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Fluorine-containing organic derivatives of polyvalent halogens

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ABSTRACT. **The methods of synthesis and properties of fluorine-containing organic derivatives of polyvalent iodine, bromine, and chlorine are examined.**

The bibliography includes 162 references.

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I. Introduction

Organic derivatives of polyvalent iodine were first obtained by Willgerodt in 1886. The methods of synthesis and properties of compounds containing iodine in the trivalent and pentavalent states have been described in a monograph[1] and in reviews.[2–4] Subsequent reviews were devoted to separate types of polyvalent iodine compounds—iodonium salts and ylides,[5,6] diacyloxyiodoarenes.[7] Iodonium ylides and the applications of polyvalent iodine compounds in organic syntheses have been considered in greatest detail in Koser's[8] and Varvoglis's[9] reviews respectively.

There have been no reviews devoted to fluorine-containing derivatives of polyvalent iodine. Nevertheless certain types of compounds have been synthesised solely as a result of the introduction of fluorine atoms into the molecule.

The chemistry of fluorine-containing organic derivatives of polyvalent iodine is developing vigorously. They are finding increasingly extensive application as selective oxidants, alkylating and fluorinating agents, and physiologically active substances.

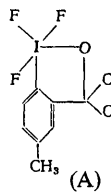
Certain fluorine-containing organic derivatives of bromine and chlorine have been synthesised in recent years.

This review deals with data on fluorine-containing organic compounds with a carbon–polyvalent-bond published up to 1987. There exist the following types of polyvalent iodine compounds of this sort.

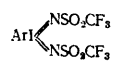
1. Compounds of trivalent iodine in which the iodine atom is linked to one carbon atom. These include iodosylperfluoroalkanes R_FIO, difluoroiodoarenes $ArIF_2$ and difluoroiodoperfluoroalkanes R_FIF_2, bis(trifluoroacetoxy)iodoarenes $ArI(OCOCF_3)_2$ and bis(trifluoroacetoxy)iodoperfluoroalkanes $R_FI(OCOCF_3)_2$, dimethoxyiodotrifluoromethane $CF_3I(OCH_3)_2$, and also μ-oxo-compounds, in which the iodine atoms are linked by an oxygen bridge, namely $ArI(OCOCF_3)-O-I(OCOCF_3)Ar$. Iminoiodoarenes, for example, $ArI=NSO_2CF_3$, belong to the same type.

2. Compounds of trivalent iodine containing an iodine atom linked to two carbon atoms. These include arylperfluoroalkyl- and aryl-αα-dihydropolyfluoroalkyliodonium salts, for example, $C_6H_5\overset{+}{I}\,C_3F_7BF_4^-$, and also iodonium ylides of the type $ArI=C(SO_2F)_2$.

3. Compounds of pentavalent iodine in which the iodine atom is linked to one carbon atom. These include iodylperfluoroalkanes R_FIO_2, difluoroiodylarenes $ArIOF_2$, and difluoroiodylperfluoroalkanes R_FIOF_2, tetrafluoroiodoarenes $ArIF_4$ and tetrafluoroiodoperfluoroalkanes R_FIF_4, tetrakis(perfluoroacyloxy)iodoarenes $ArI(OCOR_F)_4$, and bis(perfluoroacyloxy)iodylarenes $ArI(O)(OCOR)_2$. Trifluoroperiodinane (A) and bis(imino)iodoarenes (B) can also be included in this type:



(A)



(B)

4. Compounds with pentavalent iodine in which the iodine atom is linked to two carbon atoms. These include diphenyliodosyl salts, for example, $(C_6H_5)_2IF_2$ and $(C_6H_5)_2I(O)OCOCF_3$.

There are few available literature data on the fluorine-containing organic derivatives of polyvalent bromine and chlorine. The compounds R_FBRF_2, $RFBr(OCOCF_3)_2$, and R_FClF_2 have been synthesised. The available information about the synthesis of $C_6F_5Cl(F)-Cl(F)C_6F_5$ is hardly reliable.

II. Derivatives of trivalent halogen

1. Methods of synthesis

(a) Iodosyl compounds

Until recently, only aromatic iodosyl compounds ArIO were known, their stability being caused apparently by the conjugation of the positively charged iodine atom with the aromatic ring. The methods of synthesis of iodosylarenes have been described in reviews.[1–4] The most convenient of them is based on the alkaline hydrolysis of diacetoxyiodoarenes.[10]

The first representative of aliphatic iodosylperfluoro-compounds—iodosylperfluoropropane—was obtained by the hydrolysis of bis(trifluoroacetoxy)perfluoropropane in the presence of sodium bicarbonate.[11] Iodosylpentafluorobenzene was synthesised similarly:[11,12]

$$R_FI(OCOCF_3)_2 \xrightarrow{H_2,\,NaHCO_2} R_FIO, \quad R_F = C_3F_7,\ C_6F_5.$$

Contrary to the assertion[13] that iodosyl compounds are not formed when perfluoroalkyl iodides are treated with ozone, iodosyltrifluoromethane was obtained by this procedure:[14]

$$CF_3I + O_3 \xrightarrow[CCl_3F,\,-78\text{–}40\,^\circ C]{} CF_3IO + O_2.$$

The same compound is formed when difluoroiodotrifluoromethane in acetonitrile is treated with finely dispersed silica:[14]

$$2CF_3IF_2 + SiO_2 \xrightarrow[-40\text{–}0\,^\circ C]{} 2CF_3IO + SiF_4.$$

The relative stability of iodosylperfluoroalkanes is associated with the electron-accepting influence of the perfluoroalkyl group.

(b) Difluoroiodo-, difluorobromo-, and difluorochloro-compounds

The first representatives of difluoroiodo-compounds—difluoroiodoarenes—were obtained by treating iodosylarenes with 40% hydrofluoric acid.[2,4] It has also been suggested[15] that difluoroiodoarenes be obtained by the exchange of the chlorine atoms in dichloroiodoarenes with the fluorine in hydrofluoric acid in the presence of yellow mercury oxide:

$$ArICl_2 + HgO + 2HF \rightarrow ArIF_2 + H_2O + HgCl_2.$$

An important disadvantage of these methods is the presence in the reaction mixture of water, which hinders the isolation and purification of the readily hydrolysing difluoroiodoarenes. The method of synthesis of difluoroiodoarenes by treating iodosyl compounds or bis(trifluoroacetoxy)iodo-derivatives with sulphur tetrafluoride is free from this disadvantage. Apart from difluoroiodoarenes, readily removed gases—thionyl fluoride and trifluoroacetyl fluoride—are formed under these conditions:[11]

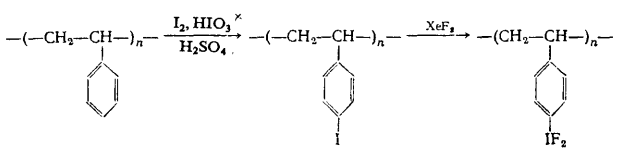
$$ArIO + SF_4 \rightarrow ArIF_2 + SOF_2,$$
$$C_6F_5I(OCOCF_3)_2 + SF_4 \rightarrow C_6F_5IF_2 + 2SOF_2 + 2CF_3COF.$$

The first representative of heterocyclic difluoroiodo-derivatives—3-difluoroiodopyridine—was also obtained by this method.[11]

Xenon difluoride can be used to synthesise difluoroiodo-compounds:[16]

$$ArI + XeF_2 \xrightarrow[20\text{–}60\,^\circ C]{} ArIF_2 + Xe.$$

Various difluoroiodoarenes[17,18] as well as polymeric difluoroiodoarene—the product of the iodination and subsequent fluorination with xenon difluoride the so called "popcorn" (cross-linked styrene–divinylbenzene copolymer)[19,20]—have been obtained with the aid of xenon difluoride:



Studies in which conditions were found for the selective fluorination of various iodoarenes by elemental fluorine have been published comparatively recently:[21,22]

$$ArI + F_2 \xrightarrow[CCl_2F,\,-100\,^\circ C]{} ArIF_2.$$

Fluorine is diluted with nitrogen in proportions of 1:20. It is then possible to avoid the fluorination of the aromatic ring even in those cases where it contains electron-donating substituents. The compound $C_6F_5IF_2$ had been obtained earlier by this procedure.[23]

The first difluoroiodoperfluoroalkane—difluoroiodotrifluoromethane—was synthesised by treating trifluoromethyl iodide with fluorine:[24]

$$CF_3I + F_2 \rightarrow CF_3IF_2$$

Subsequently various difluoroiodoperfluoroalkanes were obtained by treating the corresponding perfluoroalkyl iodides with strong fluorinating agents—elemental fluorine,[13,25,26] chlorine trifluoride, and bromine trifluoride or pentafluoride.[13] The compound $SF_5(CF_2)_2IF_2$ was also obtained with the aid of chlorine trifluoride.[27]

Difluoroiodoperfluoroalkanes[11] and difluoroiodo-αα-dihydropolyfluoroalkanes[28] are formed readily when the corresponding bis(trifluoroacetoxy)iodo-derivatives are treated with sulphur tetrafluoride.

The low-temperature fluorination of methyl iodide with elemental fluorine leads to difluoroiodotrifluoromethane.[29]

Difluoroiodoalkanes could not be obtained with the aid of elemental fluorine or strong fluorinating agents, since the C–I bond is ruptured under these conditions. Alkyl iodides cannot be oxidised to bis(trifluoroacetoxy)iodo-derivatives for the same reason. It has been found that difluoroiodomethane is formed in a quantitative yield when xenon difluoride reacts with an excess of methyl iodide:[30–32]

$$CH_3I + XeF_2 \xrightarrow[20\,^\circ C]{} CH_3IF_2 + Xe.$$

The product has been characterised only by ^1H and ^{19}F NMR spectra.

Difluoroiodoethane has been obtained from ethyl iodide using a very mild fluorinating agent—$CsSO_4F$.[33]

The formation of difluorobromoarenes in the oxidation of bromoarenes with xenon difluorides[34] and in the synthesis of diarylbromonium salts by condensing arenes with BrF_3 [35] has been detected by the ^{19}F NMR method.

The synthesis of difluorobromopentafluorobenzene by the reaction of C_6F_5Br with elemental fluorine at 128 °C was described later.[36,37] $C_6F_5BrF_2$ was isolated by preparative chromatography. However, the authors believe[38,39] that the product of the reaction of elemental fluorine with C_6F_5Br is not $C_6F_5BrF_2$. They obtained $C_6F_5BrF_2$ by substituting a fluorine atom in BrF_3 by the pentafluorophenyl residue and confirmed its formation by studying the ^{19}F NMR, IR, and mass spectra and also by means of chemical reactions:

$$C_6F_5SiF_3 + BrF_3 \rightarrow C_6F_5BrF_2 + SiF_4.$$

The formation of $C_6H_5ClF_2$ on interaction with C_6F_5Cl with elemental fluorine has been described.[40,41] It has been suggested that $C_6H_5Cl(F)-Cl(F)C_6F_5$ is formed as a side product in this reaction. A study has been devoted to the synthesis of this compound and the demonstration of its structure.[42] We believe that the existence of this compound is doubtful.

(c) Bis(trifluoroacetoxy)iodo- and bis(trifluoroacetoxy)bromo-compounds

The first representative of compounds of this kind—bis(trifluoroacetoxy)iodobenzene—was obtained by treating dichloroiodobenzene with silver trifluoroacetate or by treating iodosylbenzene with trifluoroacetic acid:[43]

$$C_6H_5ICl_2 + 2AgOCOCF_3 \rightarrow C_6H_5I(OCOCF_3)_2 + 2AgCl,$$
$$C_6H_5IO + 2CF_3COOH \rightarrow C_6H_5I(OCOCF_3)_2 + H_2O.$$

A method of synthesis of this compound from diacetoxyiodobenzene by the exchange reaction with trifluoroacetic acid at 60 °C was later proposed:[44,45]

$$C_6H_5I(OCOCH_3)_2 + 2CF_3COOH \rightarrow C_6H_5I(OCOCF_3)_2 + 2CH_3COOH.$$

Bis(trifluoroacetoxy)iodopentafluorobenzene was synthesised by oxidising iodopentafluorobenzene with nitric acid in the presence of trifluoroacetic anhydride[12] or trifluoroperacetic acid.[23]

In order to obtain bis(trifluoroacetoxy)iodoarenes containing in the benzene ring not unduly strong electron-donating and electron-accepting substituents, a method has been developed for the direct introduction of the $I(OCOCF_3)_2$ group into the aromatic ring by treatment with iodine tris(trifluoroacetate)[12,23] in trifluoroacetic acid:[46]

$$ArH + I(OCOCF_3)_3 \xrightarrow[-CF_3COOH]{} ArI(OCOCF_3)_2,$$

$$Ar = C_6H_5,\ 2,5\text{-}(CH_3)_2C_6H_3,\ 4\text{-}CH_3C_6H_4,\ 4\text{-}ClC_6H_4,\ 3\text{-}CF_3C_6H_4.$$

It was found that only the *meta*-isomer is formed from trifluoromethylbenzene, a mixture of 38% of the *ortho*-isomer and 62% of the *para*-isomer is formed from toluene, and a mixture of 6% of the *ortho*-isomer and 94% of the *para*-isomer is formed from chlorobenzene. Such composition of the isomers indicates an electrophilic mechanism of the reaction.

In the synthesis of bis(trifluoroacetoxy)iodoarenes from iodosylarenes, it is best to use trifluoroacetic anhydride instead of the acid itself. The reaction takes place with a quantitative yield:[46,47]

$$ArIO + (CF_3CO)_2O \xrightarrow[CH_2Cl_2]{-20 \text{ to } -30\,^\circ C} ArI(OCOCF_3)_2,$$

$$Ar = C_6H_5,\ 4\text{-}CH_3C_6H_4,\ 3\text{-}FC_6H_4,\ 4\text{-}FC_6H_4,\ 4\text{-}ClC_6H_4,\ 3\text{-}CF_3C_6H_4.$$

The last two methods are not applicable to the synthesis of bis(trifluoroacetoxy)iodoarenes containing strong electron-accepting substituents. In this case, the iodoarene was oxidised with fuming nitric acid in the presence of trifluoroacetic anhydride:[48]

$$XC_6H_4I + 2HNO_3 + 2(CF_3CO)_2O \rightarrow XC_6H_4I(OCOCF_3)_2 + 2NO_2 + 2CF_3COOH,$$

$$X = 3\text{-}CF_3,\ 3\text{-}NO_2,\ 4\text{-}NO_2.$$

The reaction takes place quantitatively.

The first representative of trivalent bromine carboxylates—bis(trifluoroacetoxy)bromopentafluorobenzene—was synthesised by the reaction of difluorobromopentafluorobenzene with trifluoroacetic anhydride at 0 °C in Freon 11.[39]

Until recently, saturated aliphatic di(acyloxy)iodo-compounds were unknown. The attempts to oxidise iodoalkanes to iodosyl compounds or their derivatives were unsuccessful, since this involves the dissociation of the C–I bond.

The first compounds of this type—bis(trifluoroacetoxy)iodoperfluoroalkanes and bis(trifluoroacetoxy)iodo-αα-dihydropolyfluoroalkanes—were obtained by oxidising perfluoro- and αα-dihydropolyfluoro-alkyl iodides with trifluoroperacetic acid in chloroform or trifluoroacetic acid:[11,28,49]

$$R_FI \xrightarrow[CF_3COOH]{CF_3CO_3H} R_FI(OCOCF_3)_2.$$

The reaction is general in character. The only exception is iodotrifluoromethane, which could not be oxidised by trifluoroperacetic acid. A mixture of another oxidant (nitric acid) with trifluoroacetic anhydride decomposes CF_3I, which results in the formation of iodine tris(fluoroacetate) in a quantitative yield.

Bis(trifluoroacetoxy)iodotrifluoromethane was synthesised by substituting the fluorine atoms by trifluoroacetoxy-groups in the reaction of difluoroiodotrifluoromethane with an excess of trifluoroacetic anhydride at −40 °C.[50] $CF_3IF(OCOCF_3)$ is formed as an intermediate:

$$CF_3IF_2 \xrightarrow[-CF_3COF]{(CF_3CO)_2O} CF_3IF(OCOCF_3) \xrightarrow[-CF_3COF]{(CF_3CO)_2O} CF_3I(OCOCF_3)_2.$$

Bis(trifluoroacetoxy)iodotrifluoromethane can be obtained also by treating iodosyltrifluoromethane with an excess of trifluoroacetic anhydride:[50]

$$CF_3IO + (CF_3CO)_2O \xrightarrow[-30\,^\circ C]{} CF_3I(OCOCF_3)_2.$$

(d) Fluorine-containing trivalent iodine ylides and iminoiodoarenes

Iminoiodoarenes were first obtained by the reaction of diacetoxyiodoarenes with toluene-*p*-sulphonamide in methanol in the presence of KOH.[51] Under the same conditions, trifluoroacetyliminoiodobenzene $PhI{=}NCOCF_3$ is formed from trifluoroacetamide and $PhI(OCOCH_3)_2$.[52] Compounds containing the $I{=}NSO_2CF_3$ groups could not be obtained by this method. A method consisting in the reaction of difluoroiodoarenes with *NN*-bis(trimethylsilyl)trifluoromethanesulphonamide has been developed for the synthesis of trifluoromethanesulphonyliminoiodoarenes.[53] Benzenesulphonyliminoiodoarenes have been obtained from *NN*-bis(trimethylsilyl)-benzenesulphonamide:[47,54]

$$XC_6H_4IF_2 + RSO_2N(SiMe_3)_2 \xrightarrow[-Me_3SiF]{} XC_6H_4I{=}NSO_2R,$$

$$R = CF_3,\ X = H,\ 3\text{-}F,\ 4\text{-}F;\quad R = C_6H_5,\ X = H,\ 4\text{-}CH_3,\ 3\text{-}F,\ 4\text{-}F.$$

$C_6F_5I{=}NSO_2C_6H_5$ was obtained similarly.

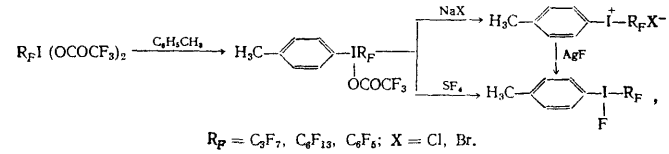
Aryliodonium di(fluorosulphonyl)methylides have been synthesised by the reaction of diacetoxyiodoarenes with methanedisulphonyl fluoride:[47,55]

$$XC_6H_4I(OCOCH_3)_2 + H_2C(SO_2F)_2 \xrightarrow[CH_2Cl_2,\ 20\,^\circ C]{} XC_6H_4I{=}C(SO_2F)_2,$$

$$X = H,\ 3\text{-}F,\ 4\text{-}F,\ 3\text{-}NO_2.$$

(e) Arylperfluoroalkyliodonium salts

These compounds were first obtained in 1971 [49] by condensing bis(trifluoroacetoxy)iodoperfluoroalkanes with benzene and toluene in trifluoroacetic acid. On treatment with sodium chloride or bromide in an aqueous acetone solution, the trifluoroacetates obtained are converted into chlorides and bromides. Arylperfluoroalkyliodonium fluorides are formed from trifluoroacetates on treatment with sulphur tetrafluoride or from chlorides by the exchange reaction with silver fluoride:



$$R_F = C_3F_7,\ C_6F_{13},\ C_6F_5;\ X = Cl,\ Br.$$

In order to increase the stability and reactivity of arylperfluoroalkyl iodonium salts, iodonium salts with the non-nucleophilic anion BF_4^- have been synthesised by the reaction of difluoroiodoperfluoroalkanes with benzene in the presence of BF_3:[56]

$$R_FIF_2 + BF_3 \xrightarrow[CH_2Cl_2,\ -60\,^\circ C]{} R_F\overset{+}{I}FBF_4^- \xrightarrow[-HF]{C_6H_6} C_6H_5\overset{+}{I}R_FBF_4^-,$$

$$R_F = C_3F_7,\ C_6F_{13}.$$

Arylperfluoroalkyliodonium salts with the trifluoromethanesulphonate (triflate) anion have been synthesised.[57] The condensation of bis(trifluoroacetoxy)iodoperfluoroalkanes with benzene or fluorobenzene was carried out in Freon 113 or in trifluoroacetic acid at

0 °C in the presence of trifluoromethanesulphonic, sulphuric, or fluorosulphonic acid:

$$R_FI(OCOCF_3)_2 \xrightarrow[XSO_3H]{ArH} ArI(OSO_2R)R_F,$$

$R_F = C_nF_{2n+1}$, $n = 2-10$; Ar = C_6H_5, 4-FC_6H_4; X = CF_3, OH, F.

Diiodonium salts—αω-bis(aryliodonium)perfluoroalkanes—with the BF_4^- [58] and $OSO_2CF_3^-$ [59] anions as well as aryl-1,1-dihydropolyfluoroalkyliodonium salts with the methylene group at the iodine atom and with the anions Br^-,[28] BF_4^-,[60] and $OSO_2SF_3^-$ [61] have also been obtained by these methods. Having replaced trifluoromethanesulphonic acid by the polymeric sulphonic acid Nafion-H in the synthesis of arylperfluoroalkyliodonium salts, an iodonium salt with a polymeric anion was obtained.[62] The synthesis of arylperfluoroalkyliodonium triflates has been surveyed.[63]

2. The properties of fluorine-containing organic compounds of trivalent iodine

(a) Iodosyl compounds

Iodosylarenes are yellowish or greenish solid substances with a characteristic smell. Their stability is low, they explode on fusion, and they disproportionate on standing:[4]

$$2ArIO \rightarrow ArI + ArIO_2.$$

Aromatic iodosyl compounds are insoluble in organic solvents and are sparingly soluble in water. On the basis of Mössbauer spectra[64] and comparison of IR and Raman spectra,[65] it has been suggested that the iodine atom in the iodosylbenzene crystals are coordinated in a T-fashion with oxygen atoms and are located in the same plane as the latter. It has been postulated that iodosylbenzene is not a polymer but a cyclic oligomer.[65]

Iodosylarenes behave as the anhydrides of the hypothetic dibasic acids $ArI(OH)_2$. They are amphoteric and form salts with a low stability after the addition of acids or bases:[4]

$$ArIO + H_3O^+ \rightleftarrows ArI^+OH + H_2O,$$
$$ArIO + OH^- \rightleftarrows ArIO_2H^-.$$

Iodosyltrifluoromethane is a colourless crystalline and very unstable substance. It can be stored in the dark at a low temperature. It decomposes with liberation of iodine at 20 °C and on rapid heating in a sealed capillary at 45 °C. When it is dissolved in methanol, the methoxide $CF_3I(OCH_3)_2$ is formed.[14]

Iodosylperfluoropropane is a more stable compound (decomposition temperature 70 °C). It does not change in air at 20 °C but decomposes gradually in the light.[11]

(b) Difluoroiodo- and difluorobromo-compounds.

Difluoroiodoarenes are colourless or yellowish crystalline substances readily hydrolysed by atmospheric moisture to iodosylarenes,[11] which corrode glass vessels on standing. They are soluble in methylene chloride, chloroform, and benzene. Solutions of difluoroiodotoluene in chloroform can be stored in glass vessels for 2–3 days.[4] The chemical shifts of the fluorine atoms in the IF_2 group in the ^{19}F NMR spectrum are presented in Table 1. The ^1H NMR and Raman spectra of these compounds have been published.[22]

The difluoroiodo-derivatives of pentafluorobenzene, perfluoro-n-alkanes, and αα-dihydropolyfluoroalkanes, obtained by the reaction of the corresponding bis(trifluoroacetoxy)iodo-compounds with sulphur tetrafluoride,[11,28] are low melting colourless crystalline substances or liquids, readily soluble in polar organic solvents. On heating above the melting point, they do not decompose and can be

Table 1. The chemical shifts of the fluorine atoms of iodine- and fluorine-containing substituents (δ_F, p.p.m.) relative to CCl_3F in benzene and perfluorocarbon derivatives.

C_6H_5X		R_FIF_2*		Solvent	Refs.	R_FIF_4*		Solvent	Refs.
X	δ_F**, p.p.m.	R_F	δ_{IF_2}, p.p.m.			R_F	δ_{IF_4}, p.p.m.		
$I(OCOCF_3)_2$	−75.99	CF_3	−175.7	CH_3CN	[25]	CF_3	−32.4	CCl_3F	[145]
			−172.7	CCl_3F	[141]				
$I(O)(OCOCF_3)_2$	−76.05	C_2F_5	−175.5	CH_3CN	[26]	C_2F_5	−30.2	CCl_3F	[145]
$I(OCOCF_3)_4$	−76.25	C_3F_7	−165.23***	—	[13]	C_3F_7	−23.03***	—	[13]
IF_2	−177.0	C_4F_9	−167.83***	—	[13]	$(F_3C)_2CF$	−17.3	CCl_3F	[145]
IF_4	−25.67	$F_5S(CF_2)_2$	−175.5	CH_3CN	[27]	n-C_4F_9	−29.2	CCl_3F	[145]
$I{=}C(SO_2F)_2$	−72.94	$F_2I(CF_2)_nIF_2$	—	—		$F_5S(CF_2)_2$	−33.0	CH_3CN	[27]
$I{=}NSO_2CF_3$	−76.96	$n=2$	−171.4	—	[58]	$F_5S(CF_2)_4$	−29.9	CH_3CN	[27]
$I(NSO_2CF_3)_2$	−77.11	$n=4$	−170.1	—	[58]	C_6F_5	−12.0	CH_3CN	[144]

* The spectroscopic characteristics have been published by Haas.[162]

** In CD_2Cl_2.[47]

*** Recalculated relative to CCl_3F.

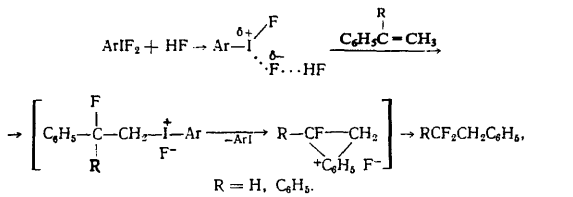
vacuum distilled. There are literature data showing that the above compounds, synthesised by other methods,[13,23,26] decompose at temperatures above 0 °C. This can probably be accounted for by the presence of impurities. The chemical shifts of the fluorine atoms of the IF_2 group in the ^{19}F NMR spectra of different difluoroiodoperfluoroalkanes are presented in Table 1 and the vibrational spectra of CF_2IF_2 have also been published.[66]

On hydrolysis of difluoroperfluoroalkanes, definite products could not be isolated. It has been suggested[13] that hydrolysis results in the formation of iodonium salts of the type $(R_F)_2\overset{+}{I}X^-$, where $X = OH^-$, IO_3^-, I^-, or F^-.

The fluorine atoms of the IF_2 group in difluoroiodotrifluoromethane can be replaced by trifluoroacetoxy-groups on treatment with an excess of trifluoroacetic anhydride,[50] while treatment with an excess of nitrogen pentoxide results in their substitution by nitrato-groups.[67] Difluoroiodotrifluoromethane forms 1:1 adducts with acetonitrile, pyridine, and quinoline. The stability of these complexes increases with increase in the electron-donating capacity of the base.[25]

Difluorobromopentafluorobenzene is a colourless crystalline substance melting at 35–36 °C and not decomposing up to 85 °C.[39]

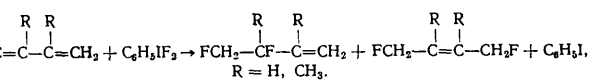
Difluoroiodoarenes and difluoroiodoalkanes are used as mild and selective fluorinating agents. The interaction of difluoroiodoarenes with 1,1-diphenylethylene,[68,69] or styrene[15] affords geminal difluoro-compounds and not 1,2-difluoro-derivatives, as was erroneously stated by Bockemüller.[68] Their formation can be explained by a rearrangement of the intermediate benzenium cation. The process is catalysed by HF:[15,18]



Rearrangements of the same type have been observed also in the fluorination with difluoroiodoarenes of 1-(3-chlorophenyl)-1-phenyl- or 1-(4-methoxyphenyl)-1-phenylethylene and also 1-phenylcyclo-pentene or 1-phenylcyclohexene.[18]

The interaction of difluoroiodoarenes with norbornene[18] results in the formation of a mixture of three products, while the reaction with norbornadiene[70] gives rise to a mixture of four products, whose proportions depend on the substituent in the benzene ring of the difluoroiodoarene.

The fluoroination of 1,3-dienes with difluoroiodobenzene[71] affords a mixture of 1,2- and 1,4-adducts in proportions of approximately 1:2:

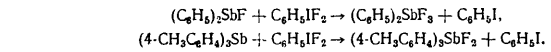


The use of aromatic difluoroiodo-derivatives as fluorinating agents was complicated by the fact that the reaction results in the formation of iodoarenes which hinder the isolation of the fluorination products. This difficulty was eliminated by employing a polymeric difluoroiodo-derivative.[19,20,72] It was found that its interaction with phenylalkenes and norbornene yields the same products as in the reaction with difluoroiodoarenes.

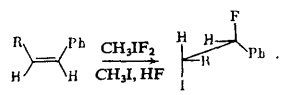
An interesting method of isolating the iodoarenes from the reaction mixture has been described.[73] 4-Difluoroiodophenylacetic acid has been proposed as a fluorinating agent. 4-Iodophenylacetic acid, formed as a result of the reaction of the fluorinating agent with substituted 1,1-diphenylethylenes, can be readily washed out with a solution of sodium carbonate.

Difluoroiodoarenes are also used to convert silylated enolic ethers into α-fluoroketones.[74]

Difluoroiodobenzene also proved to be a convenient agent for the oxidative fluorination of aromatic derivatives of trivalent antimony:[75]



As already mentioned above, difluoroiodomethane was not isolated in a pure form. However, its solutions in an excess of methyl iodide in the presence of hydrogen fluoride were made to react with phenylalkenes[76–78] and phenylalkynes.[79] It was found that this entails the addition of iodine and fluorine atoms (the elements of IF) to the double bond, which is not accompanied by a rearrangement and takes place stereoselectively in accordance with the Markovnikov rule and leads to 1-fluoro-2-iodo-derivatives:

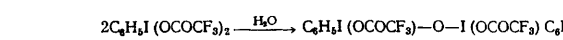


1,2- and 1,4-dihydronaphthalenes react similarly.[80] 1-Fluoro-2-iodo-1,1-diphenylethane is obtained when 1,1-diphenylethylene is treated with $C_2H_5IF_2$.[33]

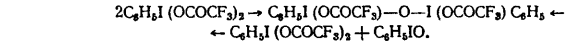
(c) Bis(trifluoroacetoxy)iodo- and bis(trifluoroacetoxy)bromo-compounds

Bis(trifluoroacetoxy)iodoarenes are colourless crystalline substances melting with decomposition at 100–150 °C, soluble in methylene chloride, chloroform, benzene, and ether, and insoluble in pentane. In solutions and during storage they decompose slowly, the decomposition being much faster on heating. Electron-donating substituents in the benzene ring reduce their stability during storage, while electron-accepting substituents increase the resistance to hydrolysis.

On hydrolysis with water, aromatic bis(trifluoroacetoxy)iodo-compounds are converted into μ-oxo-compounds:[43]



Alkaline hydrolysis yields iodosylarenes. A μ-oxo-compound is formed from bis(trifluoroacetoxy)iodobenzene on heating to 70 °C or on interaction with iodosylbenzene:[43]



μ-Oxo-compounds can be obtained by treating iodosylbenzene with a stoichiometric amount of the corresponding acid.[81] The properties, spectroscopic characteristics, and crystal structures of various μ-oxo-compounds have been examined in detail.[81]

Bis(trifluoroacetoxy)iodoarenes are reduced by sodium or potassium iodide in an acid medium to the corresponding iodo-derivatives.[46,82]

μ-Oxodiphenyldiiodosylbis(trifluoromethanesulphonate) $C_6H_5I(OSO_2CF_3)-O-I-(OSO_2CF_3)C_6H_5$, obtained by treating diacetoxyiodobenzene in chloroform with trifluoromethanesulphonic

acid[83] or by treating iodosylbenzene in methylene chloride with the anhydride of trifluoromethanesulphonic acid,[84] is a yellow substance, sparingly soluble in organic solvents, having m. p. 119–121 °C.[83]

Bis(trifluoroacetoxy)iodoperfluoroalkanes and bis(trifluoroacetoxy)iodo-αα-dihydropolyfluoroalkanes are colourless crystalline substances readily soluble in polar organic solvents. They can be stored for a long time in Teflon vessels without access of moisture. Derivatives of perfluoroalkanes are more stable than those of αα-dihydropolyfluoroalkenes.[28,49] The replacement of the aromatic groups by the more electron-accepting polyfluoro- or perfluoroalkyl group increases the tendency of bis(trifluoroacetate) to hydrolyse.[49]

In contrast to bis(trifluoroacetoxy)iodoperfluoroalkanes, bis(trifluoroacetoxy)iodo-αα-dihydropolyfluoroalkanes are converted into *meso*-oxo-compounds on treatment with water and not into iodosyl compounds.[28]

The μ-oxo-derivatives of αα-dihydropolyfluoroalkanes are colourless crystalline substances which have higher melting points and are less soluble in organic solvents than the corresponding bis(trifluoroacetoxy)iodo-derivatives. A characteristic feature of *meso*-oxo-compounds is their solubility in water (it diminishes with increase in the length of the carbon chain of the polyfluorinated group).

The hydrolysis of bis(trifluoroacetoxy)iodo-αα-dihydropolyfluoroalkanes with a 5% solution of sodium bicarbonate leads to extremely unstable iodosyl compounds, which decompose with liberation of iodine.[28]

The thermal decomposition of bis(trifluoroacetoxy)iodotrifluoromethane takes place in accordance with the scheme[50]

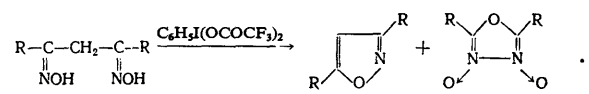
$$CF_3I(OCOCF_3)_2 \xrightarrow[-(CF_3CO)_2O]{} CF_3IO \rightarrow CF_3I + CF_3IO_2.$$

At low temperatures the reaction stops at the iodosyltrifluoromethane formation stage.

Bis(trifluoroacetoxy)bromopentafluorobenzene $C_6F_5Br(OCOCF_3)_2$ is a pale-yellow substance melting with decomposition at 54 °C. Its ^{19}F NMR, IR, and mass spectra have been published.[39] Diacetoxyiodoarenes are widely used in organic synthesis[7,9] as oxidants, acetoxylating agents, and reagents for the synthesis of iodonium salts. Bis(trifluoroacetoxy)iodoarenes are stronger oxidants and electrophiles than diacetoxyiodoarenes. The explanation is that the trifluoroacetoxy-group exhibits a greater electron-accepting inductive effect than the acetoxy-group ($\sigma_{I(OCOCH_3)} = 0.27$; $\sigma_{I(COCF_3)} = 0.65$ [85]) and a larger positive charge is concentrated on the iodine atom in bis(trifluoroacetoxy)-iodoarenes.

Bis(trifluoroacetoxy)iodoarenes have found applications in oxidation, trifluoroacetoxylation, and halogenation reactions and in the synthesis of other compounds of trivalent iodines. Bis(trifluoroacetoxy)iodobenzene is used in various dehydrogenation reactions under mild conditions. Hydrazo-compounds are converted with its aid into azo-compounds, thiophenols are converted into disulphides, hydroquinones are converted into quinones, 1,2-dioximes are converted into furoxanes, *N*-substituted hydroxylamines are converted into nitroso-compounds, and primary and secondary alcohols are converted into aldehydes and ketones.[45]

The previously unavailable furoxano[3,4-b]quinoxolines were obtained with the aid of bis(trifluoroacetoxy)iodobenzene.[9,86] 1,3-Dioximes form a mixture of isoxazoles and 1,3,4-oxadiazole 3,4-dioxides in this reaction:[7]



trans-2-Unsaturated 2,4-dioximes are oxidised to mixtures of 3a,6a-dihydroxazolo[5,4-*d*]isoxazoles and pyridazine 1,2-dioxides.[87,88]

Bis(trifluoroacetoxy)iodobenzene converts acid amides into amines (the Hofmann rearrangement) under mild conditions:[89–91]

$$R-\overset{\overset{O}{\|}}{C}-NH_2 + C_6H_5I(OCOCF_3)_2 + H_2O \rightarrow$$
$$\rightarrow R\overset{+}{N}H_3CF_3COO^- + CF_3COOH + C_6H_5I + CO_2.$$

The same reaction is used to cleave peptides with terminal COOH groups, which makes it possible to determine the aminoacid sequence[92] and also to synthesise L-2,3-diaminopropionic acid—a constituent of a polypeptide antibiotic.[93]

Arylacetylenes have been oxidised to α-diketones[94] and benzaldehydes have been oxidised to benzoic acids[95] with the aid of bis(trifluoroacetoxy)iodobenzene. It has been used in the synthesis of morphines as an agent effecting oxidative cyclisation.[96]

The oxidative cleavage of dibenzyl ethers[97] and the ring opening in oxirans (leading to hydroxyaldehydes and hydroxyketones after the hydrolysis of the trifluoroacetate[98]) and arylcyclopropanes[99–101] also belong to the class of trifluoroacetoxylation reactions.

Reactions involving the oxidative substitution of a halogen, namely iodine, in alkyl halides[102,103] lead to trifluoroacetate esters, for example:

$$n\text{-}C_7H_{15}I + C_6H_5I(OCOCF_3)_2 \rightarrow n\text{-}C_7H_{15}OCOCF_3.$$

Bis(trifluoroacetoxy)iodobenzene introduces two trifluoroacetoxy-groups into alkene molecules in a high yield, the bisesters obtained being readily hydrolysed to glycols.[9] In the interaction of bis(trifluoroacetoxy)iodobenzene with aryldiazomethanes and aryl diazoethanes, the main products are the trifluoroacetate esters $ArCH_2OCOCF_3$ or $ArCH(CH_3)OCOCF_3$.[9] The trifluoroacetoxylation reaction has been used to synthesise codeine.[104]

The phenomenon of competitive binding of superweak anions has been extended to the reactions involving the coupled addition of aryliodoso-salts to the C=C double bond in the interaction of hex-1-ene or cyclohexene with bis(trifluoroacetoxy)iodobenzene in the presence of lithium perchlorate or triflate, which leads to the formation of bistriflates or bisperchlorates of hexane-1,2-diol or cyclohexane-1,2-diol:[105,106]

$$C_4H_9CH{=}CH_2 + C_6H_5I(OCOCF_3)_2 + LiOZ \rightarrow C_4H_9CH(OZ){-}CH_2OZ,$$
$$Z = SO_2CF_3,\ ClO_3.$$

The bistriflates and bisperchlorates of hexane-1,2-diols are also formed when hex-1-ene or cyclohexene are treated with *meso*-oxodiphenyldiiodosobis(trifluoromethanesulphonate) or the corresponding perchlorate.[83] Subsequently this reaction was extended also to butadiene.[84]

The reactions involving halogenation with a mixture of bis(trifluoroacetoxy)iodobenzene with halogens are of considerable interest. It has been shown[107] that the bis(trifluoroacetoxy)-iodobenzene/iodine system is an extremely effective agent for the iodination of aromatic compounds. Iodine has been introduced by this method into a series of alkyl- and halogeno-benzenes, various polynuclear aromatic hydrocarbons, certain heterocyclic compounds,[107,108] *o*- and *m*-carbaboranes,[109] and also arylcyclopropanes.[110]

The halogenation of various aromatic compounds by mixtures of $C_6H_5I(OCOCF_3)_2$ with the halogens and also with boron and aluminium halides has been described.[111,112] A powerful halogenating agent—trifluoroacetyl hypohalite—is apparently generated in all these reactions, for example:

$$PhI(OCOCF_3)_2 + I_2 \rightarrow PhI + 2CF_3COOI,$$
$$PhI(OCOCF_3)_2 + AlCl_3 \rightarrow PhI + CF_3COOAlCl_2 + CF_3COOCl.$$

Bis(trifluoroacetoxy)iodobenzene has also been used to synthesise other trivalent iodine compounds, for example, phenyl-2-thienyliodonium trifluoroacetate.[113] The first representative of trivalent iodine compounds containing two I–N bonds, namely diphthalimidoiodobenzene, was obtained by the reaction of bis(trifluoroacetoxy)iodobenzene with potassium phthalimide.[114] It was found that similar compounds are also formed from other cyclic imides.[115]

Nitrophenyliodonium phenoxides have been obtained by the reaction of bis(trifluoroacetoxy)iodobenzene with nitrophenols.[116]

(d) Fluorine-containing trivalent iodine ylides and iminoiodoarenes

Acyliminoiodoarenes are crystalline substances melting with decomposition at 100–130 °C. Triphenylmethanesulphonylimino- and trifluoroacetylimino-iodoarenes are readily hydrolysed by atmospheric moisture, while benzenesulphonyl- and toluene-*p*-sulphonyl-iminoiodoarenes are converted into idosylarenes only on alkaline hydrolysis. In the IR spectra of these compounds, the characteristic vibrations of the SO_2 group are displaced towards shorter wavelengths compared with the corresponding sulphonamides.[51–54]

Acyliminoiodoarenes can be used in transylidation reactions. For example, the reaction of tosyliminoiodobenzene with thioanisole, dimethyl sulphoxide, and triphenylphosphine yields the corresponding iminosulphuranes and iminophosphoranes.[51] On catalysis by iron- or manganese-porphyrins, the compounds PhI=NR (R = tosyl or $COCF_3$) react with alkenes, forming *N*-substituted aziridines.[52]

Aryliodonium di(fluorosulphonyl)methylides are colourless or slightly yellowish crystalline substances which melt with decomposition at 160–170 °C,[47,55] dissolve in polar organic solvents, and do not dissolve in pentane.

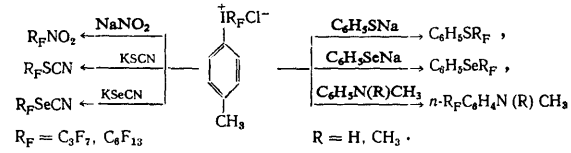
(e) Arylperfluoroalkyliodonium salts

Arylperfluoroalkyliodonium trifluoroacetates and halides are colourless crystalline substances soluble in benzene, methylene chloride, acetone, and acetonitrile. They are lower melting substances and are less stable on storage than diaryliodonium salts.[49] The low melting point can apparently be explained by the more covalent character of the bond between the iodine atom and the acid residue than in diaryliodonium salts, while their low stability is due to the intramolecular interaction of the nucleophilic anion with the onium centre.

Iodonium salts containing the BF_4^- anion are colourless crystalline substances melting with decomposition at 150–160 °C.[56] The salts containing the $OSO_2CF_3^-$ anion (the "FITS reagents")[63] melt with decomposition at lower temperatures (120–130 °C).

Arylperfluoroalkyliodonium tetrafluoroborates and triflates are stable substances which do not decompose on storage or on exposure to atmospheric moisture.

An important property of arylperfluoroalkyliodonium salts is their ability to transfer the perfluoroalkyl group to various nucleophiles. This was first demonstrated for perfluoro-n-alkyl-*p*-tolyliodonium chlorides:[117]



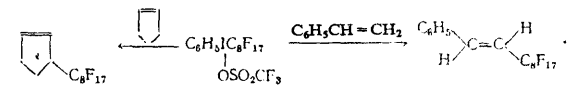
When (perfluoroalkyl)phenyliodonium tetrafluoroborates are used under the same conditions, the yields of the products of the perfluoroalkylation of sodium *p*-nitrothiophenoxide, monomethylaniline, and dimethylaniline are much higher than in the case where chlorides are used and are nearly quantitative according to GLC data.[56]

The "cationic" perfluoroalkylation reactions with the aid of FITS reagents have been extended to various carbanions,[118,119] aromatic compounds,[120] thiols,[121] phenols,[120,122] and unsaturated compounds.[123–126] The latter react with arylperfluoroalkyliodonium triflates in various ways depending on the substrate and the reaction conditions. Ethylene and other alkenes give rise to adducts in the presence of bases:[123]

$$ArI(OSO_2CF_3)-R_F + H_2C=CH_2 \xrightarrow[Na_2CO_3]{Nu^-} R_F-CH_2-CH_2-Nu,$$
$$Nu^- = HCOO^-,\ HO^-,\ CH_3O^-,\ Cl^-.$$

Alka-1,3-dienes afford exclusively 1,4-adducts.[123]

When the reaction with alkenes is carried out under other conditions, for example, in methylene chloride with added pyridine, products resulting from substitution at the vinyl or allyl carbon atom are obtained:[123]



If the reactions of iodonium triflate salts with alkenes are performed in the presence of oxygen, the perfluoroalkylation is accompanied by oxidation; perfluoroalkylated ketones are formed from alkenes, esters are formed from enol ethers, and unsaturated aldehydes and ketones are formed from dienes.[124]

The interaction of arylperfluoroalkyliodonium triflates with the trimethylsilyl ethers of enols affords high yields of α-perfluoroalkylketones, for example:

$$CH_3C(OSiMe_3)=CH_2 \xrightarrow{PhI^+C_6F_{17}\bar{O}SO_2CF_3} \underset{88\%}{CH_3COCH_2C_6F_{17}}.$$

Depending on the reaction conditions, products resulting from substitution, addition, or oxidation are formed in the reactions with various alkynes.[126]

The alkylating effect of iodonium salts in which the perfluoroalkyl group is separated from the iodine atom by the methylene group, namely aryl-1,1-dihydropolyfluoroalkyliodonium tetrafluoroborates[60] and triflates,[61] has been investigated[60,127–129] and it has been shown that these salts are stronger alkylating agents than their perfluoroalkyl analogues, apparently as a consequence of the facilitation of the heterolysis of the $I-CH_2R_F$ bond compared with $I-CF_2R_F$.

The differences between the reactivities of iodonium salts with perfluoroalkyl and 1,1-dihydropolyfluoroalkyl groups are manifested in their interaction with nitrogen-containing compounds. Whereas

arylperfluoroalkyliodonium salts do not alkylate pyridine, aryl-1,1-dihydropolyfluoroalkyliodonium salts alkylate tertiary amines, including pyridine and other heterocyclic nitrogen-containing bases[60,127] with formation of quaternary salts. Aniline, *N*-ethylaniline, and β-phenylethylamine are polyfluroalkylated only at the nitrogen atom,[60,127] while in the case of *NN*-dimethylaniline, a mixture of a quaternary salt and the product of polyfluoroalkylation in the *para*-position in the aromatic ring is obtained.[60]

The dialkylation of aniline has been achieved in a high yield with the aid of phenyl-1,1-dihydrotrifluoroethyliodonium triflate in the presence of a sterically hindered substituted pyridine:[127]

$$C_6H_5NH_2 \xrightarrow{C_6H_5\overset{+}{I}CH_2CF_3\bar{O}SO_2CF_3,\ 20\,^\circ C} C_6H_5N(CH_2CF_3)_2.$$
94%

The reaction with the trimethylsilyl ethers of enols in the presence of KF results in the formation of β-perfluoroalkylcarbonyl compounds in a satisfactory yield:[129]

$$PhI(OSO_2CF_3)CH_2R_F + PhC(OSiMe_3)=CH_2 \xrightarrow[CH_2Cl_2,\ 20\,^\circ C]{KF} PhCOCH_2CH_2R_F + PhI.$$

Aryl-(1,1-dihydropolyfluoroalkyl)iodonium triflates undergo dehydrofluorination on treatment with bases, forming aryl-(1-*H*-perfluoroalk-1-enyl)iodonium triflates:[128]

$$PhI(OSO_2CF_3)CH_2CF_2R_F \xrightarrow{NaH} PhI(OSO_2CF_3)CH=CFR_F \qquad R = CF_3,\ C_2F_5,\ C_6F_{13}.$$

On treatment with *O*-nucleophiles, a fluorine atom at the double bond is substituted, while on treatment with *S*-nucleophiles these compounds react as polyfluoroalkenylating agents:[128]

$$PhI(OPn)CH=CCF_3(OSO_2CF_3) \xleftarrow{PhO^-} PhI(OSO_2CF_3)CH=CFCF_3 \xrightarrow{ArS^-}$$
$$\rightarrow CF_3CF=CHSAr + CF_3-C(SAr)=CHSAr$$
$$Ar = p\text{-}(CH_3)_3CC_6H_4.$$

The tetrafluoroborates of αω-bis(aryliodonium)perfluoroalkanes $C_6H_5\overset{+}{I}(CF_2CF_2)_n\overset{+}{I}C_6H_5.2BF_4^-$ (n = 2, 3) exhibit a high anti-cholinesterase activity.[130]

III. Derivatives of pentavalent halogens

1. Methods of synthesis

The starting materials for the synthesis of fluorine-containing aromatic derivatives of pentavalent iodine are iodylarenes. The methods of their synthesis and their properties are therefore briefly described below. Among the perfluoroalkyl derivatives of pentavalent iodine, tetrafluoroiodoperfluoroalkanes are most readily available.

(a) Iodyl compounds

Iodylarenes were obtained almost 100 years ago.[131] The following are the most convenient methods of their synthesis; the disproportionation of iodosylarenes with steam distillation of the iodoarenes formed,[132] the oxidation of dichloroiodoarenes with sodium hypochlorite,[133] and the oxidation of iodoarenes with 40% peracetic acid.[134] Iodylpentafluorobenzene has been obtained by the disproportionation of iodosylpentafluorobenzene.[135]

A modification of the iodosylarene disproportionation method for the preparation of iodylarenes containing strong electron-accepting substituents in the benzene ring has been proposed. It consists in the steam distillation of bis(trifluoroacetoxy)iodoarenes which are more readily available in this instance. This results in the hydrolysis and disproportionation of the iodosylarenes formed.[48]

$$2XC_6H_4I(OCOCF_3)_2 \xrightarrow{H_2O} 2XC_6H_4IO \rightarrow XC_6H_4IO_2 + XC_6H_4I,$$
X=3-CF_3, 3-NO_2, 4-NO_2.

Iodylarenes, including those with electron-accepting ring substituents, are formed in 45–50% yield when iodoarenes are oxidised with potassium bromate in sulphuric acid.[136] The method is attractive because of its simplicity and safety.

The first representative of aliphatic iodyl compounds, namely iodyltrifluoromethane, has been obtained as a result of the prolonged reaction of CF_3IF_4 with finely dispersed silica in CCl_3F at 0 °C.[14]

(b) Difluoroiodyl compounds

Difluoroiodylarenes have been obtained by dissolving iodylarenes in hot 40% hydrofluoric acid:[3,137]

$$XC_6H_4IO_2 + 2HF \rightarrow XC_6H_4IOF_2 + H_2O,$$
X=H, 2-CH_3, 3-CH_3, 4-CH_3, 4-Br.

$C_6F_5IOF_2$ has been synthesised similarly.[135]

Among aliphatic difluoroiodyl compounds, only difluoroiodyltrifluoromethane CF_3IOF_2 is known. It is formed when difluoroiodotrifluoromethane is ozonised or when tetrafluoroiodotrifluoromethane reacts with finely dispersed silica.[14]

(c) Tetrafluoroiodo- and tetrafluorobromo-compounds

Tetrafluoroiodoarenes are obtained in a quantitative yield by heating iodylarenes with sulphur tetrafluoride.[138,139] Difluoroiodylarenes react similarly, their use being safer, since they are less explosive than iodylarenes:[140]

$$XC_6H_4IO_2 \xrightarrow{SF_4} XC_6H_4IF_4 \xleftarrow{SF_4} XC_6H_4IOF_2,$$
X=H, 4-CH_3, 3-F, 4-F.

The above methods are applicable only to the synthesis of the tetrafluoroiodoarenes which contain weak electron-donating or weak electron-accepting substituents in the benzene ring. The attempts to obtain tetrafluoroiodoarenes with strong electron-donating or strong electron-accepting substituents by this method have been unsuccessful.[140]

Tetrafluoroiodopentafluorobenzene has been obtained by treating iodopentafluorobenzene with chlorine trifluoride.[141,142] *p*-$F_4IC_6F_4IF_4$ is formed similarly from *p*-diiodotetrafluorobenzene.[142] $C_6F_5IF_4$ has also been synthesised by treating difluoroiodopentafluorobenzene with xenon difluoride.[16] This compound can be obtained by the reaction of IF_5 with the stoichiometric amount of $Si(C_6F_5)_4$:[143,144]

$$4IF_5 + Si(C_6F_5)_4 + 2Py \xrightarrow[CH_3CN]{80^\circ C} 4C_6F_5IF_4 + SiF_4 \cdot 2Py.$$

IF_5 reacts much more readily with aryltrifluorosilanes:[144]

$$ArSiF_3 + IF_5 \xrightarrow[CH_3CN]{35^\circ C,\ Py} ArIF_4 + SiF_4 \cdot 2Py,$$
Ar=C_6H_5, 4-$CH_3C_6H_4$, 4-FC_6H_4, C_6F_5.

The reaction involving pentafluorophenyltrifluorosilane takes place at 20 °C in the absence of pyridine.

According to Obaleye and [illegible] tetrafluorobromopentafluorobenzene has been obtained [illegible] reaction of pentafluorobromobenzene with elementa[illegible]ine at 128 °C.

Ttrafluoroiodoperfluoroalkanes are obtained by the reaction of iodoperfluoroalkanes with elemental fluorine,[13,26] chlorine trifluoride,[27,141,145] and bromine trifluoride or pentafluoride at low temperatures in inert solvents. CF_3IF_4,[141,145] $C_2F_5IF_4$, $C_4F_9IF_4$, $C_{10}F_{21}IF_4$,[13] as well as derivatives of 1,2-diiodotetrafluoroethane $F_4ICF_2CF_2IF_4$ [26] and tetrafluoroiodoperfluoroalkylsulphur pentafluoride $F_5S(CF_2)_nIF_4$ (n = 2, 4) [27] have now been described.

The first representatives of perfluoroalkyl derivatives of pentavalent bromine, namely tetrafluorobromoperfluoro-n-propane[146] and tetrafluorobromoperfluoro-n-hexane[147] have been obtained by fluorinating the corresponding perfluoroalkyl bromides with elemental fluorine at 0 °C.

(d) Tetrakis(perfluoroacyloxy)iodo-compounds

Tetrakis(trifluoroacetoxy)iodoarenes have been obtained in quantitative yields by treating iodylarenes with trifluoroacetic anhydride:[48]

$$XC_6H_4IO_2 + 2(CF_3CO)_2O \xrightarrow{[CF_3COOH]} XC_6H_4I(OCOCF_3)_4,$$
$$X=H,\ 4\text{-}CH_3,\ 4\text{-}Cl,\ 3\text{-}F,\ 4\text{-}F,\ 3\text{-}CF_3,\ 3\text{-}NO_2,\ 4\text{-}NO_2.$$

Tetrakis(perfluorobutyryloxy)iodoarenes have been obtained similarly by reaction with perfluorobutyric anhydride.[48] The reaction of iodylarenes with the anhydride of a weaker acid (acetic) affords diacetoxyiodylarenes.[48]

The reactions are carried out at 20 °C using a large excess of the anhydride, which is then regenerated. Electron-donating substituents accelerate the reaction, while electron-accepting substituents retard it somewhat. The addition of small amounts of the corresponding acid catalyses the process.

Tetrafluoroiodobenzene reacts similarly to iodylbenzene:[48]

$$C_6H_5IF_4 + (R_FCO)_2O \rightarrow C_6H_5I(OCOR_F)_4 + R_FCOF,$$
$$R_F=CF_3,\ C_3F_7.$$

(e) Diacyloxyiodyl compounds

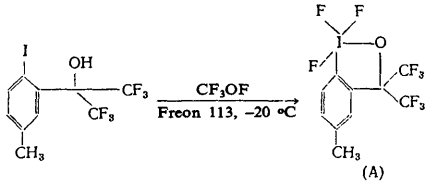
Bis(trifluoroacetoxy)iodylarenes have been obtained in quantitative yields by treating iodylarenes with trifluoroacetic acid:[148]

$$XC_6H_4IO_2 + CF_3COOH \rightarrow XC_6H_4I(OCOCF_3)_2 + H_2O,$$
$$\text{(O above I)}$$
$$X=H,\ 4\text{-}CH_3,\ 3\text{-}F,\ 4\text{-}F,\ 3\text{-}CF_3,\ 4\text{-}NO_2.$$

Diacetoxy- and bis(perfluorobutyryloxy)-iodylarenes have been synthesised similarly using an excess of acetic and perfluorobutyric acids. Small amounts of the anhydride of the corresponding acid are added to bind the water in reversible reactions. The stronger the acid, the faster the dissolution of the iodylarenes.

(f) Trifluoroperiodinanes

Trifluoroperiodinane (A) is a compound containing a pentavalent iodine atom in the ring linked to alkoxy- and aryl ligands. It has been obtained by oxidising with trifluoromethyl hypofluorite an iodoarene containing in the *ortho*-position relative to the iodine atom a tertiary carbinol residue:[149,150]



(A)

The *gem*-analogue of trifluoroperiodinane (A) has been synthesised by a procedure similar to that used for compound (A) itself.[150]

(g) Diiminoiodoarenes

Bis(sulphonylimino)iodoarenes have been obtained by the reaction of tetrafluoroiodoarenes with *NN*-bis(trimethylsilyl)derivatives of trifluoromethanesulphonamide[53] and benzene sulphonamide:[47,54]

$$XC_6H_4IF_4 + 2RSO_2N(SiMe_3)_2 \xrightarrow{\text{ether, 20 °C}} XC_6H_4I(NSO_2R)_2 + 4Me_3SiF,$$
$$R=CF_3,\ X=H,\ 3\text{-}F,\ 4\text{-}F;\ R=C_6H_5,\ X=H,\ 4\text{-}CH_3,\ 3\text{-}F,\ 4\text{-}F.$$

Instead of tetrafluoroiodoarenes, it is possible to use also tetrakis(trifluoroacetoxy)iodoarenes for the synthesis of bis(benzenesulphonylimino)iodoarenes.[54]

(h) Diaryliodosyl salts

Diphenyliodosyl hydroxide has been obtained by the self-condensation of iodylbenzene in the presence of alkali. It forms compounds with carbonic and acetic acids. They have been described as hydrogen-bonded cyclic complexes.[151]

A series of diaryliodosyl salts were subsequently obtained in accordance with the following scheme:[152]

$$ArIO_2 \xrightarrow{HO^-} Ar_2I(O)OH \xrightarrow{RCOOH} Ar_2I(O)OCOR \xrightarrow{X^-} Ar_2\overset{+}{I}(O)\ X^-,$$
$$R=CH_3,\ CF_3;\ X^-=F^-,\ Cl^-,\ Br^-,\ IO_3^-.$$

The interaction of diaryliodosyl trifluoroacetates with sulphur tetrafluoride at low temperatures leads to diaryldifluoroiodosyl trifluoroacetates.[153] On heating to 60 °C, the trifluoroacetate anion is also substituted by a fluoride ion and diphenyldifluoroiodosyl fluoride is formed:[153]

$$(XC_6H_4)_2\overset{+}{I}{=}O \xrightarrow[-10\text{–}0\,^\circ C]{SF_4} (XC_6H_4)_2\overset{+}{I}F_2\ \bar{O}COCF_3 \xrightarrow[60\,^\circ C]{SF_4} (XC_6H_4)_2\overset{+}{I}F_2\ F^-,$$
$$X=H,\ 4\text{-}F.$$

2. The properties of fluorine-containing organic compounds of pentavalent iodine

(a) Iodyl compounds

Iodylarenes are colourless crystalline substances, which explode on heating above 200 °C or on impact with liberation of iodine. They are insoluble in the majority of organic solvents and are sparingly soluble in sulpholane, dimethyl sulphoxides, and water. They are usually crystallised from water.

The structure of the solid iodylarenes has been investigated by X-ray diffraction and nuclear quadrupole resonance using *p*-chloroiodylbenzene as an example.[154] It has been shown that the iodylarene molecule is non-planar and asymmetric in the crystalline state and the IO_2 group is perpendicular to the plane of the aromatic ring. The I—O bond lengths (1.60 and 1.65 Å) are smaller than the sum of the covalent radii of oxygen and iodine (2.00 Å), which indicates a partial double bond character.[4] The effective charge on the iodine atom has been estimated from the NQR spectra. It is close to +1.7 |e|.[54] The data presented make it possible to attribute to iodylarenes the following structure:



which is similar to the structure of nitrobenzene except that the nitro-group is located in the plane of the aromatic ring.

This hypothesis has been confirmed by data obtained by comparing the IR and Raman spectra of iodylbenzene.[65] The I–O stretching vibrations in iodylbenzene occur at higher frequencies than in iodobenzene, so that the I–O distance in iodylbenzene is shorter. The Mössbauer spectra of $C_6H_5IO_2$ have been described.[64] According to the literature,[64] the O–I–O angle in the iodylbenzene molecule is close to 95 °C.

The chemical properties of iodylarenes have been little investigated. They are known to exhibit amphoteric behaviour—they react with strong acids, forming salts, and dissolve in alkalies with formation of unstable anions, which decompose on acidification.[4] Conductiometric determination of the pK_a of iodylbenzene yielded 10.4.[151]

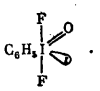
The interaction of iodylarenes with the anhydrides of carboxylic perfluoroacids and with carboxylic acids, leading to the formation of tetrakis(perfluoroacyloxy)iodoarenes[48] and diacyloxyiodylarenes,[148] proceeds via a stage involving the formation of a salt of the type $ArI^{+}(O)OH\overline{O}COR$.

The study of the chemical properties of iodylarenes is hindered by their insolubility in the usual organic solvents. The preparation of 4-t-butyliodylbenzene, soluble in hot benzene, chlorobenzene, and nitrobenzene and the study of the oxidation by this compound of alkenes, acetylenes, phenanthrene, anthracene, and tetralin have been described. The corresponding carbonyl compounds are obtained in 50–75% yield and the 4-t-butyliodobenzene dissolved can be regenerated.

Iodyltrifluoromethane is a colourless crystalline substance, stable in air, which decomposes at 50 °C with liberation of iodine. CF_3IO_2 is insoluble in CCl_3F and acetonitrile but is readily soluble in methanol, probably as a result of the formation of methoxides of the type $CF_3I(O)(OCH_3)_2$ or $CF_3I(OCH_3)_4$.[14] The IR and ^{19}F NMR spectra of iodyltrifluoromethane have been published.[14]

(b) Difluoroiodyl compounds

Difluoroiodylarenes are colourless crystalline substances, which are hydrolysed by atmospheric moisture with formation of iodylarene and hydrogen fluorides. Like iodylarenes, they are sparingly soluble in organic solvents and explode on heating above 200 °C. The following structure has been proposed for difluoroiodylbenzene on the basis of a comparison of the IR and Raman spectra:[65]



Difluoroiodyltrifluoromethane is a colourless crystalline substance which sublimes at −10 °C (0.01 mmHg). It is very readily hydrolysed by atmospheric moisture and readily dissolves in CCl_3F and acetonitrile.[14] Difluoroiodyltrifluoromethane reacts with alcohols, acids, and acid anhydrides, the fluorine atoms being substituted. All these reactions are reversible, for example:[156]

$$CF_3IOF_2 + ROH \rightleftarrows CF_3IOF(OR) + HF,$$
$$CF_3IOF(OR) + ROH \rightleftarrows CF_3IO(OR)_2 + HF.$$

When an attempt is made to isolate such compounds, they decompose. The reactions could therefore be investigated by NMR.[156]

Difluoroiodyltrifluoromethane reacts with Lewis acids (BF_3, AsF_5, and SbF_5). This probably entails the initial formation of a complex which then decomposes, being converted into tetrafluoromethane and the compounds $IO[BF_4]$, $IO[AsF_6]$, $IO[SbF_6]$, or $IO[Sb_2F_{11}]$.[157]

(c) Tetrafluoroiodo- and tetrafluorobromo-compounds

Tetrafluoroiodoarenes are colourless crystalline substances which melt without decomposition at 80–100 °C and are readily soluble in ether, benzene, and methylene chloride and less so in hexane. They are hydrolysed by atmospheric moisture to iodylarenes, they corrode glass vessels, and on heating or prolonged storage they react with quartz. On storage in platinum or Teflon vessels in the absence of moisture, they are stable.[138,140]

The ^{19}F NMR spectra of tetrafluoroiodobenzene contain one signal—an asymmetric singlet. The fluorine atoms of tetrafluoroiodobenzene are equivalent and its molecule apparently has the form of a tetragonal pyramid with fluorine atoms at the base, the iodine atom in the centre, and the phenyl residue at the apex.[138]

Tetrafluoroiodobenzene is thermally stable; it hardly changes on heating to 250 °C and decomposes at an appreciable rate only at about 300 °C.[140] On photolysis of tetrafluoroiodobenzene, atomic fluorine is evolved, which has been demonstrated by photolysing $C_6H_5IF_4$ in deuteriated benzene with subsequent mass-spectrometric analysis of the reaction products.[158]

Tetrafluoroiodobenzene is less reactive than iodine pentafluoride. In contrast to the latter, it dissolves in benzene without appreciable interaction. On dissolution in primary alcohols, a vigorous reaction takes place, leading to aldehydes (as a result of charring, the yields are 20%), iodobenzene, and hydrogen fluoride. Tetrafluoroiodobenzene dissolves in t-butyl alcohol in the cold without interaction, whilst at 30–35 °C it interacts with formation of t-butyl fluorides. Acids and their lithium salts are converted into acid anhydrides and fluorides respectively on heating with tetrafluoroiodobenzene.[140] Tetrafluoroiodobenzene fluorinates triphenylphosphine to trifluorotriphenylphosphorane, being reduced at the same time to difluoroiodo- or iodo-benzene depending on the reactant ratio employed:[138]

$$C_6H_5IF_4 + 2(C_6H_5)_3P \rightarrow C_6H_5I + 2(C_6H_5)_3PF_2.$$

Tetrafluorobromopentafluorobenzene is a colourless liquid which fumes in air. It oxidises 0.1 M KI solution and does not decolorise 0.1 M $KMnO_4$ solution.[36]

Tetrafluoroiodoperfluoroalkanes are colourless crystalline substances which are hydrolysed by atmospheric moisture and decompose at 20–60 °C. They are soluble in CCl_3F, IF_5, dioxane, and acetonitrile. The stability of the compounds R_FIF_4 increases with increase in the length of the carbon chain in the perfluoroalkyl group.[145]

On hydrolysis of tetrafluoroiodoperfluoroalkanes with water[13] or KOH in ethanol,[145] iodylperfluoroalkanes are not formed. The author suggests[13] that the iodonium salts $(R_F)_2\overset{+}{I}X^-$ are formed, but these have not been isolated in a pure form.

CF_3IF_4 decomposes in accordance with the following scheme:[145]

$$CF_3I + IF_5 \xleftarrow{[IF]} CF_3IF_4 \rightarrow CF_4 + IF_3 \rightarrow IF + IF_5 \downarrow I_2 + IF_5$$

In the reaction with methoxytrimethylsilane, the fluorine atoms are substituted in succession by methoxy-groups:[145]

$$CF_3IF_4 + (CH_3)_3SiOMe \rightarrow CF_3IF_3(OMe) + (CH_3)_3SiF.$$

Similar substitution products are obtained also in the interaction with alcohols, acids, and anhydrides:[156]

$$CF_3IF_4 + n\,ROH \rightleftarrows CF_3IF_{4-n}(OR)_n + n\,HF.$$

Tetrafluorobromoperfluoropropane[146] and tetrafluorobromoperfluoroheptane[147] are colourless liquids. They are capable of oxidising four equivalents of KI, for example:

$$n\text{-}C_7F_{15}BrF_4 + 4KI \rightarrow n\text{-}C_7F_{15}Br + 2I_2 + 4KF.$$

(d) Tetrakis(perfluoroacyloxy)iodo-compounds

Tetrakis(perfluoroacyloxy)iodoarenes are colourless crystalline substances melting with decomposition. They are readily hydrolysed by atmospheric moisture and are unstable during storage. Electron-donating substituents in the benzene ring diminish the stability of these compounds during storage, while electron-accepting substituents diminish their resistance to hydrolysis. Tetrakis(perfluoroacyloxy)-iodoarenes are readily soluble in organic solvents but their stability in solutions is low.[48]

The IR spectrum of tetrakis(trifluoroacetoxy)iodobenzene differs from the IR spectrum of iodylbenzene by the presence of an intense band at 500 cm^{-1} and two bands at 735 and 783 cm^{-1} instead of four bands at 700–800 cm^{-1} in the spectrum of iodylbenzene. The ^{19}F NMR spectrum of $C_6H_5I(OCOCF_3)_4$ has a single signal—a symmetrical singlet. This compound apparently has a structure similar to that of tetrafluoroiodobenzene.[48]

Tetrakis(trifluoroacetoxy)iodobenzene is a fairly powerful oxidant; it oxidises *m*-nitrobenzyl alcohol to the corresponding aldehyde in 3 h at 20 °C in 80% yield,[159] while bis(trifluoroacetoxy)iodobenzene oxidises benzyl alcohol to benzaldehyde in 4 h at 80 °C in 50% yield.[45]

(e) Diacyloxyiodylarenes

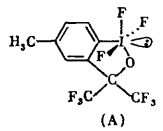
Diacyloxyiodylarenes are colourless crystalline substances melting with decomposition at higher temperatures than the corresponding tetrakis(perfluoroacyloxy)iodoarenes. They dissolve less readily in organic solvents and are more stable during storage and in hydrolysis. The IR spectra of the compounds $ArI(OCOR)_2$ are similar to the IR spectrum of $C_6H_5IOF_2$.[148]

Diacetoxyiodylbenzene has been used as an oxygen donor in the hydroxylation of steroids catalysed by cytochrome P-450.[160]

(f) Trifluoroperiodinanes

Trifluoroperiodinanes are colourless crystalline substances melting with decomposition. Trifluoroperiodinanes (A) (decomposition temperature 191–193 °C) can remain for a time in air without appreciable hydrolysis. The addition of water to this compound at 25 °C does not lead to reaction for several days. When trifluoroperiodinane is treated with an aqueous KOH solution, an iodyl derivative is probably obtained.[150] The *gem*-dimethyl analogue of trifluoroperiodinane (decomposition temperature 123–124 °C) hydrolyses faster than compound (A). In the presence of atmospheric moisture, the hydrolysis takes place over 4 h at 25 °C. The hydrolysis products have not been identified.[150] The *gem*-dimethyl analogue is also less stable during storage. It decomposes in 7 days at 25 °C and in 2–3 weeks at –20 °C.

Judging from the ^{19}F NMR spectra of perfluoroiodinanes, the fluorine atoms of the IF_3 group in these compounds are non-equivalent. An octahedral structure has been proposed for compound (A) (the sixth ligand is an electron pair):[150]



(A)

The doublet in the ^{19}F NMR spectrum of compound (A) at $\delta = -13.20$ ($J = 116$ Hz) is due to two equivalent fluorine atoms, while the triplet at $\delta = -41.57$ ($J = 116$ Hz) is due to a single fluorine atom. Other investigators[145] arrived at a similar conclusion concerning the structure of the compound $CF_3IF_3(OCH_3)$. The ^{19}F NMR spectrum of its IF_3 group consists of a doublet at $\delta = -7.0$ ($J = 113$ Hz) and a triplet at $\delta = -46.5$ ($J = 113$ Hz).

Trifluoroperiodinane decomposes slowly in acetonitrile and the solution corrodes glass in the presence of atmospheric moisture. On treatment of compound (A) with three or more equivalents of chlorotrimethylsilane, chloroiodinane, fluorotrimethylsilane, and chlorine are formed. When trifluoroperiodinane is irradiated with UV light in the presence of toluene or anisole at 50 °C, it remains unchanged.[150]

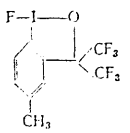
Trifluoroperiodinane reacts rapidly with phenylmagnesium bromide in accordance with the scheme

$$(A) + C_6H_5MgBr \xrightarrow{\text{ether}} \underset{90\%}{C_6H_5F}.$$

The interaction of trifluoroperiodinane with primary and secondary amines containing an α-hydrogen atom and subsequent hydrolysis afford a satisfactory yield of the corresponding carbonyl compounds.[150] In the reaction with t-butylamine, azoisobutane is formed. Trifluoroperiodinane does not react with tertiary amines.[150]

The interaction of trifluoroperiodinane with primary and secondary alcohols gives rise to aldehydes and ketones respectively.[150]

In all cases, trifluoroperiodinane is reduced as a result of the reaction to fluoroiodinane (B):



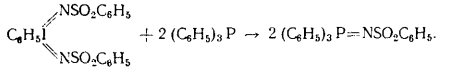
(B)

In contrast to trifluoroperiodinane, its *gem*-dimethyl analogue does not oxidise benzyl- and isopropyl-amines to the corresponding carbonyl compounds, but the reactions with alcohols proceeds with satisfactory yields.[150]

(g) Diiminoiodoarenes

Bis(trifluoromethanesulphonylimino)- [53] and bis(benzenesulphonylimino)-iodoarenes[54] are colourless or slightly yellowish crystalline substances, melting with decomposition at 100–130 °C, and are sparingly soluble in organic solvents. They are readily hydrolysed by atmospheric moisture to iodoarenes. The absorption due to the characteristic vibrations of the O_2 group are displaced in the IR spectra of these compounds towards lower frequencies compared with trifluoromethanesulphonamide and benzenesulphonamide.[53,54]

The diimino-derivatives of pentavalent iodine can be used in transylidation reactions. For example, the reaction of bis(benzenesulphonylimino)iodobenzene with triphenylphosphine afforded a high yield of *N*-benzenesulphonyltriphenylphosphine imine:[54]

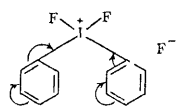


(h) Diaryliodosyl salts

Dioaryliodosyl bromides, chlorides, fluorides, and trifluoroacetates[52] are involatile and infusible crystalline substances which decompose explosively at 160–200 °C. They are readily converted into the corresponding iodonium salts on treatment with iodine, sodium bisulphite, and hydrogen peroxide.[152]

The diaryliodosyl difluoride salts are colourless crystalline substances soluble in methylene chloride, nitromethane, and acetonitrile and insoluble in ether, benzene, and hydrocarbons. In a moist atmosphere, they readily hydrolyse to diaryliodosyl salts.

The ^{19}F NMR spectra of diphenyliodosyl difluorides consist of two signals: $\delta[(C_6H_5)_2\overset{+}{I}F_2] = 22.62$ p.p.m. and $\delta(CF_3COO^-) = -13.13$ p.p.m. for the trifluoroacetate in CH_2Cl_2; $\delta[(C_6H_5)_2\overset{+}{I}F_2] = -24.5$ p.p.m. and $\delta(F^-) = 89.25$ p.p.m. (relative to trifluoromethylbenzene) for the fluoride in nitromethane.[153] As mentioned above,[138] in tetrafluoroiodobenzene all the fluorine atoms are equivalent. The replacement of one fluorine atom in tetrafluoroiodobenzene by the phenyl group led to a compound with non-equivalent fluorine atoms. The presence of two phenyl groups in the diphenyliodosyl trifluoride molecule apparently facilitates the polarisation of the I–F bond and stabilises the ionic structure $(C_6H_5)_2\overset{+}{I}F_2F^-$:[153]



IV. The electronic nature of substituents containing polyvalent iodine

The electronic nature of substituents containing an iodine atom in the trivalent and pentavalent states has been studied systematically.[47] The investigation of the ^{19}F NMR spectra of *meta*- and *para*-fluorobenzenes demonstrated a change in the character of the electronic influence of the substituent on the benzene ring in the series iodine–iodosyl group–iodyl group and on substitution of the oxygen atoms of the iodosyl and iodyl groups by fluorine and chlorine atoms and by acetoxy-, trifluoroacetoxy-, benzenesulphonylimino-, trifluoromethanesulphonylimino-, and bis(fluorosulphonyl)methylide groups. The chemical shifts of the fluorine atoms in the iodine-containing substituent (δ_F, p.p.m.) relative to CCl_3F are presented in Table 1.

The chemical shifts of the fluorine atoms in the *meta*- and *para*-derivatives of fluorobenzene relative to fluorobenzene have been measured in methylene chloride. Taft's $\delta-\sigma$ correlation equations have been used to calculate the inductive constants σ_I and the conjugation constants σ_R of the substituent.[161] The σ constants of substituents containing polyvalent iodine are listed in Table 2. The table shows that substituents containing polyvalent iodine interact with the aromatic ring mainly via the inductive mechanisms. The high values of the constants σ_I are probably caused by the high polarity of the bonds between the iodine atom and fluorine, chlorine, oxygen, and nitrogen atoms.

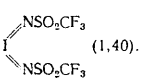
Table 2. The chemical shifts δ of the fluorine atoms in the *meta*- and *para*-derivatives of fluorobenzene relative to fluorobenzene and the σ constants of the iodine-containing substituents.[47]

Substituent	δ_m	δ_p	σ_I	σ_R	σ_m	σ_p
I	2.60	−1.25	0.45	−0.13	0.38	0.32
I=O	3.40	5.10	0.56	0.06	0.59	0.62
$I(OCOCH_3)_2$	5.45	7.13	0.85	0.06	0.88	0.91
IF_2	6.29	5.12	0.97	−0.04	0.95	0.93
$I(OCOCF_3)_2$	6.48	7.98	1.0	0.05	1.03	1.05
$I{=}NSO_2C_6H_5$	6.76	7.54	1.04	0.03	1.05	1.07
ICl_2	7.72	8.46	1.17	0.03	1.18	1.20
$I{=}NSO_2CF_3$	8.18	11.46	1.24	0.11	1.30	1.35
$I{=}C(SO_2F)_2$	8.30	9.14	1.25	0.03	1.26	1.28
$\overset{+}{I}C_6H_5BF_4^-$	8.88	9.85	1.34	0.03	1.35	1.37
IO_2	4.10	7.09	0.66	0.10	0.71	0.76
$I(OCOCF_3)_2$ ‖ O	6.55	8.42	1.01	0.06	1.04	1.07
IF_4	6.87	10.86	1.05	0.14	1.12	1.19
$I(OCOCF_3)_4$	7.46	8.43	1.14	0.03	1.15	1.17
	7.50	8.40	1.14	0.03	1.15	1.17
	8.44	12.33	1.27	0.13	1.33	1.40

The replacement of the oxygen atom in the I=O group by fluorine and chlorine atoms and by trifluoroacetoxy- or benzenesulphonylimino-groups increases appreciably the σ_I constants, while in the case of the trifluoromethanesulphonylimino- or bis(fluorosulphonyl)methylide groups the increase is by a factor greater than two.

It is of interest that the ICl_2 group is more electron-accepting than IF_2, which can be explained by the greater contribution of the polar structure $\overset{+}{I}X^-$ (X = halogen) in the dichloroiodo-derivatives compared with the difluoroiodo-derivatives.

The accumulation of fluorine atoms and the $OCOCF_3$ groups at the iodine atom [the IF_4 and $I(OCOCF_3)_4$ substituents] increases somewhat the inductive effect. In compounds with a pentavalent tricoordinate iodine atom, the difference between the σ_I constants of the trivalent and pentavalent iodine analogues diminishes with increase in the electron-accepting capacity of the second group introduced at the iodine atom (the transition from $NSO_2C_6H_5$ to NSO_2CF_3). The I–N bond in $ArI{=}NSO_2CF_3$ is apparently polarised so much that the introduction of a second NSO_2CF_3 group increases the positive charge on the iodine atom to only a slight extent. This is confirmed by the finding that, on complete charge separation in diaryliodonium tetrafluoroborates, the σ_p constant of the substituent $\overset{+}{I}C_6H_5BF_4^-$ (1.37) is very close to the σ_p constants of the groups $I{=}NSO_2CF_3$ (1.35) and

 (1,40).

It is notable that the inductive effect of the ylide groups having the I–N and I–C bonds [I=NSO_2CF_3 and I=$C(SO_2F)_2$] is very large and almost the same (σ_I = 1.24 and 1.25 respectively), which indicates a high degree of polarisation in the ylide bond in both types of compound.

The effects of the conjugation of the iodine-containing groups are insignificant. All the iodine-containing substituents investigated, except IF_2, are characterised by small positive conjugation constants.

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