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Preparation, Structure and Properties of Polyvalent Iodine Compounds

Two general approaches to the synthesis of polyvalent iodine compounds exist: the first is based on the oxidative addition of appropriate ligands to a low-valent iodine species (e.g., I_2 or PhI) and the second is based on ligand exchange in polyvalent iodine compounds. The first approach is generally used to prepare common polyvalent iodine compounds by the oxidation of readily available and cheap precursors with an appropriate oxidant. This approach, in particular, is employed for large-scale preparation of the most important hypervalent iodine reagents, such as (dichloroiodo)benzene, (diacetoxyiodo)benzene and 2-iodoxybenzoic acid (IBX), from the corresponding iodoarenes and appropriate oxidants. Once formed, λ^3 - and λ^5 -iodanes can readily exchange their ligands by treatment with appropriate nucleophiles. The ligand exchange approach is commonly used for the preparation of a broad variety of λ^3 - and λ^5 -iodanes, arylodonium salts and iodonium ylides and imides.

Only several classes of inorganic polyvalent iodine compounds are known: polyvalent iodine fluorides, chlorides, oxides and the derivatives of iodic and periodic acid. Most of the known λ^3 - and λ^5 -iodanes are organic derivatives with one or two carbon ligands at the iodine, while derivatives of polyvalent iodine with three carbon ligands, R_3I , in general have low thermal stability and cannot be isolated. The overwhelming majority of organic λ^3 - and λ^5 -iodanes have a benzene ring as a carbon ligand linked to the iodine atom. Derivatives of polyvalent iodine with an alkyl substituent at iodine are highly unstable and generally can exist only as short-lived reactive intermediates in the oxidations of alkyl iodides. However, introduction of an electron-withdrawing substituent into the alkyl moiety leads to significant stabilization of the molecule. Typical representatives of such stabilized compounds with $I-Csp^3$ -bonding are perfluoroalkyl λ^3 -iodanes (R_fIL_2), numerous examples of which have been prepared and characterized.

2.1 Iodine(III) Compounds

2.1.1 Inorganic Iodine(III) Derivatives

The known classes of iodine(III) compounds without carbon ligands are represented by the iodine(III) halides and by the derivatives of unstable iodine(III) oxide, I_2O_3 , of types $OIOR$ or $I(OR)_3$. Table 2.1 summarizes the known inorganic iodine(III) compounds.

Table 2.1 Iodine(III) compounds without carbon ligands.

Compound	Method of synthesis	Properties	Reference
IF ₃	I ₂ + F ₂ /Ar mixture, -45 °C	Decomposes at -28 °C	[1]
ICl ₃	I ₂ + liquid Cl ₂ , -78 °C	Decomposes at 47–62 °C	[2, 7]
KICl ₄	KI/water + Cl ₂ gas	Stable golden solid, mp 115 °C	[3]
(IO) ₂ SO ₄	I ₂ + I ₂ O ₅ in conc. H ₂ SO ₄	Stable yellow solid	[4]
(IO) ₂ SeO ₄	I ₂ + I ₂ O ₅ in conc. H ₂ SeO ₄	Stable yellow solid	[4]
OIOSO ₂ F	I ₂ + I ₂ O ₅ in HOSO ₂ F	Hygroscopic yellow solid	[5]
OIOtF	I ₂ + I ₂ O ₅ in HOTf, rt	Hygroscopic yellow solid	[5]
I(OTf) ₃	I(OCOCF ₃) ₃ + HOTf	Colorless solid	[6]
I(OAc) ₃	I ₂ + conc. HNO ₃ + Ac ₂ O	Colorless crystals	[6]
I(OCOCF ₃) ₃	I ₂ + CF ₃ CO ₃ H	Colorless solid	[7]

2.1.1.1 Iodine(III) Halides

Iodine(III) halides in general lack stability. Of the four known binary iodine fluorides (IF, IF₃, IF₅ and IF₇) iodine trifluoride is the least stable with a decomposition temperature of -28 °C, as established by differential thermogravimetry [8]. Even at low temperatures IF₃ readily disproportionates to IF₅ and IF or I₂ [9]. However, if iodine is treated with diluted elemental fluorine at low temperatures, iodine trifluoride can be obtained free of IF₅ as an unstable yellow solid insoluble in conventional solvents [10]. Hoyer and Seppelt were able to grow crystals of IF₃ from anhydrous hydrogen fluoride in the presence of traces of water and to perform a single-crystal X-ray structure determination [1]. In crystal form, iodine trifluoride has a polymeric structure **1** (Figure 2.1), assembled from planar distorted T-shaped molecules with one primary I–F_{eq} bond distance of 1.872(4) Å and two I–F_{ax} bonds of 1.983(3) Å each, which have an F_{ax}–I–F_{ax} bond angle of 160.3(2)°. Each iodine atom is linked to a neighboring IF₃ molecule by two intermolecular I...F secondary bonds of 2.769(3) Å, so that the resulting coordination polyhedron around the iodine atom is a planar pentagon [1].

Several computational structural studies of iodine trifluoride have been published [11–16]. According to *ab initio* calculations [16], IF₃ has a distorted T-shaped geometry with the axial I–F bond distance of 1.971 Å, the equatorial I–F bond distance of 1.901 Å and an F_{ax}–I–F_{eq} angle of 81.7°.

The chemical properties of iodine trifluoride are almost unknown. IF₃ forms 1 : 1 complexes with pyrazine or 2,2'-bipyridyl and reacts with CsF in a 1 : 3 molar ratio to give Cs₃IF₆ [8]. The ligand exchange reaction of IF₃ with trifluoroacetic anhydride leading to iodine(III) trifluoroacetates has been reported [17].

Iodine trichloride, ICl₃, is usually prepared by a low-temperature reaction of iodine with liquid chlorine by the method of Booth and Morris [2]. It is obtained in the form of a fluffy orange solid that easily decomposes

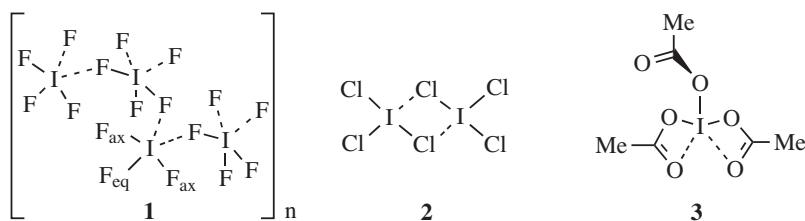


Figure 2.1 Primary and secondary bonding pattern in single-crystal X-ray structures of IF₃ (**1**), I₂Cl₆ (**2**) and I(OAc)₃ (**3**).

to ICl and Cl_2 at elevated temperatures. As established by a single-crystal X-ray analysis, iodine trichloride in the solid state exists as a dimer, I_2Cl_6 (**2**, Figure 2.1), with a planar structure containing two bridging $\text{I}-\text{Cl}\cdots\text{I}$ bonds ($\text{I}-\text{Cl}$ distances 2.68 and 2.72 Å) and four terminal $\text{I}-\text{Cl}$ bonds (2.38–2.39 Å) [18]. Iodine trichloride forms several addition products, which can be regarded as salts of the acid HICl_4 . The salts of alkali metals (e.g., KICl_4) and ammonia are best prepared by adding chlorine into an aqueous solution of the respective iodide [3].

Iodine tribromide, IBr_3 , is unstable and cannot be isolated as an individual compound. A study of solutions of iodine and bromine in hydrobromic acid by electrometric titrations provided experimental evidence for the existence of IBr_3 in the solution [19].

2.1.1.2 Derivatives of Iodine(III) Oxide

The parent iodine(III) oxide, I_2O_3 , is unknown; however, several its inorganic derivatives of types OIOR or I(OR)_3 have been reported in the literature. Historically, the first of these derivatives was iodosyl sulfate, $(\text{IO})_2\text{SO}_4$, which was first isolated as early as 1844 [20]. Iodosyl sulfate and the selenate, $(\text{IO})_2\text{SeO}_4$, can be prepared by the interaction of iodine with iodine pentoxide in concentrated sulfuric or selenic acid [4, 21, 22]. A convenient procedure for the preparation of iodosyl sulfate by heating iodine and sodium metaperiodate, NaIO_4 , in concentrated sulfuric acid was reported by Kraszkiewicz and Skulski in 2008 [23]. X-Ray crystallographic analysis of iodosyl sulfate shows a polymeric structure with infinite $(-\text{O}-\text{I}^+-\text{O}-)_n$ spiral chains linked by SO_4 tetrahedra [24]. Studies of $(\text{IO})_2\text{SO}_4$ by IR and Raman spectroscopy in the solid state [22] and by cryoscopic and conductometric measurements of the solution in sulfuric acid [25], were also reported.

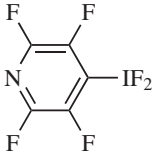
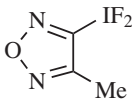

Iodosyl fluorosulfate, OIOSO_2F and the triflate, OIOTf , can be prepared as thermally stable, hygroscopic yellow solids by the reaction of iodine with iodine pentoxide or iodic acid in fluorosulfonic or trifluoromethanesulfonic acids, respectively [5]. Raman and infrared spectra of these compounds indicate a polymeric structure analogous to iodosyl sulfate [5]. Iodine tris(fluorosulfate), $\text{I(OSO}_2\text{F)}_3$ and tris(triflate), I(OTf)_3 , are also known [6, 26]. $\text{I(OSO}_2\text{F)}_3$ can be prepared by the reaction of iodine with peroxydisulfuryl difluoride [26]. Salts such as $\text{KI(OSO}_2\text{F)}_4$ have also been prepared and investigated by Raman spectroscopy [26, 27]. I(OTf)_3 was prepared from iodine tris(trifluoroacetate) and trifluoromethanesulfonic acid [6].

Several iodine(III) tris(carboxylate) derivatives, $\text{I(O}_2\text{CR)}_3$, where $\text{R} = \text{CH}_3$, CH_2Cl and CF_3 , have been reported in the literature [6]. These compounds are best synthesized by the oxidation of iodine with fuming nitric acid in the presence of the appropriate carboxylic acid and acetic anhydride. Birchall and coworkers reported an X-ray crystal and molecular structure of I(OAc)_3 [6]. The geometry about iodine in this compound consists of primary bonds to the three acetate groups ($\text{I}-\text{O}$ distances 2.159, 2.023 and 2.168 Å) and two strong intramolecular secondary bonds ($\text{I}\cdots\text{O}$ distances 2.463 and 2.518 Å) to two of the acetate groups, forming a pentagonal-planar arrangement **3** (Figure 2.1). An alternative method for the generation of I(OAc)_3 in solution involves the treatment of iodine trichloride with silver acetate in dry acetic acid [28]. $\text{I(O}_2\text{CCF}_3)_3$ can be prepared similarly from $\text{CF}_3\text{CO}_2\text{Ag}$ and ICl_3 in 90% yield or by the oxidation of iodine with peroxytrifluoroacetic acid in 80% yield [7].

2.1.2 Organoiodine(III) Fluorides

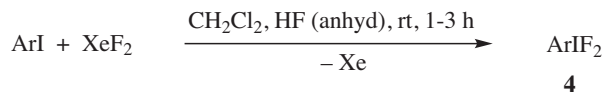
(Difluoroiodo)arenes, ArIF_2 , can be prepared by two general approaches: (i) oxidative addition of fluorine to iodoarenes using powerful fluorinating reagents and (ii) ligand exchange in iodine(III) compounds, such as ArIO or ArICl_2 , using HF or SF_4 as a source of fluoride anions. Table 2.2 summarizes the preparation methods for organic iodine(III) difluorides.

Table 2.2 Preparation of organic iodine(III) difluorides.

Compound	Method of synthesis	Yield (%)	Reference
PhIF ₂	PhI, XeF ₂ , anhyd. HF, CH ₂ Cl ₂ , room temp (rt), 1–3 h	95	[29, 37]
PhIF ₂	PhIO, 46% aq. HF, CH ₂ Cl ₂ , rt	86	[30]
3-ClC ₆ H ₄ IF ₂	ArI, XeF ₂ , anhyd. HF, CH ₂ Cl ₂ , rt, 1–3 h	95	[29]
3-NO ₂ C ₆ H ₄ IF ₂	ArI, XeF ₂ , anhyd. HF, CH ₂ Cl ₂ , rt, 1–3 h	95	[29]
3-MeOC ₆ H ₄ IF ₂	ArI, XeF ₂ , anhyd. HF, CH ₂ Cl ₂ , rt, 1–3 h	95	[29]
4-MeOC ₆ H ₄ IF ₂	ArI, XeF ₂ , anhyd. HF, CH ₂ Cl ₂ , rt, 1–3 h	95	[29]
4-MeC ₆ H ₄ IF ₂	ArIO, 46% aq. HF, CH ₂ Cl ₂ , rt	86	[30, 31]
4-ClC ₆ H ₄ IF ₂	ArIO, 46% aq. HF, CH ₂ Cl ₂ , rt	79	[30]
4-NO ₂ C ₆ H ₄ IF ₂	ArIO, 46% aq. HF, CH ₂ Cl ₂ , rt	85	[30]
2,6-F ₂ C ₆ H ₃ IF ₂	ArI, F ₂ /N ₂ , CCl ₃ F, –78 °C	Quantitative	[32]
4- <i>t</i> -Bu-2,6-Me ₂ C ₆ H ₂ IF ₂	ArH, I ₂ , Selectfluor, MeCN	78	[33]
	RI, XeF ₂ , CH ₂ Cl ₂ , –78 °C to rt, 4 h	84	[34]
	RI, XeF ₂ , MeCN, rt	Quantitative	[35]
CH ₃ IF ₂	CH ₃ I, XeF ₂ , no solvent, rt, 20 min	Quantitative	[36]
CF ₃ IF ₂	CF ₃ I, CF ₃ OCl, –50 °C, 24 h	Not reported	[37]
	RI, XeF ₂ , CCl ₄ , rt, 1 h	Quantitative	[38]

2.1.2.1 Preparation by Fluorination of Organic Iodides

Various fluorinating reagents have been used for the fluorination of iodoarenes. A very clean and selective, although relatively expensive, procedure for the preparation of (difluoroiodo)arenes **4** is based on the fluorination of iodoarenes with xenon difluoride in dichloromethane in the presence of anhydrous hydrogen fluoride (Scheme 2.1) [29, 39]. This method works well for the fluorination of iodoarenes with electron-donating or electron-withdrawing substituents; the latter, however, require longer reaction times. (Difluoroiodo)arenes (**4**) are hygroscopic and highly hydrolyzable compounds, which makes their separation and crystallization extremely difficult. Since xenon gas is the only byproduct in this reaction (Scheme 2.1), the



Ar = Ph, 3-ClC₆H₄, 3-NO₂C₆H₄, 4-MeOC₆H₄, 3-MeOC₆H₄

Scheme 2.1

resulting dichloromethane solutions contain essentially pure fluorides **4**, which can be used in the subsequent reactions without additional purification. A similar procedure, but in the absence of anhydrous hydrogen fluoride, has been employed in the synthesis of some heteroaromatic iododifluorides (Table 2.2). 4-(Difluoriodo)-2,3,5,6-tetrafluoropyridine, 4-(C₅F₄N)IF₂, was prepared in high yield by the reaction of 2,3,5,6-tetrafluoro-4-iodopyridine with xenon difluoride in dichloromethane at room temperature [34]. Likewise, the fluorination of 3-iodo-4-methylfurazan with xenon difluoride in acetonitrile at room temperature was used to prepare 3-(difluoriodo)-4-methylfurazan (Table 2.2) [35]. A relatively stable 4-(difluoriodo)tricyclene was prepared in the form of a pale yellow solid by treatment of a solution of 4-iodotricyclene in carbon tetrachloride with an excess of xenon difluoride followed by removal of solvent (Table 2.2) [38].

Various other powerful fluorinating reagents, such as F₂, ClF, CF₃OCl, BrF₅, C₆F₅BrF₂, C₆F₅BrF₄, XeF₂/BF₃, can be used for the preparation of (difluoriodo)arenes derived from polyfluoro-substituted iodoarenes [32, 40–42]. Frohn and coworkers investigated the preparation of C₆F₅IF₂ and other polyfluorinated (difluoriodo)arenes by oxidative fluorination of the appropriate iodides using F₂, ClF, CF₃OCl, BrF₅, C₆F₅BrF₂, C₆F₅BrF₄ and XeF₂ [40, 43, 44]. The highest purity and yield of C₆F₅IF₂ was achieved by a low-temperature fluorination with F₂ [40]. The C₆F₅IF₂ prepared in this work was fully characterized by multinuclear NMR, IR, Raman spectroscopy and X-ray structural analysis [40]. Another preparation of C₆F₅IF₂ in high yield (97%) involved the reaction of IF₃ with Cd(C₆F₅)₂ in dichloromethane at –78 °C [44]. Naumann and coworkers prepared 2,6-F₂C₆H₃IF₂ in quantitative yield by oxidative fluorination of the corresponding aryl iodide with XeF₂ in acetonitrile or with F₂/N₂ mixtures in CCl₃F [32].

Zefirov, Brel and coworkers developed a procedure for the preparation of [fluoro(trifluoromethylsulfonyloxy)iodo]arenes, ArIF(OTf), by oxidative fluorination of iodoarenes with FXeOTf, which can be generated *in situ* from XeF₂ and triflic acid [45–49]. The analogous mesylate, PhIF(OMs), can be prepared from iodobenzene, XeF₂ and methanesulfonic acid by a similar procedure [50, 51].

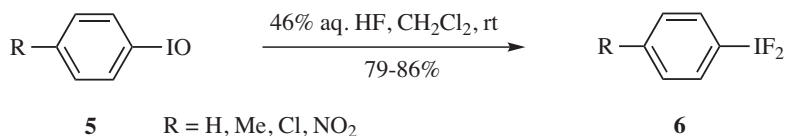
Shreeve and coworkers reported a convenient procedure for preparing (difluoriodo)arenes by direct fluorination of the respective iodoarenes with the commercially available fluorinating reagent Selectfluor® in acetonitrile solution. This procedure has been further improved by using the corresponding arene, elemental iodine and Selectfluor in a one-pot oxidative iodination/fluorination procedure [33].

para-Substituted (difluoriodo)arenes can be effectively prepared by electrochemical fluorination of the respective iodoarenes [52–54]. In the procedure developed by Fuchigami and Fujita, the electrosynthesis of ArIF₂ is accomplished by the anodic oxidation of iodoarenes with Et₃N·3HF or Et₃N·5HF in anhydrous acetonitrile using a divided cell [52]. This procedure works especially well for the preparation of 4-NO₂C₆H₄IF₂, which precipitates from the electrolytic solution in pure form during the electrolysis. Other *para*-substituted (difluoriodo)arenes, such as TolIF₂ and 4-MeOC₆H₄IF₂, can be used without isolation as in-cell mediators for subsequent reaction [52–55].

2.1.2.2 Preparation by Ligand Exchange

A classical procedure of Carpenter for the preparation of (difluoriodo)arenes involves a one-step reaction of (dichloroiodo)arenes with yellow mercuric oxide and 48% aqueous hydrofluoric acid in dichloromethane [56]. The resulting solution of (difluoriodo)arenes in dichloromethane can be used in subsequent reactions without additional purification. A drawback of this method is the use of a large quantity of harmful HgO to remove the chloride ion from the reaction mixture. A convenient modified procedure without the use of HgO consists of the treatment of iodosylarenes **5** with 40–46% aqueous hydrofluoric acid (Scheme 2.2) followed by crystallization of products **6** from hexane [30, 31]. It is important that the freshly prepared iodosylarenes **5** are used in this procedure.

The methods based on the use of hydrofluoric acid have several general disadvantages. First, (difluoriodo)arenes are often hygroscopic and highly hydrolyzable compounds, which makes their separation from



Scheme 2.2

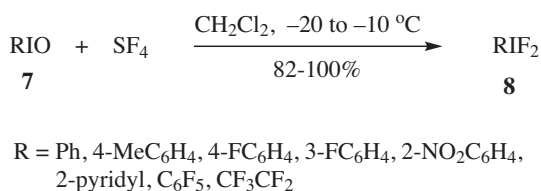
aqueous hydrofluoric acid and crystallization extremely difficult. Second, the high acidity of the reaction media complicates reactions of base- and acid-sensitive substrates, such as heterocycles. Yagupolskii, Lyalin and coworkers developed a milder procedure based on the reaction of organic iodosyl compounds **7** with SF₄ under neutral conditions [57]. In this method, SF₄ is bubbled at –20 °C through a suspension of the iodosyl compound **7** in dichloromethane (Scheme 2.3). All the byproducts in this reaction are volatile, so evaporation of the solvent under anhydrous conditions affords organic iododifluorides **8** of high purity. Owing to the mild and non-acidic reaction conditions, this method is applicable to the synthesis of the pyridine and perfluoroalkyl derivatives **8** [57].

(Difluoriodo)arenes are extremely sensitive to moisture and are commonly used as a freshly prepared solution, without isolation. DiMaggio and coauthors reported a convenient procedure for almost quantitative generation of PhIF₂ in acetonitrile solution by the reaction of PhI(OAc)₂ with anhydrous tetrabutylammonium fluoride under absolutely dry conditions [58].

2.1.2.3 Structural Studies

Only several structural studies of organo-iododifluorides, RIF₂, have been reported in the literature. Single-crystal X-ray diffraction studies of trifluoromethyl iododifluoride, CF₃IF₂, revealed a distorted T-shaped structure with the two fluorine atoms in the apical positions and the trifluoromethyl group in the equatorial position; I–C bond length 2.174(6) Å, I–F bond distances 1.982(2) Å and the F–I–F angle is 165.4(2)° [37]. The unit cell contains eight CF₃IF₂ molecules and each molecule has contacts to four adjacent molecules via I–F...I bridges resulting in a planar pentagonal coordination around the iodine atom (Figure 2.2). The lengths of all secondary F...I contacts are 2.950 Å [37], while the sum of the van der Waals radii of iodine and fluorine is significantly longer (3.45 Å [59]). Theoretical studies of CF₃IF₂ by *ab initio* and DFT (density functional theory) calculations have also been reported [60].

The X-ray crystal and molecular structures of 4-(difluoriodo)toluene and 3-(difluoriodo)nitrobenzene were reported in a PhD dissertation in 1996 [61]. More recently, Shreeve and coworkers have published single-crystal X-ray structures of two (difluoriodo)arenes, 4-MeC₆H₄IF₂ and 4-Bu^t-2,6-Me₂C₆H₂IF₂ [33]. The single-crystal structure of 4-MeC₆H₄IF₂ is similar to CF₃IF₂ and, in particular, has the same secondary bonding pattern resulting in a planar pentagonal coordination around the iodine atom. In contrast, in the crystal structure of 4-Bu^t-2,6-Me₂C₆H₂IF₂ the iodine atoms are only four coordinated with a distorted square-planar



Scheme 2.3

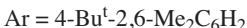


Figure 2.2 Primary and secondary bonding pattern in single-crystal X-ray structures of (a) CF_3IF_2 and (b) $4\text{-Bu}^t\text{-2,6-Me}_2\text{C}_6\text{H}_3\text{IF}_2$.

geometry. The intermolecular F...I interactions lead to self-assembly of four molecules of ArIF_2 into an unusual eight-membered chair ring formed by repeating F-I...F units (Figure 2.2) [33].

The structure of pentafluorophenyliododifluoride, $C_6F_5IF_2$, has been investigated by single-crystal X-ray crystallography and by multinuclear NMR, IR and Raman spectroscopy [40]. Frohn and coworkers reported the isolation and structural studies of adducts of several (difluoriodo)arenes with nitrogen bases [62]. In particular, the adducts of Ar_fIF_2 , ($Ar_f = C_6F_5$, $C_6F_2H_3$, $C_6F_3H_2$) with phenanthroline, 2,2'-bipyridine and quinoline were isolated and characterized by their single-crystal structure, Raman spectra and their multi-NMR spectra in the solution [62].

2.1.3 Organoiodine(III) Chlorides

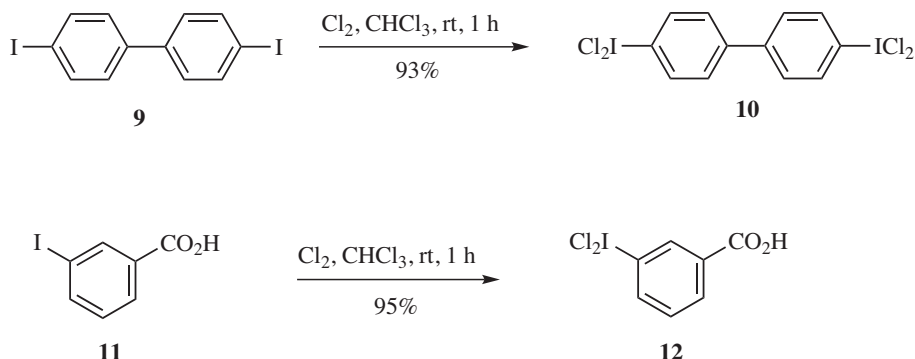
Organic iodine(III) dichlorides, RICHl_2 , are usually prepared by direct chlorination of organic iodides, or, less commonly, by ligand exchange in other iodine(III) compounds. Table 2.3 summarizes the preparation methods for organic iodine(III) dichlorides.

2.1.3.1 Preparation by Chlorination of Organic Iodides

Historically, (dichloroiodo)benzene, PhICl_2 , was the first reported organic compound of polyvalent iodine. It was prepared by Willgerodt in 1886 by the reaction of iodobenzene with ICl_3 or, preferably, with chlorine

Table 2.3 Preparation of organic iodine(III) dichlorides.

Compound	Method of synthesis	Yield (%)	Reference
PhICl ₂	PhI, Cl ₂ , CHCl ₃ , 0 °C, 3 h	94	[63]
PhICl ₂	PhI, 5.84% aq. NaOCl, conc. HCl, 15 °C	99	[64]
PhICl ₂	PhI, 30% aq. H ₂ O ₂ , conc. HCl, CF ₃ CH ₂ OH, rt (room temp.)	89	[65]
4-MeC ₆ H ₄ ICl ₂	Arl, Cl ₂ , hexane, 3 h, rt	92	[65]
3-NO ₂ C ₆ H ₄ IF ₂	Arl, Cl ₂ , hexane, 19 h, rt	76	[65]
3-HO ₂ CC ₆ H ₄ ICl ₂	Arl, Cl ₂ , CHCl ₃ , rt, 1 h	95	[66]
2,4,6-Pr ₃ C ₆ H ₂ ICl ₂	Arl, Cl ₂ , CHCl ₃ , -10 °C, 1 h	86	[67]
CF ₃ CH ₂ ICl ₂	CF ₃ CH ₂ I, Cl ₂ , no solvent, 0 °C, 2 h	85	[68]
CH ₃ I(Cl)F	CF ₃ I, CF ₃ OCl, -78 °C	Not reported	[69]
CF ₃ ICl ₂	CH ₃ I(Cl)F, Me ₃ SiCl, -40 °C	Not reported	[70]
(E)-ClCH=CHICl ₂	ICl ₃ , HC≡CH, conc. HCl, 0 °C to rt, 2 h	21	[71]

**Scheme 2.4**

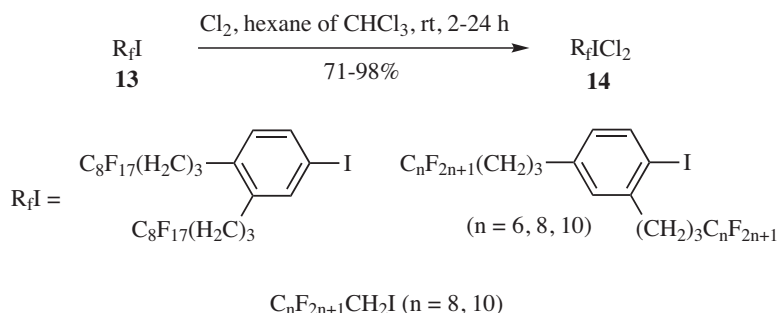
[72]. Direct chlorination of aryl iodides with chlorine in chloroform or dichloromethane is the most general approach to (dichloriodo)arenes [63].

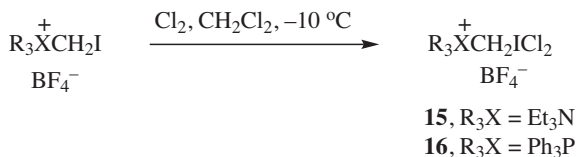
This method can be applied to the large-scale (20–25 kg) preparation of PhICl_2 by the reaction of iodobenzene with chlorine at -3 to $+4$ °C in dichloromethane [73]. (Dichloriodo)arenes are generally isolated as light- and heat-sensitive yellow crystalline solids, which are insufficiently stable for extended storage even at low temperatures.

The direct chlorination of iodoarenes **9** and **11** has been used for the preparation of 4,4'-bis(dichloriodo)biphenyl (**10**) and 3-(dichloriodo)benzoic acid (**12**) (Scheme 2.4), which are convenient recyclable hypervalent iodine reagents (Section 5.3) [66].

Gladysz and coworkers reported the synthesis of several fluorous aryl and alkyl iodine(III) dichlorides **14** in 71–98% yields by reactions of chlorine and the corresponding fluorous iodides **13** at room temperature in hexane or chloroform solutions (Scheme 2.5) [74]. A similar chlorination procedure was used to prepare $\text{CF}_3\text{CH}_2\text{ICl}_2$, $\text{CF}_3\text{CF}_2\text{CH}_2\text{ICl}_2$, $\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{ICl}_2$ and $\text{H}(\text{CF}_2)_6\text{CH}_2\text{ICl}_2$ by Montanari, DesMarteau and coworkers [68, 75, 76].

Alkyl iodine(III) dichlorides **15** and **16**, which are stabilized due to the presence of the electron-withdrawing trialkylammonium or triphenylphosphonium groups, can be prepared as relatively stable, non-hygroscopic, light-yellow microcrystalline solids by the chlorination of corresponding iodomethyl phosphonium and ammonium salts (Scheme 2.6) [77].

**Scheme 2.5**



Scheme 2.6

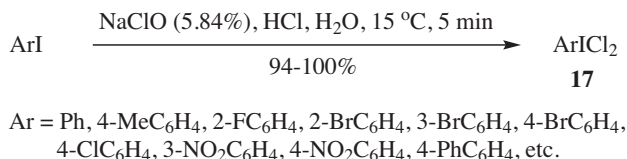
Another example of alkyl iodine(III) dichlorides stabilized by an electron-withdrawing substituent is represented by (dichloroiodo)methylsulfones, $\text{ArSO}_2\text{CH}_2\text{ICl}_2$, which are prepared similarly by chlorination of the appropriate iodomethylsulfones [78].

The preparation of several thermally unstable trifluoromethyl iodine(III) chlorides has been reported. The first spectroscopic indication for the existence of CF_3ICl_2 was reported in 1976 by Naumann and coworkers in a study of the reaction of trifluoromethyl iodide, CF_3I , with chlorine nitrate, ClONO_2 [79]. The intermediate in this reaction is a mixed chloride–nitrate $\text{CF}_3\text{I}(\text{Cl})\text{ONO}_2$, which cannot be isolated. More recently, Minkwitz and coworkers developed a better approach to trifluoromethyl iodine(III) chlorides. Specifically, the reaction of CF_3I with CF_3OCl at -78°C affords the mixed dihalide, $\text{CF}_3\text{I}(\text{Cl})\text{F}$, which is unstable even at low temperatures and decomposes to the symmetrical halides, CF_3IF_2 and CF_3ICl_2 [69]. (Trifluoromethyl)iodine dichloride, CF_3ICl_2 , can be obtained in high purity and yield by the reaction of $\text{CF}_3\text{I}(\text{Cl})\text{F}$ with chlorotrimethylsilane at -40°C [70].

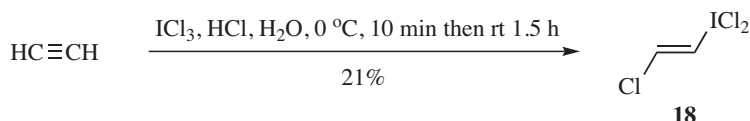
To avoid the use of elemental chlorine, iodoarenes can be chlorinated *in situ* in aqueous hydrochloric acid in the presence of an appropriate oxidant, such as KMnO_4 , activated MnO_2 , KClO_3 , NaIO_3 , concentrated HNO_3 , NaBO_3 , $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}_2$, $\text{Na}_2\text{S}_2\text{O}_8$, CrO_3 and the urea– H_2O_2 complex [80–85]. For example, the chlorination of iodoarenes in a biphasic mixture of carbon tetrachloride and concentrated hydrochloric acid in the presence of $\text{Na}_2\text{S}_2\text{O}_8$ affords the corresponding (dichloroiodo)arenes in 60–100% crude yields [81]. A modification of this method consists of the one-pot oxidative iodination/chlorination of arenes with iodine and an appropriate oxidant in hydrochloric acid [81]. Particularly useful is a solvent-free oxidative procedure involving treatment of ArI with the urea–hydrogen peroxide complex followed by addition of aqueous hydrochloric acid [85].

A convenient and mild approach to (dichloroiodo)arenes **17** consists of the chlorination of iodoarenes using concentrated hydrochloric acid and aqueous sodium hypochlorite (Scheme 2.7) [64]. Sodium chlorite, NaClO_2 , can also be used in this procedure; however, in this case the chlorination takes longer time (3 h at room temperature) and the yields of products **17** are generally lower [64].

Podgorsek and Iskra reported a procedure for the conversion of iodoarenes into (dichloroiodo)arenes in 72–91% preparative yields by the oxidative halogenation approach using 30% aqueous hydrogen peroxide and hydrochloric acid in fluorinated alcohol at room temperature [65]. In this reaction trifluoroethanol is not only the reaction medium but is also an activator of hydrogen peroxide for the oxidation of hydrochloric acid to chlorine.



Scheme 2.7



Scheme 2.8

2.1.3.2 Preparation by Ligand Exchange

The ligand exchange approach is not commonly used to prepare organic iodine(III) dichlorides and only several examples of such reactions are known. (Dichloroiodo)benzene can be conveniently prepared by treatment of iodosylbenzene with chlorotrimethylsilane, Me_3SiCl , in dichloromethane [86]. This is a very clean reaction, which allows us to generate PhICl_2 *in situ* and so use it without isolation [87]. A similar approach was employed for the low-temperature preparation of CF_3ICl_2 by the reaction of $\text{CF}_3\text{I}(\text{Cl})\text{F}$ with trimethylchlorosilane at $-40\text{ }^\circ\text{C}$ [70].

(*E*)-Chlorovinyl iodine(III) dichloride (**18**), a useful reagents for the synthesis of arylodonium salts, is prepared by addition of iodine trichloride to acetylene in concentrated hydrochloric acid (Scheme 2.8) [71,88,89]. **Caution:** product **18** should be handled with a great care; it is extremely unstable and decomposes autocatalytically within seconds. It can, however, be stored for weeks in a freezer at $-20\text{ }^\circ\text{C}$ or below [71,89].

2.1.3.3 Structural Studies

Several X-ray crystallographic studies of organo-iododichlorides, RICl_2 , have been reported in the literature. The first X-ray crystal structures of PhICl_2 [90] and $4\text{-ClC}_6\text{H}_4\text{ICl}_2$ [91] published in the 1950s were imprecise by modern standards. More recently, Chaloner and coworkers reported a good quality structure of PhICl_2 obtained at low temperature [92]. The molecule of PhICl_2 has the characteristic T-shape with primary I—Cl bond distances of 2.47 Å and 2.49 Å and Cl—I—C bond angles of 87.8 and 89.2°. In the solid state the molecules form an infinite zigzagged chain, in which one of the chlorine atoms interacts with the iodine of the next unit with an intermolecular $\text{I}\cdots\text{Cl}$ secondary bond distance of 3.42 Å. The coordination of iodine is distorted square-planar with the lone pairs occupying the *trans*-positions of a pseudo-octahedron [92].

X-Ray structures of two sterically encumbered (dichloroiodo)arenes, $2,4,6\text{-Pr}^i_3\text{C}_6\text{H}_2\text{ICl}_2$ [67] and ArICl_2 [$\text{Ar} = 2,6\text{-bis}(3,5\text{-dichloro-2,4,6-trimethylphenyl})\text{benzene}$] [93] have been reported. Both molecules have the expected T-shaped geometry; the latter molecule has Cl—I—C angles of 89.4(3) and 92.1(3)° and I—Cl distances of 2.469(4) and 2.491(4) Å. The secondary $\text{I}\cdots\text{Cl}$ bond distance in this compound is 3.816 Å, which indicates a significant reduction of intermolecular association as compared to PhICl_2 [93]. The X-ray crystal structure of 2-(dichloroiodo)nitrobenzene, $2\text{-NO}_2\text{C}_6\text{H}_4\text{ICl}_2$, does not show any significant intramolecular interaction between the iodine(III) center and the oxygen atom of the nitro group in the *ortho* position ($\text{I}\cdots\text{O}$ bond distance 3.0 Å) [94].

The X-ray structure of the PhICl_2 adduct with tetraphenylphosphonium chloride, $[\text{Ph}_4\text{P}]^+[\text{PhICl}_3]^-$, has been reported [95]. The $[\text{PhICl}_3]^-$ anions in this structure have a planar coordination environment at the iodine atom. The I—Cl bond length of the chlorine atom *trans* to the Ph group is much longer (3.019 Å) than the bond distance to the *cis* Cl atoms (2.504 Å) [95].

X-Ray crystal structures of two polyfluoroalkyl iododichlorides, $\text{CF}_3\text{CH}_2\text{ICl}_2$ and $\text{CHF}_2(\text{CF}_2)_5\text{CH}_2\text{ICl}_2$, have been reported [68]. In comparison to PhICl_2 , which has a simple chain structure, perfluoroalkyl iododichlorides have more complicated structures in which weak interactions between chains, coupled with aggregation of perfluoro groups, result in the formation of layers in the solid state.

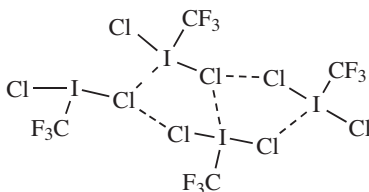


Figure 2.3 Primary and secondary bonding pattern in a single-crystal X-ray structure of CF_3ICl_2 .

Single-crystal X-ray analysis of (trifluoromethyl)iodine dichloride, CF_3ICl_2 , shows a T-shaped molecular structure with the CF_3 group in the equatorial position [70]. The axial I–Cl bonds in CF_3ICl_2 are three-center-four-electron semi-ionic bonds and have lengths of 2.478(2) and 2.457(2) Å and the angle between the iodine and the two apical chlorines is 171.62(9)°. The intermolecular I··Cl contact in CF_3ICl_2 is 3.324 Å long, which is much longer than the bridging bonds in I_2Cl_6 (2.68–2.72 Å) (Section 2.1.1.1), but shorter than in $\text{C}_6\text{H}_5\text{ICl}_2$ (3.40 Å) and 2,4,6- $\text{Pr}^i_3\text{C}_6\text{H}_2\text{ICl}_2$ (3.49 Å). In addition to the I–Cl contacts, CF_3ICl_2 also contains weak Cl–Cl contacts of 3.361 Å, some 4% under the sum of the van der Waals radii (3.5 Å), which are due to packing effects. All these contacts result in the formation of chains of side-linked five-membered rings (Figure 2.3) [70].

2.1.4 Organo-Iodosyl Compounds

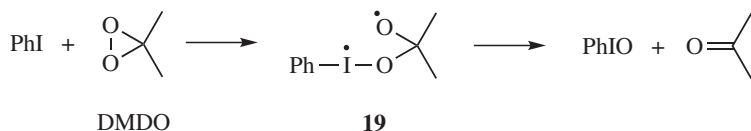
Organic iodosyl compounds usually have a polymeric structure, $(\text{RIO})_n$, with a typical, for λ^3 -iodanes, T-shaped geometry at the iodine atom; no structural evidence supporting the existence of an I=O double bond has been reported. Most known iodosyl compounds have low thermal stability and some are explosive upon heating. Iodosyl compounds can be prepared by direct oxidation of organic iodides, or, more commonly, by basic hydrolysis of other iodine(III) compounds. Table 2.4 summarizes the preparation methods for organic iodosyl compounds.

2.1.4.1 Preparation by Oxidation of Organic Iodides

Aryl iodides smoothly react with dimethyldioxirane (DMDO) in acetone to give mainly, depending on the amount of DMDO, iodosyl- or iodylarenes, which precipitate from the solution [97]. Minisci and coworkers

Table 2.4 Preparation of organo-iodosyl compounds.

Compound	Method of synthesis	Yield (%)	Reference
PhIO	$\text{PhI}(\text{OAc})_2$, NaOH, H_2O , rt (room temp), 1 h	93	[96]
PhIO	PhI, DMDO, acetone, 0 °C to rt, 3 h	26	[97]
PhIO	PhICl_2 , NaHCO_3 , NaOH, H_2O , 0 °C	63	[98]
4-MeC ₆ H ₄ IO	ArICl_2 , NaOH, THF, H_2O , rt, 1 min	81	[30]
4-MeOC ₆ H ₄ IO	$\text{ArI}(\text{OAc})_2$, NaOH, THF, H_2O , rt	88	[99]
4-NO ₂ C ₆ H ₄ IO	$\text{ArI}(\text{OAc})_2$, NaOH, THF, H_2O , rt	90	[99]
2-Bu ^t O ₂ SC ₆ H ₄ IO	$\text{ArI}(\text{OAc})_2$, NaOH, H_2O , rt, 25 min	95	[100]
3-HO ₂ CC ₆ H ₄ IO	ArI, AcOOH/AcOH, rt, 12 h	80	[101]
$\text{CF}_3\text{CF}_2\text{IO}$	$\text{CF}_3\text{CF}_2\text{I}(\text{OCOCF}_3)_2$, NaHCO_3 , ice, 0 °C	95	[102]

**Scheme 2.9**

investigated the mechanism of the reaction of iodobenzene with DMDO and suggested that this reaction occurs as the PhI-induced homolysis of the peroxide bond via the diradical intermediate **19** (Scheme 2.9) [103].

Asensio and coworkers reported a low temperature oxidation of iodomethane with DMDO to afford a pale yellow precipitate of iodosylmethane (**20**, Scheme 2.10) [104]. Upon raising the temperature to $-40\text{ }^{\circ}\text{C}$, in the presence of moisture iodosylmethane decomposes to form the unstable hypoiodous acid, HOI, which can be trapped *in situ* by an alkene to afford iodohydrins. The formation of MeIO has also been detected in the photochemical reaction of iodomethane with ozone in an argon matrix at 17 K [105]. A similar low-temperature reaction of trifluoroiodomethane affords the unstable CF₃IO, which was identified by infrared spectroscopy [106].

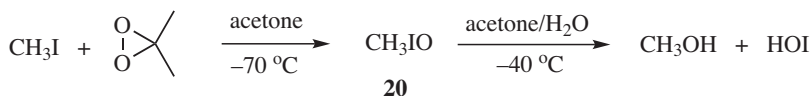
The DMDO oxidation of iodocyclohexane affords *trans*-2-iodocyclohexanol as the final product via intermediate formation of iodosylcyclohexane followed by elimination of hypoiodous acid, which then adds to the alkene generated in the elimination step [103]. The oxidative deiodination of iodoalkanes via conversion into iodosylalkanes followed by nucleophilic substitution of the iodosyl group has found some synthetic application, particularly in the synthesis of steroidal products (Section 3.1.19) [107].

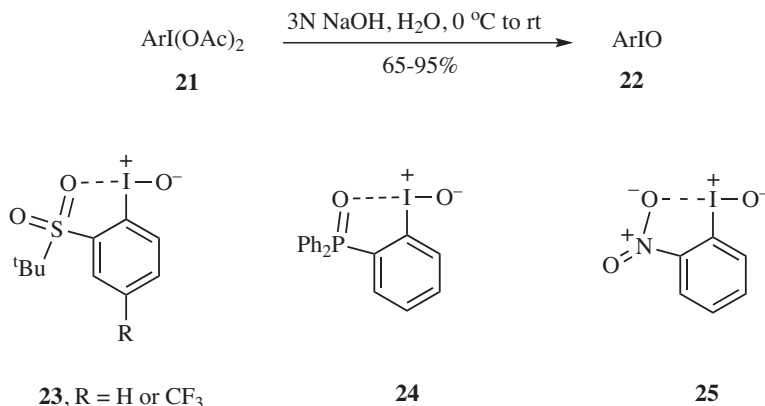
Protonated iodosylbenzene species can be generated in solution by the oxidation of iodobenzene with Oxone[®] (2KHSO₅·KHSO₄·K₂SO₄) in aqueous acetonitrile. The presence of protonated iodosylbenzene [PhIOH]⁺ in such solutions has been supported by ESI mass spectrometry [108]. This procedure has been utilized in catalytic oxidations using iodobenzene as the pre-catalyst and Oxone as the stoichiometric oxidant (Section 4.1) [109].

3-Iodosylbenzoic acid, 3-HO₂CC₆H₄IO, a useful recyclable oxidant, is conveniently prepared by the oxidation of 3-iodobenzoic acid with peracetic acid [101].

2.1.4.2 Preparation from Other Iodine(III) Compounds

Hydrolysis of diacetoxy- or (dichloroiodo)arenes is the most common approach to organic iodosyl compounds. Iodosylbenzene, PhIO, the most important member of the family of iodosyl compounds, is best prepared by hydrolysis of PhI(OAc)₂ with aqueous NaOH [96]. The same procedure can be used to prepare various *ortho*-, *meta*- and *para*-substituted iodosylarenes **22** from the respective (diacetoxy)iiodoarenes **21** (Scheme 2.11). This procedure, for example, has been used to obtain 4-methoxyiodosylbenzene [99], 4-nitroiodosylbenzene [99] and pseudocyclic iodosylarenes **23–25** bearing *tert*-butylsulfonyl [100, 110], diphenylphosphoryl [111], or nitro [94] groups in the *ortho*-position. The relatively stable iodosylperfluoroalkanes C_nF_{2n+1}IO (*n* = 2, 3, 4, 6) are synthesized similarly by the mild hydrolysis of the respective bis(trifluoroacetates) C_nF_{2n+1}I(CO₂CF₃)₂ using NaHCO₃ and water with ice [102].

**Scheme 2.10**



Scheme 2.11

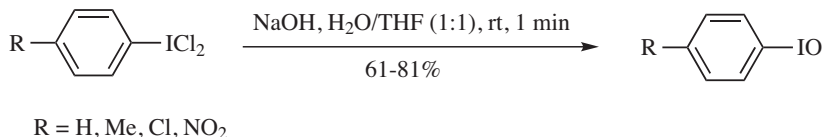
Iodosylbenzene is a yellowish amorphous powder that cannot be recrystallized due to its polymeric nature. It dissolves in methanol with depolymerization to afford PhI(OMe)₂ [112]. Heating or extended storage at room temperature results in disproportionation of iodosylbenzene to PhI and colorless, explosive iodylbenzene, PhIO₂. Drying iodosylbenzene at elevated temperatures should be avoided because of the possibility of a severe explosion. A violent explosion of iodosylbenzene upon drying at 110 °C in vacuum has been reported [113]. However, handling of even large amounts of iodosylbenzene at room temperature is relatively safe.

An alternative general procedure for the preparation of iodosylarenes is based on the alkaline hydrolysis of (dichloroiodo)arenes under conditions similar to the hydrolysis of (diacetoxyiodo)arenes [98, 114, 115]. A modified procedure employs aqueous tetrahydrofuran as a solvent for the basic hydrolysis of (dichloroiodo)arenes (Scheme 2.12) [30].

Oligomeric iodosylbenzenes **26** and **27** have been prepared by ligand exchange in λ³-iodanes under moderately acidic conditions. The oligomer **26** was obtained by the treatment of PhI(OAc)₂ with aqueous NaHSO₄ [116, 117], while product **27** precipitated from dilute aqueous solutions of PhI(OH)OTs and Mg(ClO₄)₂ [118] (Scheme 2.13). The formation of both products can be explained by self-assembly of the hydroxy(phenyl)iodonium ions (PhI⁺OH in hydrated form) and [oxo(aquo)iodo]benzene PhI⁺(OH₂)O⁻ in aqueous solution under the reaction conditions.

2.1.4.3 Structural Studies

Although iodosylbenzene has been known and widely used as a reagent for over 100 years, structural details are still limited due to its amorphous polymeric nature, insolubility and low stability. On the basis of spectroscopic studies, it was suggested that in the solid state iodosylbenzene exists as a zigzag polymeric,



Scheme 2.12

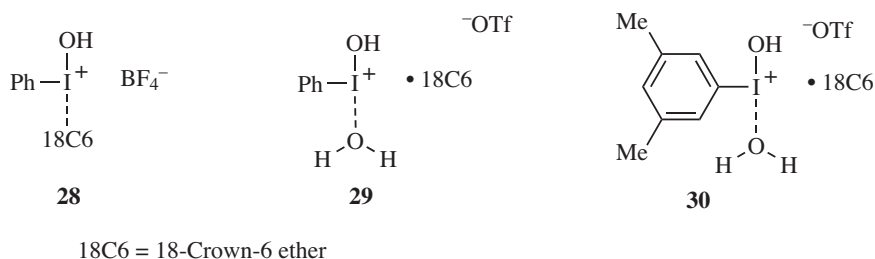


Figure 2.5 Activated iodosylbenzene monomer complexes with 18C6 crown ether.

revealed a complex structure consisting of pentaiodanyl dicationic units joined by secondary I...O bonds into an infinite linear structure of 12-atom hexagonal rings [118].

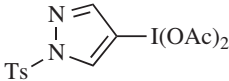
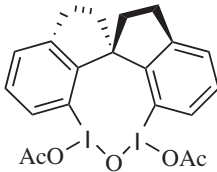
Ochiai and coworkers have reported the preparation, X-ray crystal structures and useful oxidizing reactions of activated iodosylbenzene monomer complexes with 18C6 crown ether (Figure 2.5) [124, 125]. Reaction of iodosylbenzene with $\text{HBF}_4/\text{Me}_2\text{O}$ in the presence of equimolar 18C6 in dichloromethane afforded quantitatively the stable, crystalline crown ether complex **28**, which is soluble in acetonitrile, methanol, water and dichloromethane. X-Ray analysis revealed a protonated iodosylbenzene monomer structure **28** stabilized by intramolecular coordination with the crown ether oxygen atoms [125]. The aqua complexes of iodosylarenes **29** and **30** with a water molecule coordinated to iodine(III) were prepared by the reaction of (diacetoxyiodo)benzene with trimethylsilyl triflate in the presence of 18C6 crown ether in dichloromethane. X-Ray analysis of complex **28** confirmed a T-shaped structure, ligated with one water molecule at the apical site of the iodine(III) atom of the hydroxy(phenyl)iodonium ion, with a near-linear O–I–O triad (173.96°). Including a close contact with one of the crown ether oxygens, the complex adopts a distorted square-planar geometry around the iodine [126].

Owing to the polymeric structure, iodosylbenzene is insoluble in all nonreactive solvents; however, soluble derivatives of iodosylbenzene can be realized by placing an appropriate substituent on the *ortho* position of the phenyl ring. Protasiewicz and coworkers have reported the preparation and X-ray structure of the monomeric iodosylarene $2\text{-Bu}^t\text{O}_2\text{SC}_6\text{H}_4\text{IO}$, (**23**, $\text{R} = \text{H}$, see Scheme 2.11), in which the intramolecular secondary I...O bond replaces the intermolecular interactions that are typical of polymeric iodosylbenzene [100, 127]. Iodosylarene **23** is readily soluble in organic solvents (up to 0.08 M in chloroform) and can be analyzed by NMR in solution [100]. Single-crystal X-ray analysis of **23** showed a structure resembling benziodoxoles with an intramolecular distance of 2.707 Å between one of the sulfone oxygen atoms and the hypervalent iodine center [127]. The I–O bond length in the iodosyl group of **23** is 1.848 Å and the intramolecular O–I–O bond angle is 167.3° . The iodine centers in **23** achieve a pseudo-square-planar geometry by the formation of intermolecular an I...O secondary bond (2.665 Å) to a neighboring iodosyl oxygen atom [127].

2.1.5 Organoiodine(III) Carboxylates

[Bis(acyloxy)iodo]arenes, $\text{ArI}(\text{O}_2\text{CR})_2$, are the most important, well investigated and practically useful organic derivatives of iodine(III). Two of them, (diacetoxyiodo)benzene and [bis(trifluoroacetoxy)iodo]benzene, are commercially available and widely used oxidizing reagents. The preferred abbreviations, DIB for (diacetoxyiodo)benzene and BTI for [bis(trifluoroacetoxy)iodo]benzene, were originally suggested by Varvoglis in his book published in 1992 [128]; however, the older abbreviations PIDA (phenyliodine diacetate) and PIFA [phenyliodine bis(trifluoroacetate)] are still frequently used in modern research literature. Two general approaches are used for the preparation of [bis(acyloxy)iodo]arenes: (i) the oxidation of iodoarenes in the presence of a carboxylic acid and (ii) a ligand-exchange reaction of the

Table 2.5 Preparation of organoiodine(III) carboxylates.

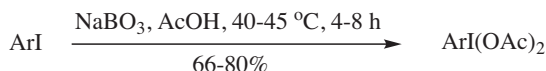
Compound	Method of synthesis	Yield (%)	Reference
PhI(OAc) ₂	PhI, AcOOH, AcOH, rt (room temp), 12 h	79	[129]
PhI(OAc) ₂	PhI, 3-ClC ₆ H ₄ CO ₂ H, AcOH, rt, 15 h	83	[130]
PhI(OAc) ₂	PhI, NaBO ₃ , TfOH, AcOH, 40–45 °C, 3 h	99	[131–139]
4-MeC ₆ H ₄ I(OAc) ₂	Arl, NaBO ₃ , TfOH, AcOH, 40–45 °C, 4 h	96	[131]
3-MeOC ₆ H ₄ I(OAc) ₂	Arl, NaBO ₃ , TfOH, AcOH, 40–45 °C, 4 h	98	[131]
3-NO ₂ C ₆ H ₄ I(OAc) ₂	Arl, NaBO ₃ , TfOH, AcOH, 40–45 °C, 6 h	94	[131]
4-FC ₆ H ₄ I(OAc) ₂	Arl, NaBO ₃ , TfOH, AcOH, 40–45 °C, 8 h	86	[131]
2,6-Me ₂ C ₆ H ₃ I(OAc) ₂	Arl, NaBO ₃ , AcOH, 40–45 °C, 4–8 h	75	[132]
	Arl, NaBO ₃ , AcOH, 50–60 °C, 8–24 h	Not reported	[133]
	Arl, Selectfluor, AcOH/MeCN, rt, 12 h	90	[134]
C ₆ F ₁₃ I(OCOCF ₃) ₂	C ₆ F ₁₃ I, Oxone, CF ₃ CO ₂ H, rt, 24 h	88	[135]
C ₆ F ₅ I(OCOCF ₃) ₂	C ₆ F ₅ I, Oxone, CF ₃ CO ₂ H, rt, 2 h	94	[135]
2-ClC ₆ H ₄ I(OCOCF ₃) ₂	2-ClC ₆ H ₄ I, Oxone, CF ₃ CO ₂ H, rt, 1.5 h	97	[135]
4-CF ₃ C ₆ H ₄ I(OCOCF ₃) ₂	Arl, HNO ₃ , (CF ₃ CO) ₂ O, –30 °C to rt, 4 days	79	[136]
CF ₃ CH ₂ I(OCOCF ₃) ₂	CF ₃ CH ₂ I, CF ₃ CO ₂ H, CF ₃ CO ₂ H, 0 °C to rt, 24 h	89	[137]
PhSO ₂ CH ₂ I(OCOCF ₃) ₂	PhSO ₂ CH ₂ I, CF ₃ CO ₂ H, CF ₃ CO ₂ H, –30 °C to rt, 4 h	99	[138]
PhI(OCOCF ₃) ₂	PhI(OAc) ₂ , CF ₃ CO ₂ H, rt	60	[139]

readily available DIB with an appropriate carboxylic acid. Table 2.5 provides an overview of preparation methods for organoiodine(III) carboxylates.

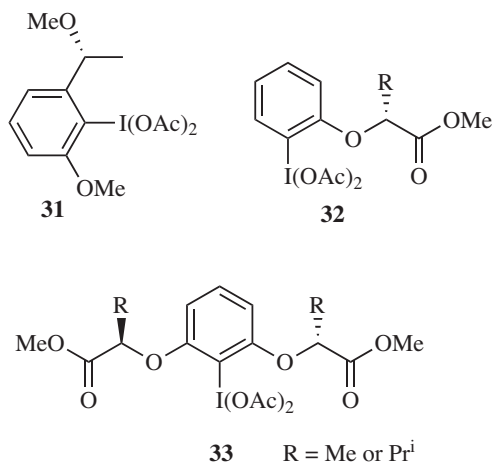
2.1.5.1 Preparation by Oxidation of Organic Iodides

The most practically important organoiodine(III) carboxylates, DIB, is usually prepared by the oxidation of iodobenzene with peracetic acid in acetic acid according to the procedure of Sharefkin and Saltzman [129]. A similar peracid oxidation of substituted iodobenzenes can be used to furnish numerous other (diacetoxyiodo)arenes, including the polymer-supported analogs of DIB from poly(iodostyrene) or aminomethylated poly(iodostyrene) [140–143] and the ion-supported (diacetoxyiodo)arenes (Chapter 5) [144, 145]. Likewise, various [bis(trifluoroacetoxy)iodo]arenes can be synthesized in high yield by the oxidation of the respective iodoarenes with peroxytrifluoroacetic acid in trifluoroacetic acid [146–148].

A modification of this method consists of the oxidative diacetoxylation of iodoarenes in acetic or trifluoroacetic acid using appropriate oxidants, such as periodates [149–151], chromium(VI) oxide [152], sodium percarbonate [153], *m*-chloroperoxybenzoic acid (*m*CPBA) [130, 154–158], potassium peroxodisulfate [159, 160], H₂O₂–urea [161], Selectfluor [33] and sodium perborate [132]. The oxidation of iodoarenes with sodium perborate in acetic acid at 40 °C is probably the most general procedure that has been used for the small-scale preparation of numerous (diacetoxyiodo)-substituted arenes and hetarenes (Scheme 2.14) [132, 133, 162–166]. For example, the chiral diacetate **31** and several analogous



Ar = Ph, 2-MeC₆H₄, 4-MeC₆H₄, 2-ClC₆H₄, 4-MeOC₆H₄,
2,4-Me₂C₆H₃, 2,6-Me₂C₆H₃, 2,3,5,6-Me₂C₆H, 3-NO₂C₆H₄, 3-CF₃C₆H₄, 2-thienyl, 3-thienyl, etc.



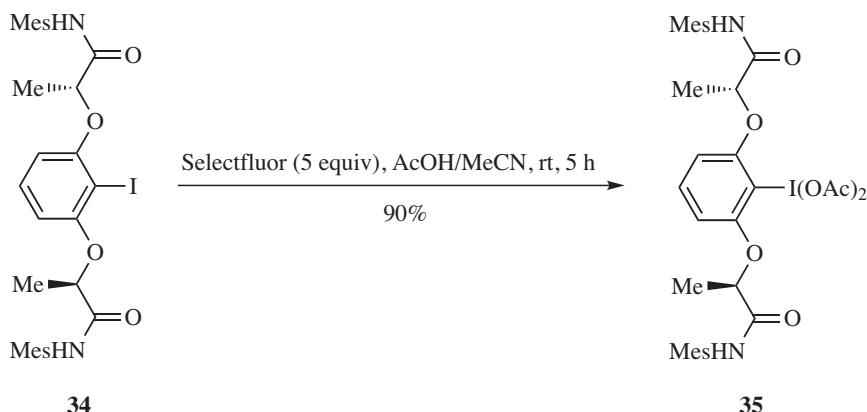
Scheme 2.14

products were prepared in 73–87% yield by the perborate oxidation of the appropriate aryl iodides [166]. These acetates serve as important precursors to the chiral [(hydroxy)tosyloxy]iodoarenes (Section 2.1.6). Fujita and coworkers used the perborate oxidation procedure for the synthesis of optically active (diacetoxyiodo)arenes **32** and **33** [165, 167, 168]. Several heteroaromatic derivatives of (diacetoxyiodo)arenes [i.e., *N*-tosyl-4-(diacetoxyiodo)pyrazole, *N*-trifluoromethanesulfonyl-4-(diacetoxyiodo)pyrazole, 2-(diacetoxyiodo)thiophene and 3-(diacetoxyiodo)thiophene] were prepared similarly by using sodium perborate in acetic acid [133]. The perborate oxidation procedure can be further improved by performing the oxidation in the presence of catalytic amounts of trifluoromethanesulfonic acid [131].

A convenient and mild experimental procedure for the preparation of (diacetoxyiodo)arenes using Selectfluor as the oxidant in acetic acid has been developed by Shreeve and coworkers [33]. This method, in particular, has been utilized in the syntheses of a chiral hypervalent iodine(III) reagent having a rigid spiro-biindane backbone [134] and the C₂-symmetric chiral (diacetoxyiodo)arene **35** from the respective iodide **34** (Scheme 2.15) [169, 170].

Kitamura and Hossain have found that potassium peroxodisulfate can be used as an efficient oxidant for the preparation of (diacetoxyiodo)arenes and [bis(trifluoroacetoxy)iodo]arenes from iodoarenes [159, 160]. A convenient modification of this approach employs the interaction of arenes with iodine and potassium peroxodisulfate in acetic acid (Scheme 2.16) [171]. The mechanism of this reaction probably includes the oxidative iodination of arenes, followed by oxidative diacetoxylation of ArI *in situ* leading to (diacetoxyiodo)-arenes **36**.

Zefirov, Stang and coworkers have developed a general procedure for the preparation of various [bis(trifluoroacetoxy)iodo]arenes by the oxidation of iodoarenes with xenon bis(trifluoroacetate), which can be generated *in situ* from XeF₂ and trifluoroacetic acid (Scheme 2.17) [172].



Scheme 2.15

Several stabilized alkyl iodine(III) dicarboxylates have been reported in the literature. [Bis(trifluoroacetoxy)iodo]perfluoroalkanes, $R_fI(CO_2CF_3)_2$, were originally prepared by Yagupolskii and coworkers in almost quantitative yield by the oxidation of 1-iodoperfluoroalkanes with peroxytrifluoroacetic acid [173]. These relatively stable compounds have found practical application for the preparation of perfluoroalkyl(phenyl)iodonium salts, which are used as electrophilic fluoroalkylating reagents (FITS reagents) (Section 2.1.9.5) [174].

A convenient newer procedure for preparing various [bis(trifluoroacetoxy)iodo]perfluoroalkanes **37** and also [bis(trifluoroacetoxy)iodo]arenes **38** involves the oxidation of the corresponding aryl and perfluoroalkyl iodides with the commercially available and inexpensive oxidant Oxone ($2KHSO_5 \cdot 3KHSO_4 \cdot 3K_2SO_4$) in trifluoroacetic acid at room temperature (Scheme 2.18) [135].

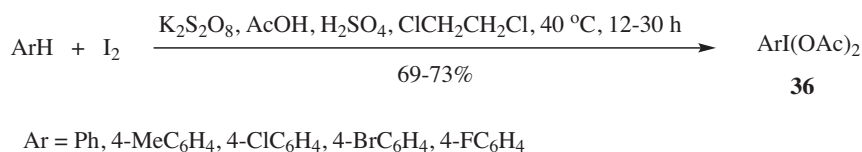
1-[Bis(trifluoroacetoxy)iodo]-1*H*,1*H*-perfluoroalkanes **39** have been prepared in almost quantitative yield by the oxidation of 1-iodo-1*H*,1*H*-perfluoroalkanes with peroxytrifluoroacetic acid as relatively stable, although moisture sensitive, white microcrystalline solids (Scheme 2.19) [137, 175, 176].

[(Arylsulfonyl)methyl]iodine(III) bis(trifluoroacetates) **41** can be prepared from the respective iodomethyl sulfones **40** using a similar oxidation procedure (Scheme 2.20) [138]. Bis(trifluoroacetates) **41** can be isolated at 0 °C, but are unstable at room temperature and can spontaneously decompose with explosion.

The reaction of 4-iodotricyclene **42** with *m*-chloroperoxybenzoic acid in dichloromethane at room temperature gives a microcrystalline precipitate of 4-[bis(*m*-chlorobenzoyloxy)iodo]tricyclene **43** (Scheme 2.21) [177]. Compound **43** has a melting point of 180–182 °C and is indefinitely stable at room temperature.

2.1.5.2 Preparation by Ligand Exchange

The second common approach to [bis(acyloxy)iodo]arenes is based on the ligand-exchange reaction of a (diacetoxyiodo)arene (usually DIB) with an appropriate carboxylic acid. A typical procedure consists of



Scheme 2.16



Ar = Ph, 4-MeC₆H₄, 2-MeC₆H₄, 4-NO₂C₆H₄, 3-NO₂C₆H₄, 2-Me-4-NO₂C₆H₃

Scheme 2.17

 $n = 4, 6, 8, 10, 12$

37



38

Ar = Ph, 4-FC₆H₄, 4-BrC₆H₄, 4-ClC₆H₄, 3-ClC₆H₄, 2-ClC₆H₄,
4-NO₂C₆H₄, 3-NO₂C₆H₄, 4-CF₃C₆H₄, 3,5-(CF₃)₂C₆H₃, etc

Scheme 2.18


$$n = 1, 2, 3, 7, \text{etc}$$

39

Scheme 2.19



Ar = Ph or 4-MeC₆H₄

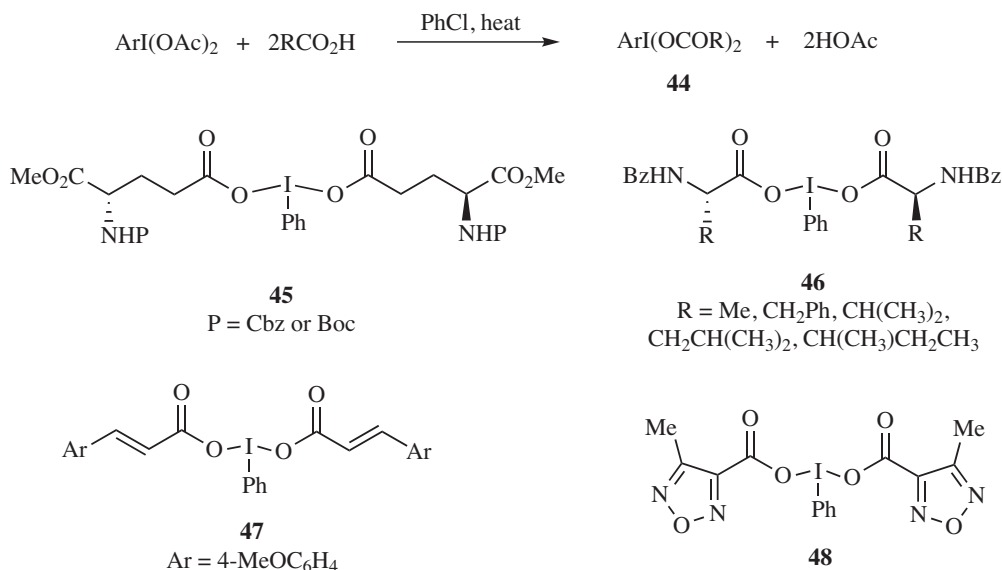
41

Scheme 2.20



43, Ar = 3-ClC₆H₄

Scheme 2.21



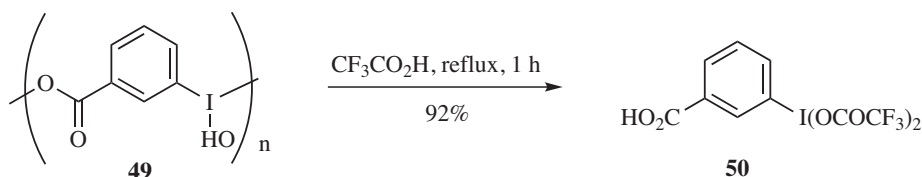
Scheme 2.22

heating DIB with a nonvolatile carboxylic acid RCO_2H in the presence of a high-boiling solvent such as chlorobenzene (Scheme 2.22) [178–183]. The equilibrium in this reversible reaction can be shifted towards the synthesis of the product **44** by distillation under reduced pressure of the relatively volatile acetic acid formed during the reaction. This procedure, for example, has been used to furnish the glutamate-derived (diacyloxyiodo)benzenes **45** [179], protected amino acid derivatives **46** [181], cinnamate derivative **47** [183] and 3-methylfuran-4-carboxylic acid derivative **48** [184].

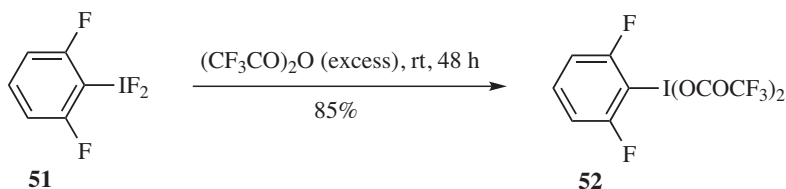
Reactions of DIB with stronger carboxylic acids usually proceed under milder conditions at room temperature. A convenient procedure for preparing $\text{PhI}(\text{CO}_2\text{CF}_3)_2$ (BTI) consists of simply dissolving DIB in trifluoroacetic acid and crystallization of the product after evaporating to a small volume [139]. Likewise, 3-[bis(trifluoroacetoxy)iodo]benzoic acid **50**, a useful recyclable oxidizing reagent, has been prepared in high yield by heating 3-iodosylbenzoic acid (which actually exists in the form of a polymeric carboxylate **49**) [185] with trifluoroacetic acid (Scheme 2.23) [186]. A similar approach has been used to prepare a series of $\text{PhI}(\text{OCOCOR})_2$ by treatment of DIB with oxalyl chloride in the respective alcohol, ROH [187].

Naumann and coworkers prepared [bis(trifluoroacetoxy)iodo]arene **52** in high yield by ligand exchange of the respective (difluoroiodo)arene **51** with trifluoroacetic anhydride (Scheme 2.24) [32].

Another common method involves the reaction of organoiodine(III) dichlorides, RICl_2 , with silver carboxylates [76, 139]. This approach has been used, for example, to prepare 1-[bis(trifluoroacetoxy)iodo]-2,2,2-trifluoroethane **54** from the respective dichloride **53** (Scheme 2.25) [76].



Scheme 2.23



Scheme 2.24

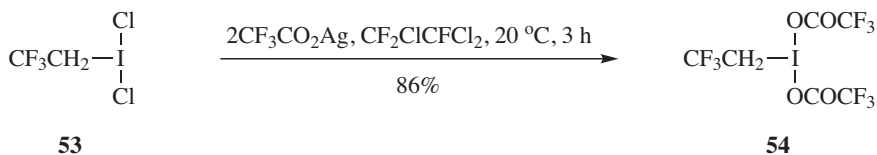
[Bis(acyloxy)iodo]arenes are generally colorless, stable microcrystalline solids, which can be easily recrystallized and stored for extended periods without significant decomposition.

2.1.5.3 Structural Studies

Numerous X-ray structural studies of organoiodine(III) carboxylates have been reported in the literature. In general, single-crystal X-ray structural data for [bis(acyloxy)iodo]benzenes indicate a pentagonal planar coordination of iodine within the molecule, combining the primary T-shaped iodine(III) geometry with two secondary intramolecular $\text{I}\cdots\text{O}$ interactions with the carboxylate oxygens. In 1979 Alcock and coworkers reported single-crystal X-ray structures of (diacetoxiodo)benzene and [bis(dichloroacetoxy)iodo]benzene, which demonstrated the importance of secondary bonding in the solid state structure of [bis(acyloxy)iodo]benzenes [188]. In the crystal structure of $\text{PhI}(\text{OAc})_2$ (**55**, Figure 2.6) the overall geometry of each iodine atom can be described as a pentagonal-planar arrangement of three strong and two weak secondary bonds. The primary $\text{I}-\text{C}$ distance in **55** of 2.090 Å and the two $\text{I}-\text{O}$ distances of about 2.156 Å are longer than the sum of the covalent radii of the elements (2.07 Å for $\text{I}-\text{C}$ and 1.99 Å for $\text{I}-\text{O}$) and the $\text{O}-\text{I}-\text{O}$ bond angle is 164° . The secondary intramolecular $\text{I}\cdots\text{O}$ bonds in the molecule of **55** are 2.817 and 2.850 Å, resulting in the overall pentagonal-planar arrangement [188]. In contrast to $\text{PhI}(\text{OAc})_2$ **55**, the molecules of $\text{PhI}(\text{OCOCF}_3)_2$ (**56**) form a dimer due to the two additional $\text{I}\cdots\text{O}$ intermolecular secondary bonds (Figure 2.6) [189]. The crystal structure of [bis(trifluoroacetoxy)iodo]pentafluorobenzene, $\text{C}_6\text{F}_5\text{I}(\text{OCOCF}_3)_2$, reported in 1989, is characterized by an additional set of $\text{I}\cdots\text{O}$ intermolecular secondary bonds, bringing the total coordination at the iodine center to seven [190].

Figure 2.7 shows several examples of [bis(acyloxy)iodo]arenes whose X-ray crystal structures have been reported in literature. These structures include the chiral diacetate **31** [191], μ -oxodiiodanyl diacetate **57** [117], *N*-tosyl-4-(diacetoxiodo)pyrazole (**58**) [133], 1,3,5,7-tetrakis[4-(diacetoxiodo)phenyl]adamantane (**59**) [154], tetrakis[4-(diacetoxiodo)phenyl]methane (**60**) [155], 3-[bis(trifluoroacetoxy)iodo]benzoic acid (**61**) [186], 1-(diacetoxiodo)-2-nitrobenzene (**62**) [94] and the chiral (diacetoxiodo)arene **63** [165] derived from methyl lactate.

In particular, μ -oxo-[bis(acetoxy)iodo]benzene (**57**), prepared by partial hydrolysis of $\text{PhI}(\text{OAc})_2$ in the presence of NaHSO_4 , in the solid state forms an isolated diamond-core dimeric structure with



Scheme 2.25

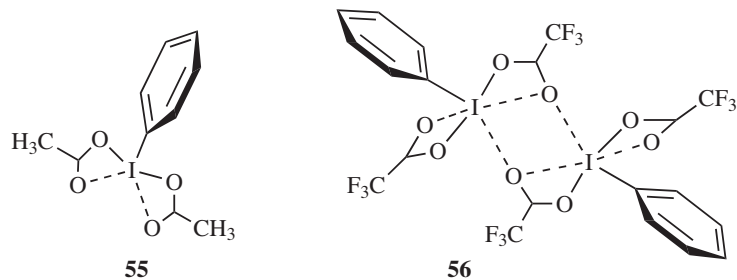


Figure 2.6 Primary and secondary bonding pattern in single-crystal X-ray structures of $\text{PhI}(\text{OAc})_2$ (**55**) [188] and $\text{PhI}(\text{OCOCF}_3)_2$ (**56**) [189].

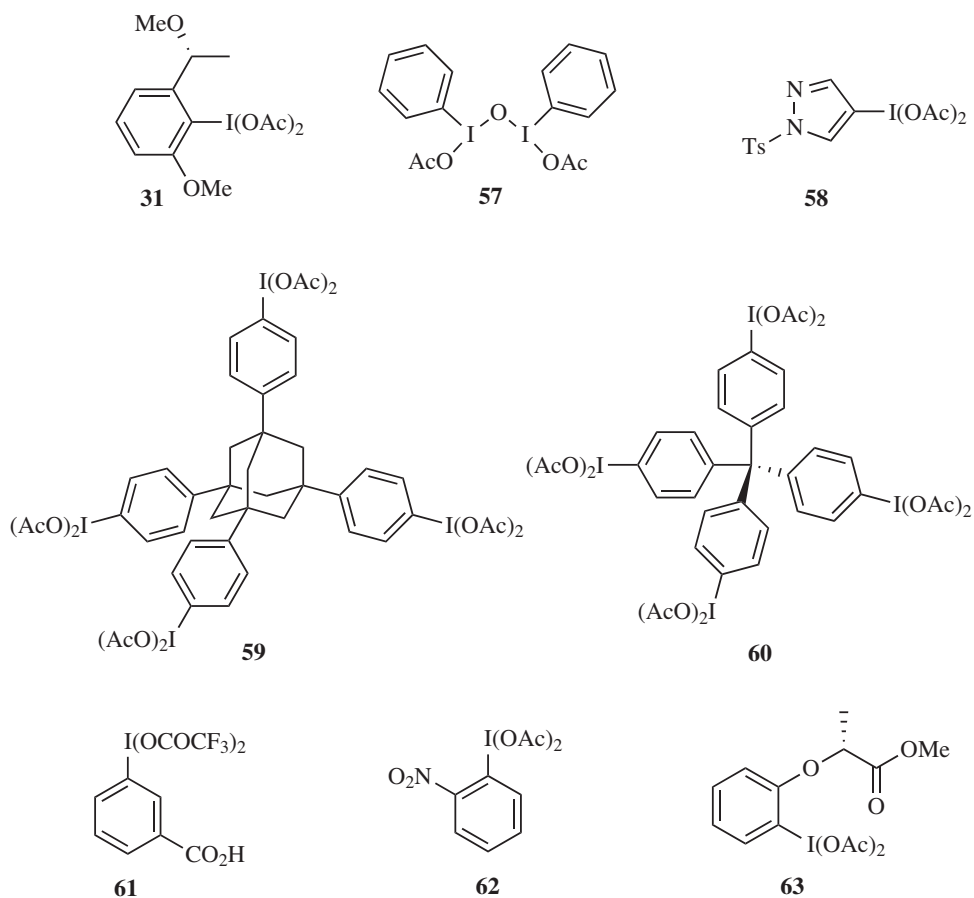


Figure 2.7 Examples of [bis(acyloxy)iodo]arenes analyzed by single-crystal X-ray diffraction.

pentagonal-planar iodine centers [117]. In the structure of **57**, both iodine centers have pentagonal-planar coordination with three short covalent and two long secondary bonds similar to that observed for μ -oxo-[bis(trifluoroacetoxy)iodo]benzene [192]. The I—O—I μ -oxo bridge is bent and consists of two short (2.03 Å, average) I—O bonds, which are close to those observed in μ -oxodiiodanyl di(trifluoroacetate) (2.02 Å) [192].

In the molecule of trifluoroacetate **61**, the C—I bond length is 2.083 Å, the primary I—O bond lengths are 2.149 and 2.186 Å and the intramolecular secondary I...O interactions with the carboxylate oxygens have distances of I(1)...O(5) 3.146 Å and I(1)...O(4) 3.030 Å; these five intramolecular interactions result in the pentagonal-planar coordination of iodine within the molecule [186]. In addition to the five intramolecular interactions, an intermolecular coordination of iodine atom to one the carboxylic oxygens of the neighboring molecule is also present (3.023 Å). Interestingly, the presence of a *meta*-carboxylic group has no noticeable effect on the molecular geometry of **61**, which is very similar to the X-ray crystal structure of [bis(trifluoroacetoxy)iodo]benzene [189]. No intermolecular interaction involving the *meta*-carboxylic group can be found in molecule **61**, which is in sharp contrast with the polymeric structure of 3-iodosylbenzoic acid [185]. The monomeric character of compound **61** leads to its improved solubility and higher reactivity compared to 3-iodosylbenzoic acid [189].

The X-ray crystal structure of 1-(diacetoxyiodo)-2-nitrobenzene (**62**) does not show any significant intramolecular interaction between the iodine(III) center and the oxygen atom of the nitro group in the *ortho* position (I...ONO bond distance 3.11 Å) [94].

Montanari, DesMarteau and Pennington reported the X-ray structural analysis of a fluoroalkyliodine(III) dicarboxylate, 1-[bis(trifluoroacetoxy)iodo]-2,2,2-trifluoroethane (**54**, Scheme 2.25) [68]. Compound **54** has a T-shaped coordination similar to other known dicarboxylates, but forms a previously unknown tetrameric array of molecules due to strong intermolecular I...O contacts.

An ^{17}O NMR study of bis(acyloxy)iodoarenes in chloroform has confirmed that the T-shaped structure of iodine(III) compounds observed in the solid state is also adopted in solution [193, 194]. The carboxylic groups of bis(acyloxy)iodoarenes show a dynamic behavior, which is explained by a [1,3]-sigmatropic shift of the iodine atom between the two oxygen atoms of the carboxylic groups [194].

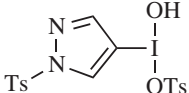
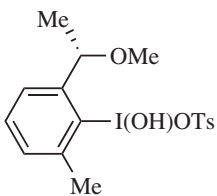
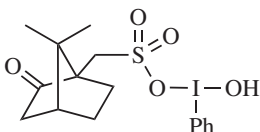
2.1.6 [Hydroxy(Organosulfonyloxy)Iodo]Arenes

In contrast to carboxylic acids, *p*-toluenesulfonic acid and other organosulfonic acids do not form stable organoiodine(III) derivatives of the type $\text{ArI}(\text{OSO}_2\text{R})_2$. The existence of several such derivatives has been proposed in the literature; however, none of them was isolated as an individual, stable compound. For example, Koser and Wettach reported in 1977 some evidence for the intermediate formation of the ditosylate $\text{PhI}(\text{OTs})_2$ in the reaction of PhICl_2 with silver tosylate, but an attempt to isolate this compound failed and the final isolated product was [hydroxy(tosyloxy)iodo]benzene, $\text{PhI}(\text{OH})\text{OTs}$ [195].

The first preparation of [hydroxy(tosyloxy)iodo]benzene (HTIB) from (diacetoxyiodo)benzene and *p*-toluenesulfonic acid monohydrate was reported in 1970 by Neilands and Karele [196]. A decade later, Koser and coworkers discovered that HTIB is an efficient reagent for the oxytosylation of unsaturated organic substrates and for the synthesis of various iodonium salts [197–201]; consequently, in modern synthetic literature HTIB is often referred to as “Koser’s reagent”.

[Hydroxy(organosulfonyloxy)iodo]arenes, $\text{ArI}(\text{OH})\text{OSO}_2\text{R}$, represent one the most common, well investigated and practically useful classes of organoiodine(III) compounds. The most important of these compounds, HTIB, is commercially available and commonly used as an oxidizing reagent in organic synthesis. [Hydroxy(organosulfonyloxy)iodo]arenes are usually prepared by a ligand-exchange reaction of (diacetoxyiodo)arenes with an appropriate organosulfonic acid (Table 2.6).

Table 2.6 Preparation of [hydroxy(organosulfonyloxy)iodo]arenes.

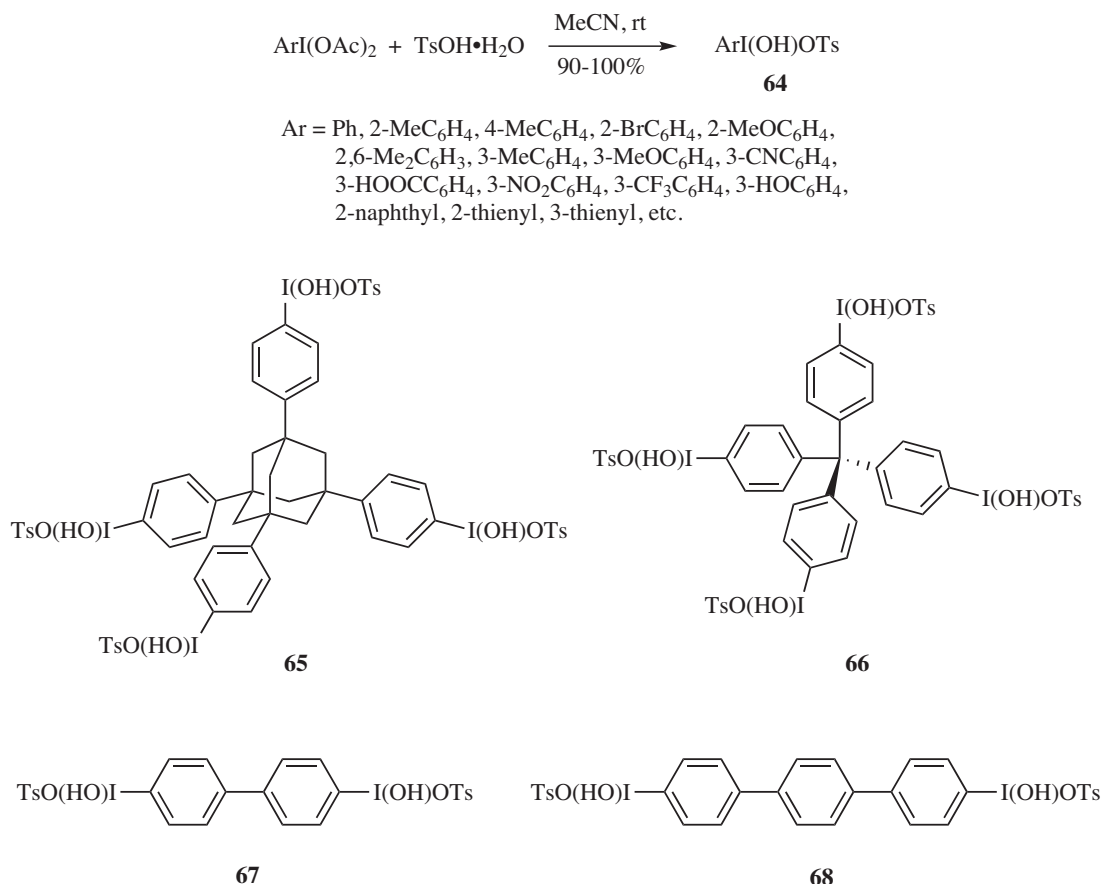
Compound	Method of synthesis	Yield (%)	Reference
PhI(OH)OTs	PhI(OAc) ₂ , TsOH·H ₂ O, MeCN, rt	93	[195]
PhI(OH)OTs	PhI(OAc) ₂ , TsOH·H ₂ O, grinding, rt, 10 min	93	[202]
PhI(OH)OTs	PhI, <i>m</i> CPBA, TsOH·H ₂ O, CHCl ₃ , rt, 2 h	95	[203]
PhI(OH)OTs	PhH, I ₂ , <i>m</i> CPBA, TfOH, TsOH·H ₂ O, CH ₂ Cl ₂ , rt	75	[204]
4-MeC ₆ H ₄ I(OH)OTs	ArI(OAc) ₂ , TsOH·H ₂ O, MeCN, rt	86	[205]
3-CF ₃ C ₆ H ₄ I(OH)OTs	ArI(OAc) ₂ , TsOH·H ₂ O, MeCN, rt, 1 h	91	[176, 204, 206]
	ArI(OAc) ₂ , TsOH·H ₂ O, MeCN, rt, 1 h	100	[206]
	ArI(OAc) ₂ , TsOH·H ₂ O, MeCN, rt, 1 h	90	[166]
C ₄ F ₉ I(OH)OTs	C ₄ F ₉ I(OCOCF ₃) ₂ , TsOH, MeCN, -20 °C to rt	91	[207]
C ₆ F ₁₃ I(OH)OTs	C ₆ F ₁₃ I(OCOCF ₃) ₂ , TsOH, MeCN, 0 °C to rt, 24 h	100	[135]
C ₆ F ₅ I(OH)OTs	C ₆ F ₅ I(OCOCF ₃) ₂ , MeCN, TsOH 0 °C to rt, 24 h	94	[135]
CF ₃ CH ₂ I(OH)OTs	CF ₃ CH ₂ I(OCOCF ₃) ₂ , TsOH, MeCN, -30 °C to rt	90	[176]
CF ₃ CH ₂ I(OH)OTs	CF ₃ CH ₂ I, <i>m</i> CPBA, TsOH, CH ₂ Cl ₂ -CF ₃ CH ₂ OH, rt	95	[204]
PhI(OH)OMs	PhH, I ₂ , <i>m</i> CPBA, MsOH, CH ₂ Cl ₂ -CF ₃ CH ₂ OH, rt	76	[204]
PhI(OH)OSO ₂ Ph	PhH, I ₂ , <i>m</i> CPBA, PhSO ₂ OH, CH ₂ Cl ₂ /CF ₃ CH ₂ OH, rt	88	[204]
	PhI(OAc) ₂ , RSO ₂ OH, MeCN, rt, 0.5 h	80	[208]

2.1.6.1 Preparation

Various [hydroxy(tosyloxy)iodo]arenes **64** can be conveniently prepared by a ligand-exchange reaction of (diacetoxyiodo)arenes with *p*-toluenesulfonic acid monohydrate in acetonitrile (Scheme 2.26). This method has been applied to the synthesis of derivatives with various substituted aromatic groups [150, 166, 186, 209, 210], [hydroxy(tosyloxy)iodo]heteroarenes [206] and the recyclable hypervalent iodine reagents **65–68** (also see Chapter 5) [154, 155, 158]. Similarly, numerous polyfluoroalkyl derivatives of the types C_{*n*}F_{2*n*+1}I(OH)OTs [135, 176, 211] and C_{*n*}F_{2*n*+1}CH₂I(OH)OTs [176, 212] can be prepared from the respective bis(trifluoroacetates) and *p*-toluenesulfonic acid.

Wirth and coworkers have reported the preparation of a series of *ortho*-substituted chiral [hydroxy(tosyloxy)iodo]arenes **69** starting from the corresponding aryl halides (Scheme 2.27) [166, 191].

A similar procedure using ArI(OAc)₂ and 4-nitrobenzenesulfonic acid, methanesulfonic acid, or 10-camphorsulfonic acid leads to the corresponding organosulfonyloxy derivatives [195, 208]. A solvent-free, solid-state version of this reaction can be carried out by simple grinding of ArI(OAc)₂ with the appropriate



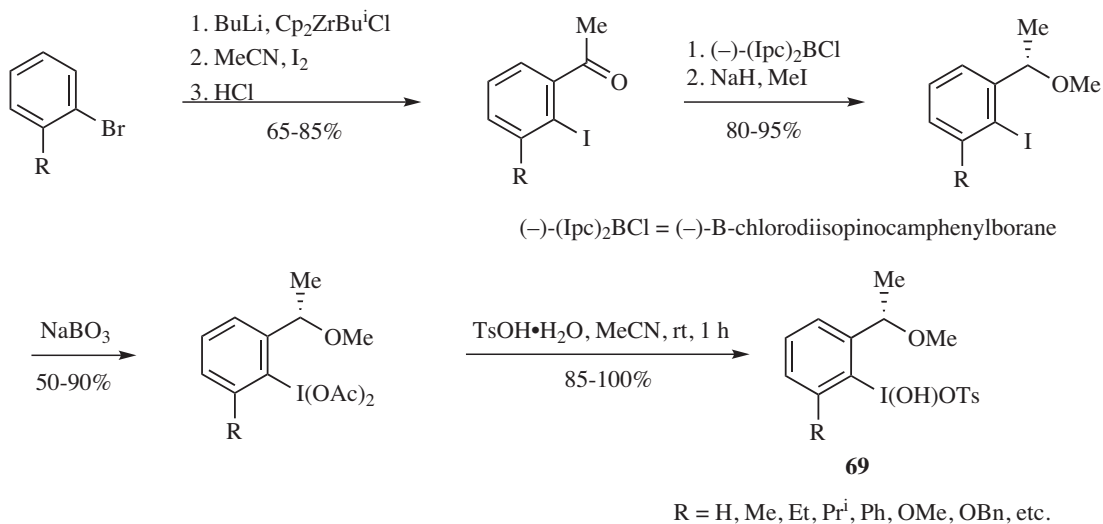
Scheme 2.26

sulfonic acid in an agate mortar followed by washing the solid residue with diethyl ether [202]. This solid-state procedure has been used for the preparation of HTIB and several other [hydroxy(organosulfonyloxy)iodo]arenes in 77–98% yields. A polymer-supported [hydroxy(tosyloxy)iodo]benzene can be prepared similarly by treatment of poly[(diacetoxyl)iodo]styrene with *p*-toluenesulfonic acid monohydrate in chloroform at room temperature (Chapter 5) [213, 214].

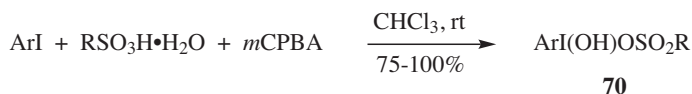
A convenient modified procedure for the preparation of various [hydroxy(organosulfonyloxy)iodo]arenes **70** consists of the one-pot reaction of iodoarenes and *m*CPBA (*m*-chloroperoxybenzoic acid) in the presence of organosulfonic acids in a small amount of chloroform at room temperature (Scheme 2.28) [203].

Further modification of this procedure, developed by Olofsson and coworkers, involves a one-pot oxidative iodination/oxidation/ligand exchange sequence of reactions leading to the synthesis of [hydroxy(organosulfonyloxy)iodo]arenes **72** from arenes **71**, iodine, *m*CPBA and the respective sulfonic acids (Scheme 2.29) [204].

Several derivatives of HTIB of type PhI(OR)OTs have been reported. In particular, [methoxy(tosyloxy)iodo]benzene, PhI(OMe)OTs, can be prepared by the treatment of HTIB with trimethyl orthoformate [215]. The methoxy ligand in [methoxy(tosyloxy)iodo]benzene (**73**) can be further substituted with a chiral menthyloxy group by treatment with menthol to give product **74** (Scheme 2.30) [216].



Scheme 2.27

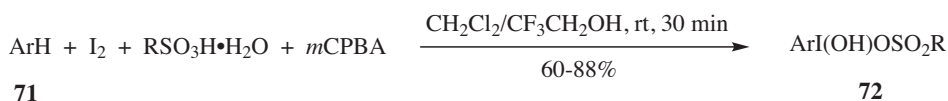


mCPBA = *m*-chloroperoxybenzoic acid

$Ar = Ph, 4\text{-MeC}_6\text{H}_4, 2\text{-MeC}_6\text{H}_4, 3\text{-CF}_3\text{C}_6\text{H}_4, 2\text{-CF}_3\text{C}_6\text{H}_4, 4\text{-ClC}_6\text{H}_4, \text{etc.}$

$RSO_3H = TsOH, MsOH, PhSO_3H, 4\text{-ClC}_6\text{H}_4SO_3H, 3\text{-NO}_2\text{C}_6\text{H}_4, (S)\text{-}(+)\text{-camphor-10-sulfonic acid, etc.}$

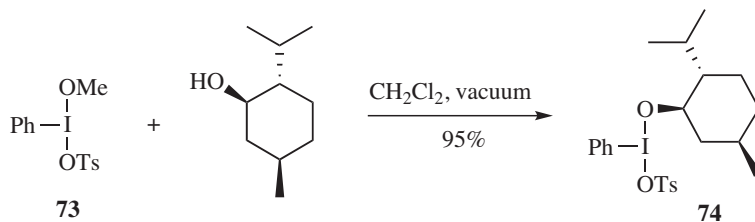
Scheme 2.28



$ArH = PhH, PhBu^t, 1,4\text{-Me}_2\text{C}_6\text{H}_4, 1,3,5\text{-Me}_3\text{C}_6\text{H}_3, PhOMe$

$RSO_3H = TsOH, MsOH, PhSO_3H, 2\text{-naphthylSO}_3H$

Scheme 2.29



Scheme 2.30

2.1.6.2 Structural Studies

Figure 2.8 shows several examples of aryliodine(III) organosulfonates whose X-ray crystal structures have been reported in the literature. Single-crystal X-ray structural data for HTIB (**75**) show the T-shaped geometry around the iodine center with almost collinear O-ligands and two different I—O bonds of 2.47 Å (I—OTs) and 1.94 Å (I—OH) [217]. The presence of a substituent in the phenyl ring has no noticeable effect on the molecular geometry of [hydroxy(tosyloxy)iodo]arenes. In particular, the X-ray single-crystal structure of 3-[hydroxy(tosyloxy)iodo]benzoic acid (**76**) is very similar to that of HTIB. The I—OTs bond in tosylate **76** (2.437 Å) is significantly longer than the I—OH bond (1.954 Å), which is indicative of some ionic character of this compound. In addition to the three intramolecular bonds, a weaker intermolecular coordination of iodine atom to one of the sulfonyl oxygens of the neighboring molecule is found with a distance of 2.931 Å. No intermolecular interaction involving *meta*-carboxylic group is present in molecule **76** [186].

The chiral, *ortho*-substituted compound **77** shows a similar T-shaped structure like HTIB (**75**). However, in contrast to HTIB, the two oxygen atoms nearest to the iodine atom in **77** are the oxygen atom of the hydroxy group (I—OH, 1.94 Å) and the methoxy oxygen atom (I—OMe, 2.47 Å), while the tosylate oxygen atom is further away from the iodine atom (I...OTs, 2.82 Å). Owing to this structural feature, the O—I—O bond angle of 166° in molecule **77** is significantly smaller than the O—I—O bond angle of 179° in HTIB [191].

In a more recent paper, Richter and coauthors reported a single-crystal X-ray structural analysis of [hydroxy(mesyloxy)iodo]benzene (**78**) and the respective oxo-bridged anhydride **79** [218]. Structural parameters of mesylate **78** are very similar to the structure of HTIB (**75**). Analogously to HTIB, compounds **78** and **79** form dimeric structures in the solid state due to the I...O secondary bonding [218].

Richter, Koser and coworkers analyzed the species present in aqueous solutions of [hydroxy(mesyloxy)iodo]benzene and [hydroxy(tosyloxy)iodo]benzene [219]. In particular, it was found that upon solution in water both PhI(OH)OMs and PhI(OH)OTs undergo complete ionization to give the hydroxy(phenyl)iodonium ion (PhI⁺OH) and the corresponding sulfonate anion (RSO₃[−]) as fully solvated species, that is, free ions, which do not form ion pairs with each other. In addition, the μ -oxo dimer, [Ph(HO)I—O—I⁺(OH₂)Ph], is present at significant levels even in relatively dilute solutions [219].

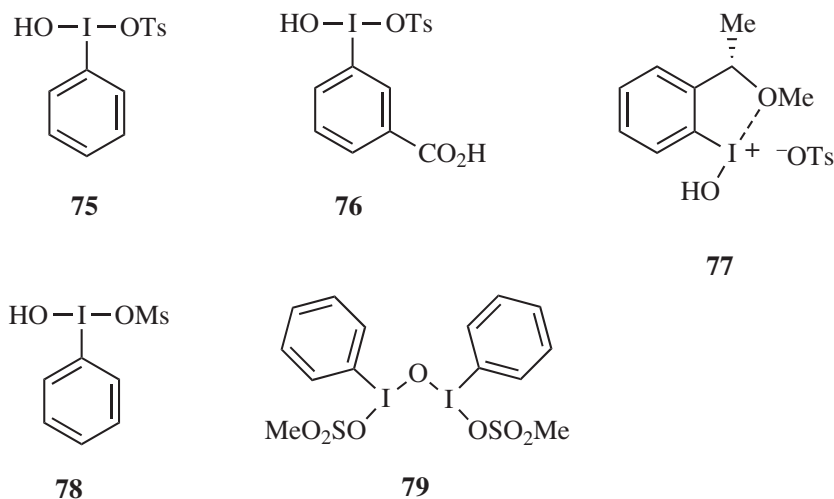
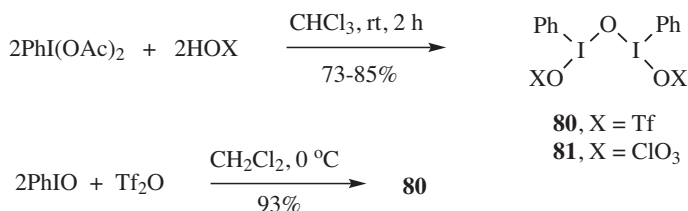


Figure 2.8 Examples of aryliodine(III) organosulfonates analyzed by single-crystal X-ray diffraction.



Scheme 2.31

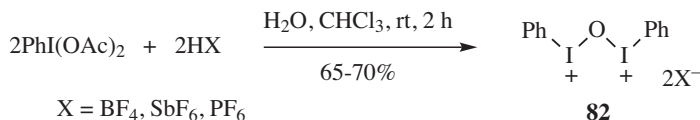
2.1.7 Organoiodine(III) Derivatives of Strong Acids

In contrast to organoiodine(III) dihalides and dicarboxylates, the analogous aryliodine(III) compounds $\text{ArI}(\text{OX})_2$ that are derived from strong acids HOX , such as H_2SO_4 , HNO_3 , HClO_4 , $\text{CF}_3\text{SO}_3\text{H}$, HSbF_6 and HPF_6 , usually lack stability and can only be generated at low temperature, under absolutely dry conditions. The existence of several such derivatives was assumed in the literature; however, none of them was isolated as an individual, stable compound. Specifically, triflate $\text{PhI}(\text{OTf})_2$ [86], perchlorate $\text{PhI}(\text{OCIO}_3)_2$ [220], sulfate PhISO_4 [221] and nitrate $\text{PhI}(\text{ONO}_2)_2$ [222] are unstable and can only be generated *in situ*, at low temperature, in the absence of water. Traces of moisture immediately convert these compounds into the μ -oxo-bridged derivatives (e.g., structures **80** and **81** in Scheme 2.31) or more complex polymeric structures, such as the oligomeric sulfate **26** and perchlorate **27** derivatives (Scheme 2.13 in Section 2.1.4.2).

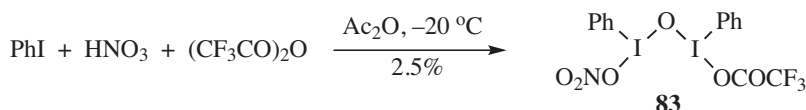
μ -Oxo-bridged iodanes are the most typical organoiodine(III) derivatives of strong inorganic acids, such as sulfuric, nitric, perchloric, trifluoromethanesulfonic and so on; however, compounds of this type are also known for carboxylic acids (e.g., structure **57**, Figure 2.7).

The most general approach to the synthesis of μ -oxo-bridged iodanes is based on the reaction of (diacetoxy)benzene or iodosylbenzene with the respective acids or anhydrides. Triflate **80** and perchlorate **81** are prepared from $\text{PhI}(\text{OAc})_2$ and aqueous perchloric or trifluoromethanesulfonic (triflic) acid (Scheme 2.31) [220]. In a convenient modified procedure triflate **80** can be generated *in situ* from iodosylbenzene (two equivalents) and triflic anhydride in dichloromethane at 0°C . Under these conditions triflate **80** is obtained as a bright yellow suspension in dichloromethane that can be used *in situ* as a useful reagent (known as Zefirov's reagent) for the preparation of iodonium salts [223]. Triflate **80** can be isolated as a yellow microcrystalline solid; however, it has a relatively low thermal stability and should be handled and stored for only brief periods. Extended storage of this reagent in the presence of trifluoromethanesulfonic acid results in self-condensation with the formation of iodonium salts [224].

A reaction of $\text{PhI}(\text{OAc})_2$ with aqueous tetrafluoroboric, hexafluoroantimonic and hexafluorophosphoric acids affords the corresponding μ -oxo-bridged iodane derivatives **82** (Scheme 2.32) [225, 226]. Compounds **82** can be isolated as relatively stable, yellow microcrystalline solids, which should be handled with care. **Caution:** a violent explosion of the tetrafluoroborate derivative **82** ($\text{X} = \text{BF}_4$) has been reported in the literature [227].



Scheme 2.32



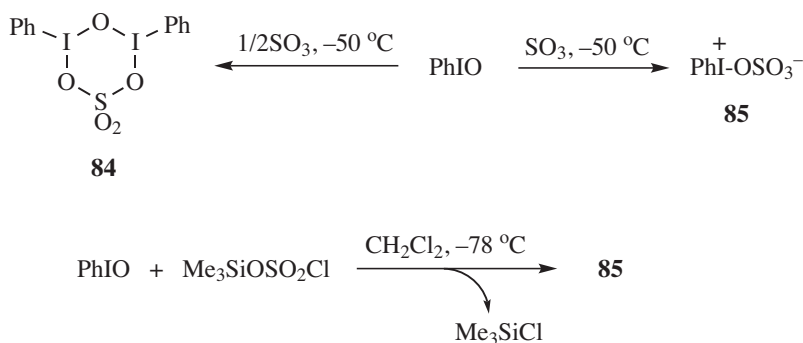
Scheme 2.33

A distinctive feature of all μ -oxo-bridged iodanes is the bright yellow color due to the $^+\text{I}-\text{O}-\text{I}^+$ bridging fragment [119]. The available X-ray structural data for the mixed μ -oxo-bridged iodine(III) nitrate-trifluoroacetate **83** (Scheme 2.33) is also consistent with the partially ionic character of the $\text{I}-\text{ONO}_2$ bonds with $\text{I}-\text{O}$ bond distances of 2.26–2.35 Å as compared to the $\text{I}-\text{O}-\text{I}$ bridge $\text{I}-\text{O}$ bond distances of 1.99–2.01 Å [228]. Product **83** was isolated in a low yield from the reaction of iodobenzene with nitric acid and trifluoroacetic anhydride in a mixture with the respective symmetrical μ -oxo-bridged iodine(III) bis(nitrate) and bis(trifluoroacetate) [228].

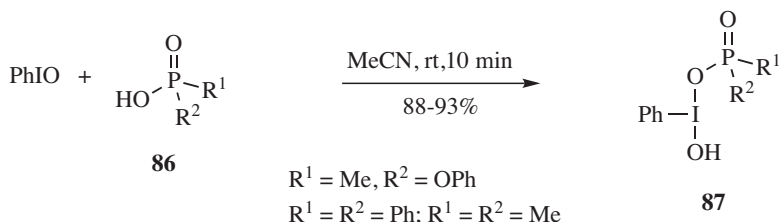
Sulfur trioxide forms two different adducts with iodosylbenzene, $\text{PhIO} \cdot \text{SO}_3$ and $(\text{PhIO})_2 \cdot \text{SO}_3$, depending on the ratio of reactants (Scheme 2.34) [221]. Both sulfates **84** and **85** are hygroscopic solids and are highly reactive toward nucleophilic organic substrates. Taylor and coworkers developed a more convenient procedure for the preparation of phenyliodosulfate (**85**) by the reaction of iodosylbenzene and trimethylsilyl chlorosulfonate followed by removal of the solvent and chlorotrimethylsilane [229]. In addition to phenyliodine(III) sulfates **84** and **85**, the oligomeric iodosylbenzene sulfate **26**, corresponding to a molecular formula of $(\text{PhIO})_3 \cdot \text{SO}_3$, has been prepared by the reaction of (diacetoxyiodo)benzene with NaHSO_4 in water (Scheme 2.13 in Section 2.1.4.2) [116, 117].

Piancatelli and coworkers reported the preparation of an unusual iodosylbenzene derivative of perchloric acid, diperchlorate $\text{PhI}(\text{OCIO}_3)_2$, by the reaction of (diacetoxyiodo)benzene with magnesium perchlorate [230]. The structure of this perchlorate was suggested on the basis of NMR and HPLC-MS data; [230] however, a more recent X-ray single-crystal structural study established a different structure for a product prepared by a similar procedure from $\text{PhI}(\text{OH})\text{OTf}$ s and aqueous magnesium perchlorate (see structure **27** in Scheme 2.13, Section 2.1.4.2) [118].

Several organoiodine(III) derivatives of phosphoric acid are known. In particular, Moriarty and coworkers reported the preparation of [hydroxy(phosphoryloxy)iodo]benzenes **87** by the reaction of iodosylbenzene with the appropriate phosphonic or phosphinic acid **86** (Scheme 2.35) [231].



Scheme 2.34



Scheme 2.35

2.1.8 Iodine(III) Heterocycles

Nearly all of the known heterocyclic λ^3 -iodanes are five-membered heterocycles, although several examples of four-membered and six-membered heterocycles with the iodine(III) atom in the ring have also been reported (Section 2.1.8.8). Several types of cyclic iodonium salts are also known (Section 2.1.8.10). Unsaturated heterocyclic systems with a hypervalent iodine atom in the ring generally do not possess any significant aromatic character due to the large iodine atom size precluding p-orbital overlap with much smaller atoms of carbon, oxygen, or nitrogen and also due to the electronic nature and the geometry of hypervalent bonding.

The five-membered iodine(III) heterocycles are represented by various cyclic compounds (**88–95**) incorporating hypervalent iodine and oxygen, nitrogen, or some other elements in the heterocyclic ring (Figure 2.9). The collective name “benziodoxoles” is commonly used for the heterocycles **88** with iodine and oxygen atoms in a five-membered ring and various substituents Y attached to iodine [128]. The first derivatives of benziodoxole, 1-hydroxy-1,2-benziodoxol-3-(1*H*)-one and 1-chloro-1,2-benziodoxol-3-(1*H*)-one, were prepared over 100 years ago by oxidation or chlorination of 2-iodobenzoic acid [232, 233]. In the mid-1980s, 1-hydroxybenziodoxoles attracted considerable interest and research activity mainly due to their excellent catalytic activity in the cleavage of toxic phosphates and reactive esters [234]. More recently, various new benziodoxole derivatives have been synthesized and their usefulness as reagents for organic synthesis and particularly for the atom-transfer reactions [235], was demonstrated. In contrast to benziodoxoles **88**, the analogous five-membered iodine-nitrogen heterocycles, benziodazoles **89**, have received much less attention and, moreover, their structural assignment in some cases was unreliable. The most important and readily available derivative of benziodazole, acetoxybenziodazole (**89**, Y = OAc, Z = H), was first prepared in 1965 by the peracetic oxidation of 2-iodobenzamide [236].

The distinctive feature of five-membered heterocyclic λ^3 -iodanes is a considerably higher thermal stability and lower reactivity compared to their acyclic analogs. This stabilization has been explained by the bridging of the apical and equatorial positions on hypervalent iodine by a five-membered ring [237] and also by better overlap of the lone pair electrons on the iodine atom with the π -orbitals of the benzene ring [238]. The greater stability of the benziodoxole system enabled the preparation and isolation of otherwise unstable iodine(III) derivatives with I–Br, I–OOR, I–N₃, I–CN, I–CF₃ and other bonds. These various benziodoxole derivatives have found practical application as reagents for organic synthesis. The chemistry of benziodoxoles and benziodazoles has previously been summarized in several reviews [235, 239, 240].

Besides benziodoxoles and benziodazoles, the other known five-membered heterocyclic systems incorporating hypervalent iodine are represented by several less common compounds (**90–95**, Figure 2.9), which include the fused benziodazoles **90** [241], benziodoxazoles **91** [242], benziodoxaboroles **92** [243], benziodoxathioles **93** [244, 245], benziodathiazoles **94** [246] and cyclic phosphonate **95** [247]. X-Ray molecular structures were reported for numerous benziodoxole derivatives **88** [237, 248–262], benziodazoles **89** [263–266], benziodoxaboroles **92** [243], benziodoxathioles **93** [244, 245] and cyclic phosphonate **95** [247]. In general, the five-membered ring in benziodoxole is highly distorted with an almost linear alignment of the

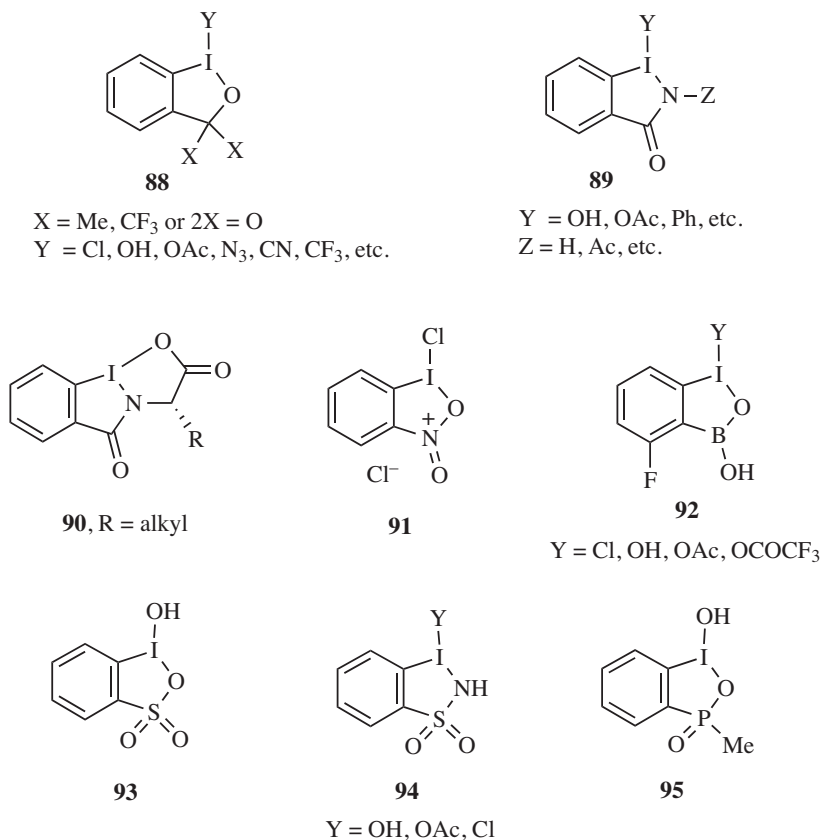
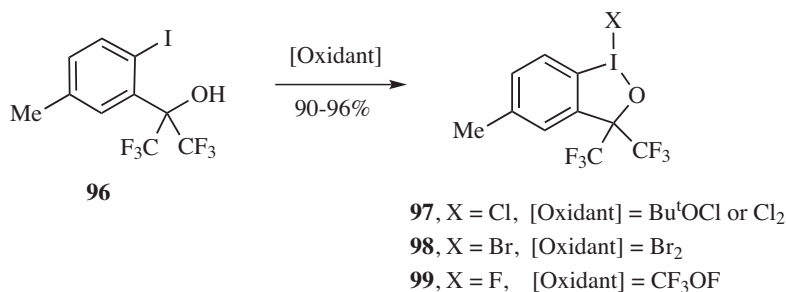


Figure 2.9 Known hypervalent iodine(III) five-membered heterocyclic systems.

two electronegative ligands. The I—O bond length in benziodoxolones (**88**, 2X = O) varies over a wide range from 2.11 Å in carboxylates (**88**, Y = *m*-ClC₆H₄CO₂) [255] to 2.48 Å in the phenyl derivative (**88**, Y = Ph) [249], which indicates considerable changes in the ionic character of this bond. The endocyclic C—I—O bond angle is typically around 80°, which is a significant deviation from the expected angle of 90° for the normal T-shaped geometry of hypervalent iodine. The structural parameters of benziodazoles **89**, Y = OAc or Ph, in general are similar to those of benziodoxoles [263–266].

2.1.8.1 Benziodoxoles

2.1.8.1.1 Halobenziodoxoles 1-Chloro-1,2-benziodoxol-3-(1*H*)-one (**88**, 2X = O, Y = Cl) can be easily prepared by direct chlorination of 2-iodobenzoic acid [233], or by the oxidation of 2-iodobenzoic acid with sodium chlorite (NaClO₂) in aqueous hydrochloric acid media [267]. The original X-ray single-crystal analysis of 1-chloro-1,2-benziodoxol-3-(1*H*)-one reported in 1976 was relatively imprecise [268]. More recently, Koser and coworkers reported the single-crystal X-ray structure of a 1 : 1 complex of 1-chloro-1,2-benziodoxol-3-(1*H*)-one and tetra-*n*-butylammonium chloride [262]. The primary bond distances at iodine in this compound are consistent with expectations for a λ³-iodane. In particular, the I—Cl and I—O bond distances of 2.454 and 2.145 Å, respectively, are greater than the sums of the appropriate covalent radii and reflect the



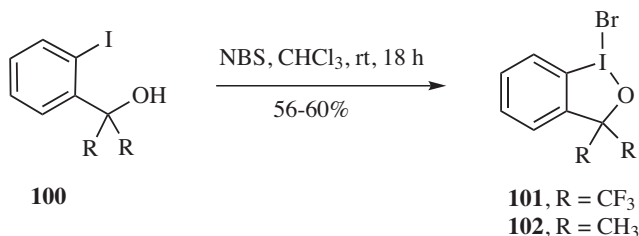
Scheme 2.36

hypervalent nature of the apical iodine–heteroligand bond. A notable structural feature of this complex is the existence of a secondary $\text{I}\cdots\text{Cl}$ bond (2.943 Å) between the chloride ion of Bu_4NCl and the iodine atom of the chlorobenziiodoxole moiety [262]. The analogous 1-fluoro- and 1-bromo-1,2-benziiodoxol-3-(1*H*)-ones are unknown.

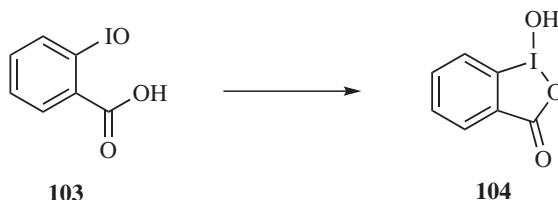
In 1979, Amey and Martin reported the synthesis of halobenziiodoxoles **97–99**, derivatives of the 3,3-bis(trifluoromethyl)-3-(1*H*)-1,2-benziiodoxole system, by the halogenation of benzylic alcohol **96** with the respective halogenating reagents (Scheme 2.36) [237]. Bromobenziiodoxole **98** represents an unusual, stable derivative of polyvalent iodine with an iodine–bromine bond.

More recently, Braddock and coworkers reported the preparation and single-crystal X-ray crystallography of two bromobenziiodoxoles (**101** and **102**, Scheme 2.37) [260]. Compounds **101** and **102** were synthesized in one step by bromination of the corresponding alcohols **100** using stoichiometric *N*-bromosuccinimide (NBS) in chloroform.

X-Ray diffraction analyses of crystals of **101** and **102** show that both iodine centers adopt a planar T-geometry, as expected. The five-membered benziiodoxole rings have an envelope conformation, with the oxygen atom lying 0.23 Å (for **101**) and 0.44 Å (for **102**) out of the C–C–C–I plane. For both compounds, the closest intermolecular distance to the iodine center is from the oxygen of a centrosymmetrically related counterpart at 3.03 Å (for **101**) and 2.94 Å (for **102**), forming discrete dimer pairs. Most notably, while the I–C bond length is essentially constant [2.120(8) Å in **101** and 2.112(7) Å in **102**], the I–O and I–Br bond lengths vary considerably in **101** and **102**, presumably due to the effect of the electron-withdrawing *gem*-trifluoromethyl groups on the three-center-four-electron O–I–Br bond. The I–O bond length is ca. 2.12 Å in **101** and ca. 2.05 Å in **102**. The I–Br bond lengths are ca. 2.59 and ca. 2.69 Å, respectively [260]. The structure of **101** is isomorphous with that of its previously reported chloro analog [269]. The X-ray structure of the fluoro analog of **102**, 1-fluoro-3,3-dimethyl-1,3-dihydro-1λ³-benzo[*d*][1,2]iodoxole, is characterized by a very short I–F distance of 2.045 Å, while the I–O and the I–C bonds (2.02 and 2.09 Å, respectively) are comparable with the analogous bonds in **102** [270].



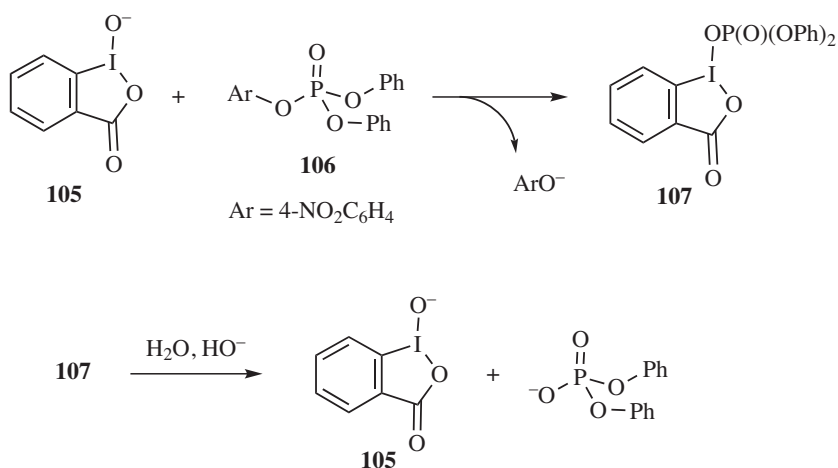
Scheme 2.37



Scheme 2.38

2.1.8.1.2 Hydroxybenziodoxoles The most important and thoroughly investigated benziodoxole derivative is 1-hydroxy-1,2-benziodoxole-3(1H)-one (**104**), the cyclic tautomer of 2-iodosylbenzoic acid (**103**) (Scheme 2.38). The tautomeric form **104** represents the actual structure of this compound, as confirmed by its unusually low acidity (pK_a 7.25 against 2.85 for the hypothetical 2-iodosylbenzoic acid) [238] and unambiguously established by a single-crystal X-ray analysis of **104** in the solid state [253, 271]. The I—O bond distance of 2.30 Å in the five-membered ring of **104** is significantly longer than the computed covalent I—O bond length of 1.99 Å, which is indicative of the highly ionic nature of this bond [252]. The early report [272] on the existence of the noncyclic tautomeric form of a ring substituted 2-iodosylbenzoic acid (**103**) was proved to be wrong in more recent work [273].

1-Hydroxy-1,2-benziodoxole-3(1H)-one (**104**) is commercially available or can be easily prepared by direct oxidation of 2-iodobenzoic acid or by basic hydrolysis of 2-(dichloroiodo)benzoic acid [232, 233, 274]. A more recent preparative procedure for **104** involves the oxidation of 2-iodobenzoic acid with acetyl nitrate in acetic anhydride at room temperature followed by aqueous work-up [275]. In the 1980s benziodoxole **104** and other hydroxybenziodoxoles attracted considerable research interest due to their excellent catalytic activity in the cleavage of toxic phosphates and reactive esters. This activity is explained by a pronounced O-nucleophilicity of the benziodoxole anion **105** due to the α -effect [234, 272, 276]. Spectroscopic and kinetic mechanistic studies indicate that the highly unstable iodoxole derivatives, such as the phosphate **107**, are reactive intermediates in catalytic cleavage of phosphates, as shown for the catalytic hydrolysis of a typical substrate **106** (Scheme 2.39) [277–279]. This mechanism was proved by the synthesis and reactivity studies of the phosphate intermediate **107**.



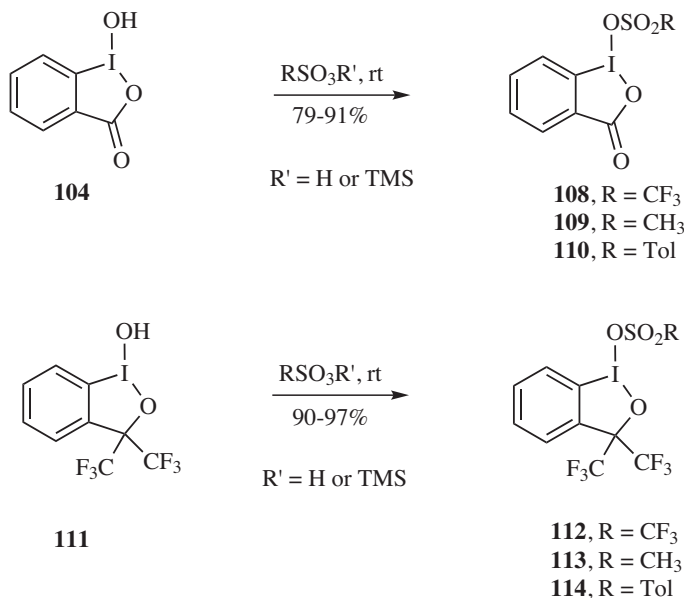
Scheme 2.39

Hydroxybenziodoxole **104** can be readily converted into its acetoxy derivative, 1-acetoxy-1,2-benziodoxole-3(1*H*)-one (**88**, $2X = O$, $Y = OAc$), by heating **104** with acetic anhydride and the acetoxy derivative can be further converted into the alkoxy derivatives by treatment with an appropriate alcohol [280]. The tetrabutylammonium salt of hydroxybenziodoxole **104** has been prepared by the reaction of hydroxybenziodoxole with tetrabutylammonium fluoride in THF; it is a mild oxidant that is useful for the preparation of epoxides from α,β -unsaturated carbonyl compounds [281]. 1-Hydroxy-1,2-benziodoxole-3(1*H*)-one and 1-acetoxy-1,2-benziodoxole-3(1*H*)-one have found wide application as starting compounds for the synthesis of various benziodoxole-based hypervalent iodine reagents by ligand exchange on iodine [239].

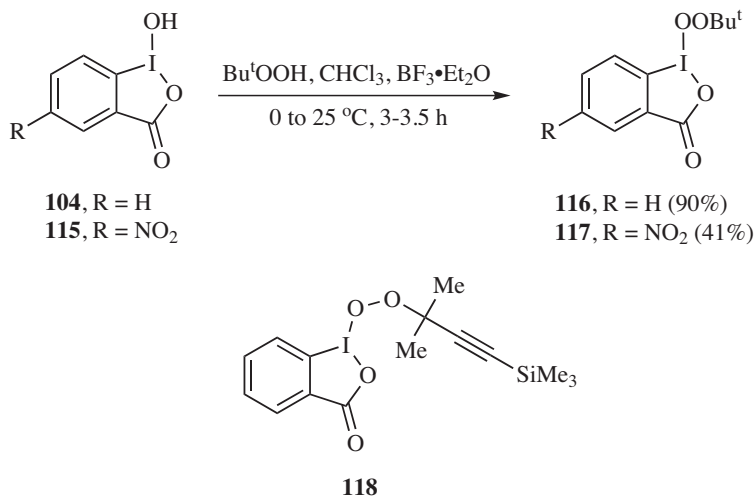
2.1.8.1.3 Organosulfonate Derivatives of Benziodoxoles 1-Organosulfonyloxy-1,2-benziodoxole-3(1*H*)-ones **108–110** and the analogous sulfonate derivatives **112–114** of the 3,3-bis(trifluoromethyl)-3-(1*H*)-1,2-benziodoxole system can be readily prepared by a simple, one-step procedure starting from **104** or **111** and the corresponding sulfonic acids or trimethylsilyl triflate (Scheme 2.40) [282, 283]. The organosulfonates **108–110** and **112–114** are isolated as moderately hygroscopic, but thermally stable, crystalline solids. The most stable to moisture are the tosylates **110** and **114**. The mesylates and triflates are more hygroscopic and can be isolated only in the form of crystallohydrates; however, for further reactions they can be conveniently used *in situ* [283]. An alternative procedure for preparing benziodoxole triflate **108** in moderate yield consists of the oxidation of 2-iodobenzoic acid with *m*-chloroperoxybenzoic acid in the presence of trifluoromethanesulfonic acid in dichloromethane at room temperature [284].

Like the other iodine(III) derivatives of strong acids, sulfonates **108–110** and **112–114** are highly reactive toward unsaturated organic substrates and other carbon nucleophiles and have found practical application for the preparation of C-substituted benziodoxoles.

2.1.8.1.4 Alkylperoxybenziodoxoles The greater stability of heterocyclic iodanes enables the isolation of otherwise unstable iodine(III) derivatives with I—OOR bonds. Ochiai and coworkers reported the preparation



Scheme 2.40

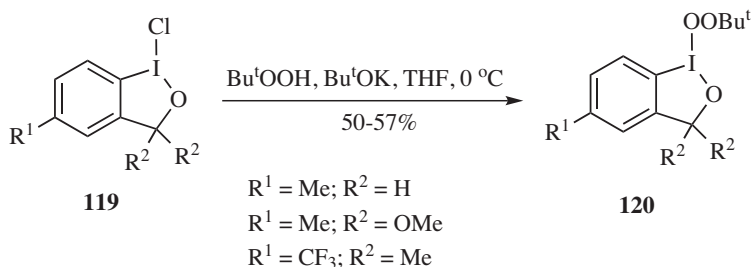


Scheme 2.41

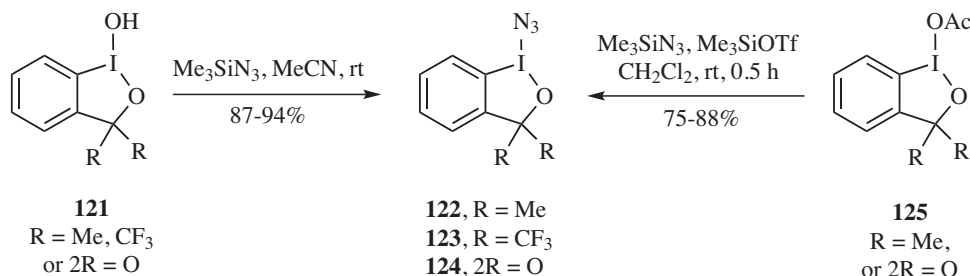
of 1-(*tert*-butylperoxy)benziodoxoles **116** and **117** by treatment of the corresponding benziodoxoles **104** and **115** with *tert*-butyl hydroperoxide in the presence of BF_3 -etherate (Scheme 2.41) [256, 285]. The structure of 1-(*tert*-butylperoxy)benziodoxole **116** was established by a single-crystal X-ray analysis. In particular, the *tert*-butylperoxy group occupies an apical position of a distorted trigonal-bipyramidal geometry around the iodine. There are two primary hypervalent I—O bonds: a considerably ionic endocyclic bond [2.181 (5) Å] to the ring oxygen and a short exocyclic bond [2.039 (5) Å] to the peroxide oxygen. The peroxide O—O bond in the molecule of **116** has a bond length of 1.459 (7) Å, which is comparable to that in anhydrous hydrogen peroxide [256]. A similar peroxybenziodoxole (**118**) was formed in an unusual reaction of **104** with 1,3-bis(trimethylsilyl)-3-methylbut-1-yne in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in dichloromethane; the structure of **118** was determined by single-crystal X-ray analysis [257]. Peroxides **116–118** are stable, crystalline products, which can be safely stored at room temperature for an indefinite period of time.

Dolenc and Plesnicar reported an alternative procedure for the preparation of 1-(*tert*-butylperoxy)benziodoxoles **120** from the corresponding chlorobenziodoxoles **119** and *tert*-butyl hydroperoxide in the presence of potassium *tert*-butoxide in THF (Scheme 2.42) [286].

Peroxyiodane **116** is a useful reagent acting as a strong oxidant toward various organic substrates, such as ethers, organic sulfides, amides and phenols [285, 287–291].



Scheme 2.42



Scheme 2.43

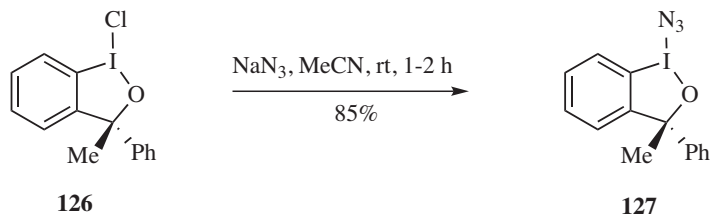
2.1.8.1.5 Azidobenziodoxoles The noncyclic azido λ^3 -iodanes, for example, $\text{PhI}(\text{N}_3)\text{OAc}$ or $\text{PhI}(\text{N}_3)_2$, in general lack stability and rapidly decompose at -25 to 0°C with the formation of iodobenzene and dinitrogen (Section 2.1.12.1). The incorporation of hypervalent iodine atom into a five-membered heterocycle leads to a significant stabilization of the azidoiodane. Stable azidobenziodoxoles **122**–**124** can be prepared by the reaction of hydroxybenziodoxoles **121** with trimethylsilyl azide in acetonitrile [251, 292], or by treatment of acetoxybenziodoxoles **125** with trimethylsilyl azide in dichloromethane in the presence of catalytic trimethylsilyl triflate (Scheme 2.43) [259]. All three azides **122**–**124** were isolated as thermally stable, non-explosive, microcrystalline solids that can be stored indefinitely in a refrigerator.

The structure of azidobenziodoxole **123** was unambiguously established by a single-crystal X-ray analysis [251]. The structural data revealed the distorted T-shaped geometry typical of hypervalent iodine, with an N—I—O bond angle of 169.5° . The lengths of the bonds to the iodine atom, I—N (2.18 Å), I—O (2.13 Å) and I—C (2.11 Å), are within the range of typical single covalent bonds in organic derivatives of polyvalent iodine [251].

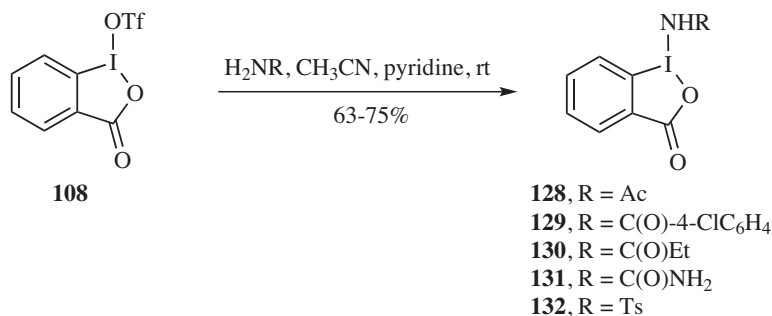
Azidobenziodoxoles can be used as efficient radical azidating reagents toward various organic substrates [251, 293].

Koser and Rabah have reported the synthesis of optically active 1-azido-1,3-dihydro-3-methyl-3-phenyl-1,2-benziodoxole (**127**) from the corresponding chlorobenziodoxole **126** (Scheme 2.44) [294]. This chiral, non-racemic azidobenziodoxole is a potentially useful reagent for asymmetric azidation reactions.

2.1.8.1.6 Amidobenziodoxoles Amidobenziodoxoles **128**–**132** are readily synthesized in one step by treatment of the triflate **108** with an appropriate amide, RNH_2 (Scheme 2.45) [295]. All five adducts (**128**–**132**) were isolated as thermally stable, white, non-hygroscopic, microcrystalline solids. Amidobenziodoxoles can be used as amidating reagents toward polycyclic alkanes under radical conditions [295].



Scheme 2.44



Scheme 2.45

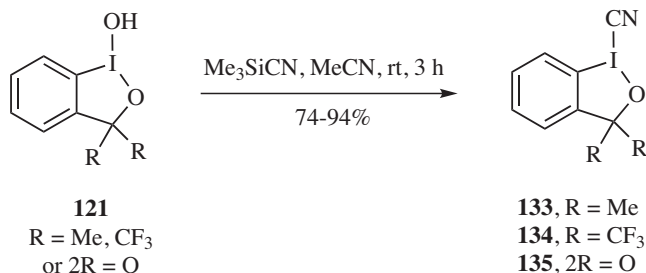
2.1.8.1.7 Cyanobenziodoxoles Cyanobenziodoxoles **133–135** can be synthesized in one step by the reaction of cyanotrimethylsilane with the respective hydroxybenziodoxoles **121** (Scheme 2.46) [258, 296], or from acetoxybenziodoxole and cyanotrimethylsilane [259].

All three products **133–135** were isolated as thermally stable, white, microcrystalline solids. The structures of two of them (**134** and **135**) were unambiguously established by single-crystal X-ray analysis [258, 259]. In particular, X-ray structural data for **134** revealed a distorted T-shaped geometry expected for hypervalent iodine with an endocyclic C–I–O bond angle of 78.2° and a NC–I–O bond angle of 169.5° [258]. The lengths of the bonds to the iodine atom, I–CN (2.167 Å), I–O (2.117 Å) and I–Ar (2.112 Å), are within the range of typical single covalent bond lengths in noncyclic organic derivatives of polyvalent iodine.

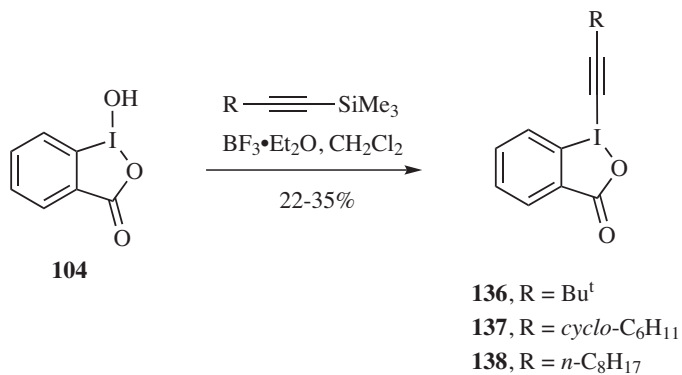
The chemical reactivity of cyanobenziodoxoles **133–135** is generally similar to that of azidobenziodoxoles and they can be used as efficient cyanating reagents toward organic substrates [258, 296].

2.1.8.1.8 Alkynylbenziodoxoles The first preparation of 1-alkynylbenziodoxoles **136–138** by a reaction of hydroxybenziodoxole **104** with alkynyltrimethylsilanes and BF₃·Et₂O (Scheme 2.47) was reported by Ochiai and coworkers in 1991 [252]. The structure of the cyclohexyl derivative **137** was established by a single-crystal X-ray diffraction analysis [252]. The structural data revealed the usual, distorted T-shaped geometry about the iodine atom. The I–O bond distance of 2.34 Å in **137** is significantly longer than the computed covalent single bond length of 1.99 Å, which is indicative of a highly ionic nature of this bond.

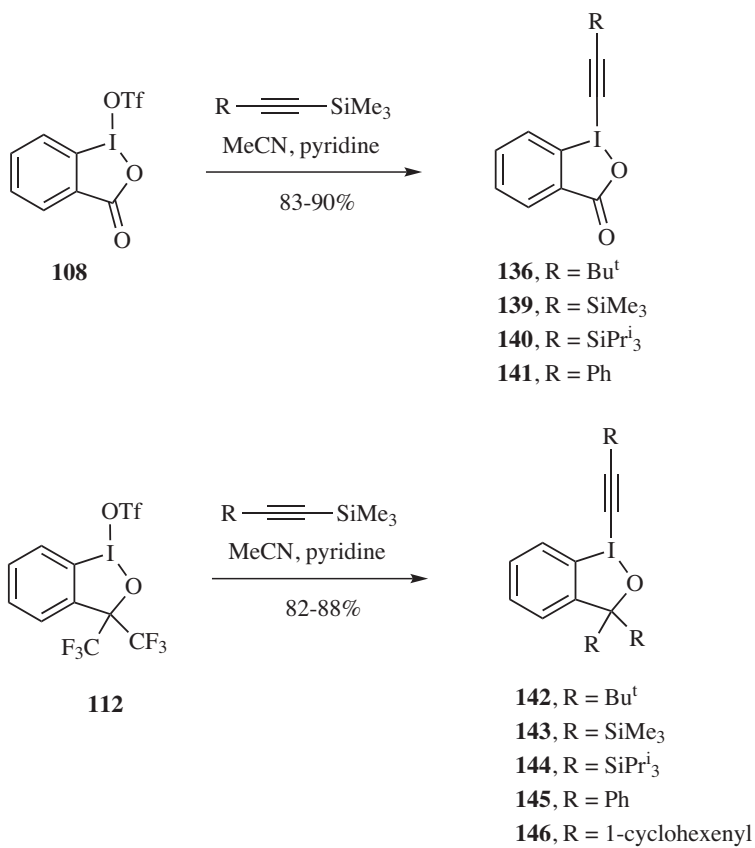
A better procedure for the preparation of various alkynylbenziodoxoles (**136**, **139–146**) in high yields involves the reaction of triflates **108** and **112** with alkynyltrimethylsilanes according to Scheme 2.48 [283]. Further modification of this approach consists of the reaction of 1-acetoxy-1,2-benziodoxol-3(1*H*)-one with 1-alkynyl(diisopropyl)boronates in acetonitrile under reflux conditions [297].



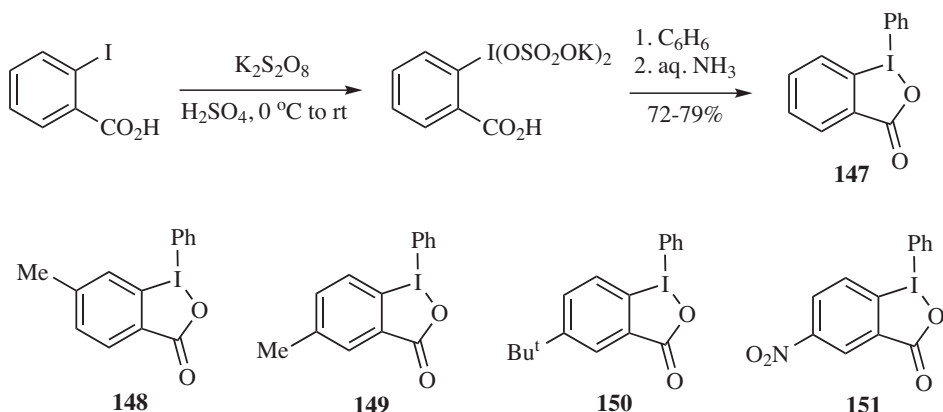
Scheme 2.46



Scheme 2.47



Scheme 2.48



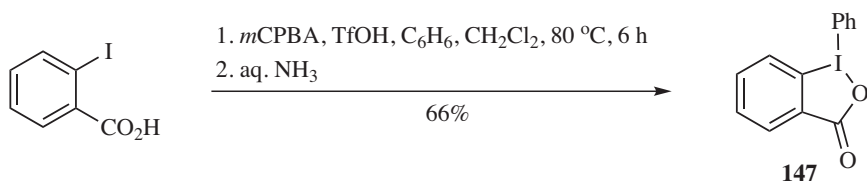
Scheme 2.49

1-[(Triisopropylsilyl)ethynyl]-1,2-benziodoxol-3(1*H*)-one (TIPS-EBX) **140** has found synthetic application as an efficient reagent for ethynylation of various organic substrates [235, 298–303].

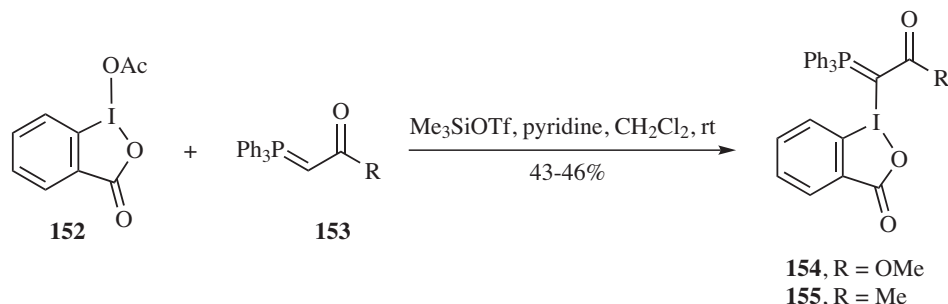
2.1.8.1.9 Arylbenziodoxoles 1-Phenyl-1,2-benziodoxole-3(1*H*)-one **147**, commonly known under the name of diphenyliodonium-2-carboxylate, is the most important representative of arylbenziodoxoles. Phenylbenziodoxole **147** is commercially available or can be prepared by the oxidation of 2-iodobenzoic acid with potassium persulfate followed by addition of benzene according to the optimized procedure published in *Organic Syntheses* (Scheme 2.49) [304]. The original procedure was reported in 1960 by Beringer and Lillien [305] and it has been used to prepare substituted phenylbenziodoxoles **148** [306], **149** [307] and **150** [308]. A more recent modification of this procedure (Scheme 2.49) consists of the use of Oxone ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) as an oxidant instead of $\text{K}_2\text{S}_2\text{O}_8$ and the use of NaHCO_3 as a base instead of NH_3 [309]. This modified method affords various arylbenziodoxoles in high yields and is also applicable for the synthesis of the 7-methylbenziodoxolone ring system using 2-iodo-3-methylbenzoic acid as starting compound [309]. The nitro-substituted phenylbenziodoxole **151** was prepared by the treatment of 5-nitro-2-iodobenzoic acid with benzene in concentrated sulfuric acid [310].

More recently, Merritt and Olofsson reported a convenient modified procedure for the synthesis of phenylbenziodoxole **147** by a one-pot reaction of 2-iodobenzoic acid with *m*-chloroperoxybenzoic acid, trifluoromethanesulfonic acid (TfOH) and benzene followed by addition of aqueous ammonia (Scheme 2.50) [284].

Batchelor, Birchall and Sawyer in 1986 reported X-ray crystal and molecular structure of phenylbenziodoxole **147** [249]. The geometry about iodine in **147** consists of primary bonds to the two phenyl rings (I–C



Scheme 2.50



Scheme 2.51

2.105 and 2.119 Å) and a strong intramolecular secondary $\text{I}\cdots\text{O}$ bond 2.478 Å long to the *ortho*-carboxylate group in an approximate trigonal-bipyramidal arrangement. The $\text{C}-\text{I}-\text{C}$ angle 95.2° is opened to accommodate the $\text{I}\cdots\text{O}$ interaction and to reduce a $\text{C}\cdots\text{H}$ interaction of 2.56 Å between the phenyl rings. Unexpectedly, no further $\text{I}\cdots\text{O}$ secondary bonding occurs and the crystal packing is dictated by hydrogen bonds involving the water molecule in the lattice. The ^{127}I Mössbauer spectral data for the structure of compound **147** is in agreement with that obtained from the crystallographic data [249].

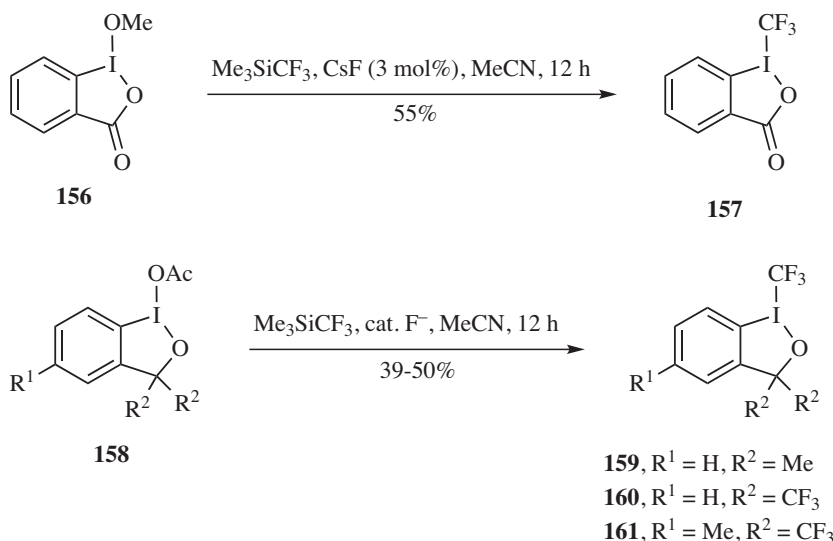
2.1.8.1.10 Phosphoranyl-Derived Benziodoxoles Phosphoranyl-derived benziodoxoles **154** and **155** have been prepared by the reaction of phosphoranes **153** with acetoxybenziodoxole **152** in the presence of trimethylsilyl triflate and pyridine (Scheme 2.51) and isolated in the form of stable, white, microcrystalline solids [250].

Both benziodoxoles **154** and **155** were characterized by a single-crystal X-ray analysis [250]. In particular, X-ray crystallographic analysis of **154** shows that the benziodoxole ring system is essentially planar with the $\text{I}-\text{O}$ bond length of 2.484 Å, which is very similar to the structure of phenylbenziodoxole **147**. The solid-state packing of **154** demonstrates the significance of secondary bonding interactions, which link individual molecules of **154** into infinite chains via interactions between a carbonyl oxygen of one molecule with the $\text{I}(\text{III})$ center of its neighbor. This secondary bonding also affords an approximately square-planar configuration about iodine, with a rather long $\text{I}\cdots\text{O}$ bond length of 3.270 Å [250].

2.1.8.1.11 Trifluoromethylbenziodoxoles The noncyclic CF_3 -substituted λ^3 -iodanes in general lack stability and cannot be isolated at room temperature; however, the incorporation of a hypervalent iodine atom into a five-membered heterocycle has a significant stabilization effect. The first synthesis of stable trifluoromethylbenziodoxoles **157** and **159–161** by treatment of corresponding methoxybenziodoxole **156** or acetoxybenziodoxole **158** with trimethyl(trifluoromethyl)silane was reported by Togni and coworkers in 2006 (Scheme 2.52) [248].

In later works, the synthesis of trifluoromethylbenziodoxole **157** was optimized to give 76% yield over three steps starting from 2-iodobenzoic acid [311] and the improved one-pot synthesis affording **159** in 89% yield starting from chlorobenziodoxole **162** was also developed (Scheme 2.53) [261].

Single-crystal X-ray structures were reported for trifluoromethylbenziodoxole **159** [261] and also for products **157**, **160** and **161** [248]. The X-ray analyzes for all four products clearly show the distorted T-shaped geometry around iodine, typical for members of the hypervalent λ^3 -iodanes. The $\text{I}-\text{CF}_3$ bond lengths increase from **157** (2.219 Å), through **160** (2.229 Å), to **161** (2.236 Å) and **159** (2.267 Å) and simultaneously the $\text{I}-\text{O}$ bond length decreases (**157**: 2.283 Å, **160**: 2.201 Å, **161**: 2.197 Å and **159**: 2.117 Å), whereas

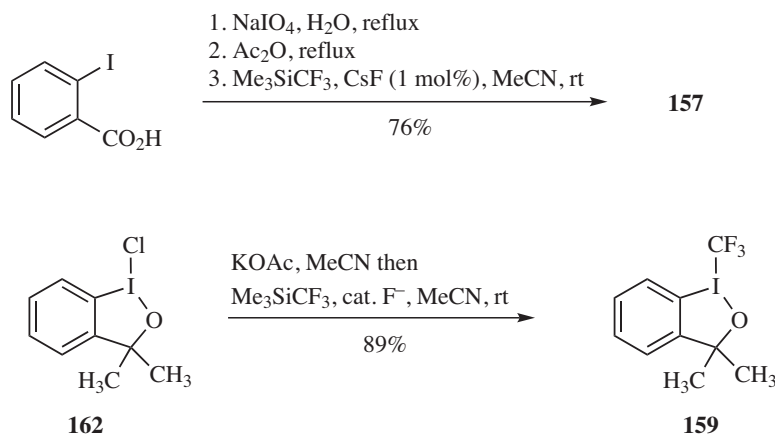


Scheme 2.52

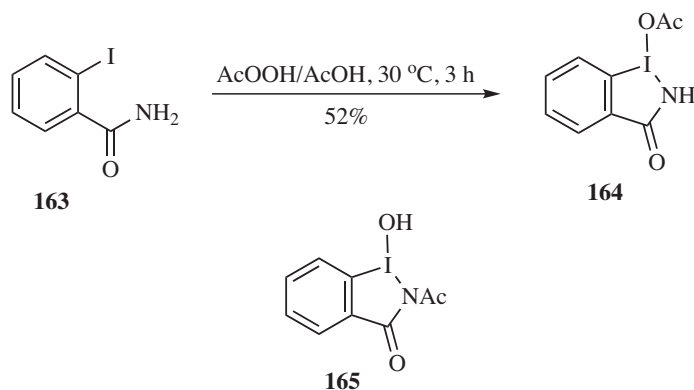
the I–C bond length remains constant within one standard deviation (2.114 Å). The $\text{CF}_3\text{—I—O}$ angles in trifluoromethylbenziodoxoles are significantly smaller than 180° due to the repulsion of the two lone pairs at iodine as predicted by VSEPR theory and are within the range of those typical of other benziodoxoles (around 170°) [248].

Trifluoromethylbenziodoxoles, especially 1-trifluoromethyl-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole **159**, have found synthetic application as efficient reagents for the trifluoromethylation of various organic substrates [248, 261, 311–325].

Two other examples of fluoroalkyl-substituted benziodoxoles have been reported in the literature. 1-Pentafluoroethylbenziodoxolone has been prepared similarly to 1-trifluoromethylbenziodoxolone **157** by reacting 1-acetoxybenziodoxolone (**152**) with $\text{C}_2\text{F}_5\text{SiMe}_3$ in the presence of CsF in acetonitrile [326]. Likewise, the analog of reagent **159** bearing a PhSO_2CF_2 -substituent on the iodine atom was synthesized



Scheme 2.53



Scheme 2.54

from 1-chloro-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (**162**) and PhSO₂CF₂SiMe₃ using the procedure outlined in Scheme 2.53 [327]. This benziodoxole derivative acts as the electrophilic (phenylsulfonyl) difluoromethylating reagent for various S-nucleophiles under mild reaction conditions.

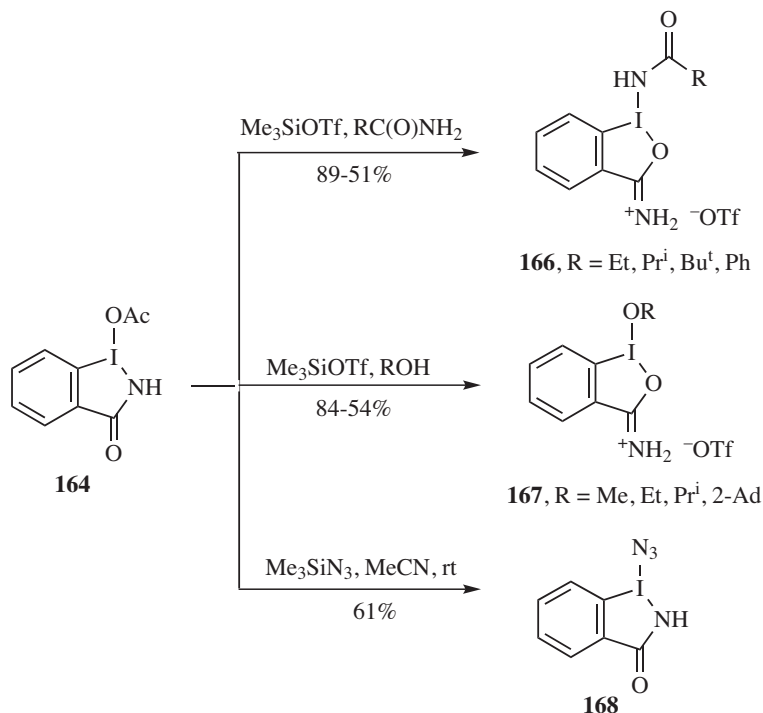
2.1.8.2 Benziodazoles

The first preparation of a benziodazole heterocyclic system was reported by Wolf and Steinberg in 1965 [236]. The authors of this paper isolated the product of peracetic oxidation of 2-iodobenzamide (**163**) and, based on the IR spectroscopy, incorrectly assigned the structure of *N*-acetyl-1-hydroxy-3-(1*H*)-1,2-benziodazole-3-one **165** to this product. Structure **165** was also adopted in several other studies [259, 328, 329]. More recently, the product of peracetic oxidation of **163** (Scheme 2.54) was investigated by a single-crystal X-ray analysis, which revealed its actual structure of acetoxybenziodazole **164**, which is different from the previously adopted **165** [266].

The structural data for acetoxybenziodazole **164** (as a solvate with acetic acid) showed the expected distorted T-shaped geometry with a N–I–O bond angle of 162.1°. The lengths of the bonds to the iodine atom, I–N (2.101 Å), I–O (2.34 Å) and I–C (2.106 Å), are all within the range of typical single covalent bonds in organic derivatives of polyvalent iodine and are in good agreement with the previously reported structures of chlorobenziodazoles [263, 330]. The results of *ab initio* molecular orbital calculations show that structure **164** is 6.31 kcal mol^{−1} more stable than **165** at the Hartree–Fock level of theory [264].

Acetoxybenziodazole **164** reacts at room temperature with carboxamides and alcohols in the presence of trimethylsilyl triflate to afford the rearranged products **166** and **167** (Scheme 2.55), the structures of which were established by X-ray analysis [264]. A plausible mechanism of this rearrangement most likely includes ring opening and ring closure in the protonated benziodazole. Molecular orbital calculations indicate that the driving force of this rearrangement of benziodazoles to 3-iminiumbenziodoxoles is the greater thermodynamic stability of the N-protonated 3-iminobenziodoxoles **166** and **167** relative to the respective O-protonated benziodazole-3-ones by about 15 kcal mol^{−1} [264]. The reaction of acetoxybenziodazole **164** with azidotrimethylsilane affords the corresponding azide **168** in the form of a yellow, microcrystalline precipitate [266]. Azide **168** has similar reactivity to that of azidobenziodoxoles and can be used as an efficient azidating reagent toward dimethylanilines.

The synthesis and structural studies of several N-functionalized benziodazoles derived from natural amino acids have been reported [265]. Acetoxybenziodazoles **170** and **171** were prepared by the peracetic oxidation



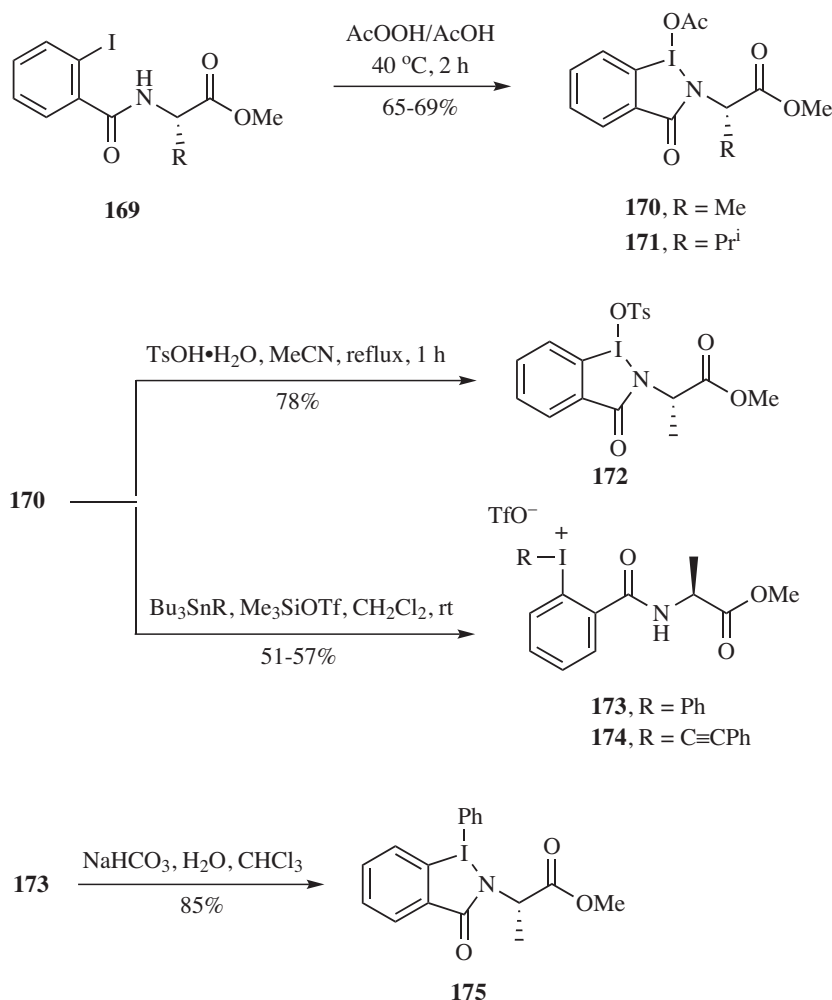
Scheme 2.55

of the readily available 2-iodobenzamides **169** (Scheme 2.56) and isolated as stable, white, microcrystalline solids. Acetoxymethylbenziodazole **170** can be further converted into the tosylate **172** by treatment with *p*-toluenesulfonic acid, or to iodonium salts **173** and **174** by the reaction with tributylphenyltin or tributylphenylethynyltin in the presence of trimethylsilyl triflate.

Treatment of iodonium triflate **173** with aqueous sodium bicarbonate resulted in a restoration of the benziodazole ring with the formation of phenylbenziodazole **175** (Scheme 2.56) [265]. X-Ray crystallographic analysis of **175** shows that the benziodoxole ring system is essentially planar and has a relatively long I—N bond of 2.445 Å. This bond is significantly longer than the analogous I—N bond in acetoxymethylbenziodazole **170**, which is indicative of a substantial ionic character. Overall, the geometry of **175** is similar to that observed for the previously reported structure of phenylbenziodoxole [265].

The oxidation of *N*-(2-iodobenzoyl) amino acids **176** with dimethyldioxirane affords chiral and optically pure hypervalent iodine macrocycles **178–181** as the final isolated products [241]. It is assumed that the initial products in this reaction are the monomeric amino acid derived benziodazoles **177**, subsequent self-assembly of which affords the final products **178–181** (Scheme 2.57). This self-assembly is directed by secondary bonding between hypervalent iodine and oxygen atoms of the amino acid fragment [241].

The structures of macrocycles **180** and **181** were established by X-ray analysis [241]. Molecule **180** consists of a slightly distorted planar macrocyclic system with three oxygens of the amino acid carboxyls inside the ring and all three alkyl groups above the plane. Each iodine atom is covalently bonded to carbon (I—C = 2.092 Å) and nitrogen (I—N = 2.064 Å) and has three longer intramolecular contacts with oxygen atoms (I—O = 2.368, 2.524 and 2.877 Å). With the consideration of primary and secondary bonds, the iodine atoms in **180** have a pentagonal-planar geometry, which is analogous to that found in the solid state for

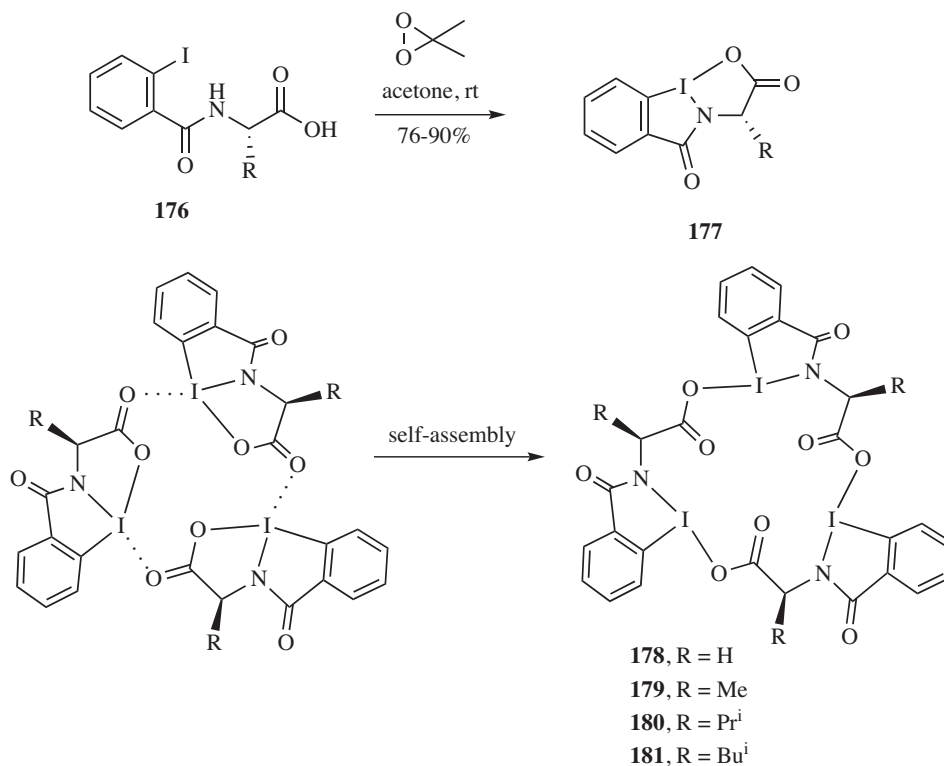


Scheme 2.56

PhI(OAc)_2 . As a result of the central oxygens, the electron-rich cavity of macrocycle **180** is suitable for complexation of metal cations. Specifically, ESI-MS data indicate that macrocycles **178–181** can selectively form complexes with sodium cations in the presence of K^+ , Li^+ , Ag^+ , or Pb^{2+} [241]. The self-assembly of monomeric benziodazoles **177** into macrocyclic molecules **178–181** was studied using molecular orbital calculations [331]. The driving force for the self-assembly is the formation of secondary bonding interactions between molecules and a rearrangement of primary and secondary bonding around iodine to place the least electronegative substituent in the equatorial position for each iodine in the trimer.

2.1.8.3 Benziodoxaboroles

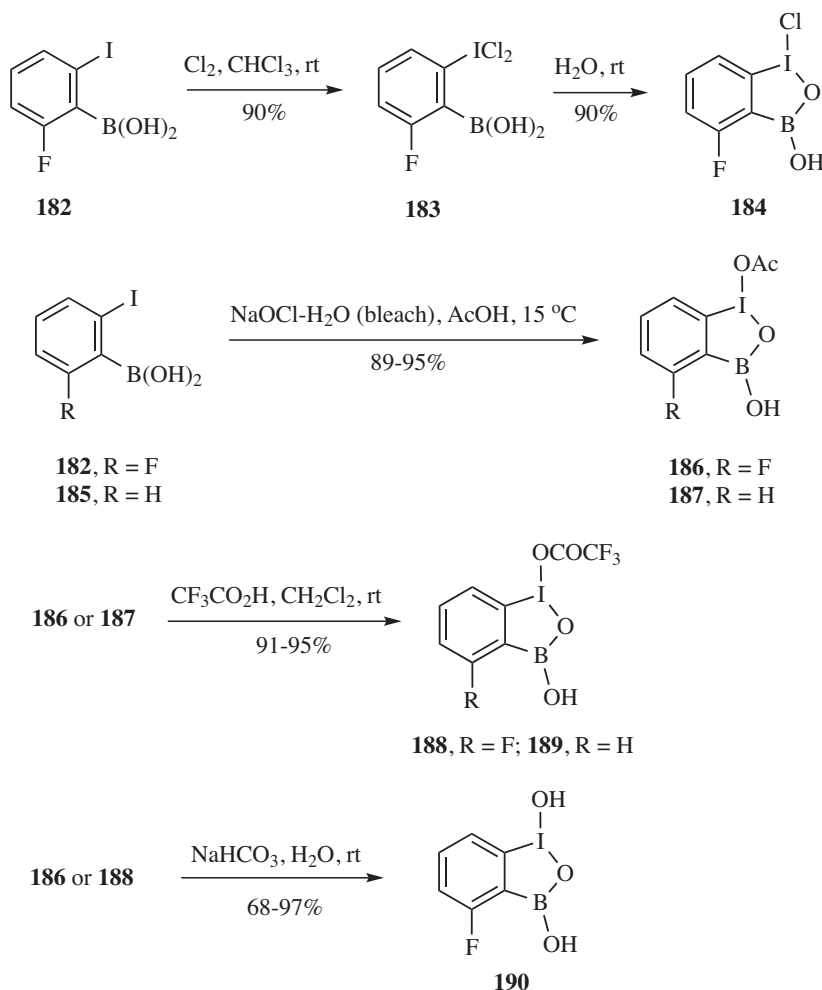
A series of heterocyclic compounds containing trivalent iodine, oxygen and boron in a five-membered ring has been prepared by oxidative cyclization of commercially available *ortho*-iodophenylboronic acids **182** and **185**



Scheme 2.57

[243]. 1-Chloro-4-fluoro-1*H*-1 λ^3 -benzo[*d*][1,2,3]iodoxaborol-3-ol (**184**) was synthesized by the chlorination of 2-fluoro-6-iodophenylboronic acid **182** followed by treatment of the intermediate iododichloride **183** with water (Scheme 2.58). The 1-substituted acetoxybenziodoxaboroles **188** and **189** were prepared by hypochlorite oxidation of 2-fluoro-6-iodophenylboronic acid (**182**) or 2-iodophenylboronic acid (**185**) in acetic acid. Acetoxybenziodoxaboroles **188** and **189** can be further converted into the respective trifluoroacetates **188** and **189** by treatment with trifluoroacetic acid and the 1-hydroxy derivative **190** can be prepared by basic hydrolysis of acetoxy- or trifluoroacetoxy-benziodoxaboroles with aqueous NaHCO₃. X-Ray structural studies of 1-chloro- and 1-trifluoroacetoxy substituted benziodoxaboroles **184**, **188** and **189** have shown the presence of a planar five-membered heterocyclic ring with an unusually short endocyclic I–O bond distance of 2.04–2.09 Å [243]. Structural parameters of the five-membered iodoxaborole ring, such as the planar geometry and the short B–O and O–I bonds lengths in **184**, **188** and **189** compared to those in known benziodoxoles, are suggestive of a partially aromatic character of this ring. The calculated NIST (0) and NIST (1) indexes for 1-chloro- and 1-trifluoroacetoxy substituted benziodoxaboroles, however, are indicative of a significantly lower aromaticity compared to the classic aromatic systems [243].

Slow crystallization of 1-trifluoroacetoxybenziodoxaborole **188** from methanol afforded the tetrameric macrocyclic structure **192** resulting from self-assembly of the initially formed 4-fluoro-1,3-dimethoxy-1*H*-1 λ^3 -benzo[*d*][1,2,3]iodoxaborole (**191**) (Scheme 2.59). The structure of macrocycle **192** was established by a single-crystal X-ray analysis [243]. The driving force for formation of the eight-membered cyclic system **192** is the transformation of initial trigonal-planar sp² hybrid boron atoms in **191** into tetrahedral sp³ hybridized atoms. Indeed, each boron atom in tetramer **192** forms one covalent bond with carbon and three covalent

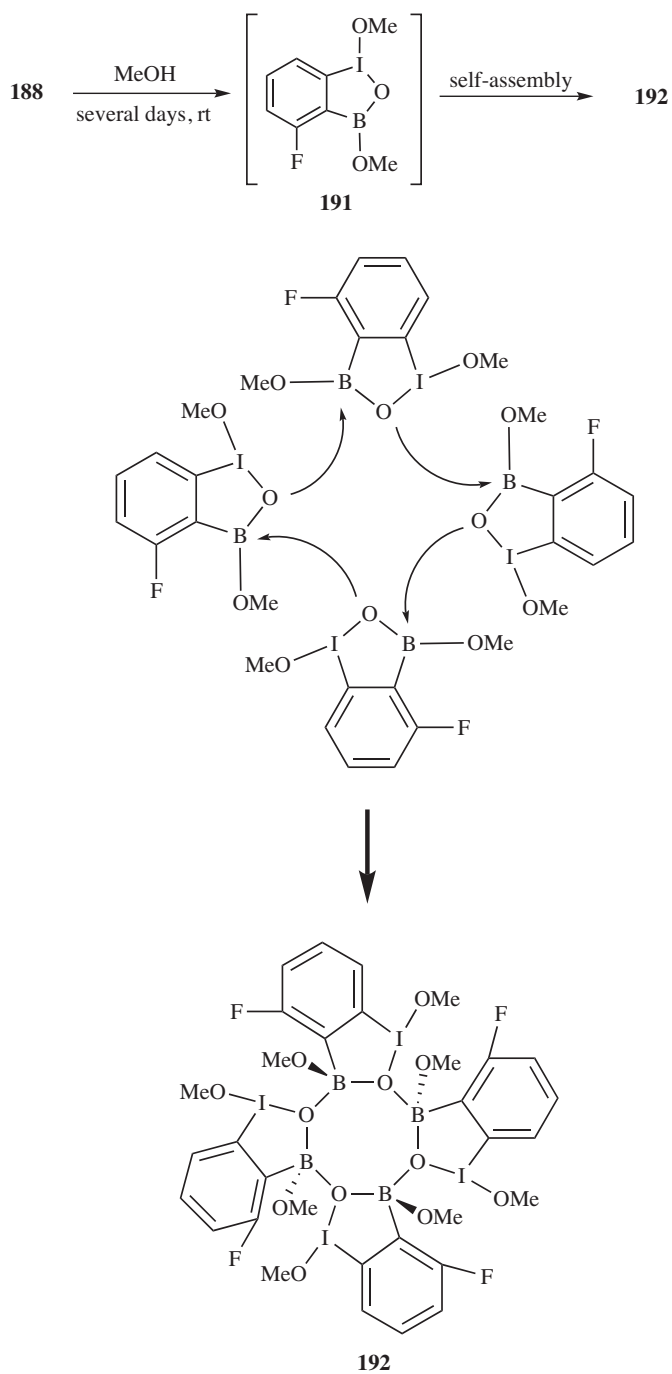


Scheme 2.58

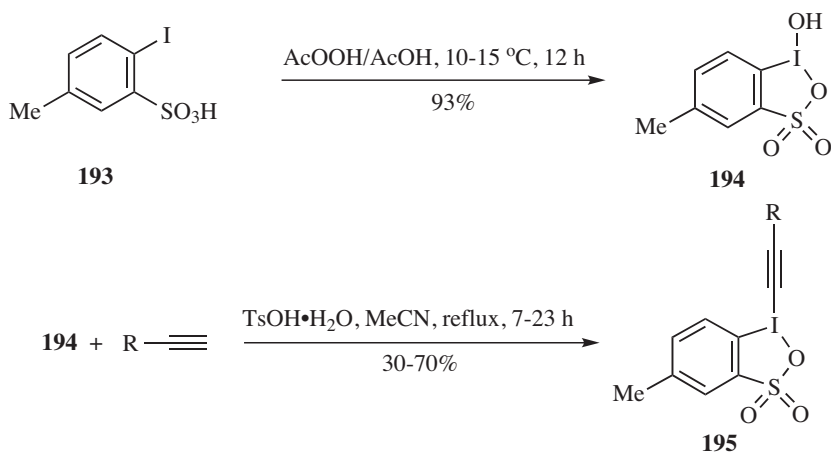
bonds with oxygen atoms. The boron–oxygen bonds, which form the eight-membered cycle (1.48–1.50 Å), are significantly longer than the B–OMe bond distances (1.43–1.44 Å). The eight-membered cycle in **192** is nonplanar with alternating larger B–O–B bond angles (126.2° , average) and smaller O–B–O bond angles (110.7° , average), with the latter being close to the expected for the sp^3 hybridized boron atoms. The change in hybridization of the boron atoms in tetramer **192** also leads to a significant elongation of boron–carbon and heterocyclic iodine–oxygen bonds compared to those observed in compounds **184**, **188** and **189**. Similarly to compounds **184**, **188** and **189** the iodine centers in **192** have the usual T-shape geometry for iodine(III) compounds, with O–I–OMe bond angles varying between 167.2 and 170.5° [243].

2.1.8.4 Benziiodoxathioles

1*H*-1-Hydroxy-1,2,3-benziiodoxathiole 3,3-dioxide (**93** in Figure 2.9) was first described as a sodium salt in 1914 in book by Willgerodt [332]. In 1993 Koser and coworkers reported the preparation of



Scheme 2.59



Scheme 2.60

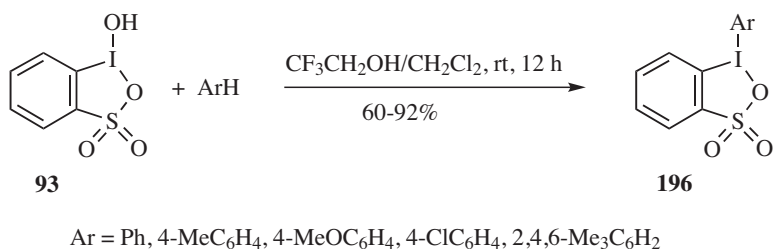
1*H*-1-hydroxy-5-methyl-1,2,3-benziodoxathiole 3,3-dioxide (**194**) by the peracetic oxidation of 2-iodo-5-methylbenzenesulfonic acid (**193**). Benziodoxathiole **194** was further converted into a series of alkynylbenziodoxathioles **195** by the reaction with corresponding terminal alkynes in the presence of toluenesulfonic acid (Scheme 2.60) [244].

The structure of hydroxybenziodoxathiole **194** was determined by a single-crystal X-ray analysis [244]. As expected for a λ^3 -iodane, molecules of **194** are approximately T-shaped about the iodine atom, although the O—I—O bond angle in **194** of 168.6° is less linear than the O—I—O angle in the noncyclic sulfonate $\text{PhI}(\text{OH})\text{OTs}$ (178.80°). The I—OH bond distances in **194** (1.933 Å) and $\text{PhI}(\text{OH})\text{OTs}$ (1.940 Å) are nearly the same and slightly shorter than the computed covalent distance of 1.99 Å for an I—O single bond. The I—O bond to the sulfonate ligand in **194** (2.372 Å) is elongated, although it is 0.1 Å shorter than in $\text{PhI}(\text{OH})\text{OTs}$ (2.473 Å).

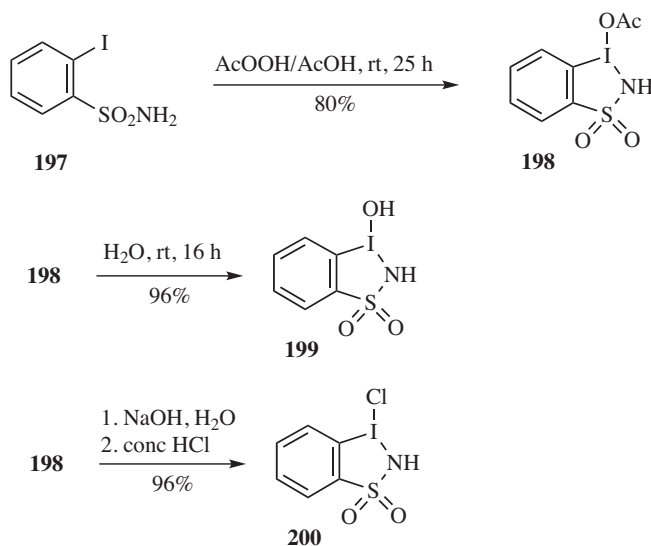
In a more recent paper, the X-ray single-crystal structure of the unsubstituted 1*H*-1-hydroxy-1,2,3-benziodoxathiole 3,3-dioxide (**93**) was reported [245]. In general, the molecular structure of **93** is very similar to that of **194**.

Justik, Protasiewicz and Updegraff have described the preparation and X-ray structural studies of several arylbenziodoxathioles **196** [333]. Compounds **196** were prepared by reacting **93** with appropriate arenes in a solution containing 2,2,2-trifluoroethanol (Scheme 2.61).

X-Ray single crystal structural analysis of compounds **196** (four structures for Ar = Ph, 4-MeOC₆H₄, 4-ClC₆H₄ and 2,4,6-Me₃C₆H₂) revealed that the I—O bond (e.g., 2.676 Å in structure **196**, Ar = Ph) is



Scheme 2.61



Scheme 2.62

markedly longer than the analogous bond in phenylbenziodoxole **147** (2.478 Å; see Section 2.1.8.1.9), suggesting reduced covalent character and a greater contribution of the betaine form rather than covalent benziodoxathiole [333]. For comparison, in the observed solid-state structure of **93** this bond is markedly shorter (2.381 Å) [245].

2.1.8.5 Benziodathiazoles

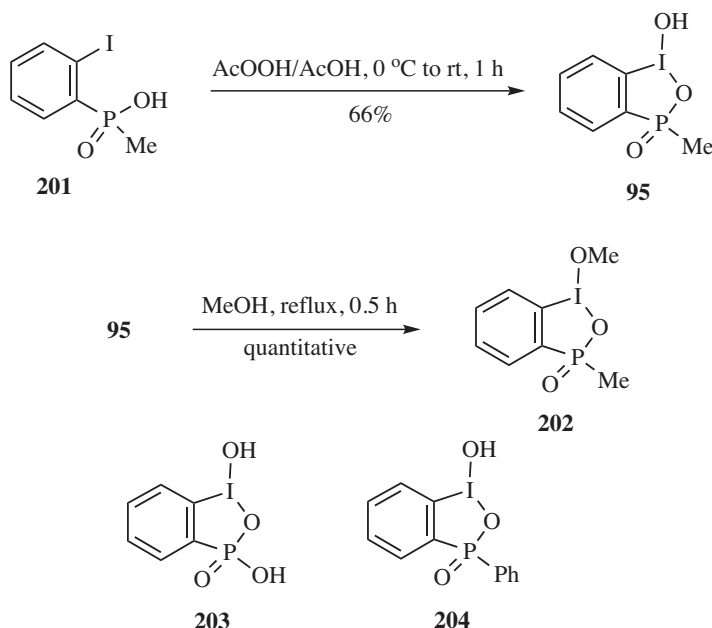
Jaffe and Leffler in 1975 achieved the entry into the benziodathiazole system via 1-acetoxy-1,2-dihydro-1,3,2-benziodathiazole 3,3-dioxide (**198**, Scheme 2.62) [246]. The acetate **198** was synthesized by the peracetic acid oxidation of 2-iodobenzenesulfonamide (**197**). Hydrolysis of **198** gives 1-hydroxy-1,2-dihydro-1,3,2-benziodathiazole 3,3-dioxide (**199**) and 1-chloro-1,2-dihydro-1,3,2-benziodathiazole 3,3-dioxide (**200**) can be obtained by treatment of a basic solution of **198** with concentrated hydrochloric acid [246].

2.1.8.6 Benziodoxaphospholes

Balthazor and coworkers reported the synthesis of 1,3-dihydro-1-hydroxy-3-methyl-1,2,3-benziodoxaphosphole 2-oxide (**95**) by the peracetic oxidation of 2-iodophenylmethylphosphinic acid (**201**) (Scheme 2.63) [247]. Benziodoxaphosphole **95** can be converted into the methoxy derivative **202** by treatment with hot methanol. Methoxybenziodoxaphosphole **202** is readily hydrolyzed in moist air to give the initial hydroxybenziodoxaphosphole **201** [247]. Freedman and DeMott reported a similar preparation of benziodoxaphospholes **203** and **204** by a peracid oxidation of 2-iodophenylphosphonic acid or (2-iodophenyl)phenylphosphonic acid, respectively [334].

The molecular structure of hydroxybenziodoxaphosphole **95** was determined by a single-crystal X-ray analysis [247]. Molecules of **95** are T-shaped about the iodine atom with an O—I—O bond angle of 171.3° , I—OH bond distance of 1.952 Å and I—O bond distance to the phosphinate oxygen of 2.286 Å.

Moss and coworkers [335] investigated catalytic activity of hydroxybenziodoxaphospholes in the hydrolysis of phosphate esters and found that the anion of **95** is 44-times less reactive than hydroxybenziodoxole anion **105** (see Scheme 2.39 in Section 2.1.8.1.2).



Scheme 2.63

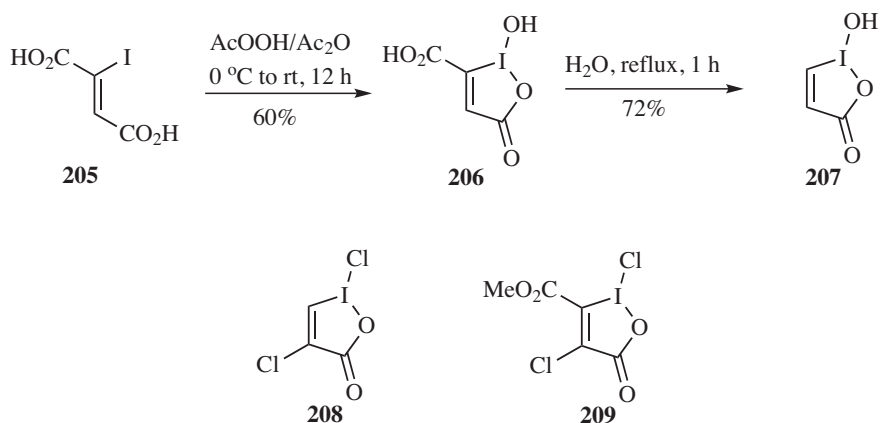
2.1.8.7 Iodoxolones

Iodoxolones represent the only known example of hypervalent iodine heterocycles in which the iodine(III) atom is not connected to an aromatic ring. The first representatives of iodoxolones were prepared by Thiele and Peter in the early 1900s by the oxidative cyclization of iodofumaric acid derivatives [336]. More recently, Moss and coworkers have prepared several iodoxolones using modified older procedures. In particular, hydroxyiodoxolone (**207**) was synthesized by the peracetic oxidation of iodofumaric acid (**205**) followed by decarboxylation of the initially formed 5-carboxylic acid derivative **206** (Scheme 2.64) [337]. Another approach to this heterocyclic system (e.g., chloriodoxolones **208** and **209**) involves the addition of ICl_3 to acetylenedicarboxylic acid followed by a spontaneous cyclization of the initially formed iododichlorides [338].

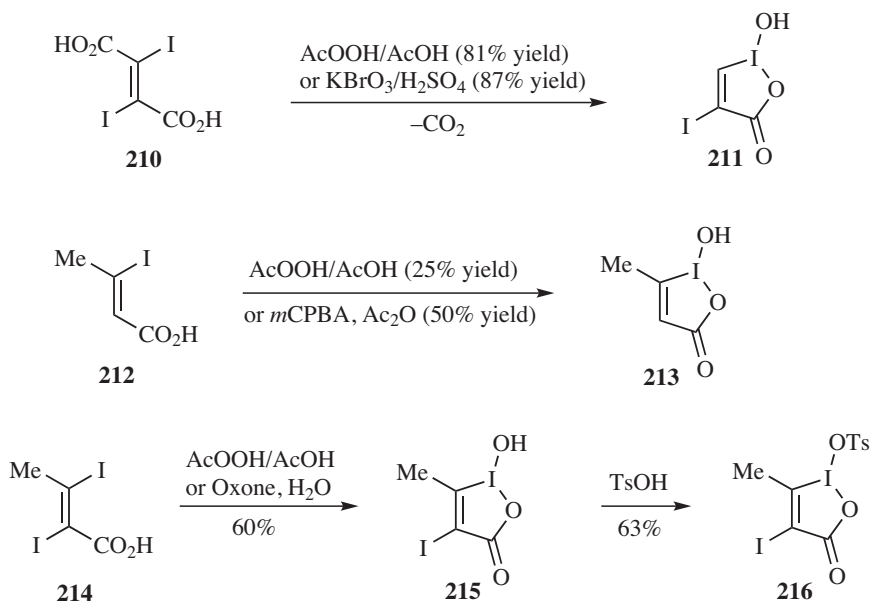
Several iodoxolones (e.g., **211**, **213**, **215** and **216**) have been prepared by the oxidation of (*Z*)-3-iodo acrylic acid derivatives **210**, **212** and **214** (Scheme 2.65) [339]. Structures of products **211** and **213** were established by X-ray analysis [339]. The angles and distances found in the five-membered iodoxolone system are very similar in structures **211** and **213** and are directly comparable to the X-ray structure of 2-iodosylbenzoic acid (**104**) (Section 2.1.8.1.2) [271] or 3,4,5,6-tetrafluoro-2-iodosylbenzoic acid [340]. Iodoxolones **211**, **213**, **215** and **216** have stabilities and reactivities similar to those of conventional hypervalent iodine(III) reagents [339].

A stable aliphatic iodoxolone **218**, the valence tautomer of *cis*-iodosylcyclopropanecarboxylic acid, has been prepared by two alternative approaches: (i) the peracetic oxidation of *cis*-2-iodocyclopropanecarboxylic acid (**217**) and (ii) by hydrolysis of the corresponding iododichloride **219** (Scheme 2.66) [341].

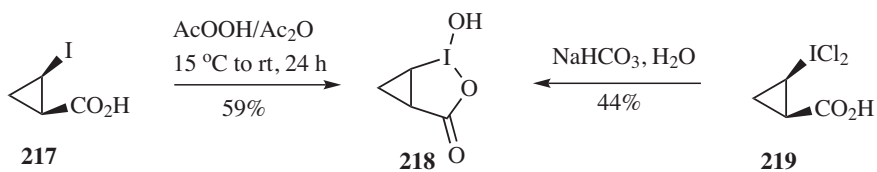
Compound **218** exists in the hydroxyiodoxolone form, not in the open *cis*-cyclopropanecarboxylic acid form, as indicated by its high pK_a of 7.55 (cf. Section 2.1.8.1.2) and by its ability to cleave phosphate esters in aqueous micellar solution [341].



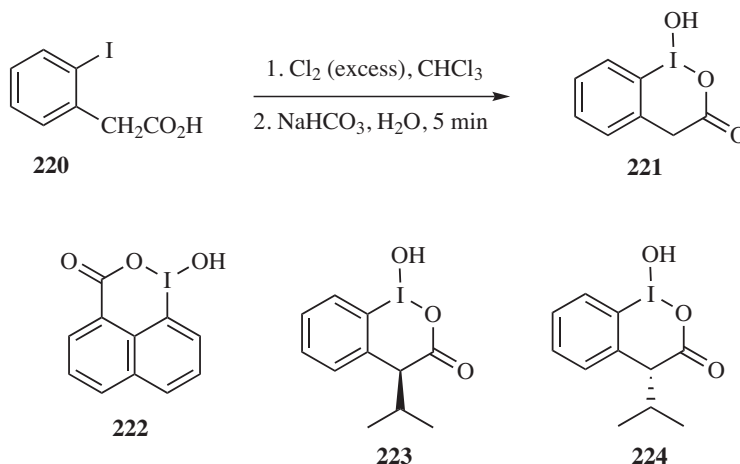
Scheme 2.64



Scheme 2.65



Scheme 2.66



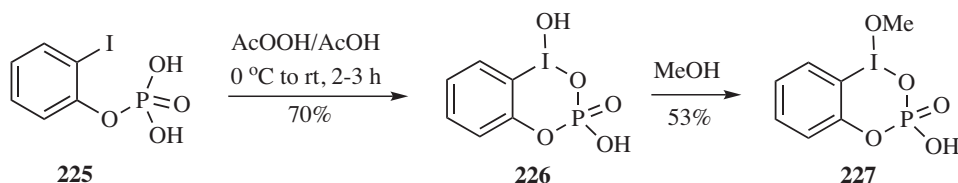
Scheme 2.67

2.1.8.8 Six-Membered Iodine(III) Heterocycles

Owing to the nature of hypervalent bonding and the T-shaped geometry of the iodine(III) center, the formation of six-membered iodine heterocycles is highly unfavorable. Several such compounds have been reported in the literature [328, 342–346]; however, X-ray structural data on six-membered iodine(III) heterocycles is not available. Moreover, based on the available X-ray single-crystal data for several pseudocyclic six-membered iodine(V) derivatives (Section 2.2.2), it can be expected that these compounds may exist as their noncyclic tautomers [345].

The first six-membered iodine(III) heterocycle, the cyclic tautomer of 2-iodosylphenylacetic acid, **221**, was reported in 1963 by Leffler and coauthors [342]. This compound was synthesized by chlorination of 2-iodophenylacetic acid (**220**) followed by hydrolysis of the initially formed, unstable 2-(dichloroiodo)phenylacetic acid (Scheme 2.67). Compound **221** is stable at room temperature but decomposes in solution at 80–100 °C; the proposed cyclic structure **221** is in agreement with its relatively low acidity ($\text{p}K_{\text{a}} = 7.45$) [342]. 8-Iodosyl-1-naphthoic acid (**222**) was prepared by the peracetic oxidation of 8-iodo-1-naphthoic acid [343]. Anions of 2-iodosylphenylacetic acid (**221**) [328] and **222** [343] have a moderate reactivity in the cleavage of phosphate esters in aqueous micellar solution. The chiral, enantiomerically pure substituted 2-iodosylphenylacetic acid derivatives **223** and **224** were synthesized from the corresponding aryl iodides by oxidation with dimethyldioxirane [344].

Leffler and Jaffe reported the synthesis of a presumably cyclic tautomer of 2-iodosylphenylphosphoric acid (**226**) and its methyl ester **227** starting from 2-iodophenylphosphoric acid (**225**) (Scheme 2.68) [346].



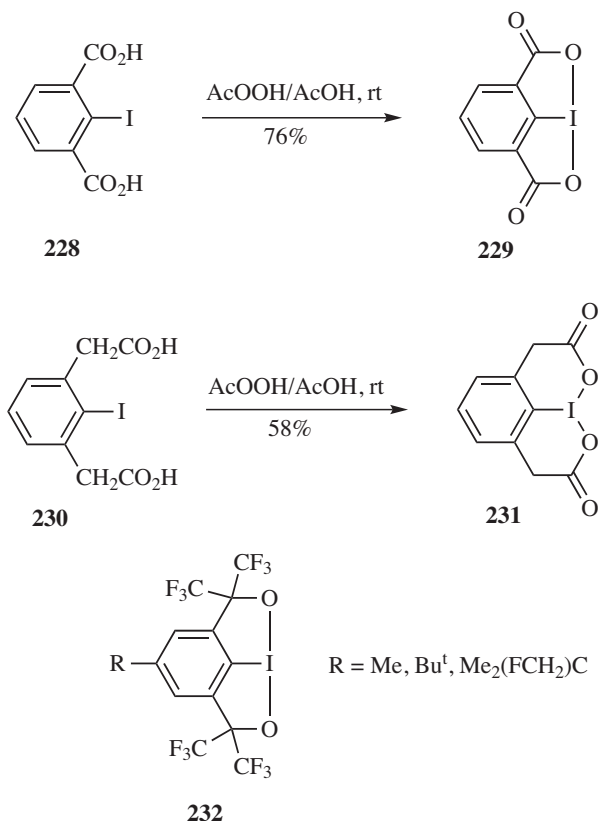
Scheme 2.68

Products **226** and **227** were identified by NMR spectroscopy; an attempted X-ray diffraction analysis of **226** was unsuccessful.

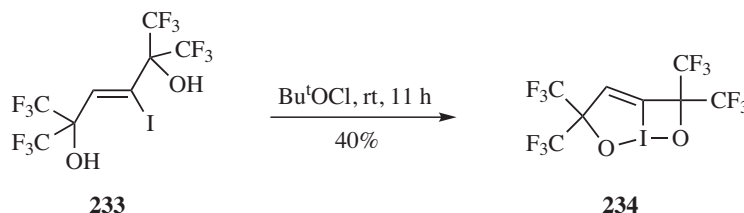
2.1.8.9 Polycyclic Heterocycles with an Iodine(III) Atom at Ring Junction

The synthesis of the first representatives of this class of fused hypervalent iodine heterocycles was described by Agosta in 1965 [347]. Compounds **229** and **231** were originally prepared by the peracetic oxidation of corresponding iodides **228** and **230** (Scheme 2.69). A few years later, Martin and Chau reported an alternative way of forming product **229** by the thermal decomposition of the dibutyl ester of 2-iodoisophthalic acid [348]. The benziodoxolone derivative **229** has high thermal stability, with a decomposition point above 260 °C; the formation of this heterocyclic system is particularly favorable due to the T-shaped geometry of hypervalent iodine. The X-ray crystallographic analysis of compound **229** showed a structure of overall planar geometry with the expected T-shape configuration at the iodine(III) center [349]. Several similarly fused iodine(III) heterocycles (compounds **232**) have also been reported [350, 351].

An unusual fused hypervalent iodine heterocycle (**234**) has been prepared by oxidative cyclization of 3-iodo-3-hexene-2,5-diol **233** with neat *tert*-butyl hypochlorite (Scheme 2.70) [352, 353].



Scheme 2.69



Scheme 2.70

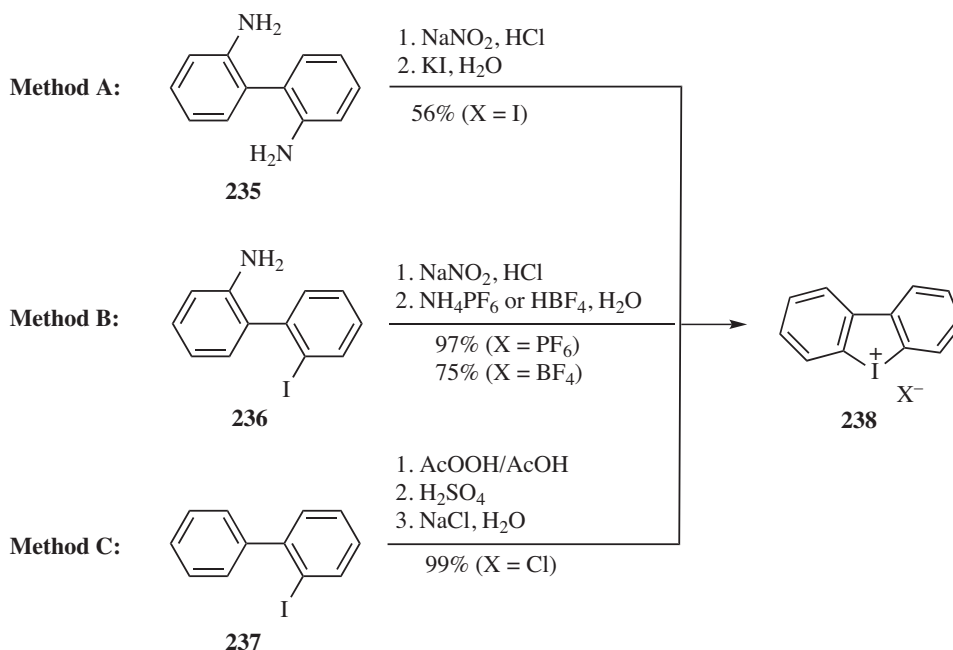
The structures of products **232** ($R = \text{Bu}^t$) [354] and **234** [353] were established by single-crystal X-ray analyses, which showed that both structures have a distorted T-shape geometry around the central iodine atom. Apical bond angles O—I—O for **234** and **232** are $144.5(1)^\circ$ and $158.2(2)^\circ$, respectively, indicating that the deviation (35.5°) of bond angle O—I—O in **234** from 180° is larger than that (21.8°) of **232**. The apical bond length [$2.142(3) \text{ \AA}$] of the four-membered ring of **234** is longer than that of the five-membered ring [$2.070(3) \text{ \AA}$]. These results explain the ring strain in the four-membered ring. The four-membered ring is almost planar, judging from the torsion angle I—C—C—O of $0.0(3)^\circ$ and the sum of bond angles of the four-membered ring of 359.9° [353].

2.1.8.10 Cyclic Iodonium Salts

The most important representative of cyclic iodonium salts, the dibenziodolium or diphenyleneiodonium (DPI) cation **238**, known in the form of iodide, chloride, hydrosulfate, hexafluorophosphate, or tetrafluoroborate salts, can be obtained by three different procedures (A, B and C) summarized in Scheme 2.71. Method A, originally developed by Mascarelli and Benati in 1909 [355], uses 2,2'-diaminodiphenyl (**235**) as the starting material, which upon diazotization with sodium nitrite in a hydrochloric acid solution followed by potassium iodide addition, gives DPI **238** as iodide salt. A similar reaction starting from 2-amino-2'-iododiphenyl **236** affords DPI as hexafluorophosphate or tetrafluoroborate in excellent yields (Method B) [356]. The third method involves the peracetic oxidation of 2-iodobiphenyl (**237**) to an iodine(III) intermediate that then cyclizes in acidic solution (Method C) [357]. More recently, these methods were used to prepare the tritium labeled DPI and of its 4-nitro derivative [358].

The structure of dibenziodolium tetrafluoroborate, **238** ($X = \text{BF}_4$), was established by a single-crystal X-ray analysis [359]. In particular, **238** is planar; deviations from the mean molecular plane are less than 0.03 \AA . The bond angle C—I—C of 83° in **238** is appreciably smaller than the corresponding angle in the structure of a noncyclic iodonium salt, diphenyliodonium chloride [360] (93°). The bond lengths C—I of 2.08 \AA are close to typical C—I bonds in hypervalent iodine compounds. A relatively long distance of 3.65 \AA between the iodine center and the nearest tetrafluoroborate anion is indicative of the ionic character of this compound. Dibenziodolium salts **238** have a relatively high thermal stability (tetrafluoroborate salt **238** has a melting point of $239\text{--}240^\circ \text{C}$) [356]; however, the X-ray structural data do not support aromatic character of the iodonium ring.

The preparation and chemistry of cyclic iodonium salts has been summarized in a review of Grushin [361]. Several examples of known cyclic iodonium salts are shown in Figure 2.10 and include 4,5-phenanthryleneiodonium salts (**239**) [362], 10*H*-dibenz[*b,e*]iodonium salt (**240**) [363], 10,11-dihydrodibenz[*b,f*]iodeponium salt (**241**) [363], phenoxiodonium salt (**242**) [363], 10-acetylphenaziodonium salt (**243**) [363], 10-oxidophenothiiodonium salt (**244**) [363], the bicyclic bis-iodonium salt **245** [364], benziodolium chloride **246** [359] and iodonium salt **247** [365].



Scheme 2.71

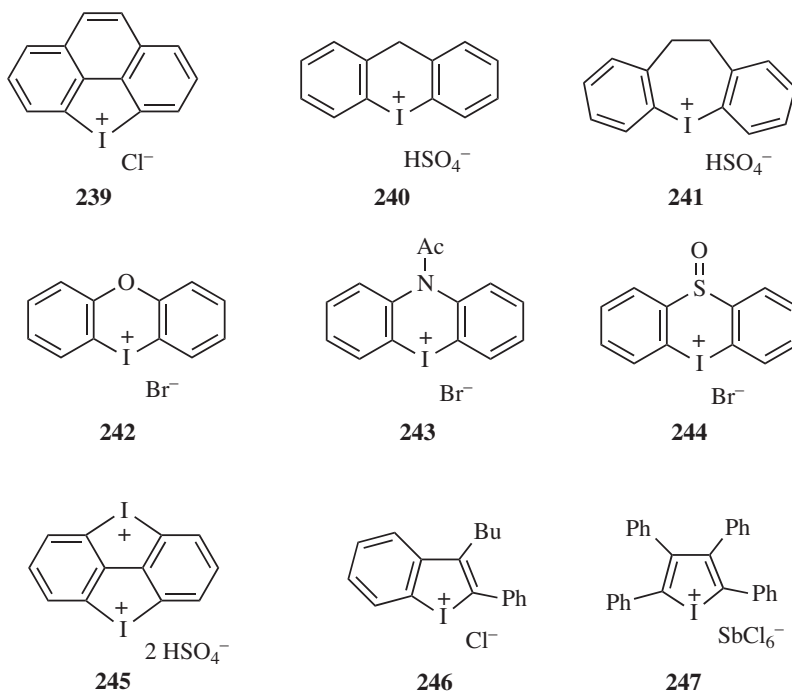


Figure 2.10 Examples of known cyclic iodonium salts.

The preparation of several macrocyclic iodonium triflates, for example, rhomboids **250**, a square (**253**) and a pentagon (**255**) has been reported (Scheme 2.72) [147,366,367]. The rhomboid-shaped molecules **250** were prepared by the treatment of compounds **248** and **249** with trimethylsilyl triflate [366]. The reaction of dication **251** with compound **252** in the presence of trimethylsilyl triflate gave the iodonium-containing molecular square **253** in good yield [147,366]. In addition, the pentagon-shaped macrocycle **255** was prepared in 60% yield from precursors **251** and **254**. Structures of these iodonium-containing charged macrocycles were established using elemental analysis, multinuclear NMR and mass spectrometry. These iodonium-containing macromolecules may find potential application in nanotechnology [366].

2.1.9 Iodonium Salts

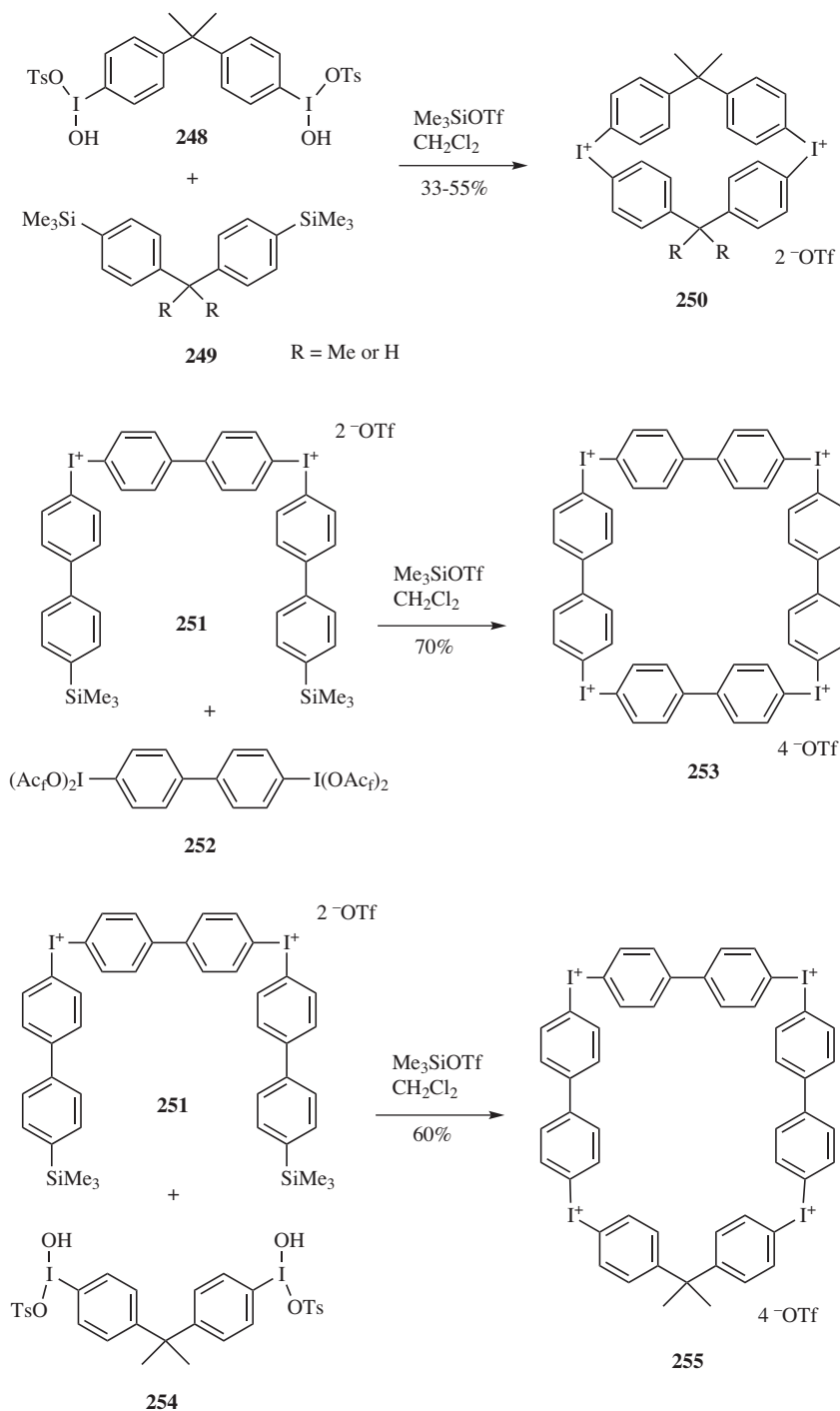
According to conventional classification, iodonium salts are defined as positively charged 8-I-2 species with two carbon ligands and a negatively charged counterion, $R_2I^+ X^-$. Formally, the iodonium cation does not belong to hypervalent species since it has only eight valence electrons on the iodine atom; however, in the modern literature iodonium salts are commonly treated as the ten-electron hypervalent compounds, taking into account the closely associated anionic part of the molecule. X-Ray structural data for the overwhelming majority of iodonium salts show significant secondary bonding between the iodine atom and the anion, with average bond distances within the range 2.3–2.7 Å. Their structure has overall trigonal-bipyramidal geometry and the experimentally determined R–I–R bond angle is close to 90°, which is similar to the geometry of λ^3 -iodanes with one carbon ligand. The most common and well-investigated class of these compounds is represented by diaryliodonium salts, which have been known for over 100 years and especially were extensively studied in the 1950s and 1960s. More recently, significant research activity has focused on aryl- and heteroaryliodonium salts bearing alkenyl, alkynyl and fluoroalkyl groups as the second ligand. Iodonium salts have found numerous practical applications as synthetic reagents and biologically active compounds.

2.1.9.1 Aryl- and Heteroaryliodonium Salts

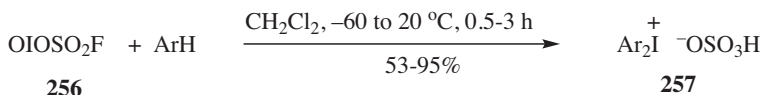
Diaryliodonium salts are the most stable and well-investigated class of iodonium salts. The first example of these compounds, (4-iodophenyl)phenyliodonium bisulfate, was prepared by Hartmann and Meyer in 1894 from iodosylbenzene and sulfuric acid [368]. Diaryliodonium salts $Ar_2I^+ X^-$ are air- and moisture-stable compounds, whose physical properties are strongly affected by the nature of the anionic part of the molecule. In particular, diaryliodonium salts with halide anions are generally sparingly soluble in many organic solvents, whereas triflate and tetrafluoroborate salts have a better solubility. The chemistry of aryl- and heteroaryliodonium salts has been extensively covered in several reviews [361,369,370].

2.1.9.1.1 Preparation Synthetic routes to diaryliodonium salts typically involve the initial oxidation of an aryl iodide to a λ^3 -iodane and then ligand exchange with an arene or a nucleophilic arylating reagent (e.g., arylborates, arylstannanes, or arylsilanes) to obtain the diaryliodonium salt. In many cases a final anion exchange step is necessary. To shorten the synthetic route to symmetric iodonium salts, preformed inorganic iodine(III) reagents can be employed. A particularly useful approach involves one-pot oxidation and ligand-exchange reactions to obtain the diaryliodonium salts directly from arenes and iodoarenes or molecular iodine. Most of these reactions are performed under acidic conditions, although several neutral or basic methods also exist.

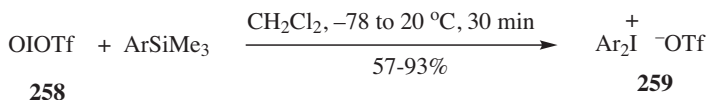
Older methods for the preparation of symmetrical diaryliodonium salts are based on the reaction of arenes with potassium iodate or KIO_3/I_2 in the presence of concentrated sulfuric acid [371,372]. It is assumed that the mechanisms of these reactions involve initial formation of the electrophilic iodyl or iodosyl species, $IO_2^+HSO_4^-$ or $IO^+HSO_4^-$, which further react with arenes, finally forming diaryliodonium salts,



Scheme 2.72



Ar = Ph, 4-MeC₆H₄, 4-Bu^tC₆H₄, 2,4-Me₂C₆H₃, 4-FC₆H₄, 4-ClC₆H₄, 4-BrC₆H₄



Ar = Ph, 4-MeC₆H₄, 2,4,6-Me₂C₆H₂, 4-BrC₆H₄, 4-(4'-BrC₆H₄)C₆H₄, etc.

Scheme 2.73

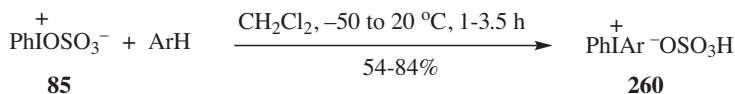
Ar₂I⁺HSO₄⁻, in several consecutive steps. Other inorganic iodosyl derivatives, such as iodosyl fluorosulfate (**256**) and iodosyl trifluoromethanesulfonate (**258**) also react with arenes or trimethylsilylarenes under mild conditions to afford the corresponding iodonium hydrosulfates **257** or triflates **259** (Scheme 2.73) [373, 374].

A modification of this procedure, which is useful for a selective synthesis of unsymmetrical aryl(phenyl)iodonium hydrosulfates **260**, consists of the reaction of arenes with phenyliodosyl sulfate **85** (Scheme 2.74) [375].

Numerous methods for the preparation of symmetrical and unsymmetrical diaryl- and hetaryl-iodonium organosulfonates have been developed. A common synthetic approach to unsymmetric diaryl- and hetaryl(aryl)iodonium tosylates (e.g., **262**, **264**, **266** and **268**) is based on the reactions of [hydroxy(tosyloxy)iido]arenes with aryltrimethylsilanes **261** [198], aryltributylstannanes **263** [376], arylboronic acids **265** [377], or the appropriate heteroaromatic precursors **267** (Scheme 2.75) [378, 379]. The reaction of HTIB with arylstannanes proceeds under milder conditions compared to arylsilanes and is applicable to a wide range of arenes with electron-withdrawing substituents. Arylboronic acids in general have some advantage over arylstannanes in the case of the electron-rich heterocyclic precursors [377].

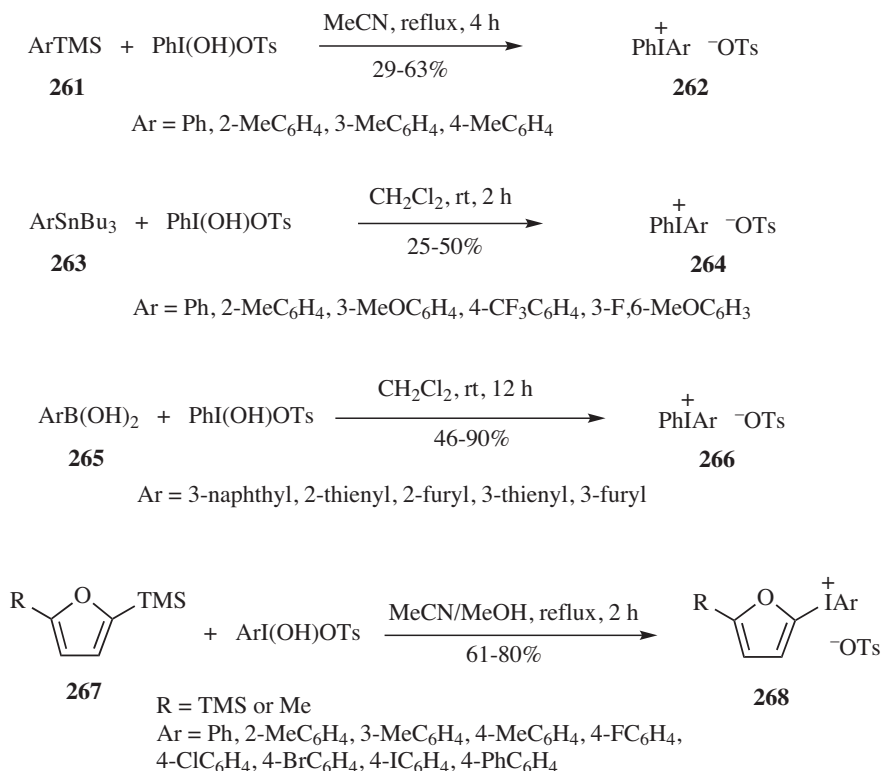
Various unsymmetrically substituted diaryliodonium triflates **269** can be synthesized by the reaction of iodosylbenzene [380] or (diacetoxyiodo)arenes [381] with arenes in trifluoromethanesulfonic acid (Scheme 2.76). This simple procedure affords diaryliodonium triflates in relatively high yields, but it is limited to aromatic substrates that are not sensitive to strong acids. In a milder, more selective variation of this procedure (diacetoxyiodo)benzene is reacted with arylboronic acids in the presence of triflic acid at -30 °C to afford aryl(phenyl)iodonium triflates in 74–97% yields [377].

Several modified procedures for the preparation of diaryliodonium triflates have been reported in a more recent literature [382–384]. Kitamura and Hossain have developed a one-pot reaction to obtain symmetrical diaryliodonium triflates in good yields directly from iodoarenes and aromatic substrates using K₂S₂O₈ as an



Ar = Ph, 4-MeC₆H₄, 4-FC₆H₄, 4-IC₆H₄, 4-Bu^tC₆H₄, 2,4-Me₂C₆H₃,
2,4,6-Me₃C₆H₂, 3-NO₂C₆H₄

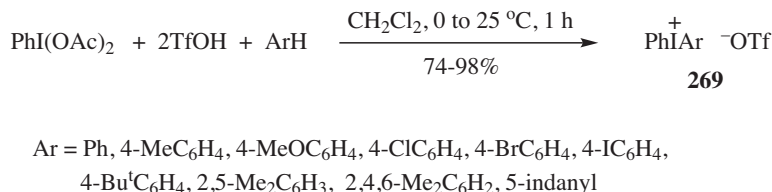
Scheme 2.74



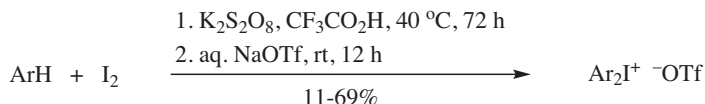
Scheme 2.75

oxidant [382]. Additional improvements of this procedure consist of the reaction of arenes with elemental iodine and $\text{K}_2\text{S}_2\text{O}_8$ in trifluoroacetic acid, followed by treatment with sodium triflate (Scheme 2.77) [383,384].

Olofsson and coworkers have developed several efficient one-pot syntheses of diaryliodonium salts [385–390]. A general and universal procedure provides both symmetrical and unsymmetrical diaryliodonium triflates **272** from both electron-deficient and electron-rich arenes **271** and aryl iodides **270** using *m*CPBA as the oxidant and triflic acid (Scheme 2.78) [385–387]. The electron-rich diaryliodonium tosylates are prepared similarly using toluenesulfonic acid instead of triflic acid as the additive [387]. Symmetrical diaryliodonium triflates can be synthesized by a modified one-pot procedure from iodine, arenes, *m*CPBA and triflic acid under similar conditions [374, 375]. A similar procedure based on a one-pot reaction of arylboronic acids, aryl iodides, *m*CPBA and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ has been used for regioselective synthesis of unsymmetrical diaryliodonium tetrafluoroborates [388, 389]. In a further improvement of this approach, a range of



Scheme 2.76

**Scheme 2.77**

symmetrical and unsymmetrical diaryliodonium triflates were prepared employing urea–H₂O₂ as the environmentally benign oxidizing agent in trifluoroethanol (TFE) [390]. Kita and coworkers have demonstrated that hexafluoroisopropanol (HFIP) can also be used as a highly efficient solvent for the synthesis of various diaryliodonium salts [391, 392].

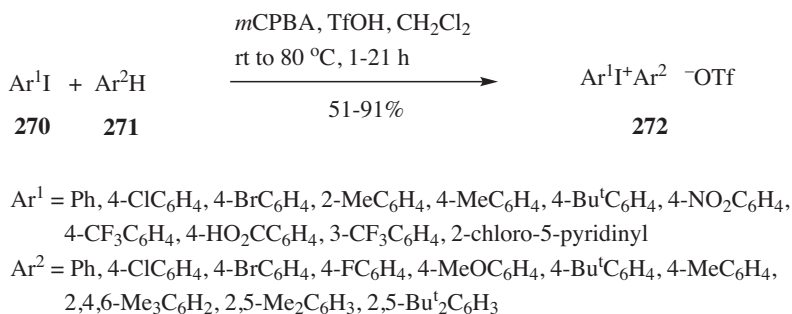
Diaryliodonium tetrafluoroborates **274** and **276** can be conveniently prepared by the boron–iodine(III) exchange reaction of (diacetoxyiodo)arenes with tetraarylborates **273** [393] or arylboronic acids **275** [394, 395] followed by treatment with a saturated sodium tetrafluoroborate solution (Scheme 2.79). A modified procedure employs aryltrifluoroborates, ArBF₃[−]K⁺, instead of tetraarylborates under mild conditions [396]. Several fluoroorgano-iodonium tetrafluoroborates, such as (C₆F₅)₂I⁺BF₄[−], (4-C₅F₄N)₂I⁺BF₄[−] and [C₆F₅(4-C₅F₄N)I]⁺BF₄[−], can be prepared by interaction of the appropriate (difluoroiodo)arenes with fluorinated organodifluoroboranes, Ar_fBF₂, in dichloromethane at 0 to 20 °C [34].

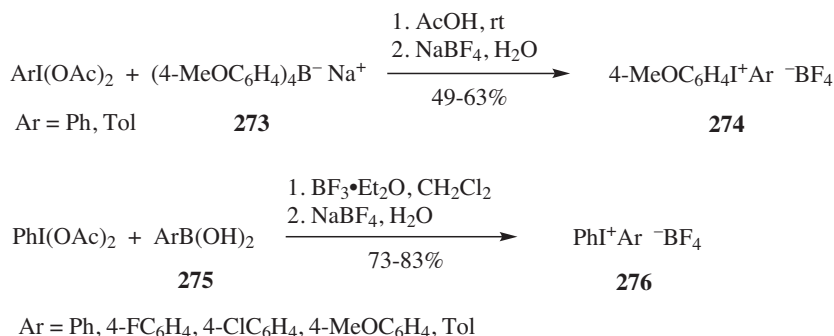
Another protocol uses a similar tin–iodine(III) and silicon–iodine(III) exchange reaction of (diacetoxyiodo)arenes or iodosylbenzene with tetraphenylstannane or (trimethylsilyl)benzene in the presence of boron trifluoride etherate [397].

Frohn and coworkers have reported the preparation of a perfluoroaryliodonium salt, (C₆F₅)₂I⁺AsF₆[−], by the electrophilic arylation of C₆F₅I with a stable pentafluorophenylxenonium hexafluoroarsenate, C₆F₅Xe⁺AsF₆[−] [398].

Skulski and Kraszkiewicz have also reported a new direct method for the preparation of various symmetrical diaryliodonium bromides (15–88% crude yields) from arenes by the reaction of ArH with NaIO₄ in sulfuric acid followed by the addition of KBr [23].

A very mild and general method for the preparation of diaryl- and heteroaryliodonium triflates is based on iodonium transfer reactions of iodine(III) cyanides with the respective aryl- or heteroarylstannanes [146, 148, 399–401]. Specifically, (dicyano)iodonium triflate (**277**), generated *in situ* from iodosyl triflate and Me₃SiCN, reacts with tributyltin derivatives of aromatic and heteroaromatic compounds to afford the corresponding symmetrical iodonium salts under very mild conditions (Scheme 2.80) [389, 390].

**Scheme 2.78**



Scheme 2.79

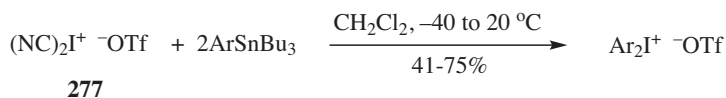
A similar iodonium exchange reaction involves aryl(cyano)iodonium triflates **278** and stannylated aromatic precursors providing many kinds of diaryl or aryl(heteroaryl) iodonium salts [145, 147, 401]. Tykwinski, Hinkle and coworkers have reported an application of such iodonium transfer reaction for obtaining of a series of mono- and bithienyl(aryl)iodonium triflates **279** with increasingly electron-withdrawing substituents on the aryl moiety (Scheme 2.81) [401]. Thienyl and bithienyl iodonium salts prepared by iodonium transfer reaction using $\text{PhI}(\text{CN})\text{OTf}$ are potentially useful as nonlinear optical materials [402].

A very mild and selective approach to aryl- and hetaryl(iodonium) chlorides **282** is based on the reaction of aryllithium **280** (generated *in situ* from bromoarenes and butyllithium) with (*E*)-chlorovinyl(iodine(III)) dichloride (**18**) (Scheme 2.82) [71, 88, 89, 403, 404]. The iodonium transfer reagent **18** is prepared by the reaction of iodine trichloride with acetylene in concentrated hydrochloric acid (Scheme 2.8 in Section 2.1.3.2) [403]; **caution:** this compound is highly unstable and should be handled and stored with proper safety precautions [71]. However, the iodonium transfer procedure with reagent **18** is particularly useful for the preparation of bis(hetaryl)iodonium chlorides **283** from the appropriate nitrogen heterocycles **282** (Scheme 2.82) [71].

A similar approach to aryl- and heteroaryl(phenyl)iodonium triflates **285** involves the ligand-transfer reaction between vinyl(iodonium) salt **284** with aryllithiums (Scheme 2.83) [405]. Likewise, the reaction of (*E*)-[β -(trifluoromethanesulfonyloxy)ethenyl](aryl)iodonium triflates **286** with aryllithiums or alkynyllithiums can be used for a selective preparation of the respective diaryl- or alkynyl(aryl)iodonium triflates in high yields [406].

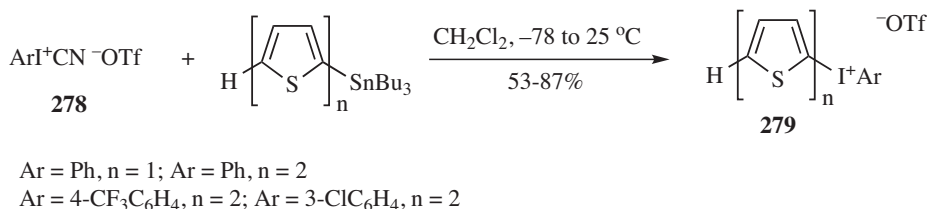
Peacock and Pletcher have reported a simple, one-step procedure for the synthesis of diaryliodonium salts by the electrochemical oxidation of aryl iodide at a carbon felt anode in acetic acid in the presence of an arene [407, 408]. This reaction gives good yields of diaryliodonium salts for aryl iodides and arenes with alkyl substituents in the benzene ring.

Several heteroaryl(phenyl)iodonium organosulfonates have been prepared by the [3+2] cycloaddition reactions of alkynyliodonium salts with 1,3-dipolar reagents. The reaction of (arylethynyl)iodonium tosylates



Ar = Ph, 3-MeOC₆H₄, 4-MeOC₆H₄, 2-furyl, 2-thienyl, 4-pyrazolyl, etc.

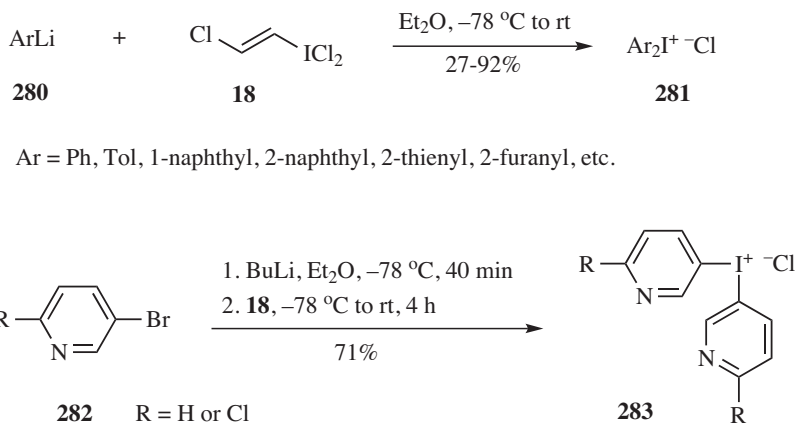
Scheme 2.80



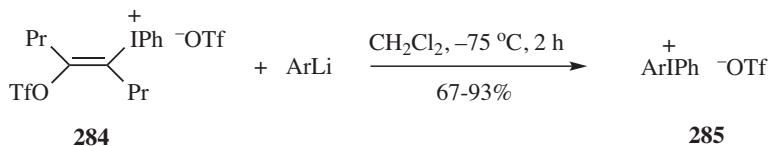
Scheme 2.81

287 with nitrile oxides **288** affords cycloadducts **289** as sole products in good yield (Scheme 2.84) [409]. The nitron **291** reacts with (phenylethynyl)iodonium tosylate **290** to give cycloaddition product **292** in moderate yield [409]. A similar cycloaddition of alkynyliodonium triflate **293** with diazocarbonyl compounds **294** affords pyrazolyliodonium salts **295** as sole regioisomers [410,411]. Methyl and phenyl azides **297** react with alkynyliodonium triflates **296** upon heating in tetrahydrofuran or acetonitrile to give triazolyliodonium salts **298** as sole regioisomers in low yields (Scheme 2.84) [410].

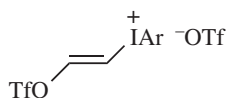
Single-crystal X-ray structures have been reported for the following aryl- and heteroaryliodonium salts: diphenyliodonium triiodide [412], (2-methylphenyl)(2-methoxyphenyl)iodonium chloride [413], (2-methoxy-5-methylphenyl)(4-methoxy-2-methylphenyl)iodonium trifluoroacetate [414], (2-methoxy-5-methylphenyl)(4-methoxyphenyl)iodonium trifluoroacetate [415], a complex of diphenyliodonium tetrafluoroborate with pyridine [416], a complex of diphenyliodonium tetrafluoroborate with 1,10-phenanthroline [417], a complex of diphenyliodonium tetrafluoroborate with 18-crown-6 [418], 1-naphthylphenyliodonium tetrafluoroborate [419], 3,10-dimethyl-10*H*-dibenzo[*b,e*]iodinium tetrafluoroborate [420], aryl(pentafluorophenyl)iodonium tetrafluoroborates [421], 4,4'-[bis(phenyliodonium)]-diphenylmethane ditriflate [422], [bis(4-methoxyphenyl)](diethylaminocarbodithioato)iodine(III) [423], di(*p*-tolyl)iodonium bromide [424], diphenyliodonium chloride, bromide and iodide [425,426], diphenyliodonium nitrate [427], diphenyliodonium tetrafluoroborate [428], thienyl(phenyl)iodonium salts [401], (*anti*-dimethanoanthracenyl)phenyliodonium tosylate and hexafluorophosphate [429] and 3-mesityl-5-phenylisoxazol-4-yl(phenyl)iodonium *p*-toluenesulfonate [409].



Scheme 2.82

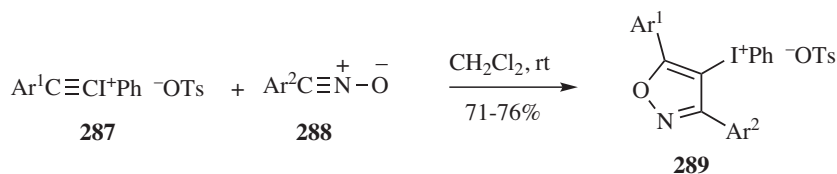


Ar = Ph, 2-MeC₆H₄, 2-MeOC₆H₄, 3-MeOC₆H₄, 2-thienyl, 2-benzothieryl



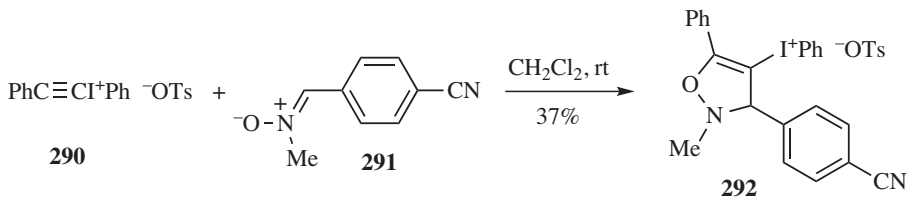
286, Ar = Ph or 4-MeC₆H₄

Scheme 2.83

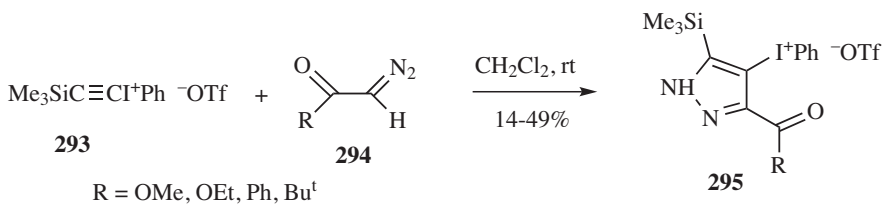


289

Ar¹ = Ph, 2-ClC₆H₄; Ar² = 2,4,6-Me₃C₆H₂, 2,6-Cl₂C₆H₃

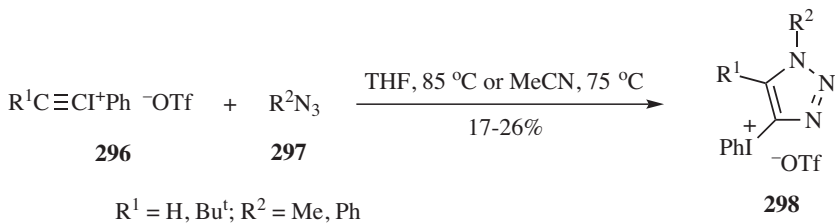


292



295

R = OMe, OEt, Ph, Bu^t



298

R¹ = H, Bu^t; R² = Me, Ph

Scheme 2.84

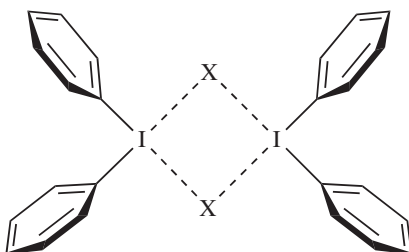


Figure 2.11 Primary and secondary bonding pattern in a single-crystal X-ray structure of a typical diaryliodonium salt Ph_2IX ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{or } \text{BF}_4$).

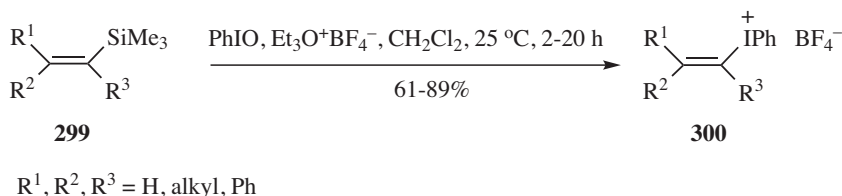
In the solid state, diaryliodonium halides and tetrafluoroborates usually exist as anion-bridged dimers held together by iodine–halogen bonds (Figure 2.11). The overall iodine coordination is square planar and the C–I–C bond angle is close to 90° . A particularly detailed X-ray structural study of diphenyliodonium chloride, bromide and iodide was published by Alcock and Countryman in 1977 [425]. All three compounds Ph_2IX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) exist in the solid state as centrosymmetric dimers, held together by halogen bridges. The dimers are precisely planar and all six I–C bonds are equal to within experimental error (mean 2.090 \AA). The C–I–C bond angles are $92.6(3)^\circ$ ($\text{X} = \text{Cl}$), $93.2(5)^\circ$ ($\text{X} = \text{Br}$) and $91.8(6)^\circ$ ($\text{X} = \text{I}$), the C–I–X bond angles vary from $179.3(3)^\circ$ ($\text{X} = \text{Cl}$) to $174.8(4)^\circ$ ($\text{X} = \text{I}$) and the $\text{I}\cdots\text{X}$ secondary bond distance increases from $3.064(3)$ ($\text{X} = \text{Cl}$) to $3.463(2)$ ($\text{X} = \text{I}$) [373]. The $\text{I}\cdots\text{Cl}$ secondary bond distance is much longer than the regular hypervalent I–Cl bond length of 2.47 \AA in PhICl_2 [92], which is indicative of the ionic character of iodonium salts. A more recently published single-crystal X-ray structure of (2-methylphenyl)(2-methoxyphenyl)iodonium chloride [413], is generally very similar to the structure of Ph_2ICl . Interestingly, this study unveiled hypervalent iodine as a stereogenic center within a dimeric structure, composed of two conformational enantiomers, which probably undergo racemization in solution [413].

Studies in solution have shown that diaryliodonium salts are in general fully dissociated in aqueous or polar media, but have also suggested that they may exist as ion pairs or dimeric structures in less polar organic solvents. In particular, freezing point depression measurements for diphenyliodonium chloride in water (25–50 mmolar concentration) gave a van't Hoff factor of 2.04, compared to one of 2.06 for sodium chloride in the same apparatus. Diphenyliodonium chloride is thus very largely dissociated in water. Dilute solutions of 4,4'-dicyclohexyldiphenyliodonium iodide in benzene gave a van't Hoff factor of about 0.5, which is indicative of ion aggregation in the nonpolar media [430].

2.1.9.2 Alkenyliodonium Salts

Several examples of alkenyliodonium salts have been known for more than a hundred years, but it was only in the 1990s that these compounds become readily available and found some synthetic application. The chemistry of alkenyl(aryl)iodonium salts has been covered in several reviews by Ochiai [431], Okuyama [432–434] and Zefirov and coauthors [435].

2.1.9.2.1 Preparation First representatives of alkenyliodonium salts, dichlorovinyl(phenyl)iodonium species, were reported by Thiele and Haakh in the early 1900s [436]. The first general synthetic approach to alkenyl(phenyl)iodonium salts was developed by Ochiai in the mid-1980s [437, 438]. This method is based on the reaction of silylated alkenes **299** with iodosylbenzene in the presence of Lewis acids, leading to the stereoselective formation of various alkenyliodonium tetrafluoroborates **300** in good yield (Scheme 2.85).



Scheme 2.85

The boron trifluoride-catalyzed silicon–iodine(III) exchange reaction of alkenylsilanes **301** with iodosylarenes followed by treatment with aqueous NaBF_4 is the most general method for the synthesis of alkenyl(aryl)iodonium tetrafluoroborates **302** (Scheme 2.86) [394, 439]. This reaction proceeds under mild conditions and in a stereoselective manner with retention of the geometry of organosilanes.

A similar boron–iodine(III) exchange of alkenylboronic acids **303** with iodosylbenzene or (diacetoxyiodo)benzene in the presence of boron trifluoride etherate is an efficient alternative method for a selective preparation of alkenyl(phenyl)iodonium tetrafluoroborates **304** in excellent yields (Scheme 2.87) [440, 441].

Likewise, the reaction of vinylzirconium derivatives **305** with (diacetoxyiodo)benzene followed by anion exchange affords alkenyl(phenyl)iodonium salts **306** stereoselectively with retention of configuration (Scheme 2.88) [442].

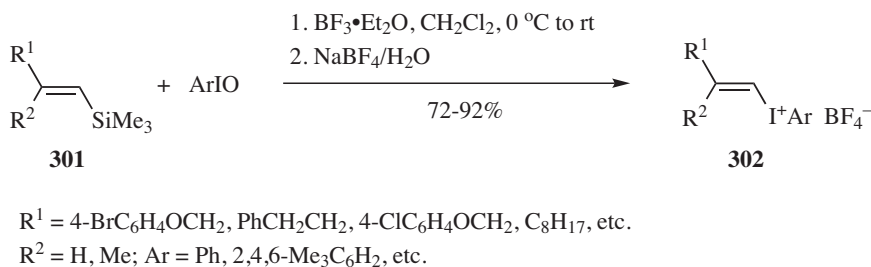
A very general and mild procedure for the stereospecific synthesis of alkenyl(aryl)iodonium triflates **309** involves aryl(cyano)iodonium triflates **308** as iodonium transfer reagents in reactions with stannylated alkenes **307** (Scheme 2.89) [367, 443, 444]. This method was also applied to the preparation of the parent vinyliodonium triflate from tributyl(vinyl)tin [445].

Several types of functionalized alkenyl(aryl)iodonium salts have been prepared by the addition of hypervalent iodine reagents to alkynes. Reactions of terminal alkynes with iodosylbenzene and triflic acid proceed as a highly stereoselective *anti*-addition to afford (*E*)-(β-trifluoromethanesulfonyloxyalkenyl)phenyliodonium triflates **310** in high yield (Scheme 2.90) [446–448]. Similar products were obtained from the reactions of internal alkynes and parent acetylene [447].

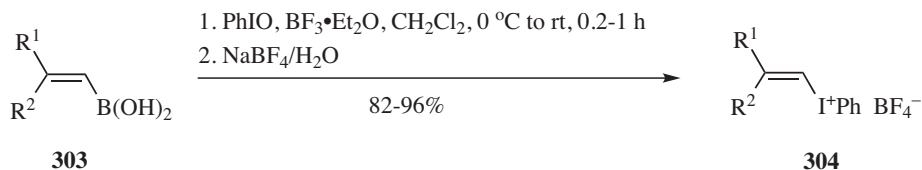
Similarly functionalized alkenyl(aryl)iodonium triflates **312** were prepared by the addition of (aryl)fluoroiodonium triflates **311** to terminal alkynes (Scheme 2.91) [45, 48].

Likewise, various alkenyliodonium fluorides **314** were prepared by the addition of 4-(difluoroiodo)toluene **313** to alkynes (Scheme 2.92) [449–452].

Alkynyl(aryl)iodonium salts can serve as precursors to some alkenyl(aryl)iodonium salts [453–455]. For example, (*E*)-β-fluoroalkenyl(phenyl)iodonium tetrafluoroborates **316** can be stereoselectively prepared by

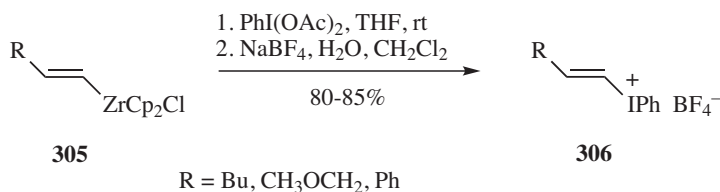


Scheme 2.86

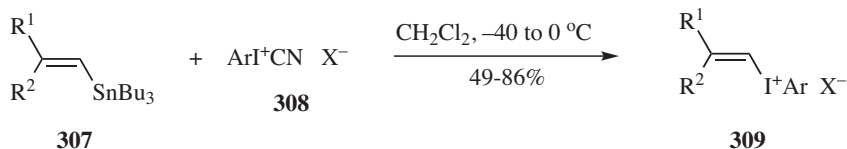


$\text{R}^1 = \text{Bu, Bu}^t, \text{Ph(CH}_2)_3, (\text{CH}_3)_2\text{CH(CH}_2)_2, \text{etc.}; \text{R}^2 = \text{H, Me}$

Scheme 2.87



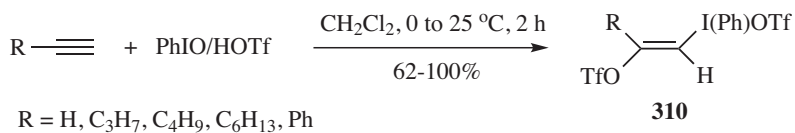
Scheme 2.88



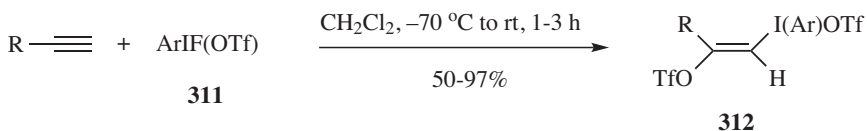
$\text{R}^1 = \text{Me, Et, Bu, Ph}; \text{R}^2 = \text{Me, Et, Bu}$

$\text{Ar} = \text{Ph, 4-CF}_3\text{C}_6\text{H}_4, 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_2; \text{X} = \text{OTf or OTs}$

Scheme 2.89



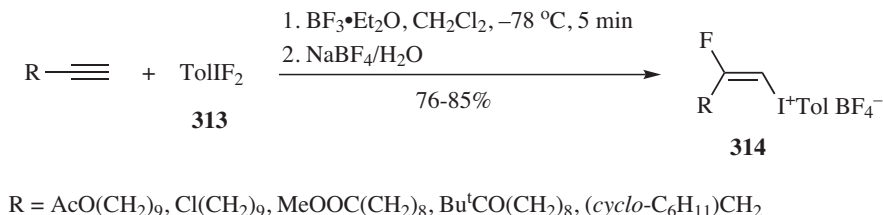
Scheme 2.90



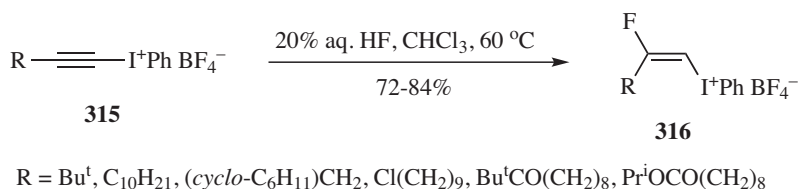
$\text{R} = \text{H, C}_3\text{H}_7, \text{C}_4\text{H}_9, \text{C}_8\text{H}_{17}, \text{CH}_2\text{OCH}_3, \text{CH}_2\text{OH, CH}_2\text{Cl}$

$\text{Ar} = \text{Ph, 4-MeC}_6\text{H}_4, 2\text{-MeC}_6\text{H}_4, 4\text{-NO}_2\text{C}_6\text{H}_4$

Scheme 2.91



Scheme 2.92



Scheme 2.93

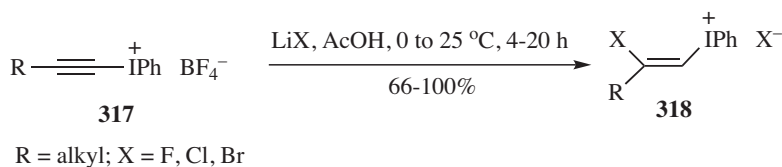
the reaction of alkynyl(phenyl)iodonium salts **315** with aqueous HF in good yields (Scheme 2.93) [453,454]. This method is applicable to the synthesis of fluoroalkenyliodonium salts having functional groups such as ketone, ester and chloride.

(Z)- β -Substituted vinyliodonium salts **318** can be prepared by a Michael-type nucleophilic addition of halide anions to alkynyliodonium salts **317** (Scheme 2.94) [456,457].

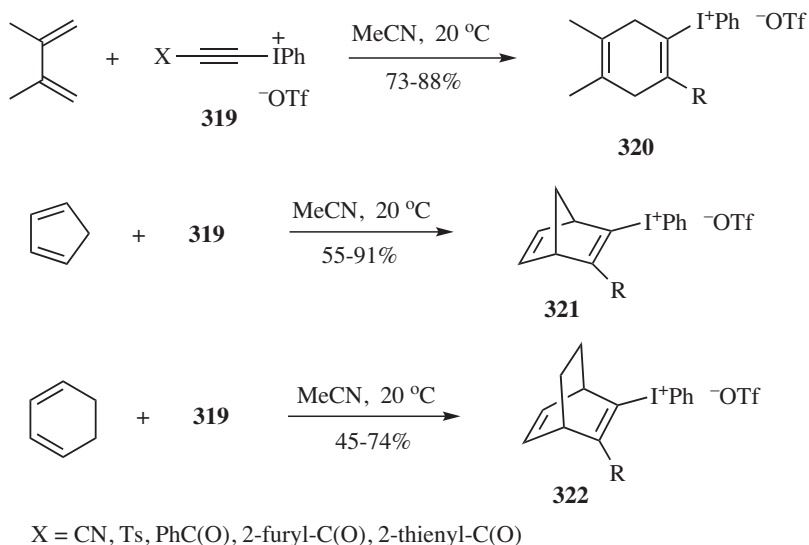
Various cyclohexadienyl(phenyl)iodonium salts have been prepared by the [4+2] Diels–Alder cycloadditions of alkynyliodonium salts **319**, functionalized with electron-withdrawing substituents in the β -position, with a wide range of dienes. Scheme 2.95 shows several examples of these cycloadditions, affording adducts **320–322** as stable microcrystalline solids [458].

The reaction of alkynyliodonium salts **319** with unsymmetrically substituted dienes **323** results in a mixture of two regioisomeric cyclohexadienes **324** and **325** (Scheme 2.96) [459]. In general, this cycloaddition shows low regioselectivity in the case of 2-substituted dienes and has a better degree of regioselectivity in the case of 1-substituted dienes. Moreover, the reaction of 1-methylbutadiene (**326**) with alkynyliodonium salt **327** selectively affords a single regioisomer (**328**), whose structure was established by X-ray analysis (Scheme 2.96) [459].

Several iodonium- and bis(iodonium) norbornadienes and other polycyclic adducts have been synthesized by [2+4] cycloaddition reactions of alkynyliodonium triflates with cyclic 1,3-dienes [458, 460–464]. In particular, the bis-iodonium acetylene **331** undergoes Diels–Alder reactions with cyclopentadiene **329**, furan



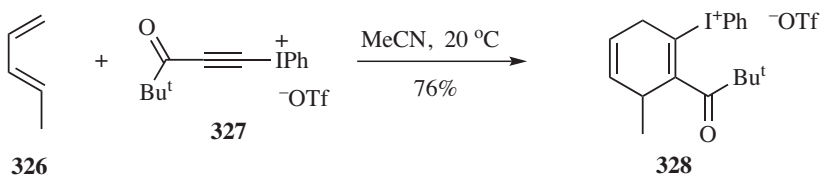
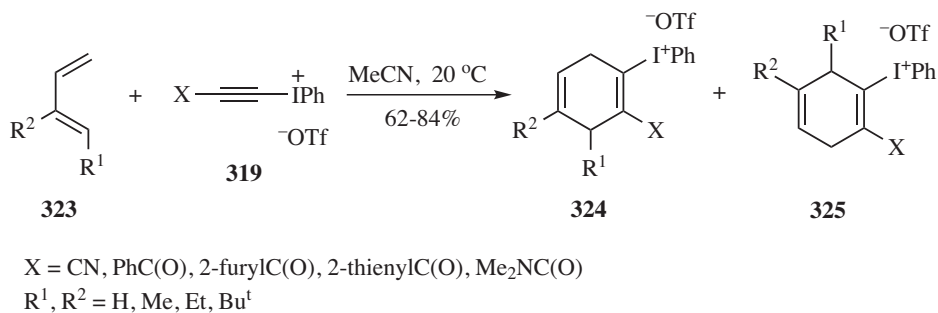
Scheme 2.94



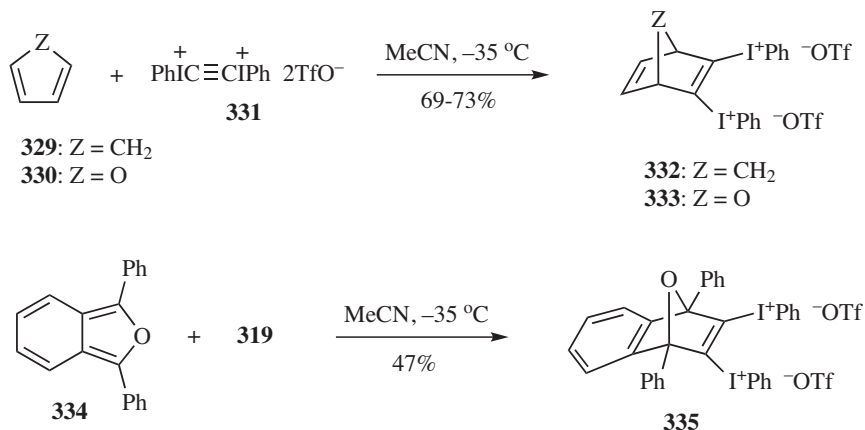
Scheme 2.95

330 and 1,3-diphenylisobenzofuran **334** in acetonitrile under very mild conditions (Scheme 2.97) [460]. All adducts (**332**, **333** and **335**) were isolated in the form of stable microcrystalline solids; the structure of adduct **332** was established by single-crystal X-ray analysis [460].

2.1.9.2.2 Structural Studies Examples of alkenyliodonium salts whose X-ray crystal structures have been reported in literature include the following: (*E*)-(β -trifluoromethanesulfonyloxyalkenyl)phenyliodonium triflate **336** [465], 2,3-bis(iodonium)norbornadiene **332** [460], 4-*tert*-butylcyclohexenyl(phenyl)iodonium



Scheme 2.96



Scheme 2.97

tetrafluoroborate (**337**) [437], phenyl(2,2-dimethyl-4-(diethylphosphono)-2,5-dihydro-3-furyl)iodonium salts **338** and **339** [466], 1-(trimethylacetyl)-2-(phenyl{[(trifluoromethyl)sulfonyl]oxy}iodo)-6-methyl-1,4-cyclohexadiene (**328**) [459], internal alkenyliodonium salt **340** [467], substituted 1-[(Z)-1-phenyl-2-phenyliodonio]vinyl]oxy}pyridinium ditosylate **341** [455], (*E*)-(β-chloroalkenyl)phenyliodonium tetrafluoroborates **342** and **343** [452] and a complex of **337** with 18-crown-6 [468] (Figure 2.12).

The structures of alkenyliodonium salts can generally be considered as ionic with a typical distance between iodine and the nearest anion of 2.8–3.1 Å. However, with consideration of the anionic part of the molecule, the overall experimentally determined geometry is T-shaped, similar to the hypervalent 10-I-3 species. The formation of dimeric structures with bridging anions is typical in the solid state; for example, 4-*tert*-butylcyclohexenyl(phenyl)iodonium tetrafluoroborate **337** has a centrosymmetric dimeric structure analogous to diphenyliodonium salts (cf. Figure 2.11) [437]. The carbon–carbon double bonds in alkenyliodonium salts have normal lengths of 1.31–1.34 Å, the C–I distances can vary from 2.07 to 2.13 Å and the C–I–C angles are in the range 91–99°.

2.1.9.3 Alkynyliodonium Salts

The first alkynyliodonium salt, phenylethynyl(phenyl)iodonium chloride, was obtained in the mid-1960s by Beringer and Galton by interaction of PhICl₂ with lithium phenylacetylide [469]. However, this product was unstable due to the relatively high nucleophilicity of the chloride counter ion and decomposed in a few hours at room temperature into a 1 : 1 mixture of iodobenzene and phenyl chloroacetylene. In 1979, Merkushev and coworkers reported the formation of the crystalline, relatively stable, albeit hygroscopic, alkynyliodonium trifluoroacetates but characterized them only by IR spectroscopy [470]. The first fully characterized, stable alkynyliodonium salts were alkynyl(phenyl)iodonium tosylates prepared by Koser and coworkers via the interaction of [hydroxy(tosyloxy)iodo]benzene with terminal alkynes [199, 471]. From then on it has been recognized that the stability of alkynyliodonium salts depends on the nature of the counterion. In general, non-nucleophilic anions such as sulfonate and tetrafluoroborate are required to stabilize the iodonium salt. The chemistry of alkynyl(aryl)iodonium salts has been previously covered in several specialized reviews [370, 472–475].

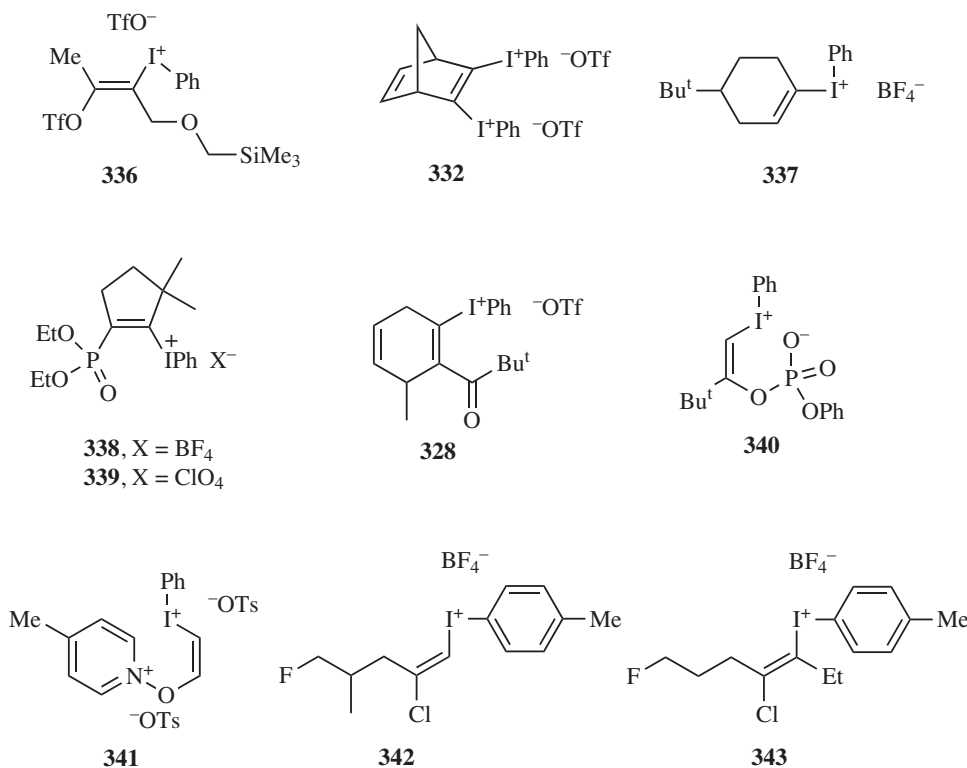
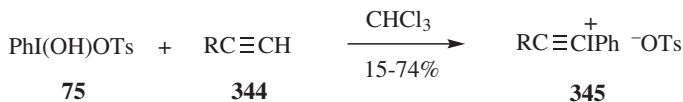


Figure 2.12 Examples of alkenyliodonium salts analyzed by single-crystal X-ray diffraction.

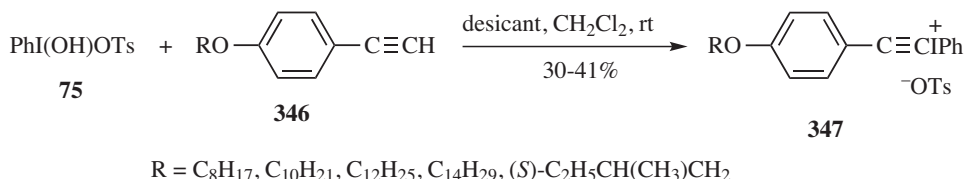
2.1.9.3.1 Preparation A common synthetic approach to alkynyliodonium salts involves the reaction of an electrophilic λ^3 -iodane with a terminal alkyne or its silylated, stannylated, or lithiated derivative. In the early 1980s, Koser and coworkers found that [hydroxy(tosyloxy)iodo]benzene **75** reacts with terminal alkynes **344** upon gentle heating in chloroform or dichloromethane to form alkynyliodonium tosylates **345** in moderate to low yield (Scheme 2.98) [199,471,476].

This reaction (Scheme 2.98) works well only for alkynes **344** with a bulky alkyl or an aryl group as the substituent R. The addition of a desiccant to the reaction mixture results in broader applicability of this procedure with a greater variety of alkynes [477,478]. This method is also applicable to the preparation of alkynyliodonium mesylates and *p*-nitrobenzenesulfonates by the reaction of the appropriate [hydroxy(organosulfonyloxy)iodo]benzenes with terminal alkynes under similar conditions [477,478]. This procedure has been applied for the preparation of arylethynyl(phenyl)iodonium tosylates **347** bearing long



R = Prⁱ, Buⁱ, Bu^s, Bu^t, cyclopentyl, cyclohexyl, Ph, *p*-Tol

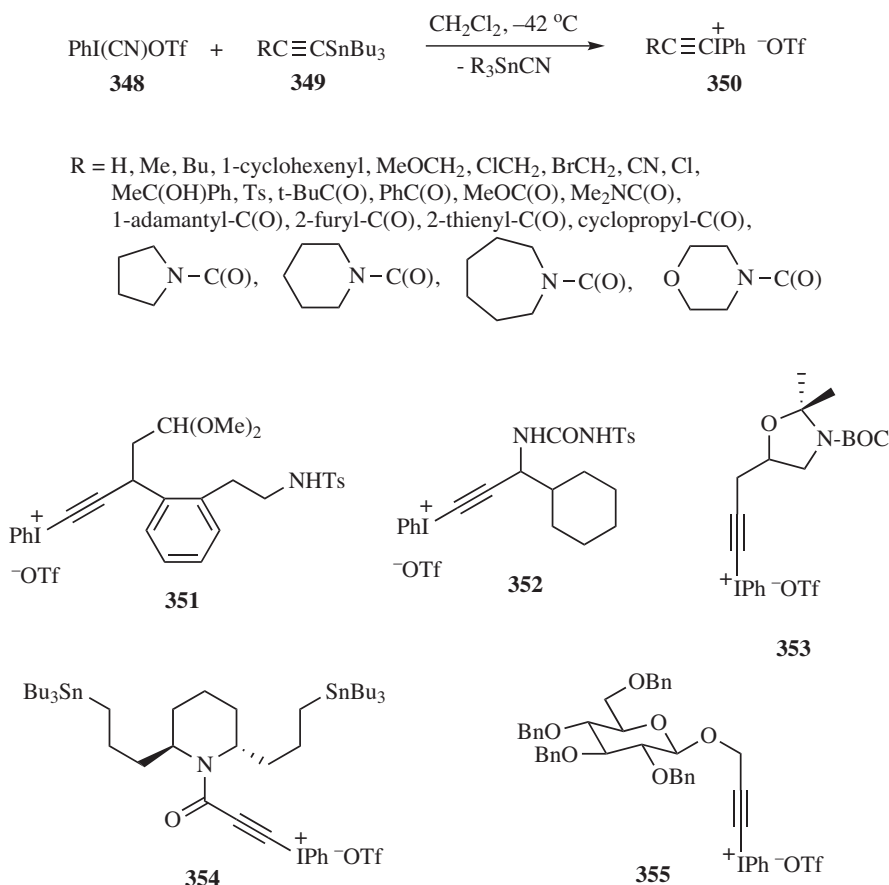
Scheme 2.98



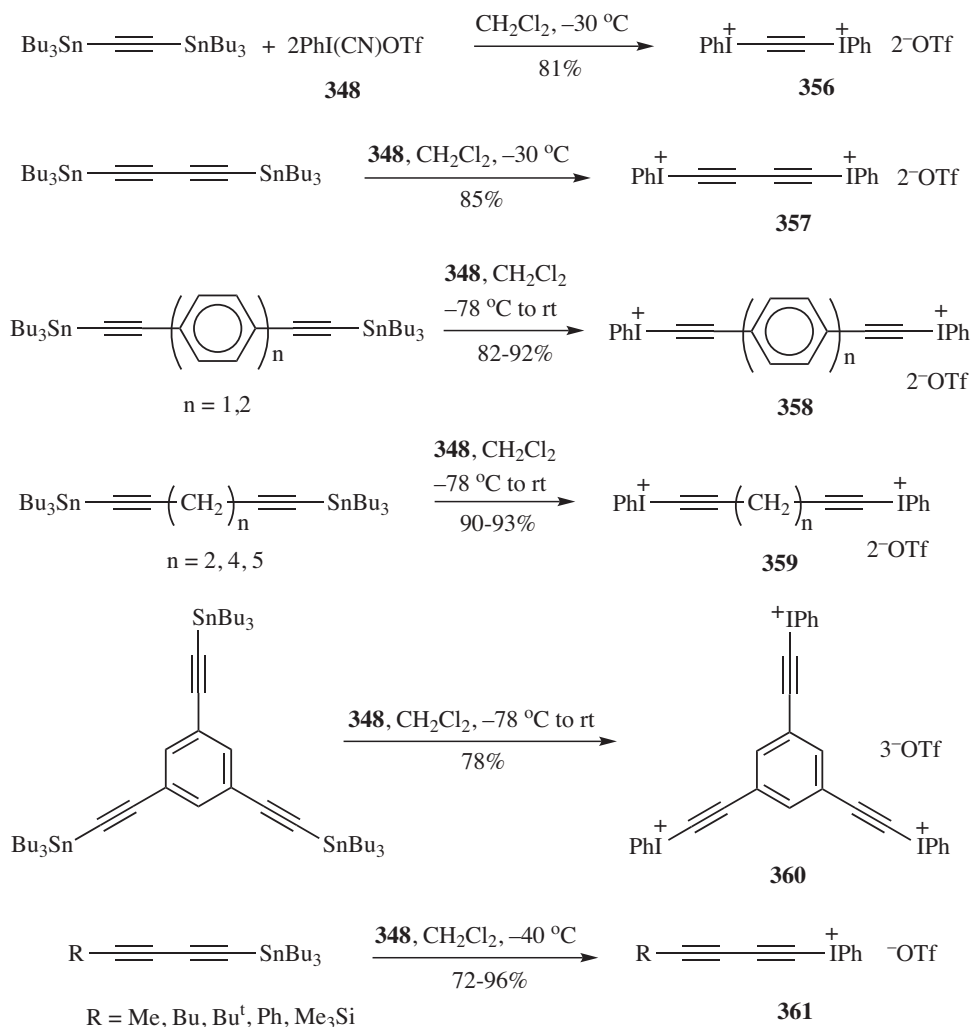
Scheme 2.99

alkoxy chains and chiral alkynyl ligands using Koser's reagent **75** and the appropriate alkynes **346** (Scheme 2.99) [479–481].

The most versatile method for preparing alkynyl(phenyl)iodonium triflates employs the iodonium transfer reaction between cyano(phenyl)iodonium triflate (**348**) and alkynylstannanes. The interaction of a large variety of readily available β -functionalized alkynylstannanes **349** with reagent **348** under very mild conditions provides ready access to diverse β -functionalized alkynyliodonium salts **350** in excellent yields (Scheme 2.100) [458, 482, 483]. This procedure is particularly useful for the preparation of various complex,



Scheme 2.100

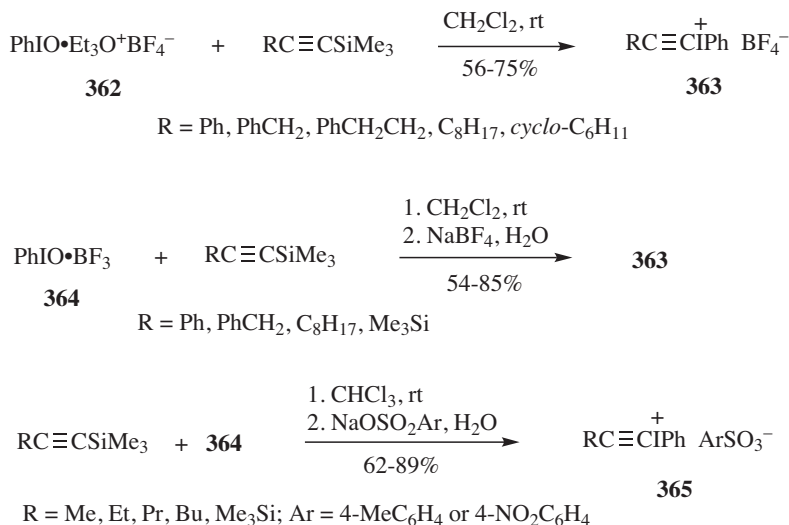


Scheme 2.101

functionalized alkynyliodonium derivatives, such as compounds **351** and **352** [484], **353** [485], **354** [486] and **355** [487]. Products **351**–**355** are formed under these very mild conditions in high yields (80–90%) and can be used in subsequent transformations without additional purification.

This procedure has been used for the preparation of the bis-iodonium acetylenes **356** and **357** [460, 488], conjugated **358** and unconjugated **359** bis(alkynyliodonium) salts [489–491], tris(alkynyliodonium) salts **360** [491] and diynyl(phenyl)iodonium triflates **361** [492] (Scheme 2.101).

An alternative, less general procedure for the preparation of alkynyl(phenyl)iodonium triflates in moderate yields employs the reaction of alkynylsilanes [493], alkynylstannanes [494], or alkynylboronates [297] with Zefirov's reagent, 2PhIO·Tf₂O. This method is also applicable to the synthesis of the parent ethynyl(phenyl)iodonium triflate [495].

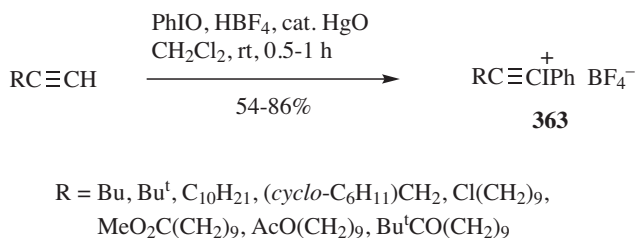


Scheme 2.102

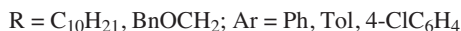
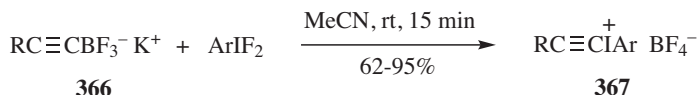
A common method for preparing alkynyl(phenyl)iodonium tetrafluoroborates involves the reaction of iodosylbenzene in the presence of triethyloxonium tetrafluoroborate or boron trifluoride etherate with alkynylsilanes. For example, the complex of iodosylbenzene with triethyloxonium tetrafluoroborate (**362**) reacts with alkynylsilanes in dichloromethane at room temperature to afford alkynyl(phenyl)iodonium tetrafluoroborates **363** in good yield [496]. A variation of this procedure employs the complex of iodosylbenzene with boron trifluoride etherate (**364**) followed by treatment with aqueous NaBF₄ [493, 497] or sodium arylsulfonates to furnish, respectively, the appropriate alkynyl(phenyl)iodonium tetrafluoroborates **363** [483, 487] or organosulfonates **365** [488, 489] (Scheme 2.102) [498, 499].

A modified method for the synthesis of alkynyl(phenyl)iodonium tetrafluoroborates **363** consists of the direct reaction of terminal alkynes with iodosylbenzene, a 42% aqueous solution of tetrafluoroboric acid and a catalytic amount of mercury oxide (Scheme 2.103) [500].

Yoshida and coauthors have reported a facile preparation of iodonium salts **367** by the reaction of potassium organotrifluoroborates **366** with (difluoroiodo)arenes under mild conditions (Scheme 2.104) [396]. A similar approach to alkynyliodonium salts by the reaction of alkynyldifluoroboranes with polyfluoroorganyliodine difluorides was developed by Frohn and Bardin [501].



Scheme 2.103



Scheme 2.104

2.1.9.3.2 Properties and Structure Most known alkynyl(aryl)iodonium salts are prepared as white micro-crystalline products, which are insoluble in water and nonpolar organic solvents and moderately soluble in acetonitrile and other polar organic solvents. Their thermal stability varies over a broad range depending on the nature of the counterion and the substituent on the acetylenic β -carbon. Alkynyl(aryl)iodonium triflates and tosylates bearing an aryl or unsubstituted alkyl group at the acetylenic β -carbon, as well as the bis-iodonium acetylene **356**, the unconjugated bis(alkynyl)iodonium salts **359** and the parent ethynyl(phenyl)iodonium triflate, in general have a decomposition point in the range 120–140 °C and can be stored for several months in a refrigerator. Functionalized iodonium alkynylidonium triflates (e.g., **351–355**) generally have lower thermal stability, while diynylidonium triflates **357** and **361** are unstable and should be handled only at low temperature.

Alkynylidonium salts can be conveniently identified by IR and NMR spectroscopy. In the infrared spectrum, the most characteristic absorption is the triple bond band between 2120 and 2190 cm^{-1} . In the ^{13}C NMR spectrum, the most distinctive signals are the acetylenic α - and β -carbons, with the former generally between 10 and 40 ppm and the latter at 110–120 ppm.

Single-crystal X-ray structural data have been reported for the following alkynylidonium compounds: the parent ethynyl(phenyl)iodonium triflate (**368**) [495], phenylethynyl(phenyl)iodonium tosylate (**369**) [477], cyanoethynyl(phenyl)iodonium triflate (**370**) [458], propynyl(phenyl)iodonium periodate (**371**) [502], trimethylsilylethynyl(phenyl)iodonium triflate (**372**) [503], 3,3,3-trifluoropropynyl(phenyl)iodonium triflate (**373**) [504], bis(alkynyl)iodonium triflate **374** [505] and complexes of ethynyl(phenyl)iodonium [506] and 1-decynyl(phenyl)iodonium [507] tetrafluoroborates with 18-crown-6 (Figure 2.13).

Single-crystal X-ray structural data are all consistent with the pseudo-trigonal bipyramidal, or T-shaped geometry, of alkynylidonium species. In all known cases, the aryl group occupies an equatorial position, whereas the alkynyl moiety and the counter ion occupy apical positions. The alkynyl–iodine bond length is about 2.0 Å and the I...O distances to the nearest sulfonate anion vary from 2.56 to 2.70 Å. The C–I–O bond angles vary from 166° to 172° and the C–I–C bond angles are between 90° and 95°.

2.1.9.4 Cyanoiodonium Salts

Two structural types of cyanoiodonium salts are known: (dicyano)iodonium triflate, $(\text{NC})_2\text{IOTf}$ [399,400] and aryl(cyano)iodonium derivatives, $\text{ArI}(\text{CN})\text{X}$ [146,460,508,509]. (Dicyano)iodonium triflate **277** can be prepared by the reaction of iodosyl triflate (**375**) (Section 2.1.1.2) with cyanotrimethylsilane in dichloromethane (Scheme 2.105). In the solid state, compound **277** is thermally unstable and air-sensitive; it completely decomposes at room temperature in 2–5 min forming cyanogen iodine, ICN and explodes when exposed to air. However, it can be stored at –20 °C under nitrogen for several days [400]. Despite its low stability, cyanide **277** can be used *in situ* for the very mild and efficient preparation of various bis(heteroaryl)iodonium salts by an iodonium transfer reaction with the respective stannylated heteroarenes (Section 2.1.9.1.1).

Aryl(cyano)iodonium triflates **348** and **278** are prepared by reactions of iodosylbenzene or [bis(trifluoroacetoxy)iodo]arenes with trimethylsilyl triflate and cyanotrimethylsilane (Scheme 2.106).

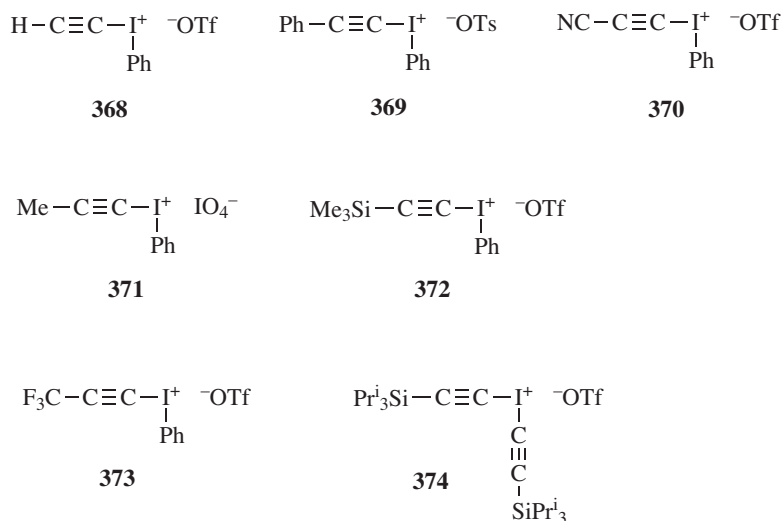
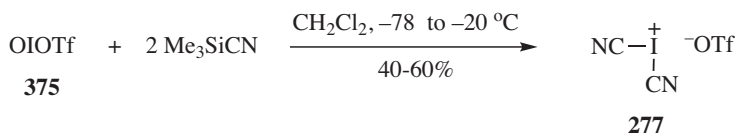
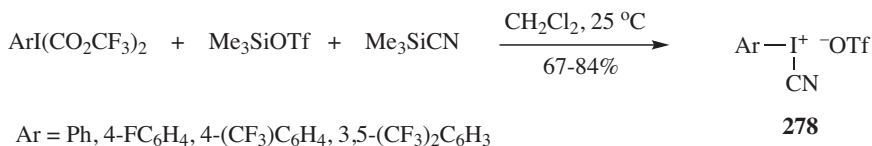
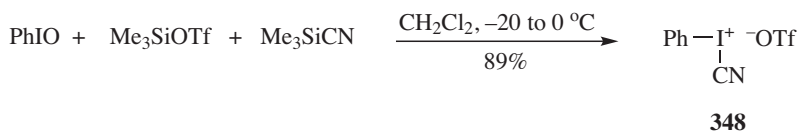


Figure 2.13 Examples of alkynyliodonium salts analyzed by single-crystal X-ray diffraction.

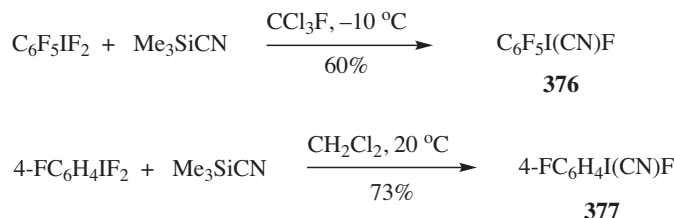
Cyanides **278** are relatively stable, white microcrystalline solids that decompose over several days at room temperature, but can be stored for extended periods in a refrigerator without change [146, 508]. Phenyl(cyano)iodonium triflate (**348**) has found some synthetic application as the iodonium transfer reagent useful for preparation of various iodonium salts (Sections 2.1.9.1.1, 2.1.9.2.1 and 2.1.9.3.1).



Scheme 2.105



Scheme 2.106

**Scheme 2.107**

Frohn and coauthors reported the preparation and structural studies of aryl(cyano)iodonium fluorides **376** and **377** by the reaction of appropriate (difluoroiodo)arenes with one equivalent of cyanotrimethylsilane (Scheme 2.107) [509].

The X-ray molecular structure and the crystal packing of both products **376** and **377** (Figure 2.14) [509] are very similar and reminiscent of the solid-state structure of $\text{C}_6\text{F}_5\text{IF}_2$ [40]. A common feature in the structures of products **376**, **377** and $\text{C}_6\text{F}_5\text{IF}_2$ is the zigzag chain motif resulting from intermolecular $\text{I}\cdots\text{F}$ interactions with a distance of 2.64–2.69 Å. The plane of the $\text{F}-\text{I}-\text{CN}$ group intersects with the aryl plane at angle of approximately 65.5° . The $\text{I}-\text{CN}$ distance of 2.112 Å is relatively short and the $\text{I}-\text{F}$ distance (2.110–2.135 Å) is elongated compared to that in $\text{C}_6\text{F}_5\text{IF}_2$ (average 1.99 Å). The $\text{Ar}-\text{I}-\text{CN}$ angle is close to 90° (86.3° in **376** and 89.0° in **377**) [509].

2.1.9.5 Alkyl- and Fluoroalkyliodonium Salts

Iodonium salts with one or two non-substituted aliphatic alkyl groups generally lack stability. However, several examples of these unstable species have been generated and investigated by NMR spectroscopy at low temperatures and some of them (e.g., $\text{Me}_2\text{I}^+ \text{X}^-$, where $\text{X} = \text{AsF}_6, \text{SbF}_6, \text{Sb}_2\text{F}_{11}$) were even isolated in the form of labile crystalline salts [510–512].

The unstable β -oxoalkyl(phenyl)iodonium salts **379** can be generated by a low-temperature reaction of silyl enol ethers with reagent **378** (Scheme 2.108) [513–515]. These and similar species were proposed as the reactive intermediates in synthetically useful carbon–carbon bond forming reactions reviewed by Moriarty and Vaid in 1990 [515].

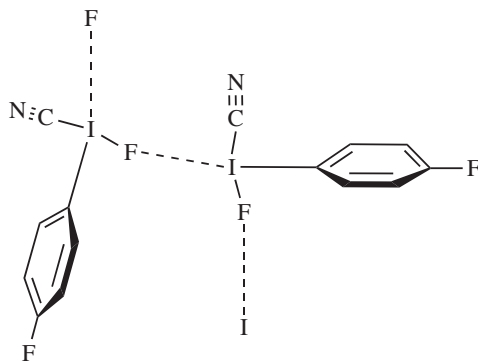
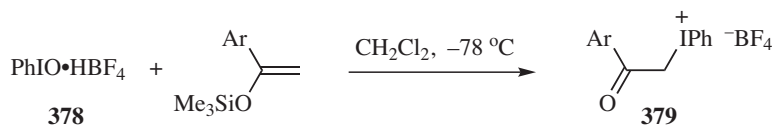
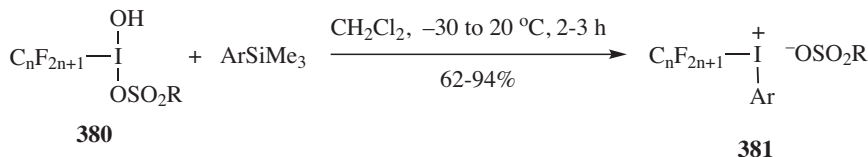


Figure 2.14 Primary and secondary bonding pattern in single-crystal X-ray structure of 4-fluorophenyl-(cyano)iodonium fluoride (**377**) [509].



Ar = Ph, 4-MeC₆H₄, 4-ClC₆H₄, 4-NO₂C₆H₄, 4-MeOC₆H₄

Scheme 2.108



n = 4 or 6; R = p-Tol, CH₃, CF₃

Ar = Ph, 4-MeC₆H₄, 4-MeOC₆H₄, 2-MeC₆H₄, 4-Me₃SiC₆H₄

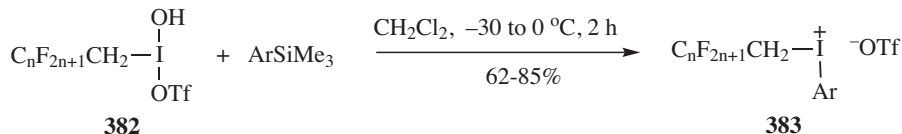
Scheme 2.109

The presence of electron-withdrawing groups in the alkyl group of iodonium salts usually has a pronounced stabilizing effect. The most stable and important derivatives of this type are polyfluoroalkyl(aryl)iodonium salts [174, 516]. These salts as chlorides were first prepared in 1971 by Yagupolskii and coworkers [517] and later widely applied as electrophilic fluoroalkylating reagents by Umemoto and coworkers [518–526]. Perfluoroalkyl(phenyl)iodonium triflates, PhIC_nF_{2n+1}OTf, were originally synthesized by the reaction of [bis(trifluoroacetoxy)iodo]perfluoroalkanes with benzene in the presence of triflic acid [527, 528]. A more recent, general method for preparing various perfluoroalkyl(aryl)iodonium sulfonates **381** involves the reaction of [hydroxy(sulfonyloxy)iodo]perfluoroalkanes **380** with arylsilanes under Lewis acid catalysis (Scheme 2.109) [207, 211, 529].

In a similar manner, 1*H*,1*H*-perfluoroalkyl(aryl)iodonium triflates **383** are prepared by the reaction of triflates **382** with trimethylsilylarenes under mild conditions (Scheme 2.110) [176, 212].

Several fluoroalkyliodonium salts of other types have been reported [77, 530, 531]. The reaction of tosylate **384** with cyclic enamines **385** affords stable iodonium salts **386** (Scheme 2.111) [530]. Mild thermolysis of salts **386** in boiling acetonitrile cleanly affords 2,2,2-trifluoroethyl tosylate and the respective iodoenaminone [530].

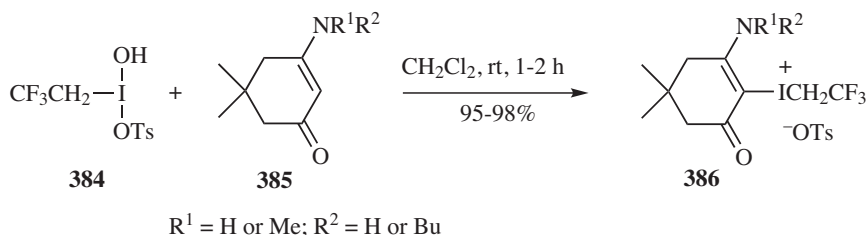
Fluoroalkyl(alkynyl)iodonium triflates **388** can be prepared by the reaction of triflates **387** and (trimethylsilyl)acetylenes (Scheme 2.112) [176].



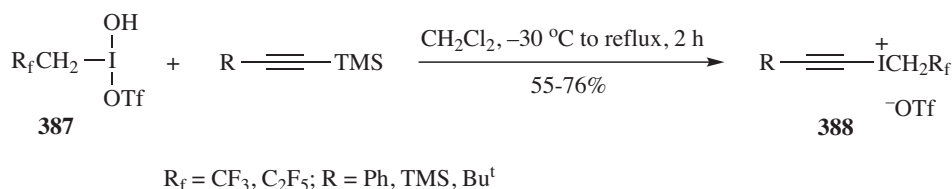
n = 1 or 2

Ar = Ph, 4-MeC₆H₄, 2-MeC₆H₄, 4-Me₃SiC₆H₄, 4-MeOC₆H₄

Scheme 2.110



Scheme 2.111

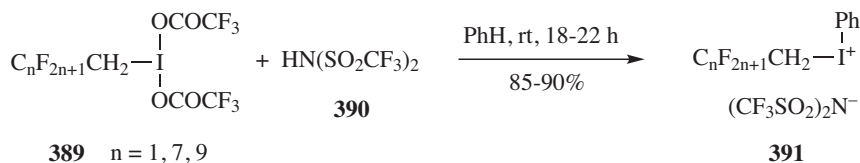


Scheme 2.112

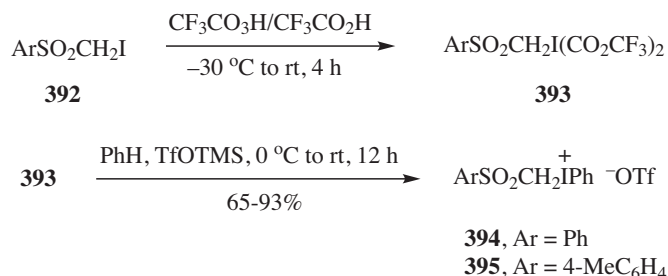
DesMarteau and coworkers reported the preparation, X-ray crystal structure and chemistry of trifluoroethylidoniun salts **391** by the reaction of fluoroalkyliodo-bis(trifluoroacetates) **389** with benzene and triflimide acid (**390**) (Scheme 2.113) [68, 531, 532]. The structure of trifluoroethyl(phenyl)iodoniun salt **391** ($n = 1$) was established by a single-crystal X-ray analysis [68]. In contrast to fluoroalkyliodonium triflates **383**, compounds **391** are stable to water and can be used as reagents for fluoroalkylation reactions in aqueous media.

(Arylsulfonylmethyl)iodoniun salts **394** and **395**, which are stabilized due to the presence of the electron-withdrawing sulfonyl group, can be prepared in two steps starting from the readily available iodomethyl sulfones **392** (Scheme 2.114) [138]. In the first step, starting iodides **392** are oxidized with peroxytrifluoroacetic acid to trifluoroacetates **393** in almost quantitative yield. Subsequent treatment of **393** with benzene and trimethylsilyl (TMS) triflate in dichloromethane affords products **394** and **395** in good yields. Both iodonium salts **394** and **395** are not moisture sensitive, can be purified by crystallization from acetonitrile and can be stored for several months in a refrigerator.

The structure of iodonium triflate **395** was unambiguously established by a single-crystal X-ray analysis [138]. The structural data revealed the expected geometry for iodonium salts with a C—I—C bond angle of 91.53° . The I—C bond distances of 2.131 and 2.209 Å are longer than the typical bond length in diaryliodonium salts (2.0–2.1 Å). The I...O distance between the iodine atom and the nearest oxygen of the triflate anion is 2.797 Å.



Scheme 2.113



Scheme 2.114

2.1.10 Iodonium Ylides

Aryliodonium ylides, ArICX_2 , where X is an electron-withdrawing substituent (e.g., carbonyl or sulfonyl group), represent the most important and relatively stable class of iodonium ylides. Alkylidonium ylides such as dimethyliodonium ylide, CH_3ICH_2 , are unknown, although they have been a subject of computational studies [533, 534]. The first example of a stable iodonium ylide (see structure **405**, $\text{R} = \text{Me}$, below in Figure 2.15), prepared by the reaction of dimedone (5,5-dimethyl-1,3-cyclohexanedione) and (difluoroiodo)benzene, was reported by Neiland and coworkers in 1957 [535]. Since then, numerous stable aryliodonium ylides have been prepared and structurally investigated. Single X-ray crystallographic studies demonstrate that the geometry of aryliodonium ylides is similar to that of iodonium salts with a $\text{C}-\text{I}-\text{C}$ angle close to 90° , which is indicative of a zwitterionic nature of the ylidic $\text{C}-\text{I}$ bond. The chemistry of aryliodonium ylides has been summarized in several reviews mainly devoted to their use as precursors for the generation of singlet carbene or carbenoid species [536–539].

2.1.10.1 Preparation

Most iodonium ylides have low thermal stability and can be handled only at low temperature or generated and used *in situ*. The relatively stable and practically important iodonium ylides, the dicarbonyl derivatives $\text{PhIC}(\text{COR})_2$ [535, 540–543] and bis(organosulfonyl)(phenyliodonium)methanides, $\text{PhIC}(\text{SO}_2\text{R})_2$ [544–547], are prepared by the reaction of (diacetoxyiodo)benzene with the appropriate dicarbonyl compound or disulfone under basic conditions. A general procedure for the synthesis of phenyliodonium ylides **397** from malonate esters **396** is based on the treatment of esters **396** with (diacetoxyiodo)benzene in dichloromethane in the presence of potassium hydroxide (Scheme 2.115) [542]. An optimized method for preparing bis(methoxycarbonyl)(phenyliodonium)methanide (**399**) by using reaction of dimethyl malonate

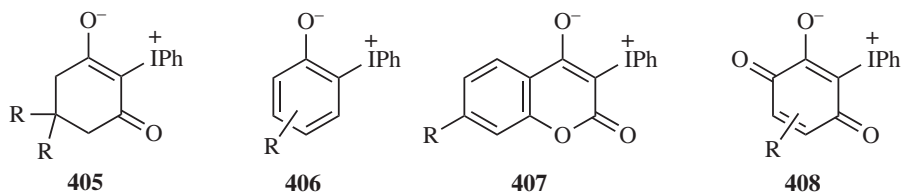
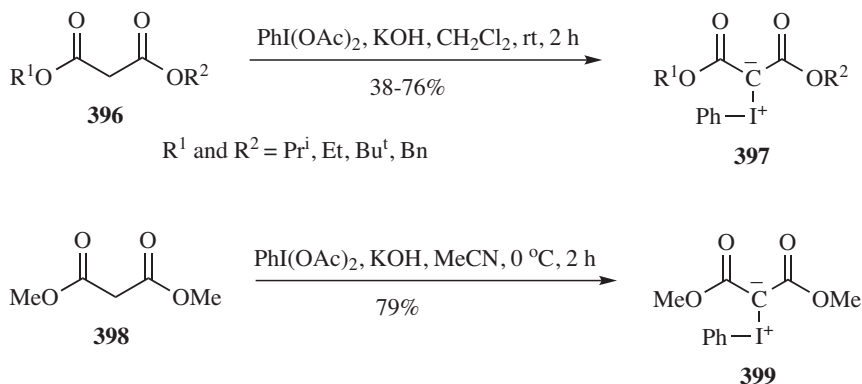


Figure 2.15 Iodonium ylides derived from cyclic 1,3-dicarbonyl compounds (**405**), phenols (**406**), coumarin derivatives (**407**) and hydroxyquinones (**408**).

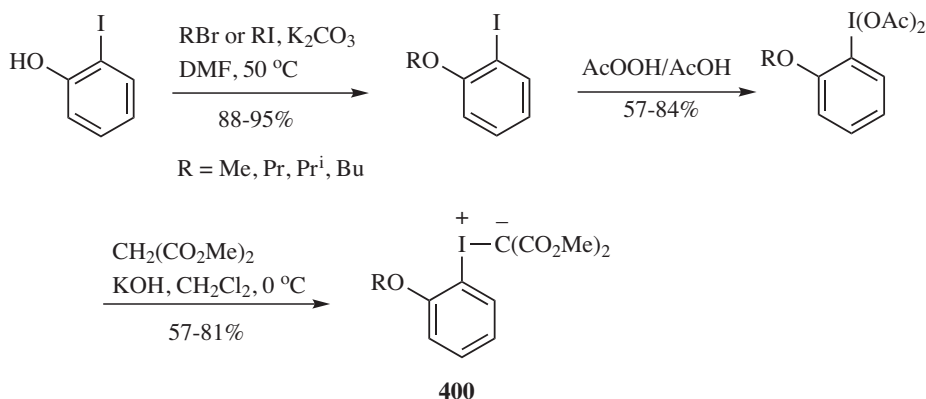


Scheme 2.115

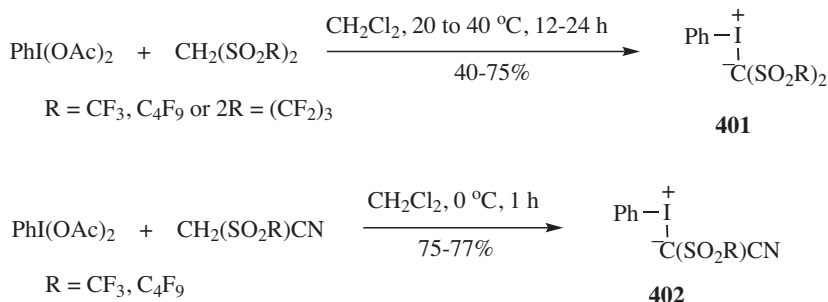
ester (**398**) in acetonitrile solution was published in *Organic Syntheses* in 2010 [548]. Ylides **397** and **399** decompose slowly at room temperature and can be kept for several weeks at $-20\text{ }^\circ\text{C}$.

Phenyliodonium ylide **399** has found some synthetic use as an efficient carbene precursor and has been especially useful as a reagent for cyclopropanation of alkenes. Practical application of ylide **399** is, however, limited by its poor solubility [insoluble in most organic solvents except DMSO (dimethyl sulfoxide)] and low stability. 2-Alkoxyphenyliodonium ylides **400** derived from malonate methyl ester and bearing an *ortho* alkoxy substituent on the phenyl ring, can be synthesized from commercially available 2-iodophenol according to the procedure shown in Scheme 2.116. Ylides **400** are relatively stable, have good solubility in dichloromethane, chloroform, or acetone (e.g., the solubility of ylide **400**, $R = Pr$, in dichloromethane is 0.56 g mL^{-1}) and have higher reactivity than common phenyliodonium ylides in the Rh-catalyzed cyclopropanation, C–H insertion and transylidation reactions under homogeneous conditions [549].

Bis(perfluoroalkanesulfonyl)(phenyliodonium)methanides **401**, synthesized from (diacetoxyiodo)benzene and bis[(perfluoroalkyl)sulfonyl]methane (Scheme 2.117), have unusually high thermal stability; they can be stored without decomposition at room temperature for several months [546]. The non-symmetric, cyano[(perfluoroalkyl)sulfonyl]-substituted ylides **402** (Scheme 2.117) [545] or bis(fluorosulfonyl)-(phenyliodonium)methanide, $PhIC(SO_2F)_2$ [550], were prepared by a similar reaction using appropriate bis(sulfonyl)methanes as starting materials.



Scheme 2.116



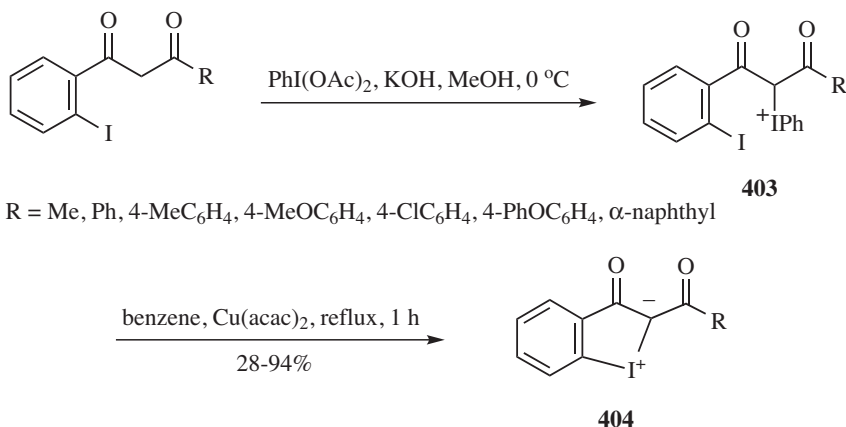
Scheme 2.117

Cyclic iodonium ylides, in which the iodonium atom is incorporated in a five-membered ring, have much higher thermal stability. The unusually stable cyclic iodonium ylides **404** can be synthesized via intramolecular transylidation of a preformed acyclic ylide **403** (Scheme 2.118) [551].

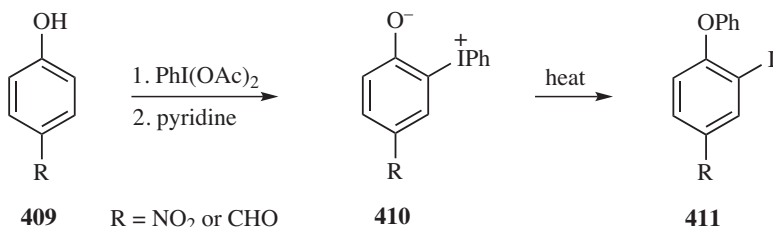
Iodonium ylides derived from cyclic 1,3-dicarbonyl compounds, phenols, coumarin derivatives and hydroxyquinones represent a particularly stable and synthetically important class of zwitterionic iodonium compounds [539, 552]. Several examples of these compounds are shown in Figure 2.15 in the major resonance form as enolate or phenolate zwitterionic structures **405–408**.

The preparation of iodonium phenolates **410** was first reported in 1977 via a reaction of phenols **409** with (diacetoxyiodo)benzene followed by treatment with pyridine (Scheme 2.119) [553]. The system of an iodonium phenolate is stabilized by the presence of at least one electron-withdrawing substituent on the aromatic ring. Monosubstituted iodonium phenolates **410** are relatively unstable and easily rearrange to iodo ethers **411** under heating. Such a 1,4 aryl migration is a very common phenomenon for iodonium ylides of types **405–408**; according to mechanistic and computational studies it is an intramolecular rearrangement via a concerted mechanism [554, 555].

Ylides of hydroxycoumarins (**413**) were prepared by the reaction of (diacetoxyiodo)arenes with 4-hydroxycoumarins **412** (Scheme 2.120) [556, 557]. X-Ray crystal structure determination [558] and the Mössbauer spectra [559] indicate that ylides **413** exist in predominantly zwitterionic form. These ylides are



Scheme 2.118

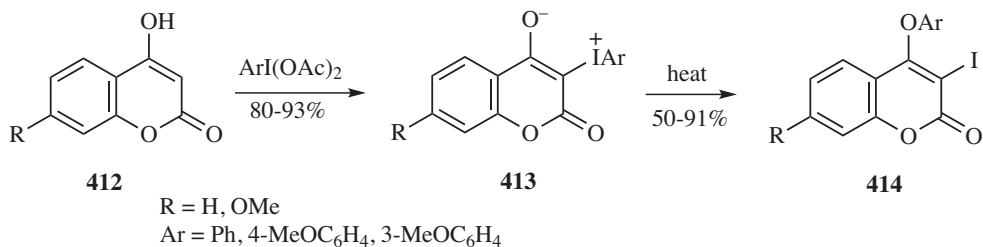


Scheme 2.119

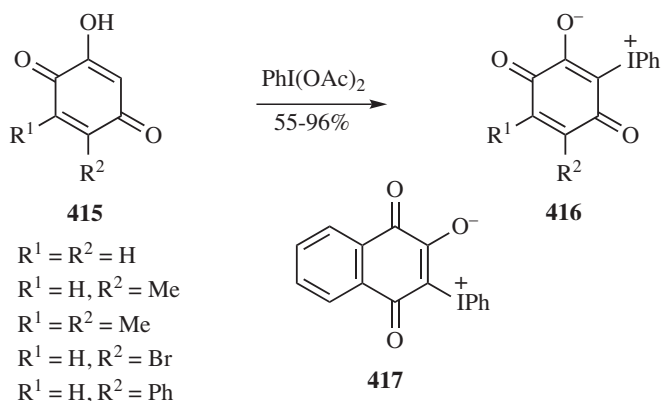
easily transformed into the corresponding iodo ethers **414** through the usual thermal aryl migration from iodine to oxygen [557].

Ylides of hydroxyquinones **416** were synthesized by treatment of 2-hydroxy-1,4-benzoquinones **415** with an equimolar amount of (diacetoxyiodo)benzene (Scheme 2.121) [560]. The most important member of this class, 2-oxido-3-(phenyliodonio)-1,4-naphthoquinone (**417**), was prepared similarly by treatment of 2-hydroxy-1,4-naphthoquinone (lawsone) with an equimolar amount of (diacetoxyiodo)benzene [561].

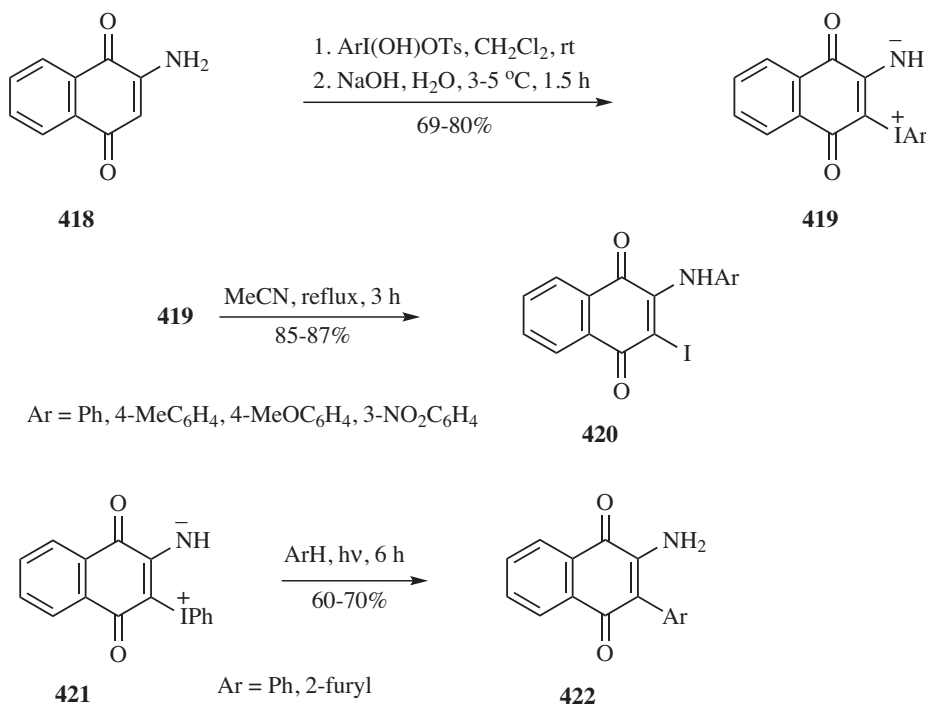
The aza analogues of **417**, iodine–nitrogen zwitterions **419**, have been prepared by the reaction of 2-amino-1,4-naphthoquinone (**418**) with [hydroxy(tosyloxy)iodo]arenes (Scheme 2.122) [205, 562, 563]. Ylides **419** show interesting reactivity: upon heating, aryl migration from iodine to nitrogen occurs, giving product **420**,



Scheme 2.120



Scheme 2.121



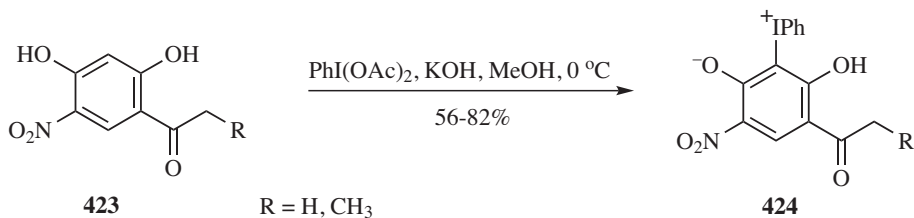
Scheme 2.122

while the photochemical reaction of ylide **421** with aromatic compounds and furan leads to substitution products **422** (Scheme 2.122).

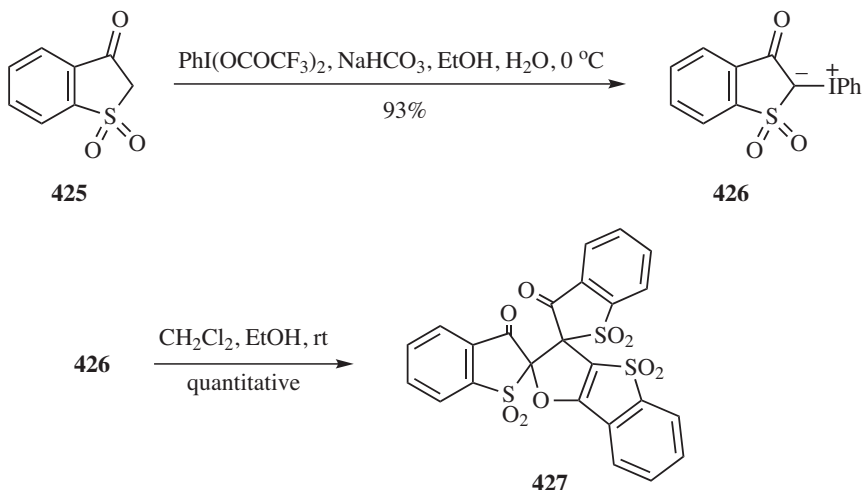
Stable zwitterionic arylidonium compounds **424** have been prepared by the reaction of 2,4-dihydroxyacetophenones **423** with (diacetoxyiodo)benzene under basic conditions (Scheme 2.123) [564]. Heating of these compounds leads to phenyl migration from iodine to oxygen with formation of the respective *o*-iodophenoxy ethers.

A relatively stable iodonium ylide (**426**) was prepared by the reaction of β -ketosulfone **425** with [bis(trifluoroacetoxy)iodo]benzene (Scheme 2.124) [565]. Ylide **426** decomposes in a solution of dichloromethane/ethanol to form quantitatively, the trimer **427**.

Ochiai and coworkers developed a new synthetic approach to various iodonium ylides **429** by the intermolecular transylidation reactions between halonium ylides under thermal or catalytic conditions (Scheme 2.125) [566, 567]. The transylidations of bromonium **428** to iodonium **429** ylides proceed under thermal



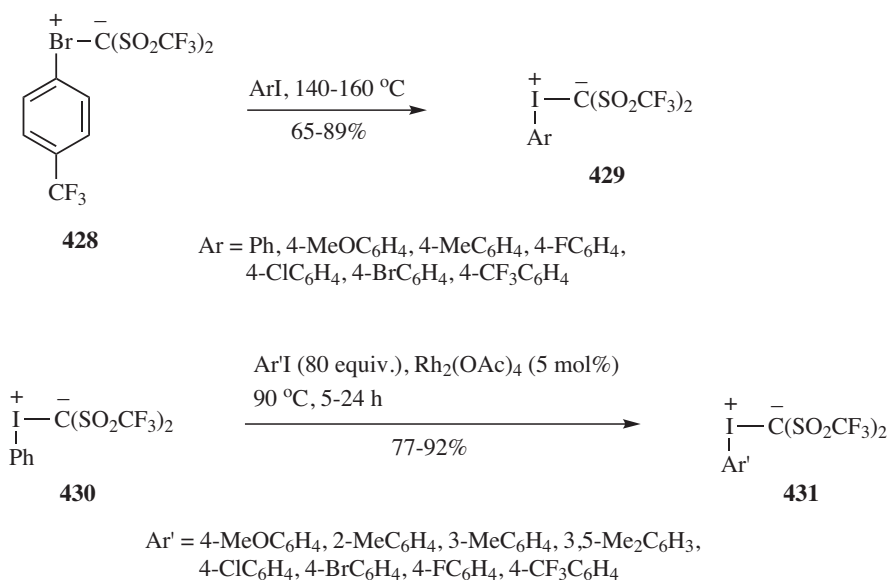
Scheme 2.123



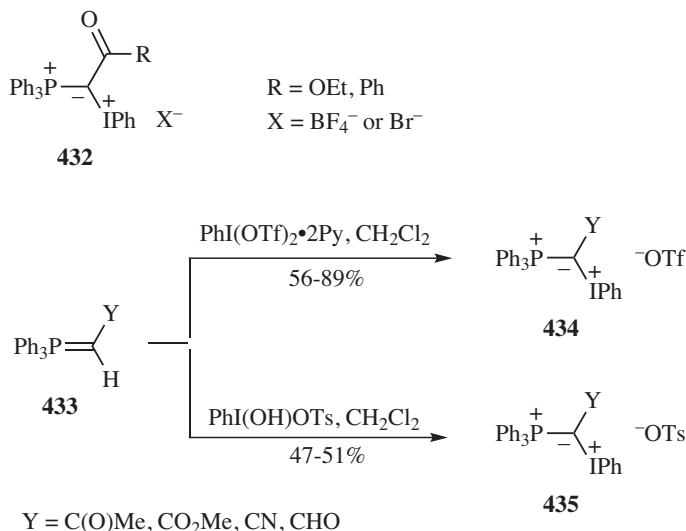
Scheme 2.124

conditions and probably involve generation of a reactive carbene intermediate [566]. Heating of phenyliodonium ylide **430** with iodoarenes in the presence of 5 mol% of rhodium(II) acetate as a catalyst results in transfer of the bis(trifluoromethylsulfonyl)methylidene group to the iodine(I) atom of iodoarene to afford substituted aryliodonium ylides **431** in good yields [567].

Mixed phosphonium–iodonium ylides **432** represent a useful class of reagents that combine in one molecule the synthetic advantages of a phosphonium ylide and an iodonium salt. The preparation of the tetrafluoroborate derivatives **432** by the reaction of phosphonium ylides with (diacetoxyiodo)benzene in the presence of HBF_4



Scheme 2.125



Scheme 2.126

was first reported by Neilands and Vanags in 1964 [568]. Later, in 1984, Moriarty and coworkers reported the preparation of several new tetrafluoroborate derivatives **432** and the X-ray crystal structure for one of the products [569]. The triflate (**434**) and tosylate (**435**) derivatives of phosphonium–iodonium ylides have been prepared in good yields by the reaction of phosphonium ylides **433** with the pyridinium complex of iodobenzene ditriflate, $\text{PhI(OTf)}_2 \cdot 2\text{Py}$ [570], or with [hydroxy(tosyloxy)iodo]benzene, respectively (Scheme 2.126) [571–574]. The analogous mixed arsonium–iodonium ylides (see structure **442** below in Figure 2.16) were synthesized using a similar procedure [574]. Preparation of hetaryl-substituted phosphonium–iodonium ylides was also reported [575].

The unstable monocarbonyl iodonium ylides **437** can be generated from (*Z*)-(2-acetoxyvinyl)iodonium salts **436** by ester exchange reaction with lithium ethoxide in tetrahydrofuran (THF) at -78°C (Scheme 2.127). ^1H NMR measurements indicate that ylides **437** are stable up to -30°C and they can be conveniently used in subsequent transformations without isolation [576–580].

The unstable ylides PhIC(H)NO_2 [581, 582] and $\text{PhIC(CO}_2\text{Me)NO}_2$ [583, 584] can be generated *in situ* from nitromethane and methyl nitroacetate, respectively and used in rhodium(II) carbenoid reactions without isolation.

2.1.10.2 Structural Studies

Single-crystal X-ray structures have been reported for the following iodonium ylides: 3-phenyliodonio-1,2,4-trioxo-1,2,3,4-tetrahydronaphthalenide (**438**) [558], 3-phenyliodonio-2,4-dioxo-1,2,3,4-tetrahydro-1-oxanaphthalenide (**439**) [558], mixed phosphonium–iodonium tetrafluoroborates **440** [569] and **441** [572], mixed arsonium–iodonium tetrafluoroborate **442** [585], mixed phosphonium iodonium triflate **443** [571], cyclic iodonium ylide **444** [551], 2-methoxyphenyliodonium bis(methoxycarbonyl)methanide (**445**) [549] and phenyliodonium bis(trifluoromethanesulfonyl)methide **446** [544] (Figure 2.16). In particular, the X-ray structural analysis for phenyliodonium ylide **446** shows a geometry typical for an iodonium ylide with the I–C ylide bond length of about 1.9 \AA and an C–I–C bond angle of 98° [544]. X-Ray structural

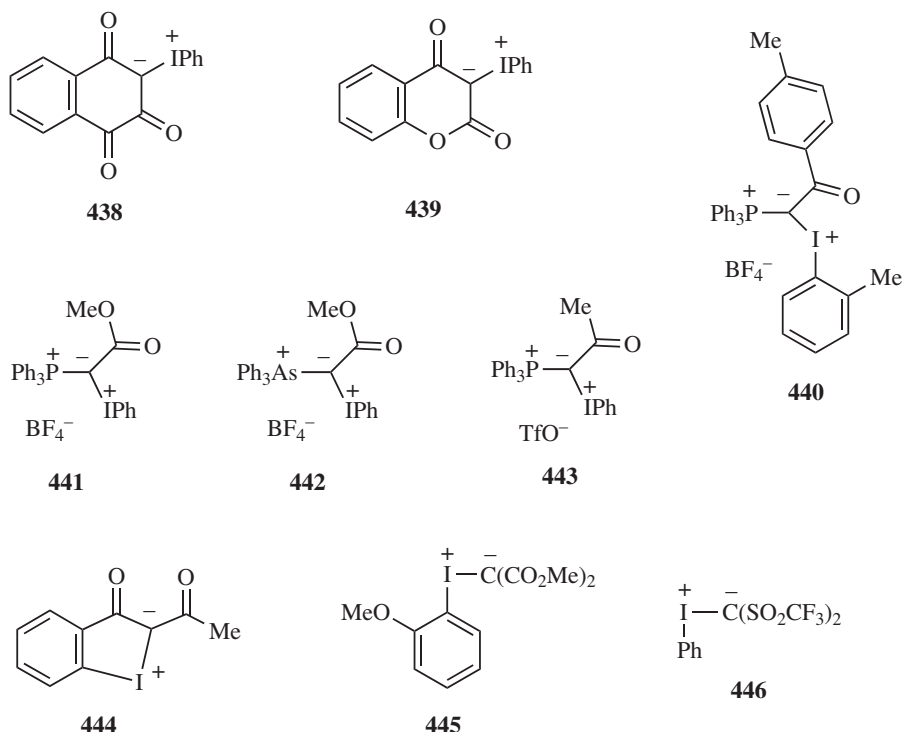
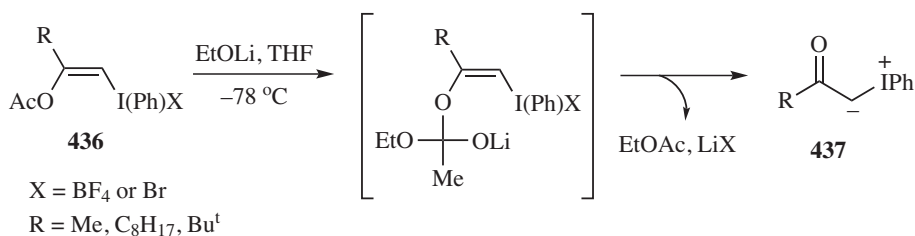
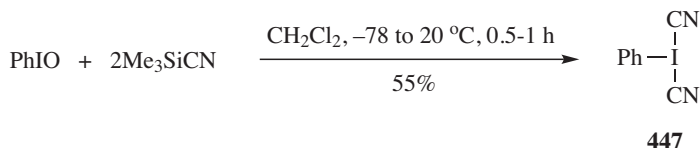


Figure 2.16 Iodonium ylides analyzed by single-crystal X-ray diffraction.

analysis for cyclic ylide **444** reveals a distorted five-membered ring with an ylidic bond length about 2.1 Å and a C–I–C bond angle of 82°, which is smaller than the usual 90° [551]. 2-Methoxyphenyliodonium bis(methoxycarbonyl)methanide **445** in the solid state has a polymeric, asymmetrically bridged structure with a hexacoordinated geometry around the iodine centers formed by two short C–I bonds [2.117 Å for I–C(Ph) and 2.039 Å for I–C(malonate)] and two relatively long iodine–oxygen intramolecular interactions between iodine and the oxygen atom of the *ortho* substituent (2.928 Å) and the carbonyl oxygen atom of the methoxycarbonyl group (3.087 Å). In addition, a relatively weak intermolecular I···O secondary interaction of 2.933 Å between the iodine center and the carbonyl oxygen atom of the neighboring molecule is also present in the solid state structure of **445** [549].



Scheme 2.127



Scheme 2.128

2.1.11 Iodine(III) Species with Three Carbon Ligands

In general, iodine(III) species with three carbon ligands are unstable at room temperature. Only a few examples of isolable compounds of this type were reported in the earlier literature, namely, triphenyl iodine, Ph_3I [586,587] and 5-aryl-5*H*-dibenziodoles [588–591]. All triaryliodanes are highly unstable and air sensitive compounds.

In 1960 Beringer and coworkers reported that diphenyliodonium chloride interacts with *n*-butyllithium to form an unstable trivalent organoiodine, presumably Ph_2IBu , which decomposes in solution at approximately -40°C [592]. More recently, in 1992, Barton and coworkers investigated a carbon–carbon bond forming reaction of dichloriodobenzene or (diacetoxyiodo)benzene with alkylolithiums [593]. One of the possible mechanistic descriptions of this reaction involves ligand coupling in the triorgano-iodane intermediate PhIR_2 ; however, these species cannot be detected even at -80°C [593].

More recent examples of relatively stable, isolable compounds of this type are represented by (dicyanoiodo)arenes, $\text{ArI}(\text{CN})_2$ [509,580]. (Dicyanoiodo)benzene (**447**) was prepared in good yield by the reaction of iodosylbenzene with trimethylsilyl cyanide in methylene chloride (Scheme 2.128) [594]. Cyanide **447** was isolated as an air-sensitive, crystalline solid that is stable at room temperature under nitrogen for several weeks.

Frohn and coworkers have synthesized and investigated structure and properties of several fluoroaryliodine(III) cyano compounds [509]. In particular, $\text{C}_6\text{F}_5\text{I}(\text{CN})_2$ and *ortho*, *meta* and *para* isomers of $\text{FC}_6\text{F}_4\text{I}(\text{CN})_2$ were isolated from reactions of the corresponding aryliodine difluorides ArIF_2 and a stoichiometric excess of Me_3SiCN in Freon[®] at 0°C or in dichloromethane at 20°C . An alternative preparation of these fluoroaryliodine(III) cyanides involves the reaction of $\text{ArI}(\text{OAc})_2$, $\text{ArI}(\text{OCOCF}_3)_2$, or ArIO with trimethylsilyl cyanide in dichloromethane at room temperature. All fluoroaryliodine(III) cyano compounds $\text{ArI}(\text{CN})_2$ are relatively unstable and exothermically decompose in the solid state at $72\text{--}100^\circ\text{C}$ [509].

Single-crystal X-ray structural data are available for $\text{C}_6\text{F}_5\text{I}(\text{CN})_2$, 3- $\text{FC}_6\text{F}_4\text{I}(\text{CN})_2$ and 4- $\text{FC}_6\text{F}_4\text{I}(\text{CN})_2$. All three products have the expected T-shape molecular structures with similar parameters. In $\text{C}_6\text{F}_5\text{I}(\text{CN})_2$ the $\text{C}(\text{aryl})\text{--I}$ distance (2.074 \AA) is significantly shorter than both $\text{C}(\text{CN})\text{--I}$ distances (average 2.25 \AA) [509]. Repulsion of the two ICN units by the two lone pairs of electrons reduces the aryliodine–CN angles to 81.72° and 82.69° . The plane defined by the $\text{I}(\text{CN})_2$ group and the aryl plane intersects by 70.7° . The nitrogen terminus of one CN group interacts with the hypervalent iodine center of a neighboring molecule with the intermolecular $\text{I}\cdots\text{N}$ distance of 2.933 \AA , which is 17% shorter than the sum of van der Waals radii for iodine and nitrogen (3.53 \AA), resulting in a zigzag chain arrangement (Figure 2.17) [509].

Fluoroaryliodine(III) cyano compounds $\text{ArI}(\text{CN})_2$ can form relatively stable adducts with nitrogen bases (phenanthroline, 2,2'-bipyridine and quinoline); the adduct of 4- $\text{FC}_6\text{F}_4\text{I}(\text{CN})_2$ with 1,10-phenanthroline has been characterized by single-crystal X-ray diffraction [62].

2.1.12 Iodine(III) Species with I–N Bonds

Iodanes with I–N bonds are generally less common than those with I–O bonds. Many of these compounds lack stability and are sensitive to moisture. In addition to the previously discussed N-substituted benziodoxoles

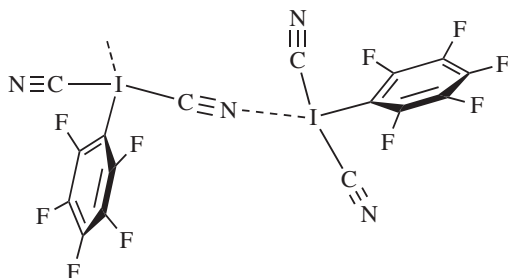


Figure 2.17 Primary and secondary bonding pattern in a single-crystal X-ray structure of $C_6F_5I(CN)_2$.

(Sections 2.1.8.1.5 and 2.1.8.1.6), benziodazoles (Section 2.1.8.2) and benziodathiazoles (Section 2.1.8.5), several other structural types of iodine(III) derivatives with one carbon ligand and one or two I–N bonds are known: azidoiodanes **448** and **449**, amidoiodanes **450–452**, bis(pyridinium) aryliodine(III) salts **453** and imidoiodanes **454** (Figure 2.18).

2.1.12.1 Azidoiodanes

Azidoiodanes **448** and **449** were proposed as reactive intermediates in synthetically useful azidation reactions involving the combination of $PhIO$, $PhI(OAc)_2$, or $PhICl_2$ with trimethylsilyl azide or NaN_3 [595–610]. Attempts to isolate these intermediates always resulted in rapid decomposition at -25 to $0^\circ C$ with the formation of iodobenzene and dinitrogen; however, low-temperature spectroscopy and the subsequent chemical reactions *in situ* provided some experimental evidence for the existence of these species. A systematic study of structure and reactivity of these unstable azidoiodanes was attempted by Zbiral and coworkers in the early 1970s [595–598]. In particular, the IR spectroscopic measurements at -60 to $0^\circ C$ indicated the existence of $PhI(N_3)_2$ and $PhI(N_3)OAc$ species in the mixture of $PhI(OAc)_2$ with trimethylsilyl azide [595]. Interestingly, the absorption band of 2040 cm^{-1} for the azido group in $PhI(N_3)OAc$ is very close to the absorption stretch of $2046\text{--}2048\text{ cm}^{-1}$ in the stable, heterocyclic azidoiodanes **122–124** (Section 2.1.8.1.5).

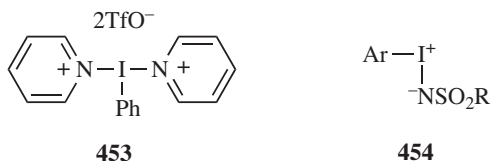
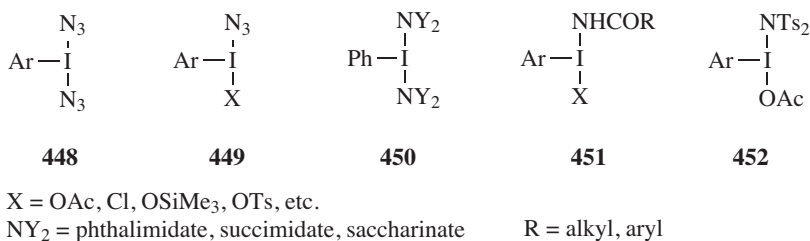
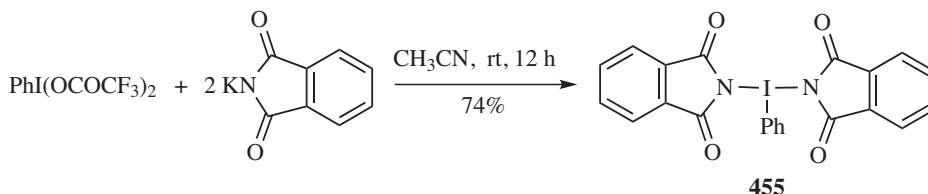


Figure 2.18 Iodine(III) derivatives with I–N bonds.

**Scheme 2.129**

The unstable and highly reactive azidoiodanes generated *in situ* from PhIO , $\text{PhI}(\text{OAc})_2$, or PhICl_2 and trimethylsilyl azide or NaN_3 have found some practical application as efficient reagents for the introduction of the azido function into organic molecules.

2.1.12.2 Amidoiodanes

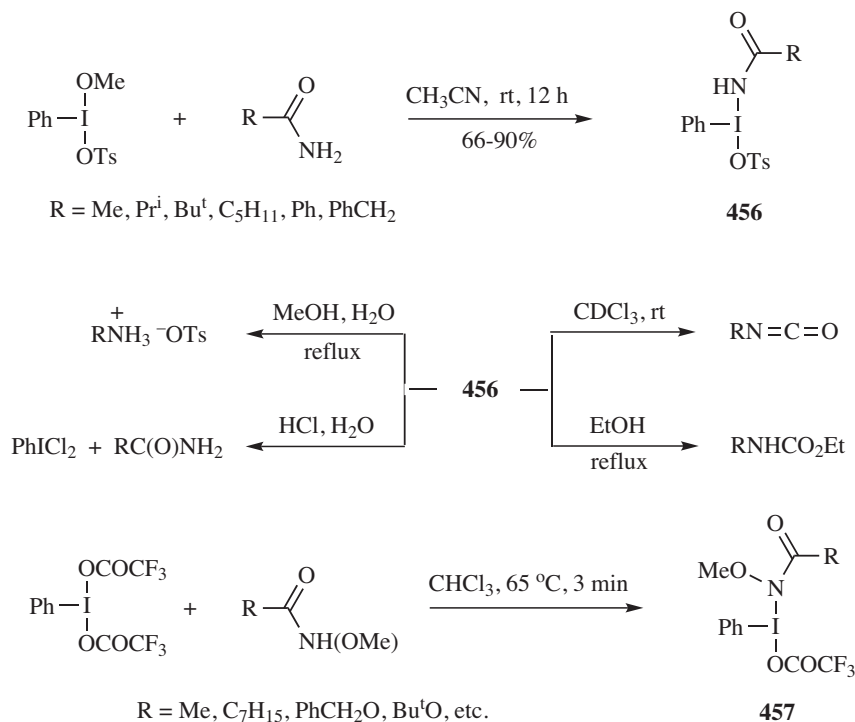
The only known amidoiodanes of type **450** with two nitrogen ligands on iodine are represented by the derivatives of cyclic imides, such as phthalimide, succinimide, glutarimide and saccharine [611–613]. For example, the thermally stable, but water-sensitive, bis(phthalimide) **455** was prepared by treatment of [bis(trifluoroacetoxy)iodo]benzene with potassium phthalimide in acetonitrile (Scheme 2.129) [611].

Amidoiodanes **451** bearing one nitrogen ligand at hypervalent iodine center are plausible intermediates in the Hofmann-type degradation of amides with [bis(acyloxy)iodo]arenes or [hydroxy(tosyloxy)iodo]benzene [614]. In most cases, these intermediates are highly unstable and instantaneously rearrange at room temperature with loss of iodobenzene to give isocyanates. However, *N*-phenyliodonio carboxamide tosylates **456** can be isolated as relatively stable, crystalline products in the reaction of [methoxy(tosyloxy)iodo]benzene with amides (Scheme 2.130) [615]. Koser and coworkers have investigated some chemical reactions of amidoiodane **456**. In particular, it decomposes in a CDCl_3 solution under anhydrous conditions at room temperature with the formation of benzyl isocyanate or gives the ammonium salt upon decomposition in the presence of water. Concentrated hydrochloric acid converts compound **456** into dichloriodobenzene and the respective amide [615]. The unstable amidoiodanes **457** can be generated by the reaction of [bis(trifluoroacetoxy)iodo]benzene with *N*-methoxyamides [215].

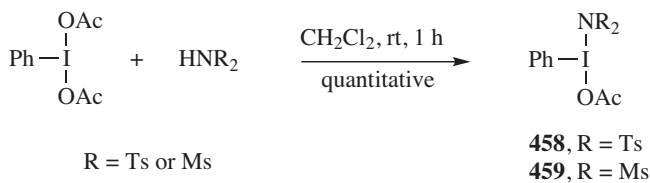
More recently, Muñiz and coworkers prepared the stable bis(sulfonylimide) derived amidoiodanes **458** and **459** by treatment of (diacetoxyiodo)benzene with bis(tosylimide) or bis(methanesulfonylimide) (Scheme 2.131) [616–618]. The structure of bis(tosylimide) **458** was established by single-crystal X-ray diffractometry [616]. Generated *in situ* amidoiodanes **458** and **459** are useful reagents for metal-free direct allylic amination or diamination of alkenes [616, 617].

2.1.12.3 Bis(Pyridinium) Aryliodine(III) Salts

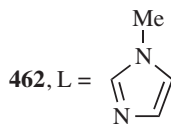
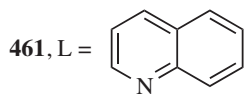
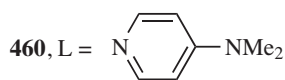
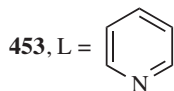
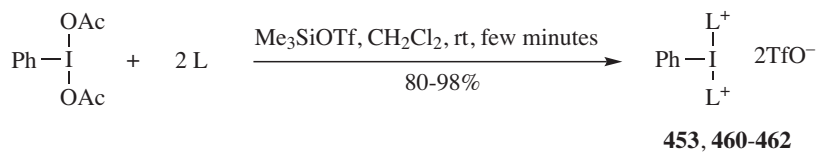
Bis(onio)-substituted aryliodine(III) salts of type **453** were originally reported in 1994 by Weiss and Seubert [570]. Treatment of (diacetoxyiodo)benzene or iodosylbenzene with trimethylsilyl triflate and a nitrogen heterocycle (L) in a molar ratio 1 : 2 at room temperature leads to the precipitation of triflate salts **453** and **460–462** (Scheme 2.132), which are sparingly soluble in dichloromethane and are stable in the absence of moisture [570]. The structures of products **453** and **460** were established by single-crystal X-ray diffraction studies [619]. The alternative procedure for the preparation of the triflate salt **453** involves the reaction of $\text{PhI}(\text{F})\text{OTf}$ with pyridine [620]. Analogous complexes of hypervalent iodine compounds with nitrogen heterocycles have also been reported for benziodoxoles and iodonium salts [416, 417, 621].



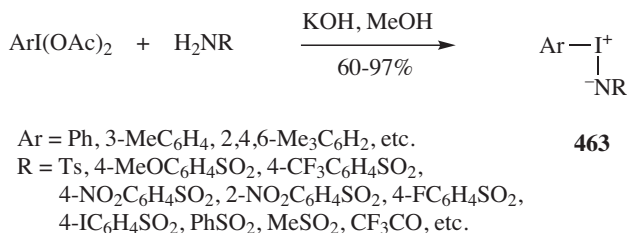
Scheme 2.130



Scheme 2.131



Scheme 2.132



Scheme 2.133

Bis(onio)-substituted aryl iodine(III) salts of type **453** are powerful oxidants. According to polarographic measurements, the E_1 value for the acceptance of the first electron by bis(pyridinium) salt **453** is 1.3 V greater than for PhI(OAc)₂, which is indicative of a dramatically increased oxidation power of **453** [570]. In particular, bis(pyridinium) salt **453** can instantaneously oxidize 1,2-bishydrazones to alkynes [570] and it reacts with diazoacetate esters at room temperature to give the corresponding α -aryliodonio diazo compounds [622].

2.1.12.4 Imidoiodanes

Imidoiodanes or iodonium imides, ArINR, are the I-N analogues of iodonium ylides and iodosylbenzene. The best known and widely used iodonium imide is *N*-tosyliminophenyliodane (PhINTs), which has found synthetic application as a useful nitrene precursor under thermal or catalytic conditions in the aziridination of alkenes and the amidation reactions of various organic substrates. The chemistry of iodonium imides was reviewed by Dauban and Dodd in 2003 [623].

2.1.12.4.1 Preparation Aryliodonium imides **463** are usually prepared by the reaction of (diacetoxyiodo)arenes with the respective amides under basic conditions (Scheme 2.133) [623]. Most iodonium imides are relatively unstable at room temperature and their storage under an inert atmosphere at low temperature is recommended. Exothermic decomposition frequently occurs at the melting point of ylides and some of them were even claimed to be explosive [623].

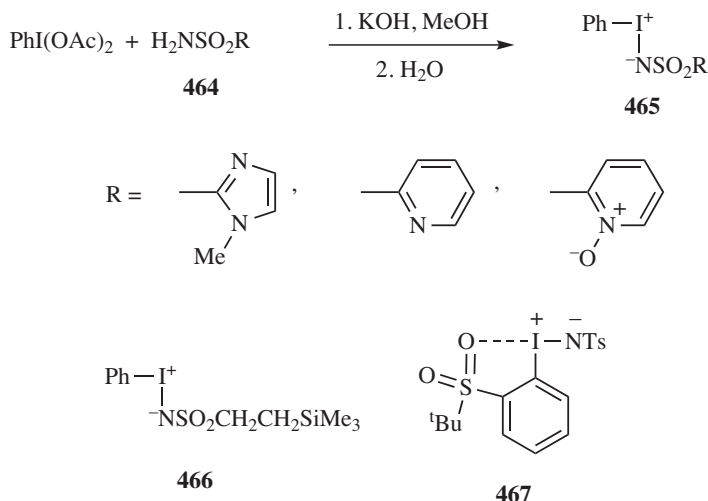
Examples of the known iodonium imides, ArINR, include *N*-tosyl- [67, 624–627], *N*-methanesulfonyl [628] and *N*-trifluoroacetyl derivatives [629]. *N*-(Trifluoroacetyl) and *N*-(methanesulfonyl) iminoiodanes are relatively unstable and explosive, while the tosylate derivatives are stable, crystalline compounds that can be stored for extended periods.

Various arenesulfonyl phenyliodonium imides, PhINSO₂Ar (Ar = Ph, 4-MeC₆H₄, 4-NO₂C₆H₄, 4-MeOC₆H₄, 4-CF₃C₆H₄, 2-NO₂C₆H₄, 4-FC₆H₄, 4-BrC₆H₄ and 4-IC₆H₄), have been prepared from (diacetoxyiodo)benzene and the appropriate sulfonylamides under basic conditions [626].

Several phenyliodonium imides **465** derived from heteroarenesulfonylamides have been synthesized from (diacetoxyiodo)benzene and the respective amides **464** (Scheme 2.134) [630]. Imides **465** can be used as sources of the corresponding heterocycle-containing nitrenes in the copper-catalyzed aziridination and sulfimidization reactions.

Imidoiodane **466** [PhINSes, where Ses = (trimethylsilyl)ethanesulfonyl] was prepared by a similar procedure from (diacetoxyiodo)benzene and the respective sulfonamide [631]. This reagent is useful for the copper-catalyzed aziridination of olefins leading to the synthetically versatile Ses-protected aziridines.

Protasiewicz and coworkers have reported the preparation and X-ray crystal structure of a highly soluble nitrene precursor **467**, in which the intramolecular secondary I...O bond replaces intermolecular interactions

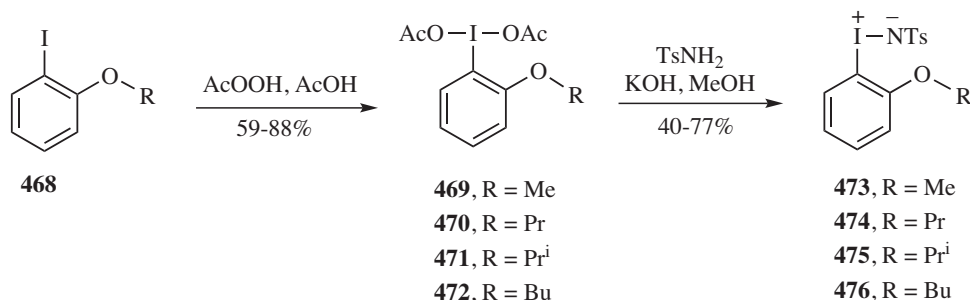


Scheme 2.134

that are typical of iodonium imides [100,632]. Imide **467** is readily soluble in organic solvents (up to 0.14 M in chloroform, which is a 50-fold increase over PhINTs) and it can be analyzed by NMR in solution [100]. Solubilization of various amides ArINTs in organic solvents can also be achieved by the addition of organic N-oxides, such as Me_3NO [633].

The highly soluble imidoiodanes **473–476**, which are derived from *ortho*-alkoxyiodobenzenes, were synthesized in two simple steps starting from readily available 2-iodophenol ethers **468** (Scheme 2.135) [634]. In the first step, iodides **468** were oxidized by peracetic acid to form diacetoxiyodo derivatives **469–472**; the structures of products **469** and **472** were established by X-ray analysis. In the second step, diacetates **469–472** were converted into imidoiodanes **473–476** by treatment with tosylamide under basic conditions in methanol. Compounds **473–476** are relatively stable at room temperature and can be stored for several weeks in a refrigerator. They also have good solubility in dichloromethane, chloroform and acetonitrile (e.g., the solubility of **472** in dichloromethane is 0.25 g ml^{-1}) [634].

2.1.12.4.2 Structural Studies Single-crystal X-ray structural data have been reported for the following iodonium imides (Figure 2.19): phenyl(*N*-tosylimino)iodane (**477**) [67, 635], mesityl(*N*-tosylimino)iodane



Scheme 2.135

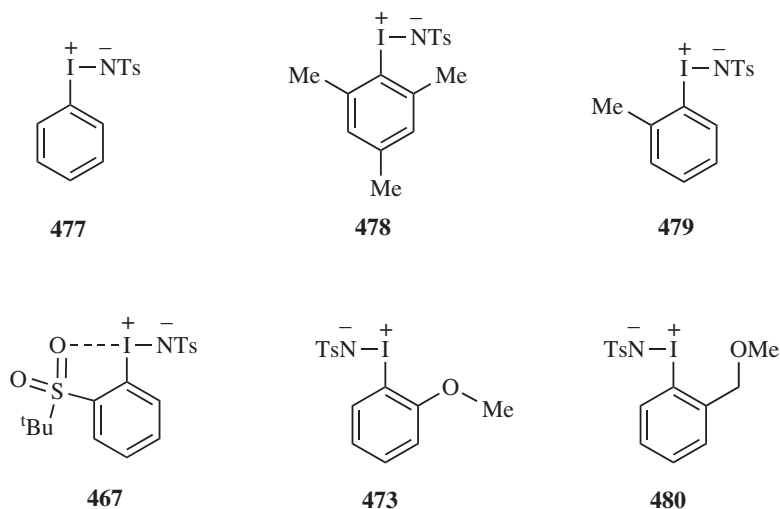


Figure 2.19 Iodonium imides analyzed by a single-crystal X-ray diffraction.

(**478**) [67], *o*-tolyl(*N*-tosylimino)iodane (**479**) [627], *ortho*-sulfonyl substituted phenyliodonium imide **467** [100], *ortho*-methoxy substituted phenyliodonium imide **473** [634] and *ortho*-methoxymethyl substituted phenyliodonium imide **480** [636].

Similar to iodosylbenzene (Section 2.1.4.3), aryl(*N*-tosylimino)iodanes have a linear polymeric, asymmetrically bridged structure with the T-shaped geometry around the iodine centers. In the case of PhINTs **477**, the monomeric units are bridged by I–N interactions, while in the more sterically hindered MesINTs **478** the bridging atom is the oxygen of the tosyl group (Figure 2.20) [67]. The structure of 2-TolINTs **479** is intermediate between the structures **477** and **478**: it can form two different polymorphic modifications, one with nitrogen and the second with oxygen as the bridging atom in the polymeric chain [627]. A polymeric, nitrogen-bridged structure was determined for 4-MeC₆H₄INTs by X-ray powder diffraction and EXAFS analyses [122]. The intramolecular I–N distance of 2.01–2.04 Å in *N*-tosyliminoiodanes is consistent with a single bond and the positive charge at iodine and the negative charge delocalized at the nitrogen and oxygen atoms of the tosylimino group.

A single-crystal X-ray analysis of *ortho*-sulfonyl substituted phenyliodonium imide **467** showed a structure of loosely associated centrosymmetric dimers with a long-range intramolecular I–N and I–O distance of more than 3.0 Å, quite unlike the infinite polymeric chains adopted in the solid state for PhINTs [100]. One of the sulfonyl oxygen atoms forms a short intramolecular I···O secondary bond to the iodine atom with a bond length of 2.667 Å. Because of the non-polymeric structure, imide **467** has excellent solubility in common organic solvents.

Similar to the structure of PhINTs (**477**, Figure 2.20), molecules of *ortho*-methoxy substituted phenyliodonium imide **473** [634] have a polymeric, asymmetrically bridged structure with a T-shaped geometry around the iodine centers formed by two iodine–nitrogen bonds and one iodine–carbon bond. However, in contrast to PhINTs, compound **473** has two additional weak intra- and intermolecular I···O contacts between the iodine center and the oxygen atoms of the alkoxy and sulfonyl groups. These weak interactions lead to an elongation of the I···N intermolecular bond in **473** (2.735 Å) compared with that observed in PhINTs (2.482 Å). As a result, the polymeric structure of **473** is weakened and the solubility is significantly increased [634].

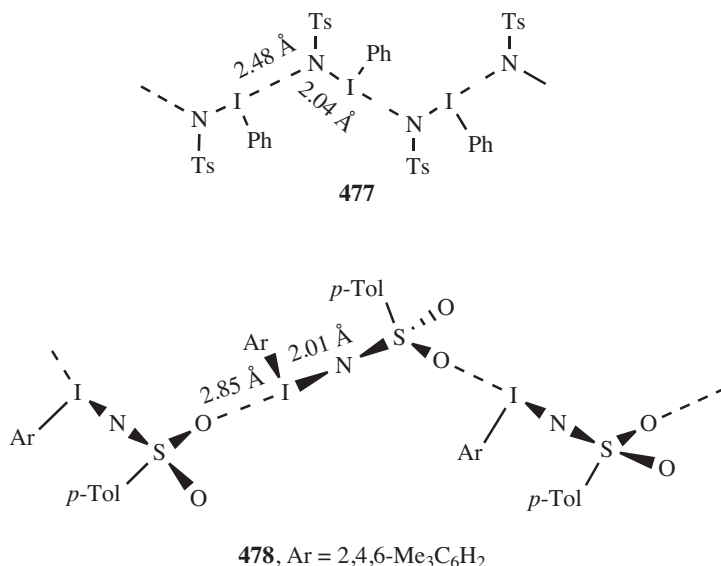


Figure 2.20 Primary and secondary bonding pattern in single-crystal X-ray structures of iodonium imides **477** and **478**.

2.2 Iodine(V) Compounds

Inorganic derivatives of iodine(V), such as salts of iodic acid, are the most common, naturally occurring derivatives of hypervalent iodine. In fact, most of the world's production of iodine comes from calcium iodate found in caliche deposits in Chile. Organic iodine(V) derivatives represent a less common, but practically important, class of hypervalent iodine compounds. Particularly useful are the cyclic derivatives of 2-iodoxybenzoic acid (IBX) and its analogues, which have found broad practical application as mild and selective oxidizing reagents in organic synthesis. The chemistry of organic iodine(V) compounds has been summarized in several reviews [637–640].

2.2.1 Inorganic Iodine(V) Derivatives

Iodine pentafluoride, the only known binary interhalogen compound of iodine(V), was first prepared in 1871 by heating iodine with silver fluoride [641–643]. This compound is a highly reactive, colorless liquid with a boiling point of 98 °C and a freezing point of 9.6 °C. According to microwave and electron-diffraction measurements, the molecule of IF₅ has a tetrahedral pyramidal geometry with four equatorial and one axial fluorine atoms with bond distances F_{eq}–I = 1.869 Å and F_{ax}–I = 1.844 Å (structure **481**, Figure 2.21) [644]. The X-ray crystal structure of the molecular addition compound XeF₂·IF₅ with more-or-less discrete IF₅ molecules was also reported [645]. The salts M⁺IF₆[–] can be prepared by the reaction of IF₅ with the respective fluorides, MF; crystal structures of (CH₃)₄N⁺ IF₆[–] and NO⁺ IF₆[–] have been reported [646]. Reaction of IF₅ with I₂O₅ gives stable, solid oxyfluorides IOF₃ and IO₂F [641–643].

Various oxygen-bonded iodine(V) derivatives are known [641–643]. Iodine pentoxide, I₂O₅, the most important and thermally stable iodine oxide, is prepared in the form of a hygroscopic, white solid by dehydration of iodic acid, HIO₃, at 200 °C. It readily absorbs water from the atmosphere, giving the hydrate,

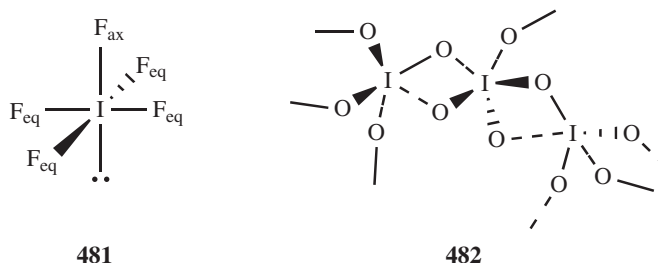


Figure 2.21 Structures of iodine pentafluoride (**481**) and iodine pentoxide (**482**).

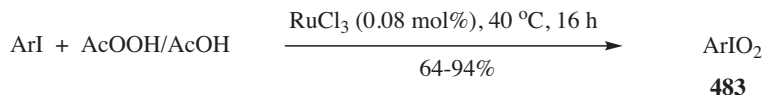
HI_3O_8 . On dissolution in water, I_2O_5 regenerates iodic acid [643]. Iodine pentoxide has a polymeric structure (**482**, Figure 2.21) with primary I—O bonds of 1.77–1.95 Å in the distinguishable molecular I_2O_5 units and intermolecular I···O distances as short as 2.23 Å [647]. Several mixed iodine(III/V) oxides, such as I_2O_4 and I_4O_9 , are also known [643]; the structure of a mixed iodine(V/VII) oxide, I_4O_{12} , has been reported [648].

Several iodyl derivatives, IO_2X , of strong inorganic acids have been synthesized and characterized. The earliest reports on iodyl derivatives of sulfuric or polysulfuric acids date well back into the twentieth century [641–643]. More recently, a crystal structure of a mixed iodine(III/V) sulfate, $(\text{IO}_2)_3\text{HSO}_4$, was reported [649]. The fluorosulfate $\text{IO}_2\text{OSO}_2\text{F}$ [650] and the triflate $\text{IO}_2\text{OSO}_2\text{CF}_3$ [5] are also known. Raman and IR spectra of these compounds indicate the presence of discrete IO_2 groups with relatively weak secondary I···O bonding [5].

2.2.2 Noncyclic and Pseudocyclic Iodylarenes

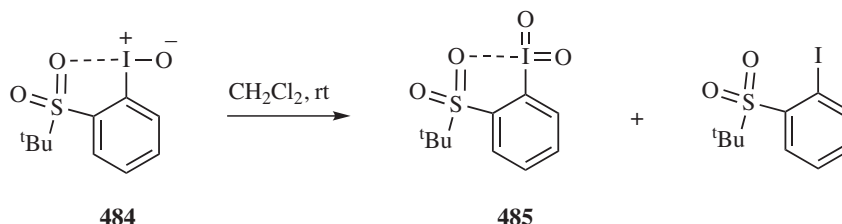
Iodylarenes, ArIO_2 , which are also known as iodoxyarenes, are commonly prepared by direct oxidation of iodoarenes, ArI , with strong oxidants or by disproportionation of iodosylarenes, ArIO . The initial oxidation of ArI usually leads to ArIO , which then slowly disproportionates to ArI and ArIO_2 upon moderate heating, or even at room temperature [111, 149, 651]. Common oxidizing reagents that are used for the preparation of iodylarenes from iodoarenes include sodium hypochlorite, sodium periodate, dimethyldioxirane and Oxone. For example, various iodylarenes have been prepared from the corresponding iodoarenes using sodium periodate as the oxidant in boiling 30% aqueous acetic acid [651].

Noncyclic iodylarenes **483**, in particular iodylarenes bearing strongly electron-withdrawing groups in the aromatic ring, can be efficiently prepared using peracetic acid as an oxidant in the presence of catalytic amounts of ruthenium trichloride (Scheme 2.136) [652, 653]. The mechanism of this reaction consists of the initial oxidation of iodobenzene by peracetic acid followed by RuCl_3 -catalyzed disproportionation of the intermediate (diacetoxyiodo)benzene to iodylbenzene and iodobenzene.



Ar = Ph, 4-MeC₆H₄, 2-MeC₆H₄, 2-ClC₆H₄, 3-ClC₆H₄, 4-ClC₆H₄, 4-BrC₆H₄,
4-FC₆H₄, 4-CF₃C₆H₄, 3,5-CF₃C₆H₃, etc.

Scheme 2.136



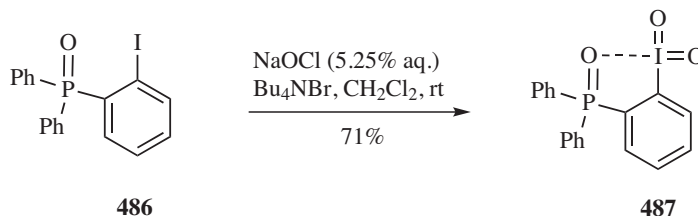
Scheme 2.137

Iodylarenes usually precipitate from the reaction mixture and can be additionally purified by recrystallization from hot water or other solvents. Iodylarenes are potentially hazardous compounds, which may explode upon impact, scratching with a spatula, or heating and therefore should be handled with appropriate precautions. A violent explosion of 2 g of 3-iodyltoluene during crystallization from boiling water with vigorous stirring has been reported [654].

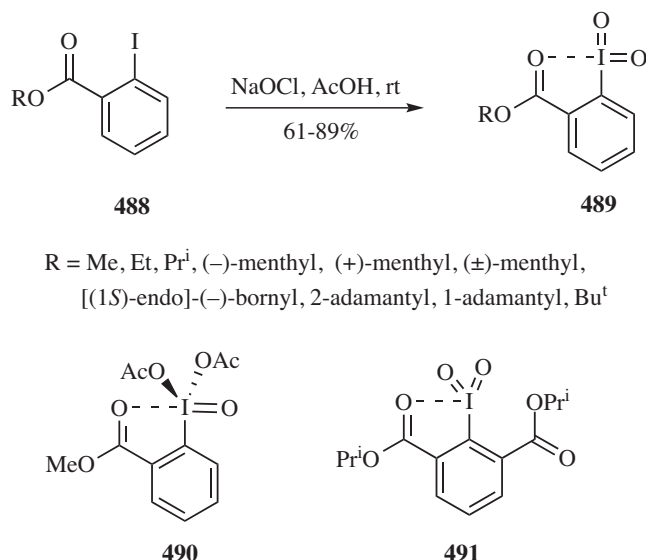
The first noncyclic iodylarene, iodylbenzene PhIO_2 , was reported by Willgerodt in 1892 [655]. Iodylbenzene is a colorless, microcrystalline solid, which detonates violently upon heating. A single-crystal X-ray structural analysis of PhIO_2 revealed a polymeric structure with a distorted octahedral arrangement at the iodine(V) center with three primary I—O bonds in the range of 1.92–2.01 Å and three secondary I...O intermolecular interactions of 2.57–2.73 Å [656]. Because of the polymeric structure, iodylbenzene is insoluble in most organic solvents, with the exception of DMSO. Iodylbenzene in general has found only very limited practical application due to its explosive properties.

Aryliodyl derivatives bearing an appropriate substituent in the *ortho*-position to the iodine are characterized by the presence of a pseudocyclic structural moiety due to a strong intramolecular secondary bonding between the hypervalent iodine center and the oxygen atom in the *ortho*-substituent. Compared to the noncyclic aryliodyl derivatives, pseudocyclic iodine(V) compounds have much better solubility, which is explained by a partial disruption of their polymeric nature due to the redirection of secondary bonding. The first pseudocyclic iodylarene of this type, 1-(*tert*-butylsulfonyl)-2-iodylbenzene **485**, was prepared by Protasiewicz and coworkers in 2000 by the disproportionation of iodosylarene **484** (Scheme 2.137) [127]. A single-crystal X-ray structure of product **485** showed a pseudooctahedral geometry with I—O bond lengths in the iodyl group of 1.796 and 1.822 Å and an intramolecular distance of 2.693 Å between one of the sulfone oxygen atoms and the hypervalent iodine center [127].

A similar, soluble *ortho*-phosphoryl substituted aryliodyl derivative **487** was obtained by the hypochlorite oxidation of the appropriate aryl iodide **486** (Scheme 2.138) [111]. A single-crystal X-ray analysis of compound **487** has shown a close contact of the phosphoryl oxygen atom and the iodine(V) atom with a distance of 2.612 Å, which is significantly shorter than the I...O distance of 3.291 Å determined for the unoxidized aryl iodide **486** [111].



Scheme 2.138

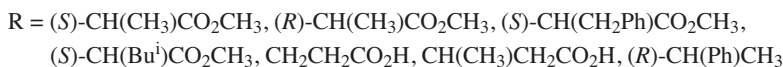
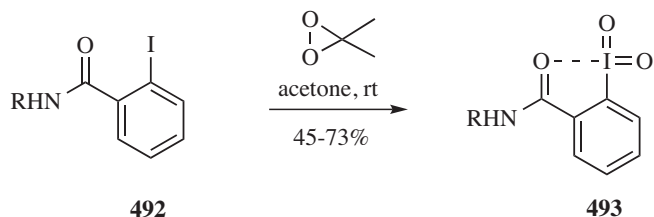


Scheme 2.139

Esters of 2-iodoxybenzoic acid (IBX-esters) **489** have been prepared by the hypochlorite oxidation of the readily available 2-iodobenzoate esters **488** (Scheme 2.139) and isolated in the form of stable microcrystalline solids [657,658]. This procedure has been used for the synthesis of IBX-esters **489** derived from various types of alcohols, such as primary, secondary and tertiary alcohols, adamantanol, optically active menthols and borneol. Single-crystal X-ray data on products **489** revealed a pseudo-benziodoxole structure in which the intramolecular I...O secondary bonds partially replace the intermolecular I...O secondary bonds, disrupting the polymeric structure characteristic of PhIO₂ and other previously reported iodylarenes [658]. This structural feature substantially increases the solubility of these compounds in comparison to other iodine(V) reagents and affects their oxidizing reactivity.

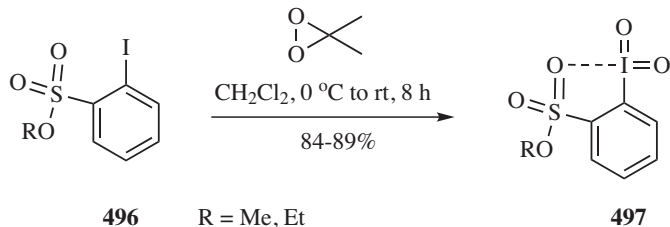
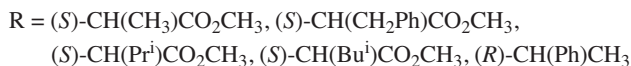
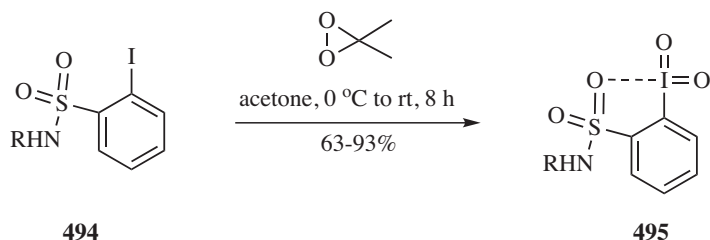
Methyl 2-iodoxybenzoate can be further converted into the diacetate **490** or a similar bis(trifluoroacetate) derivative by treatment with acetic anhydride or trifluoroacetic anhydride, respectively [658]. Single-crystal X-ray diffraction of methyl 2-[(diacetoxo)iodosyl]benzoate **490** revealed a pseudo-benziodoxole structure with three relatively weak intramolecular I...O interactions. The esters of 2-iodoxyisophthalic acid (e.g., **491**) have been prepared by oxidation of the respective iodoarenes with dimethyldioxirane. X-Ray structural analysis of diisopropyl 2-iodoxyisophthalate **491** showed intramolecular I...O interaction with the carbonyl oxygen of only one of the two ester groups, while NMR spectra in solution indicated equivalency of both ester groups [658].

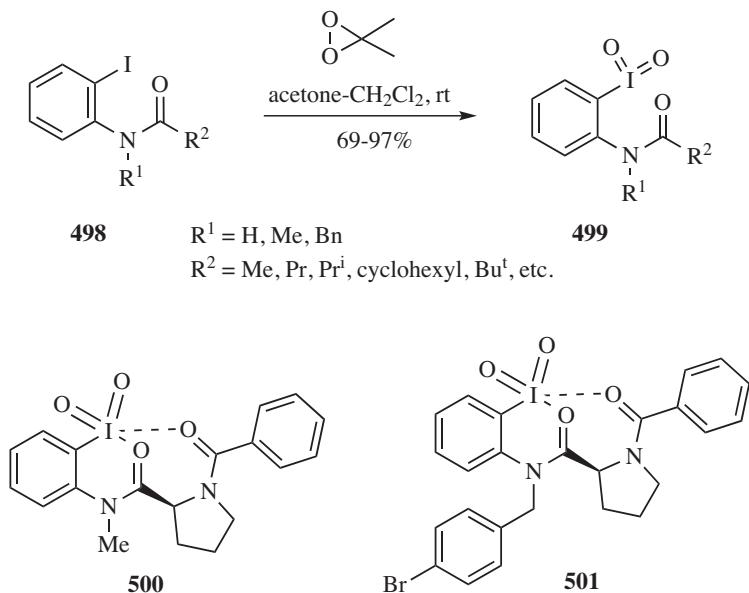
Amides of 2-iodoxybenzoic acid (IBX-amides) **493** have been prepared by the dioxirane oxidation of the appropriate 2-iodobenzamides **492** (Scheme 2.140) in the form of stable, microcrystalline solids moderately soluble in dichloromethane and chloroform [659]. This procedure has been used for the synthesis of amides **493** derived from various types of amino compounds, such as esters of α -amino acids, esters of β -amino acids and (*R*)-1-phenylethylamine. A single-crystal X-ray analysis of the phenylalanine derivative [**493**, R = (*S*)-CH(CH₂Ph)CO₂Me] revealed a close intramolecular contact of 2.571 Å between the hypervalent iodine center and the oxygen atom of the amido group within each molecule. This enforces a planar geometry of the resulting five-membered ring, a geometry that is analogous to that observed for IBX and other benziodoxoles [659].

**Scheme 2.140**

Amides of 2-iodoxybenzenesulfonic acid **495** were prepared by dioxirane oxidation of the corresponding 2-iodobenzenesulfamides **494** and isolated as stable, microcrystalline products (Scheme 2.141) [660]. A single-crystal X-ray structural analysis of the alanine derivative **495** [R = (*S*)-CH(CH₃)CO₂Me] showed a combination of intra- and intermolecular I⋯O interactions leading to a unique heptacoordinated iodine(V) center in this molecule [661]. The analogous esters **497** were prepared similarly from the respective sulfonate esters **496** [662].

The soluble and stable IBX analogues having pseudo-benziodoxazine structure, *N*-(2-iodylphenyl)acylamides **499**, have been prepared in good yields by the oxidation of 2-iodoaniline derivatives **498** with 3,3-dimethyldioxirane under mild conditions (Scheme 2.142) [663]. X-Ray data on compounds **499** revealed a unique pseudo-benziodoxazine structure with an intramolecular secondary I⋯O

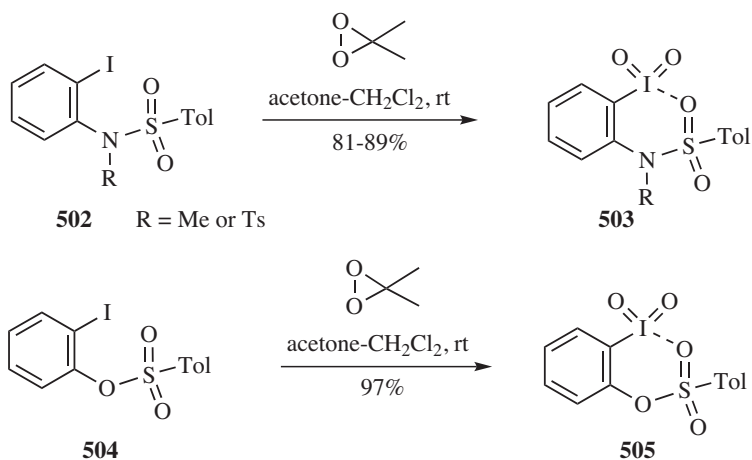
**Scheme 2.141**



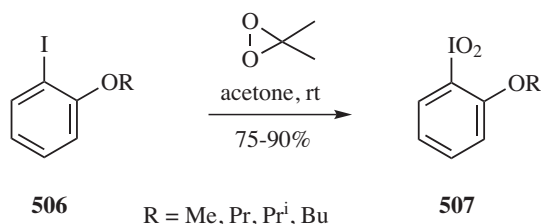
Scheme 2.142

bond distance of 2.647 Å. The synthesis of chiral pseudo-benziodoxazine reagents **500** and **501** has been achieved based on commercially available and inexpensive (*S*)-proline [664].

Similarly to *N*-(2-iodylphenyl)acylamides, the tosyl derivatives of 2-iodylaniline **503** and 2-iodylphenol **505** were prepared by the dimethyldioxirane oxidation of the corresponding 2-iodophenyltosylamides **502** or 2-iodophenyl tosylate (**504**) (Scheme 2.143) and isolated as stable, microcrystalline products [665]. A single-crystal X-ray diffraction analysis of tosylamide **503** (*R* = Me) revealed a pseudocyclic structure formed by intramolecular I...O interactions between the hypervalent iodine center and the sulfonyl oxygens in the



Scheme 2.143



Scheme 2.144

tosyl group [665]. This tosylamide has excellent solubility in organic solvents and is a potentially useful hypervalent iodine oxidant.

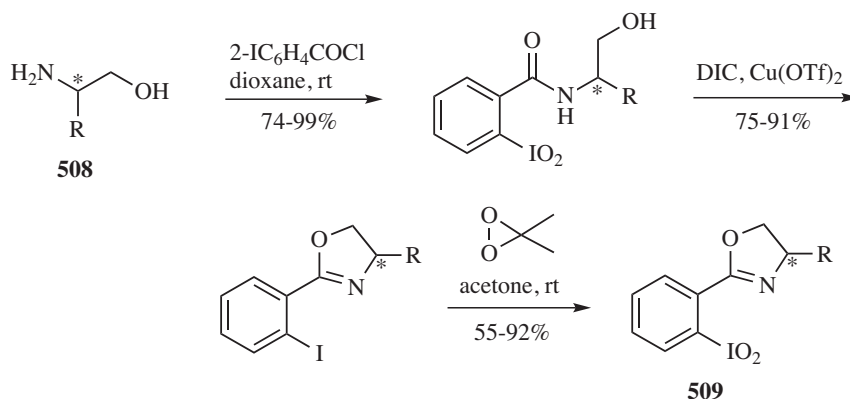
2-Iodylphenol ethers **507** have been prepared by the dioxirane oxidation of the corresponding 2-iodophenol ethers **506** (Scheme 2.144) and isolated as chemically stable, microcrystalline products [666]. A single-crystal X-ray diffraction analysis of 1-iodyl-2-isopropoxybenzene and 1-iodyl-2-butoxybenzene showed pseudopolymeric arrangements in the solid state formed by intermolecular interactions between the IO₂ groups of different molecules.

Several chiral 2-(*o*-iodylphenyl)-oxazolines **509** have been synthesized starting from chiral 2-amino alcohols **508** (Scheme 2.145) [667]. Compounds **509** were obtained as white microcrystalline powders that are soluble in most organic solvents.

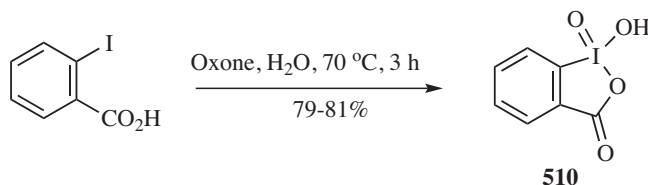
Alkyl iodyl derivatives, RIO₂, usually lack stability and cannot be isolated. For example, the matrix isolation and FTIR spectra was reported of the unstable iodylalkanes, generated by the co-deposition and photolysis of ozone with iodoethane, 2-iodopropane, pentafluoroiodoethane, 1,1,1-trifluoroiodoethane, 1,1,2,2-tetrafluoroiodoethane, 1,1,1,2-tetrafluoroiodoethane, or iodine cyanide in an argon matrix at 14–16 K [668–670]. A relatively stable iodyltrifluoromethane, CF₃IO₂, was prepared by the reaction of CF₃IF₄ with silicon dioxide [671].

2.2.3 Iodine(V) Heterocycles

Within the broad field of hypervalent iodine chemistry, five-membered iodine(V) heterocycles occupy a special place. There has been significant interest in the cyclic λ⁵-iodanes, mainly 2-iodoxybenzoic acid (IBX)



Scheme 2.145



Scheme 2.146

and Dess–Martin periodinane (DMP), which have found broad practical application as mild and selective reagents for the oxidation of alcohols and some other useful oxidative transformations. Several comprehensive reviews on the chemistry and synthetic applications of IBX and DMP have been published [637–640, 672].

2.2.3.1 2-Iodoxybenzoic Acid (IBX) and Analogues

The most important pentavalent iodine heterocycle, 2-iodoxybenzoic acid (IBX, **510**), was first prepared in 1893 by Hartman and Mayer [673]. IBX has the structure of the cyclic benziodoxole oxide (1-hydroxy-1-oxo-1*H*-1 λ^5 -benzo[*d*][1,2]iodoxol-3-one according to the IUPAC nomenclature), as determined by X-ray structural analysis [674–676]. The original preparation of IBX involved the oxidation of 2-iodobenzoic acid with potassium bromate in an aqueous solution of sulfuric acid [673]; more recently, an optimized procedure for the bromate oxidation was published in *Organic Syntheses* [677]. The samples of IBX prepared by this procedure were reported to be explosive under heating or impact [678], possibly due to the presence of bromate impurities [679]. In 1999 Santagostino and coworkers published a convenient and safe procedure for the preparation of IBX (**510**) by the oxidation of 2-iodobenzoic acid using Oxone (2KHSO₅·KHSO₄·K₂SO₄) in water at 70 °C (Scheme 2.146) [680]. This convenient protocol has become the most commonly used method for the large-scale preparation of IBX.

IBX in the solid state has a three-dimensional polymeric structure due to strong intermolecular secondary I···O contacts and hydrogen bonding. A detailed X-ray diffraction study of IBX samples, prepared by the oxidation of 2-iodobenzoic acid with potassium bromate, revealed the presence of the powder and the macrocrystalline forms of IBX [674]. It was also noticed that the powder form of IBX is more reactive in the reaction with acetic anhydride than the macrocrystalline form and thus is more useful as the Dess–Martin periodinane precursor (Section 2.2.3.2). Treatment of macrocrystalline IBX with aqueous sodium hydroxide and then with hydrochloric acid can be used to convert it into the more reactive powder form [674].

A single-crystal X-ray structural study of the macrocrystalline form of IBX has shown that the iodine(V) atom is chiral and in the solid state IBX is a racemic mixture of two enantiomers. Figure 2.22 shows the molecular geometry of IBX (**510**), with primary and secondary bonds at the iodine(V) center [674]. The crystal structure of racemic IBX consists of chains of molecules linked by I···O secondary bonds (2.808 Å) and also by additional hydrogen bonding. There is also a second iodine–oxygen contact of 2.782 Å linking the chains to form a two-dimensional sheet. Overall, the molecules of IBX are linked together via one O–H···O, four C–H···O hydrogen bonds and two I···O secondary bonds to form a three-dimensional, hydrogen and iodine–oxygen bonded network in which the iodine atoms have distorted octahedral coordination (Figure 2.22). This three-dimensional network is further stabilized by π – π stacking of the phenyl rings with C···C contacts of 3.2 Å and H–ring center contacts of 2.4 Å [674].

IBX is a potentially explosive compound and even the bromate-free samples of IBX are not safe. Santagostino and coworkers reported that as a rule pure IBX explodes at 233 °C [680]. The explosibility tests of analytically pure IBX samples (over 99% purity) confirmed the earlier observations by Plumb and Harper

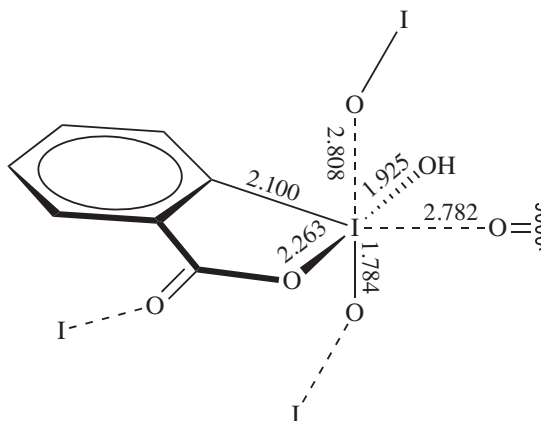
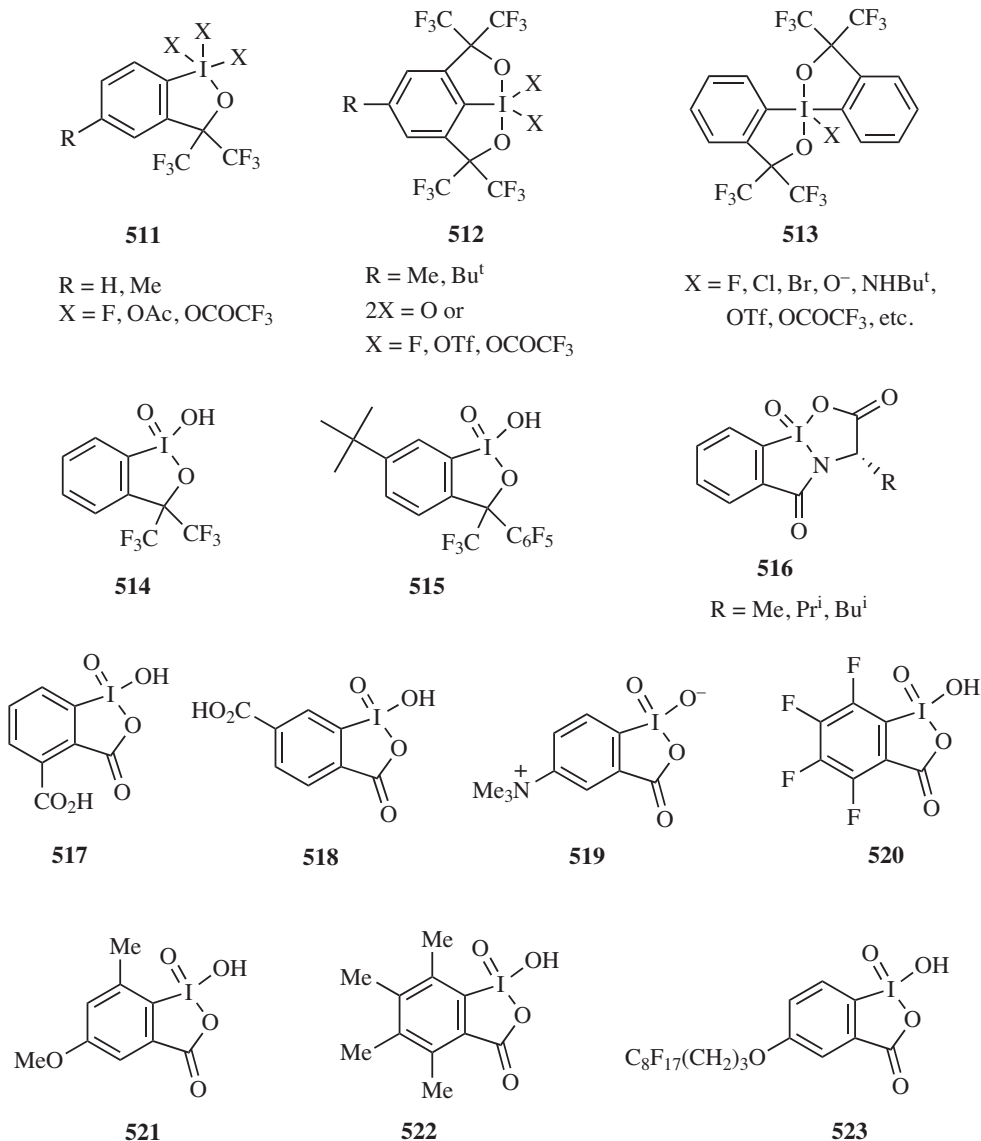


Figure 2.22 Molecular structure of IBX (**510**) with primary and secondary bonds at the iodine(V) center (bond lengths in Å) [674].

[678] that IBX is explosive under impact or heating above 200 °C. A non-explosive formulation of IBX (SIBX), consisting of IBX, benzoic acid and isophthalic acid, was introduced by Quideau and coworkers in 2003 [681]. SIBX has similar reactivity to IBX in the reactions of hydroxylative phenol dearomatization [682–684], oxidation of sulfides into sulfoxides [685], oxidative demethylation of phenolic methyl aryl ethers [681] and other useful oxidative transformations [681].

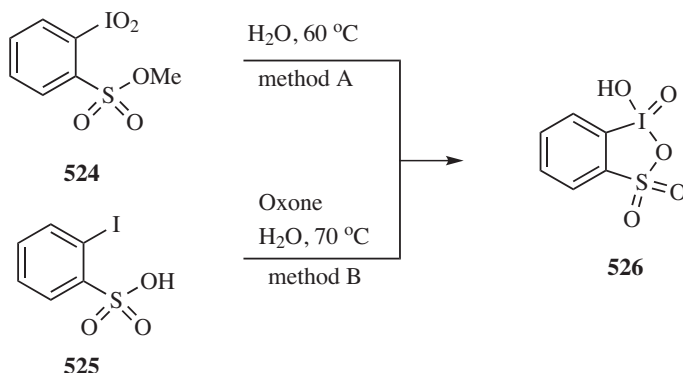
Theoretical and experimental studies of the pK_a value and proton affinity of IBX solutions in aqueous media and DMSO have been published. In particular, the aqueous pK_a value of 2.40 for IBX was obtained by using standard potentiometric titration methods [686]. The relatively high acidity of IBX should be taken into consideration while using this important reagent in the oxidation of complex organic molecules. The gas-phase proton affinities of the anions of IBX ($1300 \pm 25 \text{ kJ mol}^{-1}$) and 2-iodosylbenzoic acid ($1390 \pm 10 \text{ kJ mol}^{-1}$) using mass spectrometry-based experiments were reported [687]. The experimental results were supported by theoretical calculations, which yielded proton affinities of 1336 and 1392 kJ mol^{-1} for the anions of IBX and 2-iodosylbenzoic acid, respectively, at the B3LYP/aug-cc-PVDZ level of theory [687].

Numerous analogues of IBX have been reported in the literature (Figure 2.23). In the early 1990s, Martin and coworkers reported the synthesis, structure and properties of several cyclic λ^5 -iodanes **511–513** [350,679,688]. Martin and coworkers also introduced bis(trifluoromethyl)benziodoxole oxides **514** and **515**, which are stable and non-explosive oxidizing reagents that are soluble in a wide range of organic solvents [688,689]. Chiral derivatives of pentavalent iodine, benziodazole oxides **516**, were prepared by the oxidation of the corresponding amino acid derived 2-iodobenzamides with potassium bromate [690]. Vinod and coworkers have developed water-soluble analogs of IBX, *m*-iodoxyphthalic acid (mIBX) **517** [691] and a similar derivative of terephthalic acid (**518**) [692], which are useful oxidizing reagents in aqueous solutions. A zwitterionic, water-soluble IBX analog (**519**) was prepared by oxidation of the corresponding iodide with dimethyldioxirane and was characterized by single-crystal X-ray diffraction [693]. Wirth and coworkers have developed the tetrafluoro-IBX derivative (FIBX, **520**), which is more soluble and has higher reactivity than its non-fluorinated counterpart [340]. Moorthy and coworkers have prepared *o*-methyl-substituted IBX (Me-IBX, **521**) [694] and tetramethyl-IBX (TetMe-IBX, **522**) [695], the modified analogues of IBX that can oxidize alcohols in common organic solvents at room temperature due to the hypervalent twisting-promoted rate enhancement. Fluorous IBX **523** is a recyclable oxidant that can also be used as a catalyst for the

**Figure 2.23** IBX analogues.

oxidation of alcohols to the corresponding carbonyl compounds [696]. Several recyclable polymer-supported IBX derivatives are discussed in Section 5.2.

A pyridinium salt of IBX has been prepared, by treatment of IBX with pyridine, in the form of stable, non-explosive, colorless crystals [697]. Pyridinium 2-iodobenzoate has a similar reactivity pattern to that of IBX and can be used as a safe oxidant that is soluble in organic solvents. IBX can also form relatively stable complexes with *N*-oxides, sulfoxides (DMSO) and tetrahydrofuran [698, 699]. Such ligand complexation allows us to fine-tune the reactivity profile of IBX [698].



Scheme 2.147

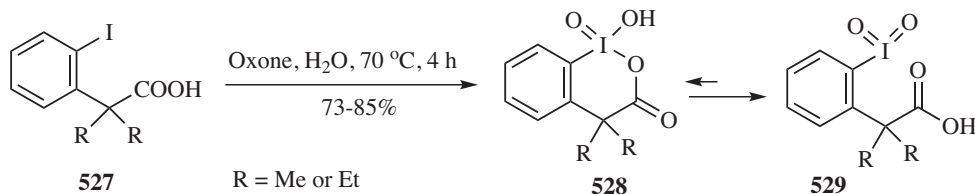
2-Iodoxybenzenesulfonic acid **526** (in a cyclic tautomeric form of 1-hydroxy-1*H*-1,2,3-benziodoxathiole 1,3,3-trioxide), a thia-analog of IBX and a powerful oxidizing reagent, has been prepared by two different pathways: (A) hydrolysis of the methyl ester of 2-iodylbenzenesulfonic acid (**524**) and (B) direct oxidation of 2-iodobenzenesulfonic acid (**525**) (Scheme 2.147) [245]. 2-Iodoxybenzenesulfonic acid **526** was found to be thermally unstable and highly reactive towards organic solvents. The structure of its reductive decomposition product, 2-iodosylbenzenesulfonic acid in its cyclic tautomeric form, was established by single-crystal X-ray diffraction [245]. It has been demonstrated that thia-IBX **526** is the most powerful catalyst in the iodine(V)-catalyzed oxidation of alcohols using Oxone as a terminal oxidant [700].

The six-membered cyclic IBX analogues **528** have been synthesized by oxidation of the corresponding 2-iodophenylacetic acids **527**. Interestingly, an X-ray structural study demonstrated that products **528** exist in the solid state as pseudocyclic acids **529** (Scheme 2.148) [345].

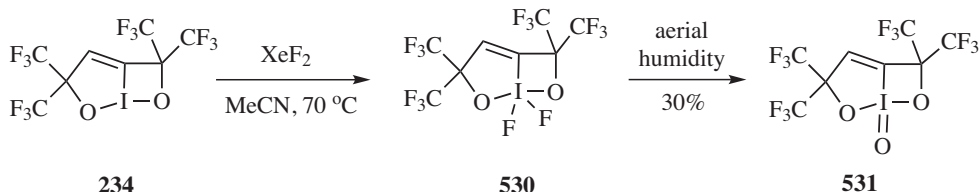
The bicyclic fused iodoxole oxide **531**, the aliphatic analog of IBX, has been prepared by the fluorination of a tricoordinate 1,2-iodoxetane **234** (Section 2.1.8.9) with xenon difluoride followed by hydrolysis of the intermediate, non-isolable, difluoride **530** (Scheme 2.149) [701]. Compound **531** has a similar reactivity to that of IBX and can oxidize alcohols and sulfides to the corresponding carbonyl compounds and sulfoxides, respectively, in good yields under mild conditions.

2.2.3.2 Dess–Martin Periodinane (DMP)

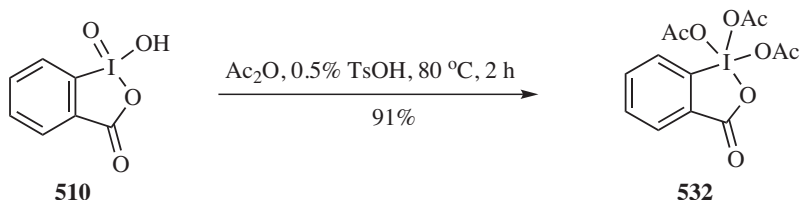
In 1983 Dess and Martin first reported the preparation of triacetoxybenziodoxolone (**532**) by heating IBX with acetic anhydride to 100 °C [702]. In subsequent years the triacetate **532** has emerged as a reagent of choice for the oxidation of alcohols to the respective carbonyl compounds [679] and in the present literature



Scheme 2.148



Scheme 2.149

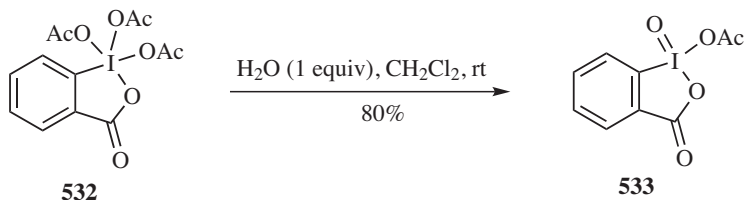


Scheme 2.150

it is commonly referred to as Dess–Martin periodinane (DMP). An improved procedure for the preparation of **532** consists of the reaction of IBX with acetic anhydride in the presence of *p*-toluenesulfonic acid at 80 °C (Scheme 2.150) [703]. DMP is also commercially available from several chemical companies. An optimized procedure for the preparation of DMP has been published in *Organic Syntheses* [677]. The synthetic applications of DMP are highlighted in two overviews [704, 705].

Freshly prepared, crystalline DMP is completely soluble in dichloromethane and chloroform. It should be stored and handled under dry conditions; exposure to atmosphere should be avoided. Careful hydrolysis of DMP (**532**) by slow addition of one equivalent of water in dichloromethane furnishes the monoacetate **533**, which can be isolated in 80% yield (Scheme 2.151) [706]. The freshly prepared or generated *in situ* monoacetate **533** is a stronger oxidant than DMP.

A single-crystal X-ray structural study has shown that DMP (**532**) crystallizes as a dimer; the molecular geometry of the iodine(V) center with primary and secondary bonds is shown in Figure 2.24 [707]. The central iodine atom resides in a distorted octahedral environment that is in accordance with a simple VSEPR model. The equatorial positions are occupied by acetoxy groups, whereas the apical positions are occupied by the phenyl ring and the lone electron pair, respectively. Owing to the steric demands of the electron pair, which is engaged in supramolecular interactions, the acetoxy substituents are pushed toward the phenyl ring. As a consequence, the iodine atom lies 0.315(1) Å below a plane formed by oxygens of the three acetoxy



Scheme 2.151

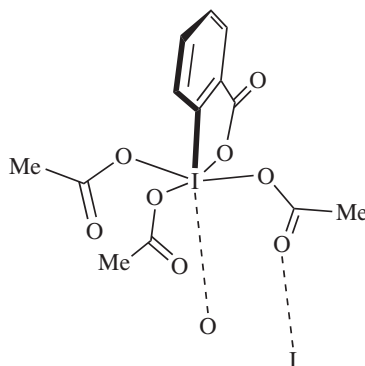


Figure 2.24 Molecular structure of DMP 532 with primary and secondary bonds at the iodine(V) center.

groups. All three acetoxy groups are bound in covalent fashion, showing typical iodine–oxygen bond lengths between 2.06 and 2.11 Å. The length of the iodine–oxygen bond of the iodoxolone ring (2.089 Å) is also well within the range of a covalent iodine–oxygen bond. The iodine–carbon bond is 2.10 Å long and forms a C–I–O angle of 79.6° within the iodoxolone ring. The unit cell is occupied by a centrosymmetric dimer that is held together, in part, by two intermolecular I...O bonds between the iodine atom and a carbonyl group of the adjacent molecule. The intermolecular iodine–oxygen distance of 3.3 Å is well below the sum of the van der Waals radii (3.46 Å). In addition to I...O bonds, the dimer is stabilized by two weak hydrogen bonds of C–H...O type.

2.2.4 Organoiodine(V) Fluorides

Several organoiodine(V) fluorides RIF_4 are known. The trifluoromethyl derivative, CF_3IF_4 , has been prepared by the reaction of ClF_3 with CF_3I in perfluorohexane at -78°C as a white, moisture sensitive solid, which decomposes at 20°C [708, 709]. It was characterized by NMR spectroscopy [710] and single-crystal X-ray diffraction [711]. Other perfluoroalkyl iodine(V) fluorides R_fIF_4 [$\text{R}_f = \text{C}_2\text{F}_5$, $(\text{CF}_3)_2\text{CF}$, or $n\text{-C}_4\text{F}_9$] can be prepared similarly as relatively stable products [708, 709].

Aryl- or perfluoroaryl substituted organoiodine(V) fluorides are thermally stable compounds. (Tetrafluoroiodo)benzene, $\text{C}_6\text{H}_5\text{IF}_4$, was first reported in 1968 by Yagupolskii and coworkers [712]. Aryl iodine tetrafluorides can be prepared by three different methods: (i) fluorination of ArI [713], (ii) arylation of IF_5 [714] and (iii) conversion of ArIO_2 into ArIF_4 with SF_4 [712]. The reaction of PhIO_2 with SF_4 is the method of choice for the preparation of PhIF_4 [712]. The reaction is nearly quantitative and the gaseous byproducts can be removed easily. PhIF_4 is crystalline material, thermally stable to about 300°C , that is sensitive to hydrolysis.

Single-crystal structures of $\text{C}_6\text{F}_5\text{IF}_4$ [715], CF_3IF_4 [711] and PhIF_4 [716] have been reported. In all three molecular structures the expected square-pyramidal geometry with the organic substituent in the apical position has been observed. The I–F bond lengths in PhIF_4 (average 1.94 Å) are longer than in IF_5 (average 1.87 Å), CF_3IF_4 (average 1.92 Å), or $\text{C}_6\text{F}_5\text{IF}_4$ (average 1.91 Å), which is a consequence of the weaker electron-withdrawing power of the Ph group compared to F, CF_3 , or C_6F_5 substituents. The I–C bond length of 2.077 Å in PhIF_4 is nearly the same as in $\text{C}_6\text{F}_5\text{IF}_4$ (2.08 Å) and is much shorter than in CF_3IF_4 (2.22 Å). The average C–I–F angle of 85.36° in PhIF_4 is slightly larger than the average C–I–F angles in IF_5 (81.98°), CF_3IF_4 (82.18°) and $\text{C}_6\text{F}_5\text{IF}_4$ (84.38°). Molecules of PhIF_4 form a zigzag chain due to the I...F intermolecular interactions [716].

The iodine atom in PhIF_4 can act as a fluoride ion acceptor in the reaction with 1,1,3,3,5,5-hexamethylpiperidinium fluoride (pip^+F^-) as a source of nearly naked fluoride ions. PhIF_4 reacts with pip^+F^- in acetonitrile at -30°C to form the colorless, hydrolytically sensitive adduct $\text{pip}^+\text{C}_6\text{H}_5\text{IF}_5^-$, which has been characterized by Raman and NMR spectroscopy and its single X-ray crystal structure [716].

2.3 Iodine(VII) Compounds

Only inorganic compounds of iodine(VII) are known. Iodine(VII) fluoride, IF_7 , has been known since 1930 [717] and numerous papers dealing with its properties and structure have been published. It can be prepared, by heating IF_5 with fluorine at 150°C , as a colorless gas with a musty odor [718]. On cooling this gas, colorless crystals are formed, which melt under slight pressure at 6.5°C . Iodine(VII) fluoride is a unique, neutral, simple binary compound in which heptacoordination is present. Numerous attempts at crystal structure determination of solid IF_7 were inconclusive due to disorder problems. A powder neutron diffraction study demonstrated that there are three solid-state phases of IF_7 at ambient pressure. Although the neutron diffraction study is more sensitive to the fluorine atom distribution than earlier X-ray diffraction studies, the high degree of thermal motion prohibits a definitive assessment of the molecular geometry of IF_7 [719]. However, important structural information was obtained from ^{19}F NMR, microwave, vibrational spectra and gas-phase electron diffraction data [720]. The isolated IF_7 molecule **534** (Figure 2.25) has the form of a pentagonal bipyramid belonging to the symmetry group D_{5h} , in which the bonds of the axial F-I-F unit (1.786 \AA) are shorter than those of the more congested equatorial IF_5 unit (1.858 \AA). An attempt to prepare an iodine(VII) compound with a carbon ligand (e.g., Ar_fIF_6) by the reaction of IF_7 with $\text{C}_6\text{F}_5\text{SiX}_3$ ($\text{X} = \text{Me}, \text{F}$), $\text{C}_6\text{F}_5\text{BF}_2$, or $1,4\text{-C}_6\text{F}_4(\text{BF}_2)_2$ was unsuccessful [721].

Two oxyfluorides, IO_2F_3 [722, 723] and IOF_5 [724], were reported in the literature. IO_2F_3 can be synthesized by the reaction of tetrafluoroorthoperiodic acid, HOIOF_4 and SO_3 in the form of a yellow sublimable solid with a melting point of 41°C [723]. According to ^{19}F NMR and Raman spectroscopy, in the liquid state IO_2F_3 exists as a cyclic trimer with *cis*-oxygen bridges, in the boat conformation [722]. The second oxyfluoride, IOF_5 , can be prepared by the interaction of IF_7 with SiO_2 [718]. The high symmetry, C_{4v} , of IOF_5 renders its structure determination very difficult. Nevertheless, on the basis of a combined electron diffraction–microwave study [725] and *ab initio* calculations [724], the structure **535** (Figure 2.25) was determined. In this structure, the axial and the equatorial I-F bonds are of comparable lengths (about 1.826 \AA), the I-O bond distance is 1.725 \AA and the O-I-F_{eq} bond angle is close to 97.2° [724]. IOF_5 reacts with tetramethylammonium fluoride to give a stable, crystalline salt, $\text{Me}_4\text{N}^+\text{IOF}_6^-$ [726]. X-Ray analysis of this salt showed the expected, pentagonal bipyramidal structure for the IOF_6^- anion with the oxygen atom occupying one of the axial positions (structure **536**, Figure 2.25). The I-O bond in this compound is

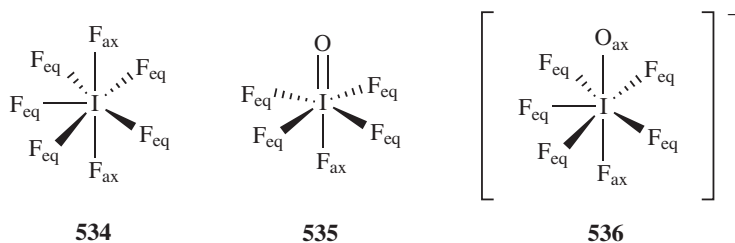


Figure 2.25 Derivatives of iodine(VII).

relatively short (1.75–1.77 Å), which is indicative of a significant double bond character. The axial I–F bonds (1.823 Å) and the equatorial I–F bonds (average 1.88 Å) in IOF_6^- are significantly longer than the corresponding bonds in IF_7 , which can be attributed to greater I–F bond polarities due to the formal negative charge on IOF_6^- [726].

Iodine(VII) oxide, I_2O_7 , is unknown. A mixed iodine(V/VII) oxide, I_4O_{12} , has been reported [648]. The crystal structure of this oxide includes the basic molecular unit I_4O_{12} with two octahedrally coordinated iodine(VII) atoms and two trigonal pyramidal iodine(V) atoms.

Periodic acid and periodates are the most important, commercially available compounds of iodine(VII). Periodates were first prepared in 1833 by oxidation of NaIO_3 with chlorine in alkaline solutions [727]. The industrial preparation of periodates is based on electrolytic oxidation of iodates. Aqueous solutions of periodic acid are best obtained by treating barium paraperiodate with concentrated nitric acid. In solution it exists as a fairly weak orthoperiodic acid, H_5IO_6 , which can be dehydrated to HIO_4 by heating to 100 °C in vacuum [643]. Structural investigations indicate an octahedral configuration about iodine in most periodates [643, 728].

Periodic acid and periodates have found wide application in organic chemistry as powerful oxidizing reagents [729–731]. The well-known periodate glycol oxidation involves the cyclic periodate esters as key intermediates; however, none of the organic periodate esters have been isolated as stable compounds.

References

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