbF_5;\ SbF_3]]{I_2+IF_5} F(CF_2CF_2)_nI + ICF_2CF_2I + \text{cyclo-}C_4F_8 + C_2F_6,$$

$$n=1-8.$$

Iodoperfluoroalkane polyfluorides have been proposed for the electrophilic iodofluorination of hexafluoropropene (HFP).[78]

The principles of the electrophilic addition of interhalogen compounds have been reviewed.[79]

Nucleophilic iodofluorination. This was first put forward by several authors[80–82] in the 1960s and is achieved in aprotic polar solvents on heating. The reaction is initiated with the addition of a fluoride anion to perfluoroalkene. Thus, for example, 2-iodoperfluoropropane is obtained by reaction of HFP with iodine and potassium fluoride in acetonitrile at 100 °C in an autoclave.[80]

$$CF_3CF{=}CF_2 \xrightarrow[CH_3CN]{KF} CF_3{-}\overline{C}F{-}CF_3 \xrightarrow[CH_3CN]{I_2} \underset{60\%}{CF_3CFICF_3}.$$

Even perfluoro-2-butene,[80] which is extremely stable towards iodofluorination,[63] reacts under such conditions. The nucleophilic iodofluorination of perfluoroisobutene takes place the most readily,[82–84] giving 2-iodoperfluoro-2-methylpropane in high yield. In this case even bound iodine (from an organic compound) adds to the intermediate perfluoro-t-butylcarbanion.[85–87]

$$(CF_3)_2C{=}CF_2 \xrightarrow{CHI_3+KF} \underset{7\%}{(CF_3)_3CI}.$$

Iodoperfluorocyclobutane is formed in a nucleophilic iodofluorination reaction of perfluorocyclobutene.[80] Conjugated nucleophilic addition of (IF) to perfluoro(methyl vinyl ether) only occurs under severe conditions, giving 1-iodoperfluoro-1-methoxyethane in negligible yield.[67] Lur'e, et al.[67] attribute this to destabilisation of the intermediate $CF_3O\overline{C}FCF_3$ by the electron pair of the neighbouring oxygen. An industrial method for the iodofluorination of TFE using hydrogen fluoride and lead(II) oxide has been reported in a French patent.[88]

$$CF_2{=}CF_2 \xrightarrow[200^\circ C]{I_2,\ HF,\ PbO} \underset{90\%}{CF_3CF_2I}.$$

2-Iodoperfluoro-2-butene has been obtained in a similar manner from perfluoro-2-butyne.[89]

$$CF_3C{\equiv}CCF_3 \rightarrow CF_3CF{=}ClCF_3.$$

A modification of this reaction occurs in the preparation of iodoperfluoroalkoxyalkanes with a branched chain[90,91] by reaction of hexafluoroacetone with the respective alkene and I_2 in the presence of excess alkali metal fluoride in a solvent.[90–95]

$$(CF_3)_2C{=}O \xrightarrow{F^-} (CF_3)_2CF{-}O^- \xrightarrow{RCF=CF_2} (CF_3)_2CFOCF_2\bar{C}FR \xrightarrow{I_2} \rightarrow (CF_3)_2CFOCF_2CFIR.$$

R=F (17%), CF_3 (13%) [89].

The nucleophilic iodofluorination of perfluoroalkenes has been studied in greater detail in a review by Joung,[96] and the mechanism of the reaction between alkoxide anion and fluorine-containing alkenes in the presence of iodine is examined in a report by Evans, et al.[97]

Radical iodofluorination. Radical iodofluorination of perfluoroalkenes has not been used very extensively. Only the preparation of 2-iodoperfluoropropane from hexafluoropropane has been reported.[98]

$$CF_3CF{=}CF_2 \xrightarrow{F_2+I_2} \underset{60\%}{CF_3CFICF_3}.$$

With the methods for preparing iodoperfluoroalkanes and iodoperfluoroalkoxyalkanes examined above it is possible to obtain mainly compounds with a short carbon chain containing up to eight carbon atoms.

Radical addition. For the synthesis of higher IPFAs, radical addition of lower iodoperfluoroalkanes and iodoperfluoroalkoxyalkanes to perfluoroalkenes is normally used, frequently with

oligomerisation of the latter occurring at the same time. The process is usually carried out in solution under pressure in the presence of metal salts.[99–102]

Thus, IPFAs with 5–29 carbon atoms in the chain have been obtained by addition of CF_3I to TFE.[102] This method is important industrially. However, on exposure to radiation IPFAs are formed containing not more than 11 carbon atoms in the chain.[103] Higher IPFAs are also obtained by electrophilic iodofluorination of TFE[76] together with C_2F_5I (see above). These methods have future potential for the production of higher perfluorocarboxylic acids from the corresponding IPFAs.[104]

The addition of CF_3I to HFP is not regiospecific and occurs with a low conversion. The formation of specific products depends on the conditions. Thus, Deev, et al,[27] on conducting the reaction in a nickel tube at a temperature of up to 380 °C, succeeded in obtaining about 77% 2-iodoperfluoro-2-methylpropane.

$$CF_3I + CF_3CF{=}CF_2 \xrightarrow{h\nu} CF_3CFIC_2F_5 + (CF_3)_2CFCF_2I \quad [105]$$
$$80\% \qquad 20\%$$
$$CF_3I + CF_3CF{=}CF_2 \xrightarrow[320-380^\circ C]{[Ni]} CF_3CFIC_2F_5 + (CF_3)_2CFCF_2I + (CF_3)_3CI \quad [27]$$
$$9\% \qquad 6\% \qquad 77\%$$

It was possible to obtain trifluoromethyl-substituted IPFAs containing more than 33 carbon atoms from HFP and higher IPFAs by oligomerisation on exposure to radiation.[106] Branched perfluoroalkenes containing more than three carbon atoms on exposure to radiation with iodotrifluoromethane give products derived from the replacement of fluorine at vinyl and allyl positions together with addition products.[107]

$$CF_3I + (CF_3)_2CFCF{=}CF_2 \xrightarrow{h\nu}$$
$$\longrightarrow (CF_3)_2CFCFICF_2CF_3 \quad 22\%$$
$$\longrightarrow (CF_3)_2CFCF(CF_3)CF_2I \quad 5\%$$
$$\longrightarrow (CF_3)_2CFCI{=}CF_2 \quad 16\%$$
$$\longrightarrow (CF_3)_2C{=}CFCF_2I \quad 12\%$$
$$\longrightarrow (CF_3)_2CFCFICF_3 \quad 2\%$$

Oligomerisation of tetrafluoroethylene with C_2F_5I in the presence of antimony pentafluoride or organic peroxides under pressure and at an elevated temperature[108,109] gives IPFAs with an even number of carbon atoms in the chain.

$$C_2F_5I + nCF_2{=}CF_2 \xrightarrow[(CCl_2{=}CClCOO)_2]{65-75\ ^\circ C,\ 7-10\ atm} C_2F_5(CF_2CF_2)_nI \quad n=1-5,\ 95-97\%$$
$$C_2F_5I + nCF_2{=}CF_2 \xrightarrow[(C_6H_5COO)_2]{125^\circ C} C_2F_5(CF_2CF_2)_nI \quad n=5-7,\ 95\%$$

Both of the isomeric iodoperfluoropropanes undergo a similar reaction, forming IPFAs with 21–25 carbon atoms.[110,111] IPFAs with an isomeric structure containing from 5 to 23 carbon atoms are obtained by oligomerisation of $(CF_3)_2CFI$ with TFE in the presence of peroxides.[110,112,113] In the absence of catalysts IPFAs can be obtained under pressure.[114]

The aqueous-emulsion oligomerisation of TFE with $(CF_3)_2CFI$ or C_2F_5I at 15–30 °C in the presence of ammonium persulphate or emulsifying agents has been reported.[115]

$$(CF_3)_2CFI + nCF_2{=}CF_2 \xrightarrow[[NaHSO_4+C_8F_{17}COONH_4]]{[(NH_4)_2S_2O_8]} (CF_3)_2CF(CF_2CF_2)_nI$$
$$n=2-5,\ 63\%.$$

Thus, by varying the initial reactants and their ratio, using different catalysts and solvents, and changing the process conditions it is possible to obtain iodoperfluoroalkanes and iodoperfluoroalkoxyalkanes with quite a long carbon chain. Even though the use of a telomerisation process leads to the formation of a wide range of products that are difficult to separate, the production of iodoperfluoroalkanes with seven or more carbon atoms in the chain is actually based on this process.

4. Other methods for preparing iodoperfluoroalkanes

It was shown by Knunyants, et al.[26] that reaction between nitrosoperfluoroalkanes with iodine in an aprotic polar solvent leads to the formation of IPFAs in high yield.

$$R_fNO + I_2 \xrightarrow{50-70^\circ C} R_fI \quad 80-95\%$$
$$R_f{=}CF_3,\ C_3F_7,\ (CF_3)_3C.$$

Iodotrifluoromethane is formed by prolonged UV irradiation of methyl trifluoromethyl sulphide[116] and bis(trifluoromethyl) sulphide[117] in the presence of sources of iodine radicals.

$$CF_3SCF_3 \xrightarrow[h\nu]{n\text{-}C_3F_7I} CF_3I \xrightarrow[h\nu]{CH_3I} CF_3SCH_3$$
$$64\%\ [117] \qquad 30\%\ [116]$$

On treatment of perfluoropropane-2-sulphinic acid with iodine monochloride, 2-iodoperfluoropropane was formed in 33% yield.[118] The action of an alcoholic solution of iodine on perfluoroalkanesulphonyl chloride at an elevated temperature results in the replacement of the sulphonyl chloride group by iodine.[119]

$$R_fSO_2X \xrightarrow[R_f'=(CF_3)_2CF,\ X=H]{ICl} (CF_3)_2CFI$$
$$R_fSO_2X \xrightarrow[R_f=R_f'OCF_2CF(CF_3)OCF_2,\ X=Cl]{I_2} R_f'OCF_2CF(CF_3)OCF_2I.$$

Oxidation of the triiodomethyl ester of n-perfluoropropanesulphonic acid on exposure to UV radiation gives 1-iodoperfluoropropane through removal of iodine from the triiodomethyl group.[120]

$$n\text{-}C_3F_7SO_3CI_3 \xrightarrow{\text{UV irradiation, } O_2} n\text{-}C_3F_7I.$$

The progress made by different research workers[121,122] in the 1980s in studies on the chemistry of perfluoroalkenyl fluorosulphates led to the development of a preparative method for the synthesis of 1-iodoperfluoro-2-propene and other 1-iodoperfluoro-2-alkenes through replacement of the fluorosulphate group by iodine and made this class of compounds, which was previously little-studied but very promising in terms of synthesis, quite accessible.

$$R_fCF_2OSO_2F \xrightarrow{NaI,\ solvent} R_fCF_2I$$
$$R_f=CF_2=CF,\quad CCl_2=CCl,\quad (CF_3)_2CFCF=CF,\quad (CF_3)_3CCF=CF.$$

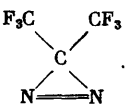
Iodoperfluoroalkanes are also formed by reaction of perfluoroalkyl-containing organoelemental compounds with iodine[123–129] or iodine monochloride.[130] Thus, reaction of iodine with $(CF_3)(CH_3)_2Bi$ or iodine monochloride with $(CF_3)_3Bi$ [123] gives iodotrifluoromethane, while reaction of iodine with bis-(perfluoroisopropyl)mercury gives 2-iodoperfluoropropane.[124] The replacement of halogens in haloperfluorocycloalkenes by iodine in the presence of ethylmagnesium bromide constitutes a variant of this method.[45]

Mixed alkylpolyfluoroalkylsilanes[125] and organolithium compounds behave in a similar manner. The latter are obtained at quite low temperatures.[126,129] It has been shown that the reaction is nucleophilic in nature towards iodine.[126]

$$(R_f)_n - M - R_m + I_2 \xrightarrow[\text{acetonitrile}]{DMF\ or} R_fI.$$

Small quantities of 2-iodoperfluoro-2-methylpropane are obtained from perfluoro-t-butyl chloroformate and potassium iodide or bis(trifluoromethyl)diazirine and iodotrifluoromethane.[26]

$$(CF_3)_3COCOCl \xrightarrow[\text{yield 30\%}]{KI,\ 180-200\ ^\circ C} (CF_3)_3Cl \xleftarrow[\text{yield 10–12\%}]{CF_3I,\ 150-200\ ^\circ C}$$



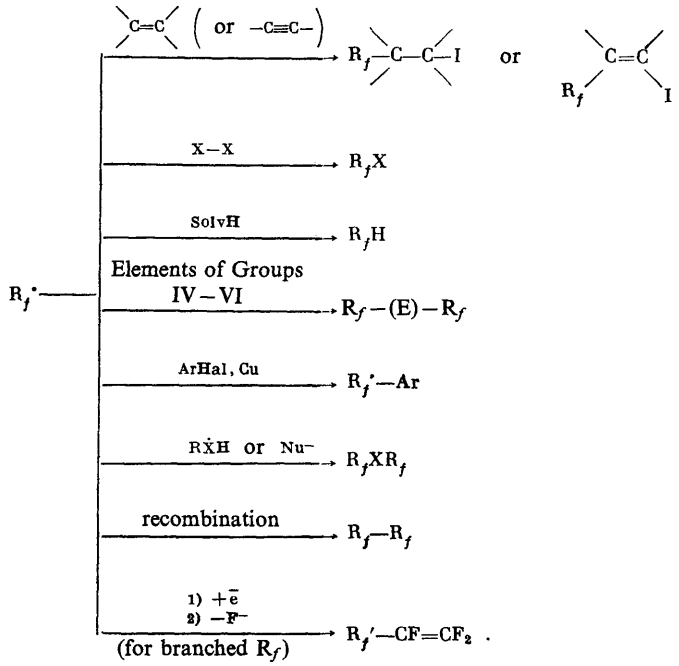
Thus, it is possible to approach the synthesis of IPFAs in different ways, but only some of the methods examined can be used in industry. Amongst these are the reaction of perfluorocarboxylates of Group I metals with iodine, the catalytic electrophilic iodofluorination of perfluoroalkenes, fluorination of diiodoperfluoroalkanes, and the oligomerisation of TFE and HFP with iodotrifluoromethane, iodopentafluoroethane, and iodoperfluoropropanes. The reaction between polyfluoroalkyl fluorosulphates and sodium iodide also appears to have considerable potential.

III. Chemical properties of iodoperfluoroalkanes

The energy of the C–I bond in iodoperfluoroalkanes is low, and they readily undergo homolytic dissociation to form $R_f^{\cdot}$ and $I^{\cdot}$ radicals on thermal or photochemical excitation. They yield an $R_f^{\cdot}$ radical from the action of radical initiators (RIs) or $R_f^{\cdot}$ and I^- on capture of an electron from an electron donor [optical electron detector (OED)] although in far from every case is it possible strictly to distinguish these reactions.

$$R_f^{\cdot} + I^- \leftarrow R_fI^{\cdot-} \xleftarrow{OED} R_fI \xrightarrow{RI} R_f^{\cdot}.$$

The resulting perfluoroalkyl radicals $R_f^{\cdot}$ are highly reactive and are stabilised through addition to carbon–carbon multiple bonds, homolytic cleavage of the bonds of molecules of substrate or solvent, and as a result of perfluoroalkylation of aromatic compounds, nucleophiles, and certain elements, and to a lesser degree by recombination or reduction to a perfluorocarbanion followed by ejection of F^- and formation of an alkene:



On the whole the above scheme almost completely governs the chemical properties and general trend for the synthetic use of IPFAs, which are characterised exclusively by radical or radical anion processes rather than by ionic reactions as proposed in early studies.[22,84,131] Beyond the scope of our review is a small group of reactions, also partly radical in nature, related to the oxidative conversions of iodine itself in an IPFA molecule, the oxidative degradation of $R_f^{\cdot}$, the formation of donor-acceptor complexes, and the halodefluorination of the CF_2I group, which are also examined in the present review.

Through lack of sufficient space we shall not examine the radical addition reactions of IPFAs to multiple bonds, as analysed in a monograph,[7] except for those reactions with unsaturated compounds that contain in addition to the multiple bond other functional groups. Reactions that are initiated by one-electron transfer have also been excluded.

1. Addition to unsaturated functional compounds

Radical reaction of iodoperfluoroalkanes with alkenes containing functional groups occurs exclusively as an addition to the C=C bond without affecting the functional groups[132,133] whereas radical-ion reactions can also occur on the functional groups. As a rule the reactions take place on treatment with conventional radical initiators such as azo compounds,[134,135] and hydrocarbon[136] and fluorinated[137] peroxides. In certain cases initiation is achieved photochemically, with the reaction carried out in a solvent.[132]

Thus, CF_3I adds to methyl vinyl ketone at its C=C bond with an anti-Markownikoff orientation.[138]

$$CF_3I + CH_2{=}CHCOCH_3 \xrightarrow{h\nu} CF_3CH_2CHICOCH_3.$$

The radical reaction of other iodoperfluoroalkanes[133–135,139–153] and iodoperfluoroethers[154,155] with unsaturated alcohols,[133–135,139–144] alkoxy alcohols,[134,147–152] and diols[153] occurs in a similar manner. Most frequently the reactions are carried out in the presence of azobis(isobutyronitrile) (ABN) at its decomposition temperature (70–85 °C),[134,135] while peroxides[136] or UV irradiation with heating[155] are used less often.

$$CH_2{=}CH{-}R{-}CH_2OH + R_fI \xrightarrow{\text{[initiator]}} R_fCH_2CHI{-}R{-}CH_2OH,$$

$R_f = C_3F_7,\ C_4F_9,\ (CF_3)_2CF,\ (CF_3)_2CFO(CF_2)_8;$

$R = -CH_2OCH_2\underset{|}{C}HOH,\ -CH_2OCH_2\underset{|}{C}HCH_3,\ -CH_2OCH_2-,$
$-(CH_2)_9-$ [133–135, 147–154].

Unsaturated carboxylic acids,[137,156–158] their amides,[159] and nitriles and esters[137,138,158,160–164] behave in a similar manner.

$$R_fI + CH_2{=}CH(CH_2)_nC(O)X \xrightarrow[ABN]{70-80^\circ C} R_fCH_2CHI(CH_2)_nC(O)X,$$

X=OH: $R_f = CF_3,\ C_3F_7,\ C_4F_9,\ C_6F_{13},\ C_7F_{15}$,

n=0–4 [137, 156–158];

$X=NH_2$: $R_f = C_7F_{15}$, n=8 [159];

X = OR: $R_f = (CF_3)_2CFO(CF_2)_m$,
where m = 2, 5, 6, n = 8 — 18 [160, 162, 163, 165];

$R_f = (CF_3)_2CF,\ CF_3(CF_2)_m$,

where m = 1 — 7, n = 1, 2 [162, 163].

$$R_fI + CH_2{=}CH(CH_2)_nCN \xrightarrow{\text{[initiator]}} R_fCH_2CHI(CH_2)_nCN,$$
$R_f = CF_3$, n=0 [138]; $R_f = C_3F_7$, n=1, 2 [158, 163].

Carboxylic acids with two or three CH_2 groups between the carboxyl group and the double bond constitute an exception. After addition of R_fI to the double bond these acids undergo lactonisation through intramolecular nucleophilic dehydroiodination. The process is assisted by *gem*-substitution.[137]

$$R_fI + CH_2{=}CHCH_2\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}COOH \xrightarrow{\text{[initiator]}} R_f{-}CH_2{-}CHICH_2\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}COOH \xrightarrow[-HI]{}$$

$$\longrightarrow R_f{-}CH_2{-}\underset{\displaystyle H_3C\ CH_3}{\overset{\displaystyle O}{\overset{|}{\underset{|}{C}}}}{=}O \quad .$$

With initial esterfication of the carboxyl group it is possible to obtain esters of unsaturated carboxylic acids with perfluoroalkyl substituents from these acids.[137]

$$CH_2{=}CHCH_2\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}COOR \xrightarrow[2)\ -HI]{1)\ C_6F_{13}I,\ [ABN]} C_6F_{13}CH{=}CHCH_2\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}COOR.$$

There is no information available on the addition of IPFAs to unsaturated functional compounds with a trifluorovinyl group.

The products of the addition of IPFAs to unsaturated compounds as listed above have considerable industrial value since they are the starting compounds for the synthesis of organofluorine surfactant and textile-auxiliary materials (see, for example, several studies).[133–136,147–163,166–168]

The radical addition of IPFAs to vinyl and allyl esters of carboxylic acids occurs in a similar manner.[161,166–170] All of the members of the homologous series of iodoperfluoroalkanes up to n = 14 undergo a reaction with vinyl acetate.[166,170] The reaction provides a preparative method for the synthesis of higher homologues of carboxylate esters with a terminal polyfluoroalkyl group and an iodine atom at the β-position relative to the R_f substituent.[168,171]

$$C_3F_7I + CH_2{=}CH(CH_2)_nOCOCH_3 \xrightarrow[70^\circ C]{\text{[ABN]}} C_3F_7CH_2CHI(CH_2)_nOCOCH_3,$$
n=3–9.

The characteristics of the reaction between vinyl and allyl acetates and IPFAs in the presence of peroxides have been reviewed in a monograph.[7] Iodoperfluoro(isopropyl alkyl ethers)[160,162] react with vinyl acetates to form monomers for the synthesis of fluorine-containing polymers with unique properties.

$$(CF_3)_2CFO(CF_2)_{1-20}I + CH_2{=}CH(CH_2)_{0-8}OCOCH_3 \xrightarrow{\text{[initiator]}}$$
$$\longrightarrow (CF_3)_2CFO(CF_2)_{1-20}CH_2CHI(CH_2)_{0-8}OCOCH_3.$$

The addition of nonbranched IPFAs to unsaturated carbocyclic acids occurs stereospecifically (up to 97% *exo* isomer is formed), whereas branched IPFAs form *endo* and *exo* isomers in a ratio of about 1 : 1.[171]

Radical addition of IPFAs to amines containing a double bond in the carbon chain[147] and perfluorovinyl sulphur pentafluoride[172] also results in saturation of the C=C bond.

$$CF_3CF_2CFISF_5 \xleftarrow[R_f = CF_3]{CF_2{=}CFSF_5,\ h\nu} R_fI \longrightarrow$$

$$\xrightarrow[\text{[ABH]};R_f = C_7F_{15}]{CH_2{=}CHCH_2NHC_2H_5} C_7F_{15}CH_2CHICH_2NHC_2H_5.$$

The radical reaction of iodoperfluoroalkanes with acetylenic compounds containing other functional groups,[164] including silicon[173] and germanium[174] atoms, generally occur in a similar manner with these groups remaining unaffected. A characteristic of these reactions is the inability of the resulting perfluoroalkyl-substituted alkenes to react further with IPFAs, apparently because of the inductive effect of R_f, which renders the double bond inert. For example, the addition of 1-iodoperfluoropropane to diethyl propargylmalonate[164] stops when the monoadduct is formed.

$$\begin{array}{c} CH_2C{\equiv}CH \\ | \\ C_2H_5OCOCHCOC_2H_5 \end{array} \xrightarrow{C_3F_7I} \begin{array}{c} CH_2CI{=}CHC_3F_7 \\ | \\ C_2H_5OCOCHCOC_2H_5 \end{array}.$$

Radical addition of IPFAs to functionally substituted olefins and acetylenes is a convenient method of preparing polyfluoroalkyl-substituted compounds.

2. Stabilisation of $R_f^{\cdot}$ radicals by addition to elements of Groups IV–VI and their derivatives

Apart from the addition to unsaturated carbon–carbon bonds, a set of radical reactions with elements of Groups IV–VI (S, Se, P, As) and their compounds, occurring as a result of the unfilled state of the outer electron shells of these elements, is also characteristic of IPFAs. Thus, the reaction of iodoperfluoroalkanes with sulphur at 250 °C gives a mixture of di- and tri-sulphides,[175,176] while at 300 °C a mixture of mono-, di-, and tri-sulphides is formed. The reaction of branched IPFAs with sulphur occurs in a similar manner.[177]

$$R_fI \xrightarrow{250-300^\circ C} R_f^{\cdot} + I^{\cdot},$$
$$R_f^{\cdot} + S \rightarrow R_fS^{\cdot},$$
$$R_fS^{\cdot} + R_fS^{\cdot} \rightarrow R_fSSR_f + R_fSS^{\cdot} + R_f^{\cdot},$$
$$R_fS^{\cdot} + S \rightarrow R_fSS^{\cdot},$$
$$R_fSSR_f + R_fSS^{\cdot} \rightarrow R_fSSSR_f + R_fS^{\cdot},$$
$$R_fSS^{\cdot} + S \rightarrow R_fSSS^{\cdot},$$
$$R_fSSS^{\cdot} + R_fSR_f \rightarrow R_fSSSR_f + R_fS^{\cdot},$$
$$R_fS^{\cdot} + R_f^{\cdot} \rightarrow R_fSR_f.$$

At the same time, when IPFAs were reacted with HgS,[177] only 22% bis(perfluoroisopropyl) disulphide was formed, with 74% conversion of 2-iodoperfluoropropane leading to the formation of 2,3-perfluorodimethylbutane through recombination of perfluoroisopropyl radicals.

Under more severe conditions perfluorinated iodine-containing ethers react with sulphur to give mainly disulphides.[178]

$$2(CF_3)_2CFOCF_2CF_2I \xrightarrow{S;\ 450^\circ C} [(CF_3)_2CFOCF_2CF_2S]_2.$$

Reactions of IPFAs with selenium can be carried out in continuous flow systems,[179] with diselenides mainly being formed in good yield.

$$CF_3I + Se \xrightarrow[40-160\ s]{300-350\ ^\circ C} \underset{79\%}{CF_3—Se—Se—CF_3}.$$

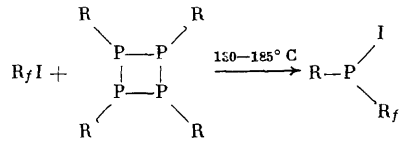
A characteristic of reactions of IPFAs with sulphur and selenium is the participation of the resulting $I^{\cdot}$ radicals solely in chain termination.

In reactions of IPFAs with phosphorus and arsenic[180–185] different types of phosphines and arsines are obtained depending on the structure of the perfluoroalkyl radicals. For the reaction of iodotrifluoromethane the formation of all three possible iodotrifluoromethylphosphines, apparently through the participation of iodine atoms along with $R_f^{\cdot}$ in chain termination, has been detected.[181,182]

$$CF_3I + P \xrightarrow[pressure]{220\ ^\circ C;\ 48\ h} (CF_3)_3P + (CF_3)_2PI + CF_3PI_2.$$

The formation of tris(perfluoroalkyl)phosphines and tris(perfluoroalkyl) arsines does not occur in the case of longer perfluoroalkyl radicals (C_2-C_{10}).[183–185]

Asymmetric iodophosphines have been obtained in reactions of IPFAs with tetrakis(alkyl or perfluoroalkyl)cyclotetraphosphines.[186–188]



$R=CF_3,\ C_3F_7,\ (CF_3)_2CF,\ C_2H_5;\quad R_f=C_2F_5,\ (CF_3)_2CF.$

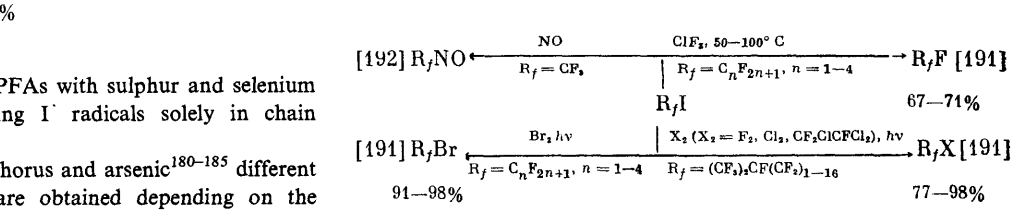
It has been established kinetically that on changing from n-C_3F_7I to $(CF_3)_2CFI$ the rate constant and energy of activation of the reaction are reduced [*sic*. The latter is presumably increased, (Ed. of Translation)], namely, the reactivity of the iodoperfluoroalkanes decreases as the degree of chain branching increases, because of both the increasing electronegativity of the fluoroalkyl group and steric hindrance.

A general reaction of nonbranched iodoperfluoroalkanes is their addition to silicon difluoride.[189]

$$R_fI + SiF_2 \rightarrow R_fSiIF_2,$$
$R_f=CF_3,\ C_2F_5,\ C_3F_7.$

3. Stabilisation of $R_f^{\cdot}$ radicals through cleavage of single bonds

In addition to radical reactions involving the addition to carbon–carbon multiple bonds, IPFAs exhibit a wide range of reactions with stabilisation of $R_f^{\cdot}$ through cleavage of the single bonds of organic and inorganic molecules and the subsequent formation of products that are more stable under the conditions of radical decomposition than the initial IPFAs. During radical initiation the iodine atom of IPFAs is readily replaced by more electronegative halogens or groups,[190–194] resulting in the formation of more stable polyfluoroalkyl-containing compounds. In this case the primary radical source can be a halogen molecule,[192,193] if the energy of its homolytic dissociation is lower than that of the IPFA.



On the other hand, in the radical reaction of IPFAs with cyanogen, in which it is possible to obtain nitriles of the corresponding perfluoroalkylcarboxylic acids in quantitative yield, the IPFAs act as a radical source.[194] The radical nature of the reaction is confirmed by the presence of a small quantity of product derived from the coupling of polyfluoroalkyl radicals:

$$R_fI + (CN)_2 \xrightarrow[pressure]{350^\circ C} R_fCN + \underset{\text{trace amounts}}{R_f—R_f}.$$

On reacting with hydrogen, IPFAs are converted to monohydroperfluoroalkanes.[195] The involvement of hydrocarbon iodoalkanes in radical reactions is also possible. Thus, 1,1,1-trifluoroethane and 1,1-difluoroethylene are formed from iodomethane. The latter is formed as a result of stabilisation of the excited state of 1,1,1-trifluoroethane through elimination of HF.[198,199]

$$CF_3I + CH_3I \xrightarrow{h\nu} CF_3CH_3^* + I_2 \xrightarrow[-HF]{} CF_2{=}CH_2.$$

Stabilisation of an $R_f^{\cdot}$ radical may also be achieved by the removal of a proton from a C–H bond of alcohols,[152] alkanes, cycloalkanes,[200–202] and alkylsilanes.[203]

$$CF_3H \xleftarrow[h\nu;\ 100^\circ C]{(CH_3)_3SiSi(CH_3)_3} CF_3I \xrightarrow[C_3H_8 \text{ or cycloalkane}]{h\nu} CF_3H.$$

Reactions of IPFAs by a radical mechanism depend in many respects on the process conditions and are principally governed by initiation (thermal, photochemical, or using initiators). The addition of IPFAs to multiple bonds and elements of Groups IV–VI as well as reactions with cleavage of X–X bonds (X = CN, Hal) occur most frequently by this mechanism. By varying the methods of generating radicals and the length and branching of the hydrocarbon chain of IPFAs it is possible to influence the reaction route, achieving the formation of given products. A characteristic of all these processes is that other functional groups present in the molecule, such as a nitrile group as well as the perfluoroalkyl-substituted double bond formed from alkynes, are stable towards IPFAs during reaction.

A radical mechanism is in doubt for certain cases of these reactions, since in addition to energetic excitation of the molecules there is the theoretical possibility of electron transfer, and this in turn can alter the process mechanism.[204]

4. Oxidation of iodoperfluoroalkanes

The oxidation of IPFAs is one of the few reactions which, depending on the conditions and nature of the oxidising agent, occurs either on the iodine atom or on the perfluoroalkyl group leading to its degradation.

Oxidation of IPFAs on the iodine atom. This gives perfluoroalkyl compounds of polyvalent iodine and takes place with all of the bonds being preserved in the molecule. Of reactions of this type, prominence should be given to oxidative halogenation. This reaction was first carried out using chlorine trifluoride,[205,206] and then subsequently with fluorine diluted with nitrogen[207] and with xenon difluoride.[208] Depending on the reagent, oxidative fluorination occurs with the formation mainly of perfluoro-alkyliodine tetrafluorides and perfluoroalkyliodine difluorides. A similar reaction may be carried out when other oxidising agents such as chlorine nitrate or perchlorate[210–212] and trifluoroperacetic acid[209] are used. The ratio of the iodine oxidation products depends on the reaction conditions.

R_fI —

- $\xrightarrow[T<0^\circ C]{ClF_3}$ $R_fIF_4 + R_fIF_2$ ($R_f = C_nF_{2n+1}$), trace amounts, $n = 2-22$ [205, 206]; (when $R_f = CF_3$ yield of R_fIF_4 100%)
- $\xrightarrow[-78^\circ C]{F_2/N_2,\ CCl_3F}$ R_fIF_2 ($R_f = CF_3$ [207])
- $\xrightarrow[20^\circ C]{XeF_2}$ R_fIF_2 ($R_f = C_3F_7$; (60%) [208])
- $\xrightarrow[\text{pressure}]{ClONO_2}$ $R_fI(NO_2)_2$ ($R_f = CF_3$ [210])
- $\xrightarrow[-78\text{—}-20^\circ C]{ClONO_2,\ CCl_3F}$ $R_fICl(NO_2)$ + $R_fI(NO_2)_2$ ($R_f = CF_3$ [211])
- $\xrightarrow{ClOClO_3}$ $R_fI(OClO_3)_2$ ($R_f = (CF_3)_2CF$ [212])
- $\xrightarrow[(CF_3CO)_2O,\ CF_3COOH]{80\%\ H_2O_2}$ $R_fI(OCOCF_3)_2$ ($R_f = C_3F_7$; (65%) [209]).

The resulting perfluoroalkyliodine difluorides and tetrafluorides are sensitive to hydrolysis. The stability of the tetrafluorides at 20 °C increases in the series

$$CF_3 < (CF_3)_2CF < C_6F_5 \ [206].$$

Perfluoroalkyliodine dinitrates and diperchlorates are obtained in low yield, probably because of their low stability at room temperature compared to the corresponding polyfluorides. The decomposition of perfluoroalkyliodine dinitrates may evidently occur according to the following scheme:[210,211]

$$10CF_3I(NO_3)_2 \rightarrow 5CF_3I + 5COF_2 + 10N_2O_5 + I_2 + IF_5 + I_2O_5.$$

Starting from perfluoroalkyliodine difluorides and acetates, L M Yagupol'skii, et al.[6,209,213] developed a preparative method for the previously inaccessible arylperfluoroalkyliodonium salts, which are convenient reagents for the preparative perfluoroalkylation of

different nucleophiles, which determines the considerable synthetic value of these compounds.

$$R_fIF_2 + BF_3 \longrightarrow R_f\overset{+}{I}FBF_4^- \xrightarrow{C_6H_5CH_3} CH_3C_6H_4\overset{+}{I}R_fBF_4^-;$$
87% (R_f=C_3F_7)
83% (R_f=C_6F_{13})

$$CH_3C_6H_4\overset{+}{I}R_fX^- + MNu \rightarrow R_fNu \quad [6]$$

M=Na, K; Nu=PhS, PhSe, NO_2, SCN, SeCN.

Oxidation with degradation of the perfluoroalkyl chain. Photochemical oxidation of perfluoroalkanes with oxygen occurs quite rapidly and is accompanied by stepwise degradation and the formation of carbonyl fluoride. When the oxidation is carried out in a quartz vessel, silicon tetrafluoride is also found amongst the reaction products. It is thought that decomposition of the perfluoroalkyl residue occurs via the formation of a perfluoroalkoxy radical. The latter, by eliminating COF_2, forms a new perfluoroalkyl radical which contains one less CF_2 group and which undergoes further oxidation.[22,214]

$$C_3F_7I \xrightarrow{h\nu} C_3F_7^{\cdot} + I^{\cdot} \xrightarrow{O_2} C_3F_7OO^{\cdot} \xrightarrow{C_3F_7I} C_3F_7OOI + C_3F_7^{\cdot} \xrightarrow{O_2} \text{etc.}$$

$$C_3F_7OOI + C_3F_7^{\cdot} \xrightarrow{C_3F_7I} C_3F_7O^{\cdot} + IO^{\cdot} \longrightarrow C_2F_5^{\cdot} + COF_2$$

$$C_2F_5^{\cdot} + COF_2 + I^{\cdot} \longleftarrow C_3F_7OI + C_3F_7^{\cdot}$$

$C_2F_5^{\cdot}$ + O_2 → etc.; $C_2F_5^{\cdot}$ + O_2 → etc.

In the presence of water or mixtures of water and chlorine and bromine, which is better, the radicals formed during oxidation undergo side reactions, giving perfluoroalkylcarboxylic acids. Thus, a mixture of acids is obtained on photochemical oxidation of 1-iodoperfluoropropane with oxygen in the presence of moist bromine.[22]

$$C_3F_7I \xrightarrow[h\nu]{O_2,\ Br_2,\ H_2O} \underset{45\%}{C_2F_5COOH} + \underset{23\%}{CF_3COOH}.$$

On treatment with other oxidising agents, such as oleum, degradation of the carbon skeleton does not usually occur, and polyfluorocarboxylic acid fluoride and a small quantity of perfluoroalkyl fluorosulphate are formed. Both products contain one less CF_2 group compared to the initial IPFAs.[215]

$$R_fCF_2I \xrightarrow[130-200\ ^\circ C,\ 1-20\ h]{\text{oleum}} \underset{88\%}{R_fCOF} + \underset{1.8\%}{R_fCOOH} + \underset{2.7\%}{R_fCF_2OSO_2F}.$$

When iodoperfluoroisopropoxyalkanes were oxidised with oleum, the product derived from the replacement of the fluorine atom of the fluorosulphate group in the by-product fluorosulphate by a second fluorosulphate group was identified together with the normal acid fluoride:[216]

$$(CF_3)_2CFO(CF_2)_6I \xrightarrow[140^\circ C]{SO_3} \begin{cases} \longrightarrow (CF_3)_2CFO(CF_2)_5COF \\ \longrightarrow (CF_3)_2CFO(CF_2)_6OSO_2OSO_2F. \end{cases}$$

The temperature of the process can be reduced by the addition of chlorine and zinc sulphates to oleum.[217] A number of methods for the oxidation of IPFAs to perfluorocarboxylic acid fluorides are currently available. It may be assumed that the process for preparing acid fluorides by oxidation of IPFAs (provided that iodine is returned to the process cycle) can compete successfully with the traditional method for preparing them—electrochemical fluorination in anhydrous hydrogen fluoride. Complex equipment design, high energy consumption, and low yields of acid fluorides because of degradation of the carbon skeleton of the initial molecule are characteristic of the latter.[16]

5. Formation of charge-transfer complexes

The polarisation of the C–I bond in IPFAs, which is the reverse of that in CH_3I, gives rise to their ability to form molecular complexes (1:1) with electron-donating solvents in which the iodine acts as the acceptor.[218–225] This is supported experimentally by the shift of absorption bands that are characteristic of IPFAs in the UV spectra[218,219] and by changes of the chemical shifts in the ^{19}F NMR spectra.[219]

$$R_f\overset{\curvearrowleft}{I} + :B \longrightarrow R_fI-B$$

R_f=CF_3, C_2F_5, C_3F_7, $(CF_3)_2CF$, $(CF_3)_3C$;
B:=$C_6H_5NR_2$, C_5H_5N, $(CH_3)_3N$, C_2H_5OH, $(C_2H_5)_2O$.

In the complexes the C–I bond in IPFAs changes its nature and becomes similar to the corresponding bond in hydrocarbon iodoalkanes. The reactivity of the complexes differs slightly from that of IPFAs. Thus, $(CF_3)_2CI$ in a solution of diethyl ether reacts with diethylamine to form the corresponding enamine:[84]

$$-\overset{|}{N}: + I-C(CF_3)_3 \longrightarrow \left[-\overset{|}{N}^{\delta+}\cdots I^{\delta-}\cdots C^{\delta-}(CF_3)_3\right] \longrightarrow$$

$$\longrightarrow -\overset{|}{N^+}-I + {}^-C(CF_3)_3 \xrightarrow[-F^-]{} CF_2=C(CF_3)_2 + \left[-\overset{|}{N}-I\right]^+F^- \xrightarrow[-HF]{(C_2H_5)_2NH}$$

$$\rightarrow (CF_3)_2C=CFN(C_2H_5)_2.$$

It should be noted that the greatest shifts of the absorption bands occur in the UV spectra of a mixture of 2-iodoperfluoro-2-methylpropane with diethyl ether and ethanol.

6. Reaction between iodoperfluoroalkanes and aluminium halides

Iodotrifluoromethane readily reacts with aluminium halides, forming a mixture of substitution products.[226] Eapen, et al.[227] found that its higher homologues and iodoperfluoroalkoxyalkanes also undergo such a reaction in the presence of a 1.5- to 3-fold excess of $AlCl_3$ or $AlBr_3$.

$$R_fCF_2I \xrightarrow[75-120\ ^\circ C,\ 24-74\ h]{AlX_3} \underset{55-56\%}{R_fCX_3}$$

R_f=C_3F_7, C_8F_{17}, $C_{10}F_{21}$; X=Cl, Br.

It follows from the experimental results that the formation of trichloro derivatives occurs via the intermediate formation of R_fCCl_2I. The latter can be isolated at a lower temperature with a

yield of about 15%. In our opinion, cleavage of the stronger C–F bond occurs in this case because the formation of AlF_3 is thermodynamically more favourable compared to AlX_3 (X = Cl, Br). The reaction with branched iodoperfluoroalkoxyalkanes is complicated by dechlorofluorination and more extensive substitution of fluorine atoms, probably because of the close proximity of the electron-donating oxygen atom.

$$(CF_3)_2CFOCF_2CF_2I \xrightarrow[60\ h]{AlCl_3,\ 100-105\ ^\circ C} \begin{cases} \longrightarrow (CF_3)_2CFOCF_2CCl_3 \quad 26\% \\ \longrightarrow (CF_3)_2CFOCF{=}CCl_2 \quad 19\% \\ \longrightarrow (CF_3)_2CFOCCl{=}CCl_2 \quad 19\% \\ \longrightarrow (CF_3)_2CFOCCl_2CCl_3\ . \quad 2\% \end{cases}$$

IV. Use of iodoperfluoroalkanes and perfluorinated iodine-containing ethers

Iodoperfluoroalkanes and perfluorinated iodine-containing ethers have found extensive use in chemical technology and in different areas of science and engineering—in laser technology, etching of dielectrics, separation of carbon isotopes, and as intermediates in the synthesis of surfactants, textile-auxiliary materials, and biologically active compounds.

1. Use of IPFAs in chemical technology and engineering

In 1971 the use of iodopentafluoroethane on a support was proposed as a source of radicals for the initiation of polymerisation processes.[228,229] Highly fluorinated oils were subsequently obtained by polymerisation of tetrafluoroethylene[230] and other perfluoroalkenes[231] in the presence of C_2F_5I. It should be noted that IPFAs can be used in polymerisation processes not only for initiation but also for modification of the polymers obtained.[323]

Long-chain branched IPFAs with the general formula $(CF_3)_2CF(CF_2CF_2)_nI$ (n = 6–16) are used as components of self-lubricating compositions (at a level of 5–30%).[233,234]

Starting in 1979 there has been an increase in the number of publications on the use of IPFAs in photodissociation iodine lasers (FIL). Laser generation from the transition of an excited iodine atom (obtained by pulsed photolysis of CF_3I) to an unexcited state was first achieved in 1964.[8]

For the last 20 years the processes that occur during pulsed photolysis of CF_3I and after it and the parameters of a CF_3I laser have been thoroughly investigated. In order to improve the energetic characteristics of a FIL and to simplify its use, including the ability to use an active medium repeatedly, the use of homologues of iodotrifluoromethane—n-C_3F_7I, n-$C_5F_{11}I$, n-$C_6F_{13}I$ and their isomers and also $C_2F_5CFICF_3$ and $(CF_3)_3CI$—has been proposed.[9–11,235–238] Amongst these compounds there is considerable interest in 2-iodoperfluoro-2-methylpropane because, in contrast to other IPFAs, the $(CF_3)_3C^{\cdot}$ radical formed during its photochemical decomposition mainly gives the initial compound on account of its structural characteristics and high stability in recombination processes, thus preventing the formation of molecular iodine and making it theoretically possible to produce a frequency FIL.[11]

The use of IPFAs in laser technology is not restricted solely to FILs. The use of a mixture of CF_3I with hydrogen-containing components such as iodomethane, hydrogen bromide, and fluorine and hydrogen has been proposed for obtaining an HF-laser emission.[13–15,198] Studies have been conducted on the production of a laser based on molecular iodine by excitation of a mixture of CF_3I and argon with an electron beam.[239]

The coincidence of the absorption spectrum of iodotrifluoromethane containing a small quantity of $^{13}CF_3I$ with the wavelength of a CO_2 laser forms the basis of the use of iodotrifluoromethane in the separation of carbon isotopes by multiphoton dissociation of CF_3I at –80 °C in the field of a CO_2 laser.[17] The efficiency of this method is very high (enrichment coefficient 600); in future it is likely to evolve as the principal method for ^{13}C isotope enrichment.

2. Surfactants based on iodoperfluoroalkanes

At the beginning of the 1960s Brace[156,159] and then Litt and Blöchl[93,240] established that starting from 1-iodo-1,1,2,2-tetrahydroperfluoroalkanes or iodoperfluoroalkoxyalkanes it is possible to obtain compounds that can produce a marked change in the surface tension of solutions and which are considerably superior to known surfactants. Research in this field has been considerably extended.[168,178,195,241–250] Current methods for the synthesis of surfactants based on IPFAs are exhibited in the scheme given in a monograph.[16] This scheme can be supplemented by the following:

$$C_3F_7I \begin{cases} \longrightarrow C_3F_7CH_2CHI(CH_2)_nO(CH_2CH_2O)_m\text{–}CH_2OH \quad [165] \\ \longrightarrow C_3F_7CH_2CHI(CH_2)_nOCH_2OCOCH_3 \longrightarrow C_3F_7CH_2CHI(CH_2)_nOCH_2OH \\ \longrightarrow C_3F_7(CH_2CH_2)_{3\div5}SO_3Na \quad [91] \\ \longrightarrow C_3F_7CH_2CH_2\text{–}\overset{+}{N}(CH_2COO^-)\text{–}C_4H_4O \quad [244]\ . \end{cases}$$

Acids whose salts have surfactant properties have also been synthesised from iodoperfluoroalkoxyalkanes. Sulphonic acids[178] and sulphonyl fluorides and sulphonyl chlorides[241] obtained from these compounds have similar properties. Fluorine-containing surfactants have a number of specific properties, in particular, stability towards acids and alkalis and also high thermal stability. They are effective at very low concentrations and are suitable for use not only in aqueous solution but also in organic media.

3. Textile-auxiliary materials

The imparting of hydrophobicity and oleophobicity to polymers on introduction of perfluoroalkyl groups has formed the basis of the widespread use of IPFAs in the synthesis of textile-auxiliary materials for impregnating fabrics, cellulose goods, and other fibrous materials, including synthetic fibres.[133–136,150,155,162,166,167,170,216,251] The most effective textile-auxiliary materials have been obtained from higher IPFAs with the number of C atoms $\geqslant$ 7.[147–150] Saturated polyfluoroalkoxy-alcohols and -amines and organophosphorus compounds used for imparting water- and oil-repellent properties to cellulose and textile goods have been obtained from

1-iodoperfluoroheptane.[147,252,253] 1-Iodoperfluorooctane is used in the synthesis of antisoiling agents for fabrics.[149–152,156] A more extensive group of iodoperfluoroalkanes R_fI (R_f = C_4-C_{16} perfluoroalkyl) is used in the synthesis of ammonium polyhydroxyalkylselenates and their derivatives, which impart oil and water resistance to textile fibres.[150] Members of the homolytic series of IPFAs with the number of C atoms $\leqslant 4$ are used less frequently for this purpose.[133,135,254–256]

Iodoperfluoroalkoxyalkanes are the starting materials for the preparation[162,163,257] of esters that are used in the synthesis of the corresponding acids and their complexes with chromium hypochlorite. The latter are efficient oil-repellent agents.

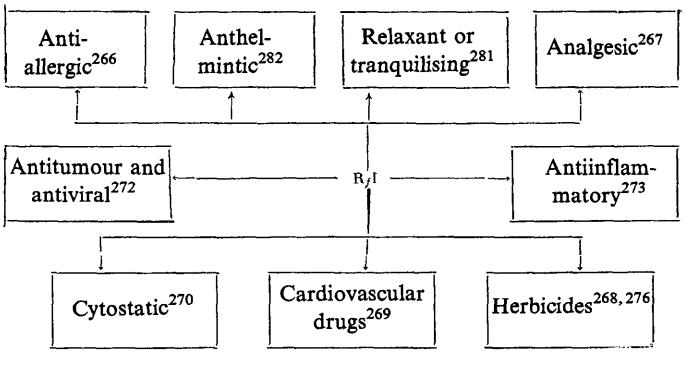
IPFAs and iodoperfluoroalkoxyalkanes have been used to synthesise novel monomers and polymers,[134,153,154,258,259] such as fluorine-containing polyurethanes,[153,260] with dust- and soil-resistant properties. The monomers obtained using IPFAs with the number of carbon atoms ranging from 1 to 10 have proved promising for the synthesis of novel polymer materials having the properties of rubbers,[261] vulcanised rubber,[262] and other vulcanised materials,[263] as well as vulcanising agents.[139]

By using 1-iodoperfluoropropane in the synthesis of fluorine-containing benzoxazoles, the authors of one patent[264] discovered novel anticorrosive lubricant additives.

4. Biologically active compounds

The use of IPFAs in the synthesis of biologically active compounds has assumed a prominent position. Reaction of CF_3I and certain of its homologues with organic substrates gives cyclic, aromatic, and heterocyclic perfluoroalkylated compounds that have diverse forms of biological activity (Scheme 1).[265–282] Iodotrifluoromethane is used most frequently in the syntheses of biologically active compounds because the compounds prepared from it have the greatest activity and also because of the high stability of CF_3I. As a consequence of the latter, the trifluoromethylation reactions, which are usually carried out at a temperature not lower than 110 °C, are not accompanied by side reactions due to the degradation of the perfluoroalkyl substituent. This is a considerable advantage in the synthesis of pharmacological compounds.

Scheme 1. Spectrum of biological effect of perfluoroalkyl-containing compounds obtained by perfluoroalkylation of aromatic and heteroaromatic substrates.



Research into novel alkylating agents for the preparation of biologically active fluorine-containing compounds has recently been undertaken. Halodifluoroacetic acids and their derivatives have been used in particular for this purpose. Thus, Delyagina, et al.[283] pointed out their ability to undergo nucleophilic substitution, while in subsequent syntheses with methyl iododifluoroacetate it was shown that they are characterised by addition and substitution reactions that are normal for IPFAs, including the alkylation of aromatic and heterocyclic compounds.[284] As a result of these studies it was possible to introduce the CH_3OOCCF_2 group into complex organic molecules, considerably extending the synthetic possibilities of the resulting compounds.

5. Other areas of application

In addition to the traditional areas of application, IPFAs and iodoperfluoroalkoxyalkanes are used as intermediates in the synthesis of various materials with useful properties,[16] including the production of dyes.[262] Iodoperfluoroalkanes are used as sources of fluorine for etching glass surfaces in order to improve their stability towards water and aqueous solutions.[18] An assessment of the possibility of using CF_3I in radiation dosimetry has been carried out.[19] In certain cases IPFAs are convenient solvents in IR spectroscopy.[285]

V. Conclusion

The presence of the highly fluorinated R_f residue in IPFAs gives rise to a basic difference between them and their hydrocarbon analogues, involving a withdrawal of electron density for the C–I bond. This almost completely deprives the molecule of the ability to participate in nucleophilic substitution reactions. Radical and radical-ion reactions are typical. Nevertheless, IPFAs, like their nonfluorinated analogues, are convenient alkylating agents, and by using simple methods they enable fluorine-containing substituents to be introduced into complex organic molecules without causing them to degrade, thus establishing their main use in organic synthesis.

The independent practical value of IPFAs results from their use in areas of modern technology such as mechanical engineering, laser technology, isotope separation, etc.

IPFAs (in particular CF_3I and n-C_3F_7I) have disadvantages in terms of their practical application because of their relatively high costs, since at the present time no technologies for synthesising them have been developed that can compete with the Borodin–Hunsdiecker method. Therefore, the development of alternative and oxygen-containing iodoperfluoroalkanes based on available products is a useful and promising trend.

We do not claim that the bibliography presented in this review is comprehensive in its coverage. However, the main directions of research into the preparative methods as well as the reactivity of iodoperfluoroalkanes are fully reflected in it. We hope that the contents of this review will be useful not only to researchers working in the field of the organic chemistry of fluorine but also to a wider circle of synthetic chemists.

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