Review

# Chemistry of Polyvalent Iodine

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# Chemistry of Polyvalent Iodine

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## *1. Introduction*

Starting from the early 1990s, the chemistry of polyvalent iodine organic compounds has experienced an explosive development. This surging interest in iodine compounds is mainly due to the very useful oxidizing properties of polyvalent organic iodine reagents, combined with their benign environmental character and commercial availability. Iodine(III) and iodine(V) derivatives are now routinely used in organic synthesis as reagents for various selective oxidative transformations of complex organic molecules. Several areas of hypervalent organoiodine chemistry have recently attracted especially active interest and research activity. These areas, in particular, include the synthetic applications of 2-iodoxybenzoic acid (IBX) and similar oxidizing reagents based on the iodine(V) derivatives, the development and synthetic use of polymer-supported and recyclable polyvalent iodine reagents, the catalytic applications of organoiodine compounds, and structural studies of complexes and supramolecular assemblies of polyvalent iodine compounds.

The chemistry of polyvalent iodine has previously been covered in four books[1−4] and several comprehensive review papers.[5−17] Numerous reviews on specific classes of polyvalent iodine compounds and their synthetic applications have recently been published.[18−61] Most notable are the specialized reviews on [hydroxy(tosyloxy)iodo]benzene,[41]

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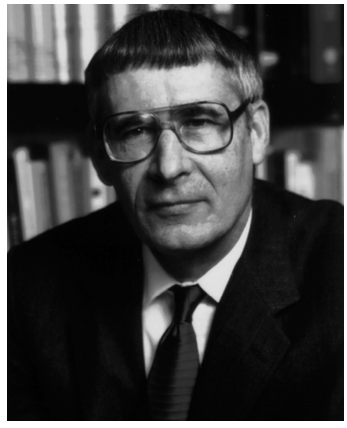
Viktor V. Zhdankin was born in Ekaterinburg, Russian Federation. His M.S. (1978), Ph.D. (1981), and Doctor of Chemical Sciences (1986) degrees were earned at Moscow State University in the research laboratories of Professor Nikolay S. Zefirov. He moved to the University of Utah in 1990, where he worked for three years as Instructor of organic chemistry and Research Associate. In 1993, he joined the faculty of the University of Minnesota Duluth, where he is currently a Professor of Chemistry. He has published over 200 scientific papers, including 21 reviews and book chapters. His main research interests are in the fields of synthetic and mechanistic organic chemistry of hypervalent main-group elements (iodine, xenon, selenium, sulfur, and phosphorus) and organofluorine chemistry.



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the chemistry and synthetic applications of iodonium salts,[29,36,38,42,43,46,47,54,55] the chemistry of iodonium ylides,[56−58] the chemistry of iminoiodanes,[28] hypervalent iodine fluorides,[27] electrophilic perfluoroalkylations,[44] perfluoroorgano hypervalent iodine compounds,[61] the chemistry of benziodoxoles,[24,45] polymer-supported hypervalent iodine reagents,[30] hypervalent iodine-mediated ring contraction reactions,[21] the application of hypervalent iodine in the synthesis of heterocycles,[25,40] the application of hypervalent iodine in the oxidation of phenolic compounds,[32,34,50−53,60] the oxidation of carbonyl compounds with organohypervalent iodine reagents,[37] the application of hypervalent iodine in (hetero-)biaryl coupling reactions,[31] the phosphorolytic reactivity of *o*-iodosylcarboxylates,[33] the coordination of hypervalent iodine,[19] transition metal-catalyzed reactions of hypervalent iodine compounds,[18] radical reactions of hypervalent iodine,[35,39] stereoselective reactions of hypervalent iodine electrophiles,[48] catalytic applications of organoiodine compounds,[20,49] and synthetic applications of pentavalent iodine reagents.[22,23,26,59]

The main purpose of the present review is to summarize the data that appeared in the literature following publication of our previous reviews in 1996 and 2002. In addition, a brief introductory discussion of the most important earlier works is provided in each section. The review is organized according to the classes of organic polyvalent iodine compounds, with emphasis on their synthetic application. Literature coverage is through July 2008.

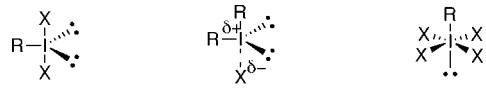
## 2. Structure and Bonding

### 2.1. General Features

Structural aspects of polyvalent iodine compounds have previously been discussed in our original 1996 review[5] and in the 1992 monograph by Varvoglis.[2] More recently, general aspects of structure and bonding in hypervalent organic compounds have been summarized by Akiba in the book *Chemistry of Hypervalent Compounds*[62] and by Ochiai in a chapter in the volume on Hypervalent Iodine Chemistry in the Topics in Current Chemistry Series.[1] A brief summary of the key structural features of iodine(III) and iodine(V) compounds is provided below.

All known organic polyvalent iodine derivatives belong to two general structural types: (1) iodine(III) compounds **1** and **2**, also named $\lambda^3$-iodanes according to IUPAC recommendations, and (2) iodine(V) compounds **3**, or $\lambda^5$-iodanes. The iodine atom in $\lambda^3$-iodanes **1** has a total of 10 electrons and the overall geometry of a distorted trigonal bipyramid with two heteroatom ligands X occupying the apical positions and with the least electronegative carbon ligand R and both electron pairs residing in equatorial positions. Iodonium salts **2**, which have two carbon ligands and a closely associated anionic part of the molecule, have a similar pseudo-trigonal bipyramidal geometry and also belong to $\lambda^3$-iodanes. In agreement with this model, the experimentally determined bond angle R−I−R in iodonium salts and ylides is close to 90°. In the hypervalent model, bonding in $RIX_2$ uses the nonhybridized 5p orbital of iodine in the linear X−I−X bond. Such a linear three-center, four-electron (3c-4e) bond is highly polarized and is longer and weaker compared to a regular covalent bond. This bond is termed "hypervalent", and the presence of this bond in $\lambda^3$-iodanes is responsible for their high electrophilic reactivity.

Organic $\lambda^5$-iodanes **3** have a distorted octahedral structure with the organic group R and the electron pair in the apical positions and four heteroatom ligands X in basal positions. Two orthogonal hypervalent 3c-4e bonds accommodate all ligands X, while the apical group R is connected to iodine by a normal covalent bond using a 5sp-hybridized orbital.[2] In general, only $\lambda^3$- and $\lambda^5$-iodanes with an aromatic group R (R = aryl or hetaryl) have sufficient stability and can be isolated. A few examples of alkyl-substituted $\lambda^3$-iodanes stabilized by strong electron-withdrawing groups (perfluoroalkyl or arylsulfonylmethyl $\lambda^3$-iodanes) have also been isolated. The stable aryl-substituted $\lambda^3$- and $\lambda^5$-iodanes possess high chemical reactivity and are widely used in organic synthesis as oxidants and electrophilic agents, which are commonly referred to as "hypervalent iodine reagents".



1 2 3

R = carbon ligand; X = halogen, O-, or N-ligand

## 2.2. Computational Studies

A relatively small number of theoretical computational studies concerning the structure and reactivity of hypervalent iodine compounds have appeared in the last 10 years.[63−76] Hoffmann and co-workers analyzed the nature of hypervalent bonding in trihalide anions by applying ideas from qualitative MO theory to computational results from density-functional calculations.[63] This systematic, unified investigation showed that the bonding in all of these systems can be explained in terms of the Rundle−Pimentel scheme for electron-rich three-center bonding. The same authors reported an analysis of intermolecular interaction between hypervalent molecules, including diaryliodonium halides $Ar_2IX$, using a combination of density functional calculations and qualitative arguments.[64] Based on fragment molecular orbital interaction diagrams, the authors concluded that the secondary bonding in these species can be understood using the language of donor−acceptor interactions: mixing between occupied states on one fragment and unoccupied states on the other. There is also a strong electrostatic contribution to the secondary bonding. The calculated strengths of these halogen−halogen secondary interactions are all less than 10 kcal $mol^{-1}$.[64]

The self-assembly of hypervalent iodine compounds to macrocyclic trimers was studied using MO calculations. The principal driving force for the self-assembly of iodonium units is the formation of secondary bonding interactions between iodonium units as well as a rearrangement of primary and secondary bonding around iodine to place the least electronegative substituent in the equatorial position for every iodine in the trimer.[65]

Kiprof has analyzed the iodine oxygen bonds of hypervalent 10-I-3 iodine(III) compounds with T-shaped geometry using the Cambridge Crystallographic Database and *ab initio* MO calculations. The statistical analysis of the I−O bond lengths in $PhI(OR)_2$ revealed an average of 2.14 Å and a strong correlation between the two bond lengths.[66] Further theoretical investigation of the mutual ligand interaction in the hypervalent L-I-L′ system has demonstrated that ligands' *trans* influences play an important role in the stability of hypervalent molecules.[67] In particular, combinations of ligands with large and small *trans* influences, as in PhI(OH)OTs, or of two moderately *trans* influencing ligands, as in $PhI(OAc)_2$, are favored and lead to higher stability of the molecule. *Trans* influences also seem to explain why iodosylbenzene, $(PhIO)_n$, adopts an oxo-bridged zigzag polymer structure in contrast to $PhI(OH)_2$, which is monomeric.[67]

The structure and reactivity of several specific classes of hypervalent iodine compounds were theoretically investigated. In particular, Okuyama and Yamataka investigated the reactivity of vinyliodonium ions with nucleophiles by *ab initio* MO (MP2) calculations at the double-ζ (DZ) + d level.[68] It was proposed that interaction of methyl(vinyl)iodonium ion with chlorine anion leads to chloro-$\lambda^3$-iodane $CH_2$═CHI(Me)Cl. Transition states for the $S_N2$, ligand-coupling substitution and for β-elimination were found for reactions at the vinyl group. The barrier to ligand-coupling substitution is usually the lowest in the gas phase, but relative barriers to $S_N2$ and to β-elimination change with the substituents. Effects of solvent on this reaction were evaluated by a dielectric continuum model and found to be large on $S_N2$ substitution but small on ligand-coupling.[68]

Widdowson, Rzepa, and co-workers reported *ab initio* and MNDO-d SCF-MO computational studies of the extrusion reactions of diaryliodonium fluorides.[69,71] The results of these studies, in particular, predicted that the intermediates and transition states in these reactions might involve dimeric, trimeric, and tetrameric structures. The regioselectivity of nucleophilic substitution in these reactions was investigated theoretically and supported by some experimental observations.[69−71]

Goddard and Su have theoretically investigated the mechanism of alcohol oxidation with 2-iodoxybenzoic acid (IBX) on the basis of density functional quantum mechanics calculations.[72] It has been found that the rearrangement of hypervalent bonds, so-called hypervalent twisting, is the rate-determining step in this reaction. Based on this mechanism, the authors explain why IBX oxidizes large alcohols faster than small ones and propose a modification to the reagent predicted to make it more active.[72]

Bakalbassis, Spyroudis, and Tsiotra reported a DFT study on the intramolecular thermal phenyl migration in iodonium ylides. The results of this study support a single-step mechanism involving a five-membered ring transition-state. The frontier-orbital-controlled migration also confirms the different thermal behavior experimentally observed for two different ylides.[77]

Molecular orbital computational studies of (arylsulfonylimino)iodoarenes ($ArINSO_2Ar'$),[73] benziodazol-3-ones,[74] and a series of *ortho*-substituted chiral organoiodine(III) compounds[75] have been reported in the literature. Results of these calculations were found to be in good agreement with X-ray structural data for these compounds.

In a very recent communication, Quideau and co-workers presented DFT calculations of spiroheterocylic iodine(III) intermediates to validate their participation in the $PhI(OAc)_2$-mediated spiroketalization of phenolic alcohols.[76]

## 2.3. Experimental Structural Studies

Numerous X-ray crystal structures have been reported for all main classes of organic polyvalent iodine compounds, and the results of these studies will be briefly discussed in the appropriate sections of this review. Several general areas of structural research on hypervalent organoiodine compounds have recently attracted especially active interest. These areas, in particular, include the preparation and structural study of complexes of hypervalent iodine compounds with crown ethers[78−82] or nitrogen ligands,[83−85] self-assembly of hypervalent iodine compounds into various supramolecular structures,[86−88] and the intramolecular secondary bonding in *ortho*-substituted aryliodine(V) and iodine(III) derivatives.[73,89−99]

Typical coordination patterns in various organic derivatives of iodine(III) in the solid state with consideration of primary and secondary bonding have been summarized by Sawyer and co-workers[100] in 1986 and updated in recent publications.[101−104] Structural features of organic iodine(V) compounds have been discussed in older papers of Martin and coauthors[105,106] and in numerous more recent publications on IBX and related $\lambda^5$-iodanes.[89,93−98,107]

Several important spectroscopic structural studies of polyvalent iodine compounds in the solution have been published.[108−112] Hiller and co-workers reported NMR and LC-MS studies on the structure and stability of 1-iodosyl-4-methoxybenzene and 1-iodosyl-4-nitrobenzene in methanol solution.[108] Interestingly, LC-MS analyses provided evidence that unlike the parent iodosylbenzene, which has a polymeric structure, the 4-substituted iodosylarenes exist in the monomeric form. Both iodosylarenes are soluble in methanol and provide acceptable $^{1}H$ and $^{13}C$ NMR spectra; however, gradual oxidation of the solvent was observed after several hours. Unlike iodosylbenzene, the two compounds did not react with methanol to give the dimethoxy derivative $ArI(OMe)_2$.[108]

Cerioni, Mocci, and co-workers investigated the structure of bis(acyloxy)iodoarenes and benzoiodoxolones in chloroform solution by $^{17}O$ NMR spectroscopy and also by DFT calculations.[109,110] This investigation provided substantial evidence that the T-shaped structure of iodine(III) compounds observed in the solid state is also adopted in solution. Furthermore, the "free" carboxylic groups of bis(acyloxy) iodoarenes show a dynamic behavior, observable only in the $^{17}O$ NMR. This behavior is ascribed to a [1,3] sigmatropic shift of the iodine atom between the two oxygen atoms of the carboxylic groups, and the energy involved in this process varies significantly between bis(acyloxy)iodoarenes and benzoiodoxolones.[110]

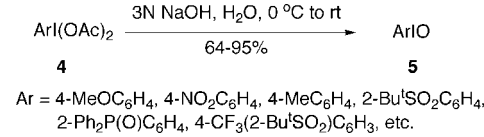
Richter, Koser, and co-workers investigated the nature of species present in aqueous solutions of phenyliodine(III) organosulfonates.[111] It was shown by spectroscopic measurements and potentiometric titrations that PhI(OH)OTs and PhI(OH)OMs upon solution in water undergo complete ionization to give the hydroxy(phenyl)iodonium ion ($PhI^{+}OH$ in hydrated form) and the corresponding sulfonate ions. The hydroxy(phenyl)iodonium ion can combine with [oxo(aquo)iodo]benzene $PhI^{+}(OH_2)O^{-}$, a hydrated form of iodosylbenzene that is also observed in the solution, producing the dimeric $\mu$-oxodiiodine cation $Ph(HO)I-O-I^{+}(OH_2)Ph$ and dication $Ph(H_2O)I^{+}-O-I^{+}(OH_2)Ph$.[111]

Silva and Lopes analyzed solutions of iodobenzene dicarboxylates in acetonitrile, acetic acid, aqueous methanol, and anhydrous methanol by electrospray ionization mass spectrometry (ESI-MS) and tandem mass spectrometry (ESI-MS/MS).[112] The major species found in the solutions of $PhI(OAc)_2$ in acetonitrile, acetic acid, and aqueous methanol are $[PhI(OAc)_2Na]^{+}$, $[PhI(OAc)_2K]^{+}$, $[PhI]^{+}$, $[PhIOAc]^{+}$, $[PhIOH]^{+}$, $[PhIO_2Ac]^{+}$, $[PhIO_2H]^{+}$, and the dimer $[Ph_2I_2O_2Ac]^{+}$. On the other hand, the anhydrous methanol solutions showed $[PhIOMe]^{+}$ as the most abundant species. In contrast to the data obtained for $PhI(OAc)_2$, the ESI-MS spectral data of $PhI(O_2CCF_3)_2$ in acetonitrile suggest that the main species in solutions is iodosylbenzene.[112]

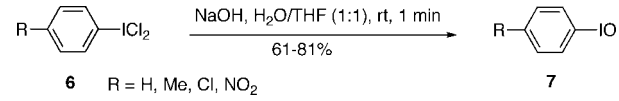
## 3. Iodine(III) Compounds

Iodine(III) compounds (structures **1** and **2**), or $\lambda^3$-iodanes according to the IUPAC nomenclature, are commonly classified by the type of ligands attached to the iodine atom.[2,3,5,6] This section of the review is organized according to the traditional classification and will cover the preparation, structure, and reactivity of iodosylarenes, aryliodine(III) halides, carboxylates, sulfonates, cyclic $\lambda^3$-iodanes, iodonium salts, ylides, and imides with emphasis on their synthetic application.

**Scheme 1**




**Scheme 2**




### 3.1. Iodosylarenes

#### 3.1.1. Preparation

The most important representative of iodosylarenes, iodosylbenzene, is best prepared by alkaline hydrolysis of (diacetoxy)iodobenzene.[113] The same procedure can be used for the preparation of a variety of *ortho*-, *meta*-, and *para*-substituted iodosylbenzenes from the respective (diacetoxy) iodoarenes (Scheme 1).[90−92,108,114] This procedure, for example, was recently used for the preparation of 4-methoxyiodosylbenzene,[108] 4-nitroiodosylbenzene,[108] and pseudocyclic iodosylarenes bearing *tert*-butylsulfonyl[91] or diphenylphosphoryl[92] groups in the *ortho*-position.

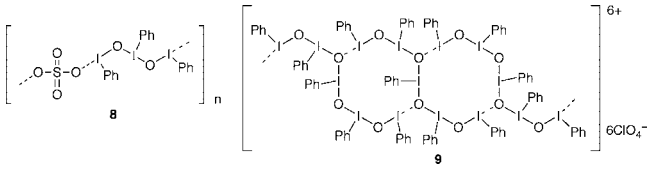
An alternative general procedure for the preparation of iodosylarenes **7** employs the alkaline hydrolysis of (dichloroiodo)arenes under conditions similar to the hydrolysis of (diacetoxyiodo)arenes.[115] A modified procedure employs aqueous tetrahydrofuran as the solvent for the hydrolysis of (dichloroiodo)arenes **6** (Scheme 2).[116]

Iodosylbenzene is a yellowish amorphous powder, which cannot be recrystallized due to its polymeric nature; it dissolves in methanol with depolymerization affording $PhI(OMe)_2$.[117] Heating or extended storage at room temperature results in disproportionation of iodosylbenzene to PhI and a colorless, explosive iodylbenzene, $PhIO_2$. Drying iodosylbenzene at elevated temperatures should be avoided; a violent explosion of 3.0 g of PhIO upon drying at 110 °C in vacuum has recently been reported.[118]

#### 3.1.2. Structural Studies

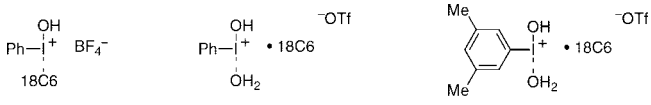
Based on spectroscopic studies, it was suggested that in the solid state iodosylbenzene exists as a zigzag polymeric, asymmetrically bridged structure, in which monomeric units of PhIO are linked by intermolecular I•••O secondary bonds.[6] The I−O bond distances of 2.04 and 2.37 Å and the C−I−O bond angle near 90° have been deduced from EXAFS analysis of polymeric iodosylbenzene.[119] The polymeric structure of iodosylbenzene was also theoretically analyzed by density functional theory computations at the B3LYP level, and in particular, the importance of the presence of a terminal hydration water in its zigzag polymeric structure HO-$(PhIO)_n$-H was established.[120] The zigzag asymmetrically bridged structure of $(PhIO)_n$ has recently been confirmed by single crystal X-ray diffraction studies of the oligomeric sulfate **8** and perchlorate **9** derivatives.[87,121] In particular, iodine atoms in the $(PhIO)_3$ fragment of the oligomeric sulfate **8** exhibit a T-shaped intramolecular geometry typical of trivalent iodine with O−I−O and O−I−C bond angles close to 180° (166.54−177.99) and 90° (79.18−92.43), respectively. The I−O bond distances in the $(PhIO)_3$ fragment of sulfate **8** vary in a broad range of

1.95−2.42 Å.[121] The single crystal X-ray crystal study of the oligomeric perchlorate **9** 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.[87] The oligomer **8** was prepared by the treatment of $PhI(OAc)_2$ with aqueous $NaHSO_4$, while product **9** precipitated from dilute aqueous solutions of PhI(OH)OTs and $Mg(ClO_4)_2$. 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 $PhI^+(OH_2)O^-$ in aqueous solution under reaction conditions.



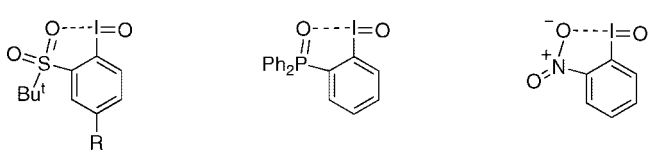
**8** **9**

Ochiai and co-workers have reported the preparation, X-ray crystal structures, and useful oxidizing reactions of activated iodosylbenzene monomer complexes with 18C6 crown ether.[19,78] Reaction of iodosylbenzene with $HBF_4-Me_2O$ in the presence of equimolar 18C6 in dichloromethane afforded quantitatively the stable, crystalline crown ether complex **10**, which is soluble in MeCN, MeOH, water, and dichloromethane. X-ray analysis revealed a protonated iodosylbenzene monomer structure **10** stabilized by intramolecular coordination with the crown ether oxygen atoms.[78] The aqua complexes of iodosylarenes **11** and **12** 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 **11** revealed a T-shaped structure, ligated with one water molecule at the apical site of the iodine(III) atom of 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.[122]



**10** **11** **12**

The *ortho*-substituted iodosylarenes **13**−**16** bearing *tert*-butylsulfonyl,[91] diphenylphosphoryl,[92] or nitro[99] groups have a monomeric, pseudocyclic structure due to the replacement of intermolecular I•••O interactions with intramolecular secondary bonding. The structure of product **13** was established by single crystal X-ray analysis.[89]



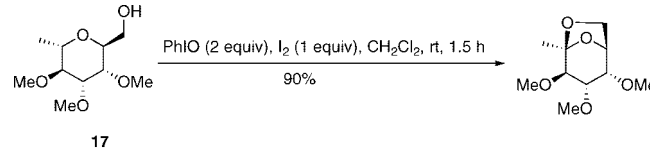
**13** (R = H)
**14** (R = $CF_3$)

**15** **16**

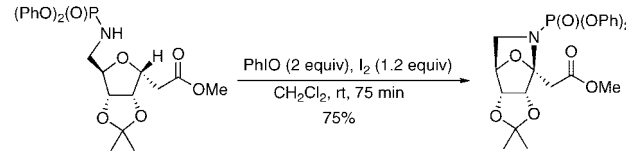
### 3.1.3. Oxidations with Iodosylarenes

Iodosylbenzene is an effective oxidizing reagent, but its insolubility, due to the polymeric structure, significantly restricts its practical usefulness. The overwhelming majority

**Scheme 3**

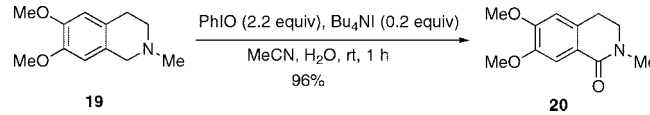


**17**



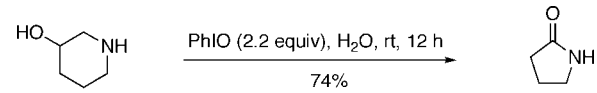
**18**

**Scheme 4**



**19** **20**

**Scheme 5**



**21** **22**

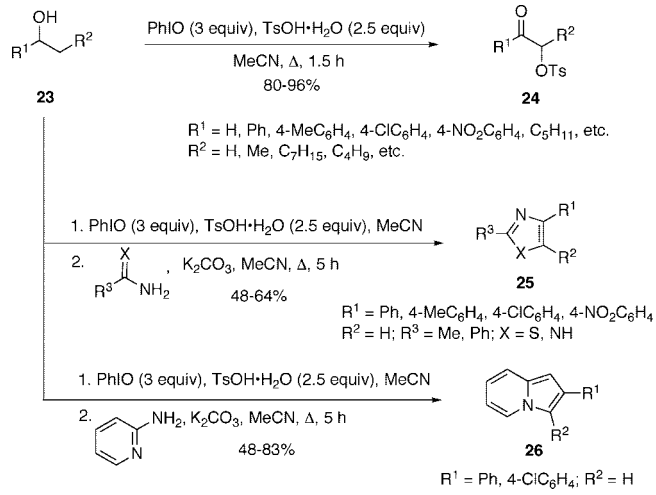
of the known reactions of iodosylbenzene require the presence of a hydroxylic solvent (water or alcohols) or a catalyst (Lewis acid, bromide or iodide anions, transition metal complex, etc.) that can effectively depolymerize $(PhIO)_n$, generating the reactive monomeric species. Numerous examples of such oxidations have been reported in our previous reviews[5,6] and include, for example, selective oxidation of alcohols[123,124] or sulfides[125] with $(PhIO)_n$/KBr/$H_2O$, the oxidation of silyl enol ethers to α-hydroxy- and α-alkoxy-substituted carbonyl compounds using $(PhIO)_n$/$BF_3$•$Et_2O$ in water or an alcohol,[126,127] the generation and sequential fragmentation of radicals from alcohols or amides (e.g., **17** and **18**) with the PhIO-$I_2$ system (Scheme 3),[128−130] and the oxidation of tetrahydroisoquinolines **19** by $(PhIO)_n$/$Bu_4NI$/$H_2O$ to the respective lactams **20** (Scheme 4).[131]

Several new oxidations with $(PhIO)_n$ have been recently reported. The oxidation of 3-hydroxypiperidine **21** with iodosylbenzene in water affords 2-pyrrolidinone **22** directly in good yield (Scheme 5).[132] The mechanism of this reaction probably involves oxidative Grob fragmentation yielding imino aldehyde, which upon hydrolysis affords 2-pyrrolidinone by a cyclization−oxidation sequence.

Togo and co-workers have reported the preparation of α-tosyloxy ketones and aldehydes **24** in good yields from alcohols **23** by treatment with iodosylbenzene and *p*-toluenesulfonic acid monohydrate. This method can also be used for the direct preparation of thiazoles (**25**, X = S), imidazoles (**25**, X = NH), and imidazo[1,2-a]pyridines **26** from alcohols in good to moderate yields by the successive treatment with iodosylbenzene and *p*-toluenesulfonic acid monohydrate, followed by thioamides, benzamidine, and 2-aminopyridine, respectively (Scheme 6).[133]

The reactions of 4-acyloxybut-1-enylsilanes **27** with iodosylbenzene in the presence of $BF_3$•$OEt_2$ afford 4-acyloxy-2-oxobutylsilanes **28**, **31**, and 3-acyloxytetrahydrofuran-2-ylsilanes **29** and **32** via a 1,3-dioxan-2-yl cation intermediate, which is generated by participation of the acyloxy group

**Scheme 6**




during the electrophilic addition of iodine(III) species to the substrate (Scheme 7).[134]

Ochiai and co-workers have reported several useful oxidations employing the activated iodosylbenzene species.[19,78,122,135,136] The monomeric iodosylbenzene complex **10** in the presence of water can cleave the carbon−carbon double bond of indene **33** with the formation of dialdehyde **34** (Scheme 8).[135] Similar oxidative cleavage of various alkenes can be performed by using iodosylbenzene in water in the presence of $HBF_4$. This convenient procedure provides a safe alternative to the ozonolysis of alkenes.[135]

Reaction of 3-phenylpropanol **35** with activated iodosylbenzene complex **10** in dichloromethane in the presence of $BF_3$•$OEt_2$ afforded directly the 6-chromanyl(phenyl)iodonium salt **36** (isolated as a complex with 18C6 crown ether) through tandem oxidative intramolecular cyclization, yielding chroman, and its subsequent regioselective reaction with complex **10**, leading to the final product **36** (Scheme 9).[136]

The oligomeric iodosylbenzene sulfate $(PhIO)_3$•$SO_3$ (structure **8**) is a readily available, stable, and water-soluble reagent with a reactivity pattern similar to that of activated iodosylbenzene. It reacts with alkenes, alcohols, and aryl alkyl sulfides in aqueous acetonitrile at room temperature to afford the respective products of oxidation **37**−**40** in good yields (Scheme 10).[88]

Iodosylbenzene is a useful reagent for nucleophilic epoxidation of electron-deficient alkenes, such as tetrasubstituted perfluoroalkenes[137] and α,β-unsaturated carbonyl compounds.[118,138] In a specific example, iodosylbenzene reacts with enones **41** to furnish the corresponding epoxides **42** in generally high yields (Scheme 11).[118]

Only very few ArIO other than iodosylbenzene have been used as reagents. The only exception is represented by *ortho*- and *meta*-iodosylbenzoic acids. The *o*-iodosylbenzoic acid (IBA) has a cyclic structure of benziodoxolone and is discussed in section 3.8 of this review. The *m*-iodosylbenzoic acid has recently found some synthetic application as an efficient, safe, and recyclable oxidant.[103,139,140] In particular, *m*-iodosylbenzoic acid in the presence of iodine is a convenient reagent for oxidative iodination of arenes at room temperature in acetonitrile solution. Separation of pure products is conveniently achieved by scavenging any aryl iodide by ion exchange with ion-exchange resin IRA-900 (hydroxide form). The reduced form of the reagent, *m*-iodobenzoic acid, can be easily recovered from the ion-exchange resin or from the basic aqueous solution by simple acidification with HCl.[140]

### 3.1.4. Transition Metal-Catalyzed Oxidations

The oxidation reactions of iodosylarenes can be effectively catalyzed by metal salts and complexes.[6] Iodosylbenzene is widely used as the most efficient terminal oxidant—source of oxygen in biomimetic oxidations catalyzed by metalloporphyrins and other transition metal derivatives.[141−145] Recent examples of transition metal-catalyzed oxidations employing iodosylbenzene include the hydroxylation of hydrocarbons,[146−151] the transition metal-mediated epoxidation of alkenes,[138,152−169] oxidation of alcohols[170,171] or silyl ethers[172] to carbonyl compounds, δ-sultone formation through Rh-catalyzed C−H insertion,[173] and oxidation of organic sulfides[163,174,175] to sulfoxides.

Iodosylarenes other than iodosylbenzene have also been used in the transition metal-catalyzed oxidation reactions. The soluble, monomeric *ortho*-substituted iodosylarene **13** (see section 3.1.2) can serve as an alternative to iodosylbenzene in the (porphyrin)manganese(III)-catalyzed alkene epoxidation reactions.[157] A convenient recyclable reagent, *m*-iodosylbenzoic acid, selectively oxidizes primary and secondary alcohols to the respective carbonyl compounds in the presence of $RuCl_3$ (0.5 mol %) at room temperature in aqueous acetonitrile.[139] Separation of pure products in this case is achieved by simple extraction of the basic aqueous solution, and the reduced form of the reagent, *m*-iodobenzoic acid, can be easily recovered from the aqueous solution by simple acidification.

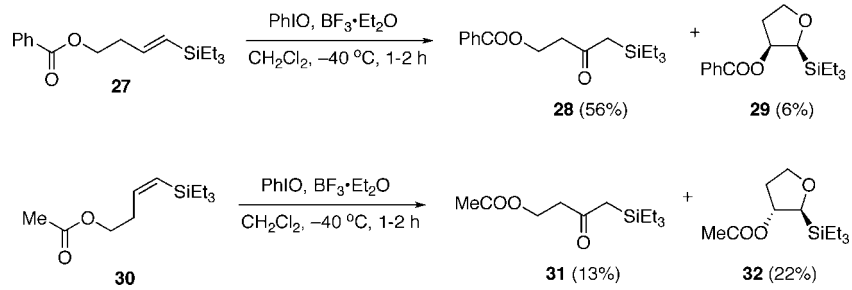
## 3.2. Fluorides

### 3.2.1. Preparation

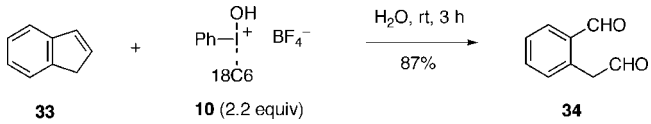
A clean and selective, although relatively expensive procedure for the preparation of (difluoroiodo)arenes **43** consists of the treatment of iodoarenes with xenon difluoride in dichloromethane (Scheme 12) in the presence of anhydrous hydrogen fluoride.[176,177] This method works well for the fluorination of iodoarenes with electron-donating or electron-withdrawing substituents; the latter, however, require longer reaction times. (Difluoroiodo)arenes **43** are hygroscopic and highly hydrolizable compounds, which make their separation and crystallization extremely difficult. Since xenon is the only byproduct in this reaction (Scheme 12), the resulting dichloromethane solutions contain essentially pure fluorides **43**, 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. 2,3,5,6-Tetrafluoropyridin-4-yliodine difluoride, 4-$(C_5F_4N)IF_2$ was prepared in 84% yield by the reaction of 4-$(C_5F_4N)I$ with $XeF_2$ in dichloromethane at room temperature.[178] Likewise, the fluorination of 3-iodo-4-methylfurazan with xenon difluoride in acetonitrile at room temperature was recently used for the preparation of 3-(difluoroiodo)-4-methylfurazan.[179]

A variety of other powerful fluorinating reagents, such as $F_2$, ClF, $CF_3OCl$, $BrF_5$, $C_6F_5BrF_2$, $C_6F_5BrF_4$, and $XeF_2/BF_3$, can be used for the preparation of (difluoroiodo)arenes derived from polyfluoro-substituted iodoarenes.[180−182] A convenient procedure for the preparation of (difluoroiodo)-benzene and 4-(difluoroiodo)toluene consists of direct fluo-

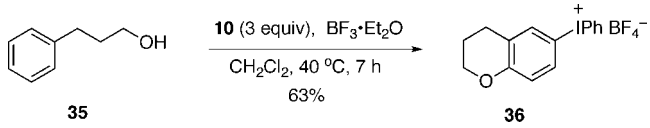
**Scheme 7**



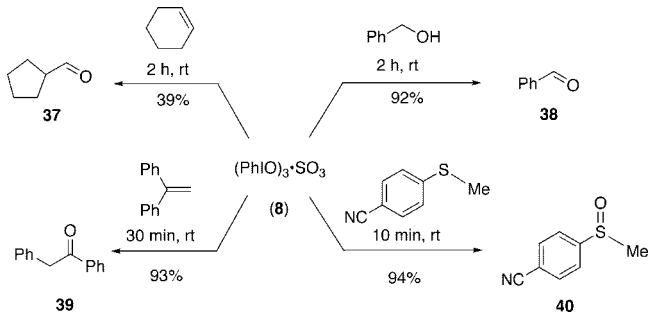

**Scheme 8**



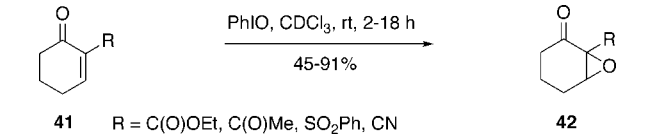

**Scheme 9**



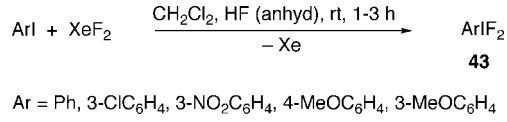

**Scheme 10**




**Scheme 11**



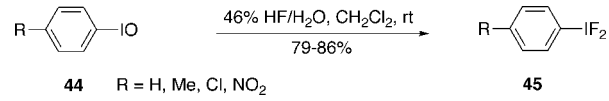

**Scheme 12**




rination of the respective iodoarenes with the commercially available fluorinating reagent Selectfluor in acetonitrile solution.[183] Various mixed (fluoroiodo)arene triflates, ArIF(OTf), can be generated in situ by fluorination of the respective iodoarenes with xenon fluorotriflate, FXeOTf.[184,185]

The *para*-substituted (difluoroiodo)arenes can be effectively prepared by the electrochemical fluorination of the respective iodoarenes.[186,187] In this procedure, the electrosynthesis of $ArIF_2$ is accomplished by the anodic oxidation of iodoarenes with $Et_3N•3HF$ or $Et_3N•5HF$ in anhydrous acetonitrile using a divided cell. This procedure works especially well for the preparation of 4-$NO_2C_6H_4IF_2$, which precipitates from the electrolytic solution in pure form during the electrolysis. The other *para*-substituted (difluoroiodo)arenes, such as $TolIF_2$ and 4-$MeOC_6H_4IF_2$, can be generated

**Scheme 13**




similarly and used without isolation as in-cell mediators for the following reactions.[186,187]

An older, common procedure for the preparation of (difluoroiodo)arenes involves a one-step reaction of mercuric oxide and aqueous hydrofluoric acid with the (dichloroiodo)arenes in dichloromethane.[188] The resulting solution of (difluoroiodo)arenes in dichloromethane can be used in the subsequent reactions without additional purification. A drawback of this method is the use of a large quantity of harmful HgO in order to remove the chloride ion from the reaction mixture. A convenient modified procedure without the use of HgO consists of the treatment of iodosylarenes **44** with 40−46% aqueous hydrofluoric acid (Scheme 13) followed by crystallization of products **45** from hexane.[116,189] It is important that the freshly prepared iodosylarenes **44** are used in this procedure.

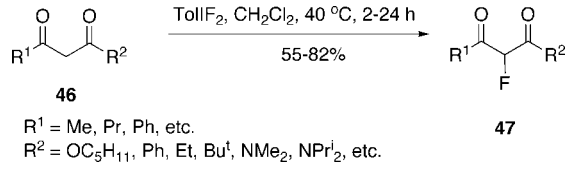
### 3.2.2. Structural Studies

Only a few examples of structural studies of organoiodofluorides, $RIF_2$, have been reported in the literature. Single crystal X-ray diffraction studies of trifluoromethyliodofluoride, $CF_3IF_2$, revealed a distorted T-shaped structure with the I−F bond lengths 1.982(2) Å and the F−I−F angle 165.4(2)°.[190] Theoretical studies of $CF_3IF_2$ by *ab initio* and DFT calculations have also been reported.[191] The structure of pentafluorophenyliodofluoride, $C_6F_5IF_2$, has been investigated by single crystal X-ray crystallography and by multinuclear NMR, IR, and Raman spectroscopy.[180] The X-ray crystal and molecular structures of *p*-(difluoroiodo)toluene and *m*-(difluoroiodo)nitrobenzene had been reported in a Ph.D. dissertation in 1996.[192]

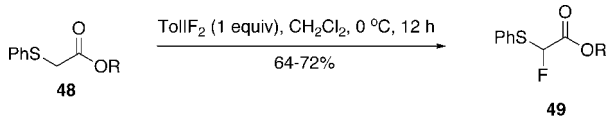
### 3.2.3. Reactions

(Difluoro)iodoarenes are powerful and selective fluorinating reagents toward various organic substrates. Various β-dicarbonyl compounds can be selectively fluorinated at the α-position by 4-(difluoroiodo)toluene and HF-amine complex.[193] This fluorination can also be performed electrochemically using 4-(difluoroiodo)toluene generated in situ from iodotoluene in $Et_3N−5HF$ in an undivided cell under constant potential.[187] More recently, Hara and co-workers have reported a modified procedure that allows us to prepare monofluorinated products **47** from β-ketoesters, β-ketoamides, and β-diketones **46** in good yields under mild conditions without the addition of the HF−amine complexes (Scheme 14).[194] Ketones cannot be directly fluorinated by (difluoro)-

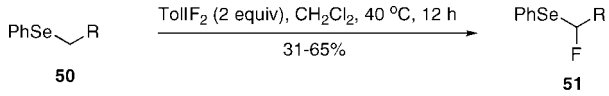
**Scheme 14**



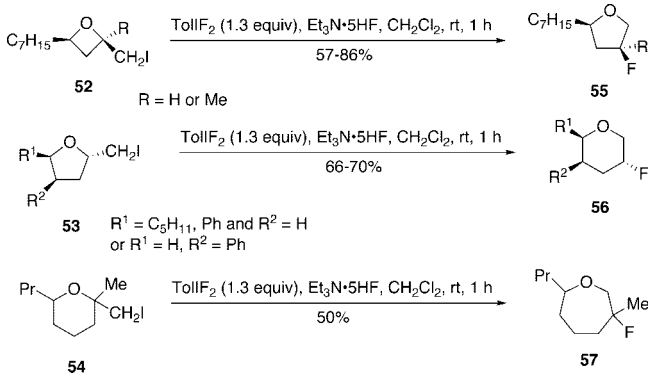

**Scheme 15**




**Scheme 16**




**Scheme 17**




iodoarenes; however, α-fluoroketones can be prepared by the reaction of silyl enol ethers with 4-(difluoroiodo)toluene in the presence of $BF_3$•$OEt_2$ and the $Et_3N$-HF complex.[195]

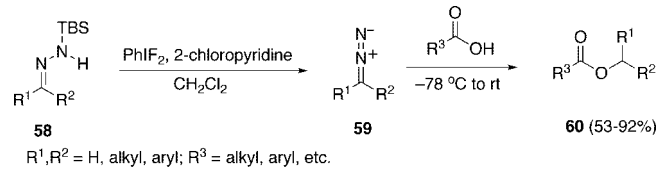
Treatment of α-phenylthio esters **48** with 1 equiv of 4-(difluoroiodo)toluene affords the α-fluoro sulfides **49** in good overall yield through a fluoro-Pummerer reaction (Scheme 15).[196] Addition of a second equivalent of 4-(difluoroiodo)toluene in this reaction produced α,α-difluoro sulfides, and a third led to α,α-difluoro sulfoxides. This sequential fluorination−oxidation behavior was exploited in the one-pot synthesis of 3-fluoro-2(5*H*)-furanone starting from (3*R*)-3-fluorodihydro-2(3*H*)-furanone.[196] The α-monofluorination of sulfanyl amides can be achieved by treatment of *σ*-phenylsulfanylacetamides with 1 equiv of 4-(difluoroiodo)toluene under similar conditions.[197]

Arrica and Wirth have reported the monofluorination of a series of *σ*-acceptor-substituted selenides **50** using (difluoroiodo)toluene (Scheme 16).[189] Although the yields of products **51** are only moderate, the reactions are usually very clean and, under the reaction conditions used, no further oxidized products are observed.

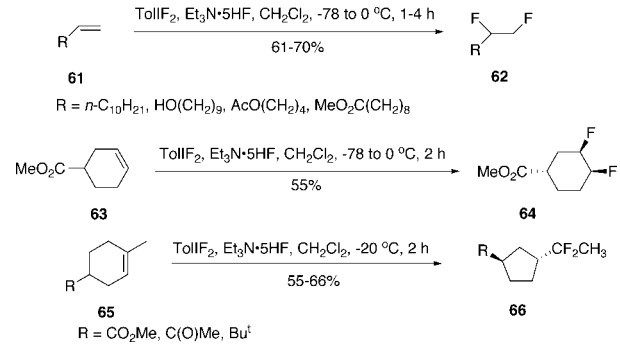
Fluorinated five- to seven-membered cyclic ethers **55**−**57** were stereoselectively synthesized from iodoalkyl-substituted four- to six-membered cyclic ethers **52**−**54** by a fluorinative ring-expansion reaction using (difluoroiodo)toluene (Scheme 17).[198]

Furrow and Myers have developed a convenient general procedure for the esterification of carboxylic acids with

**Scheme 18**




**Scheme 19**




diazoalkanes **59** generated in situ by the oxidation of *N*-*tert*-butyldimethylsilylhydrazones **58** with (difluoroiodo)benzene (Scheme 18).[199] This protocol affords various esters **60** from a broad range of carboxylic acids and, compared to the traditional esterification using diazoalkanes, offers significant advantages with regard to safety, because the diazo intermediates **59** neither are isolated nor achieve appreciable concentrations during the reaction.

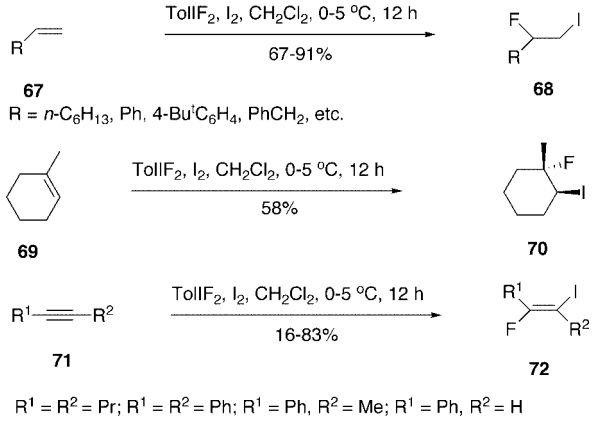
4-(Difluoroiodo)toluene reacts with terminal alkenes **61** to give *vic*-difluoroalkanes **62** in moderate yields (Scheme 19).[200] The cyclohexene derivative **63** reacts with this reagent under similar conditions with the stereoselective formation of *cis*-difluoride **64**.[200] The observed *syn*-stereoselectivity of this difluorination is explained by a two-step mechanism involving the *anti*-addition of the reagent to the double bond through a cyclic iodonium intermediate at the first step and then nucleophilic substitution of iodotoluene with fluoride anion in the second step. The reaction of substituted cyclic alkenes **65** with 4-(difluoroiodo)toluene and $Et_3N$−5HF results in a fluorinating ring-contraction with the selective formation of difluoroalkyl-substituted cycloalkanes **66** (Scheme 19).[201]

The fluorination of alkenes **67** and **69** and alkynes **71** with 4-(difluoroiodo)toluene in the presence of iodine affords *vic*-fluoroiodoalkanes **68** and **70** and fluoroiodoalkenes **72** in moderate to good yields (Scheme 20).[202] This reaction proceeds in a Markovnikov fashion and with prevalent *anti*-stereoselectivity via the initial addition of the electrophilic iodine species followed by nucleophilic attack of fluorine anion. The analogous reaction of alkenes and alkynes with 4-(difluoroiodo)toluene in the presence of diphenyl diselenides affords the respective products of phenylselenofluorination in good yields.[203]

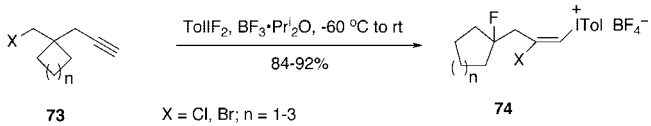
The reaction of 4-(difluoroiodo)toluene with 5-halopentynes with a four-, five-, or six-membered carbocycle **73** afforded the ring-expanded (*E*)-*δ*-fluoro-*β*-halovinyl iodonium tetrafluoroborates **74** stereoselectively in high yields (Scheme 21).[204] This reaction proceeds via a sequence of $\lambda^3$-iodanation-1,4-halogen shift-ring enlargement-fluorination steps.

4-(Difluoroiodo)toluene and other (difluoroiodo)arenes are commonly employed as reagents for the preparation of iodonium salts (see also section 3.9).[205−208] Especially useful

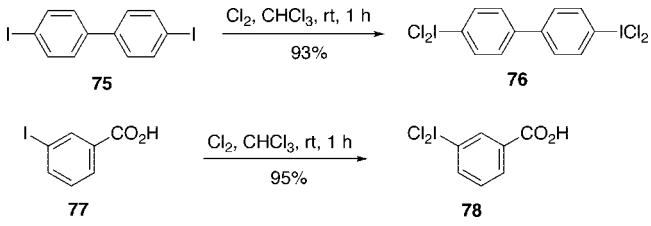
**Scheme 20**




**Scheme 21**




**Scheme 22**




is the reaction of potassium organotrifluoroborates with 4-(difluoroiodo)toluene, affording various iodonium tetrafluoroborate salts under mild conditions.[205]

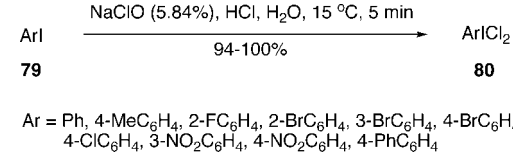
## 3.3. Chlorides

### 3.3.1. Preparation

The most general approach to (dichloroiodo)arenes involves the direct chlorination of iodoarenes with chlorine in a suitable solvent, such as chloroform or dichloromethane.[209] 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.[210] The direct chlorination of iodoarenes **75** and **77** has recently been used for the preparation of 4,4′-bis(dichloroiodo)biphenyl **76** and 3-(dichloroiodo)benzoic acid **78** (Scheme 22), which are convenient recyclable hypervalent iodine reagents.[211]

In order to avoid the use of elemental chlorine, the chlorination of iodoarenes can be effected 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 $HNO_3$, $NaBO_3$, $Na_2CO_3•H_2O_2$, $Na_2S_2O_8$, $CrO_3$, and the urea−$H_2O_2$ complex.[212−214] For example, the chlorination of iodoarenes in a biphasic mixture of carbon tetrachloride and concentrated hydrochloric acid in the presence of $Na_2S_2O_8$ affords the corresponding (dichloroiodo)arenes in 60−100% crude yields.[213] A recently reported convenient and mild approach to (dichloroiodo)arenes **80** consists of the chlorination of iodoarenes **79** using concentrated hydrochloric acid and aqueous sodium hypochlorite (Scheme 23).[215] Sodium chlorite, $NaClO_2$, can also be used in this procedure; however, in this case, the chlorination takes a longer time

**Scheme 23**




(3 h at room temperature) and the yields of products **80** are generally lower.[215]

The other synthetic approaches to (dichloroiodo)arenes are represented by the one-pot oxidative iodination/chlorination of arenes with iodine and the appropriate oxidant in hydrochloric acid[216] and by the treatment of iodosylbenzene with trimethylsilyl chloride.[217,218]

(Dichloroiodo)arenes are generally isolated as light and heat sensitive yellow crystalline solids, which are insufficiently stable for extended storage even at low temperatures.

### 3.3.2. Structural Studies

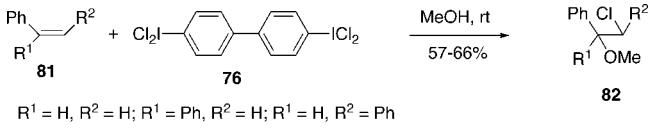
Several X-ray crystallographic studies of organoiododichlorides, $RICl_2$, have been reported in the literature. The first X-ray crystal structures of $PhICl_2$[219] and 4-$ClC_6H_4ICl_2$[220] published in 1953 and 1956 were imprecise by modern standards. More recently, a good quality structure of $PhICl_2$ obtained at low temperature has been reported.[221] The molecule of $PhICl_2$ has the characteristic T-shape with primary I−Cl bond distances of 2.47 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 zig-zagged chain, in which one of the chlorine atoms interacts with the iodine of the next unit with an intermolecular I•••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 pseudooctahedron.[221]

X-ray structures of two sterically encumbered (dichloroiodo)arenes, 2,4,6-$Pr^i_3C_6H_2ICl_2$[222] and $ArICl_2$ [Ar = 2,6-bis(3,5-dichloro-2,4,6-trimethylphenyl)benzene],[223] 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 I•••Cl bond distance in this compound is 3.816 Å, which indicates a significant reduction of intermolecular association as compared to $PhICl_2$.[223] The recently reported X-ray crystal structure of *o*-nitrobenzeneiododichloride, 2-$NO_2C_6H_4ICl_2$, does not show any significant intramolecular interaction between the iodine(III) center and the oxygen atom of the nitro group in the *ortho* position (I•••O bond distance 3.0 Å).[99]

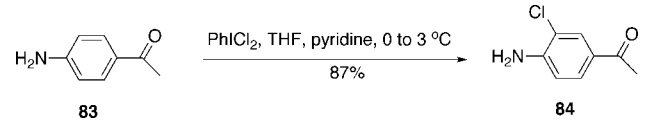
The X-ray structure of the $PhICl_2$ adduct with tetraphenylphosphonium chloride, $[Ph_4P]^+[PhICl_3]^-$, has been reported.[224] The $[PhICl_3]^-$ anions in this structure have a planar coordination environment at the iodine atom. The I−Cl bond length of the chlorine atom *trans* to the Ph group is much longer (3.019 Å) than the bond distance to the *cis* Cl atoms (2.504 Å).[224]

X-ray crystal structures of two perfluoroalkyliododichlorides, $CF_3CH_2ICl_2$ and $CHF_2(CF_2)_5CH_2ICl_2$, have been reported.[225] In comparison to $PhICl_2$, which has a simple chain structure, perfluoroalkyliododichlorides have more complicated structures in which weak interactions between chains, coupled with aggregation of perfluoro groups, result in the formation of layers.

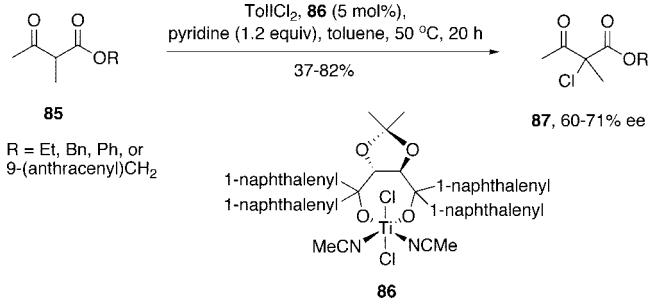
**Scheme 24**



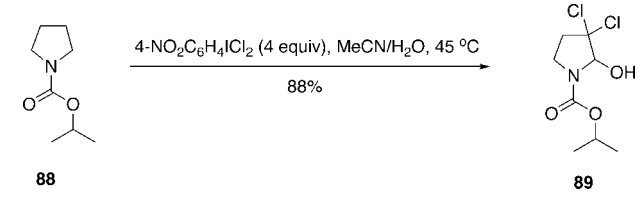

**Scheme 25**



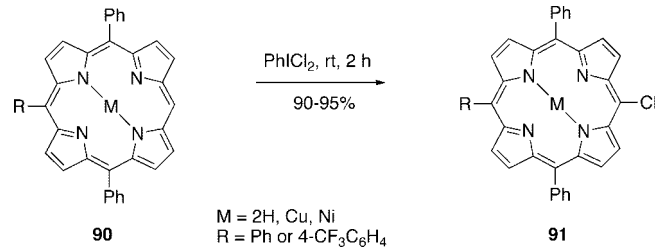

**Scheme 26**



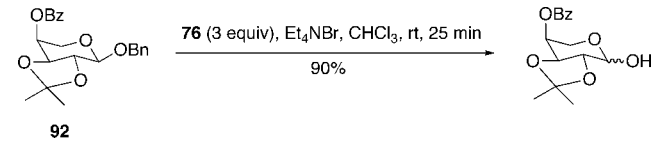

**Scheme 27**




**Scheme 28**




**Scheme 29**




### 3.3.3. Reactions

(Dichloroiodo)arenes have found practical application as reagents for chlorination or other oxidative transformations of various organic substrates. Chlorinations of alkanes with (dichloroiodo)arenes proceed via a radical mechanism and generally require photochemical conditions or the presence of radical initiators in solvents of low polarity, such as chloroform or carbon tetrachloride.[5] The chlorination of alkenes may follow a radical or ionic mechanism depending on the conditions.[211,226−228] For example, norbornene reacts with (dichloroiodo)benzene under radical conditions in nonpolar solvents with the formation of 1,2-dichlorides as the only detectable products.[226] In contrast, reactions of (dichloroiodo)benzene with various monoterpenes in methanol have an ionic mechanism and afford the respective products of chloromethoxylation of the double bond with high regio- and stereoselectivity.[228] Likewise, the reaction of 4,4′-bis(dichloroiodo)biphenyl **76** with styrene derivatives **81** in methanol affords exclusively the products of electrophilic chloromethoxylation **82** (Scheme 24).[211]

(Dichloroiodo)arenes can also be used for the chlorination of electron-rich aromatic compounds. Aminoacetophenone **83** is selectively chlorinated with (dichloroiodo)benzene to give product **84** in good yield (Scheme 25). This process can be scaled up to afford 24.8 kg of product **84** with 94% purity.[210]

(Dichloroiodo)toluene was found to be a suitable chlorinating agent in the catalytic asymmetric chlorination of $\beta$-keto esters **85**, catalyzed by the titanium complex **86**, leading to the respective α-chlorinated products **87** in moderate to good yields and enantioselectivities (Scheme 26). The enantioselectivity of this reaction showed a remarkable temperature dependence, and the maximum selectivity was obtained at 50 °C.[229]

The reaction of *N*-protected pyrrolidine **88** with 4-nitrobenzeneiododichloride affords α-hydroxy-$\beta$,$\beta$-dichloropyrrolidine **89** as the main product (Scheme 27) via a complex ionic mechanism involving a triple C−H bond activation. This oxidative pathway has been demonstrated to be general for several saturated, urethane protected nitrogen heterocyclic systems.[218]

Treatment of 5,10,15-trisubstituted porphyrins **90** with (dichloroiodo)benzene affords the corresponding meso-chlorinated porphyrins **91** (Scheme 28).[230] The reactions of trisubstituted Zn-porphyrins lead to the products of coupling, meso, meso-linked bisporphyrins, along with the meso-chlorinated products. The chlorination of 5,10,15,20-tetraarylporphyrins, in which all meso-positions are substituted, under similar conditions affords $\beta$-monochlorinated products in high yields.[230]

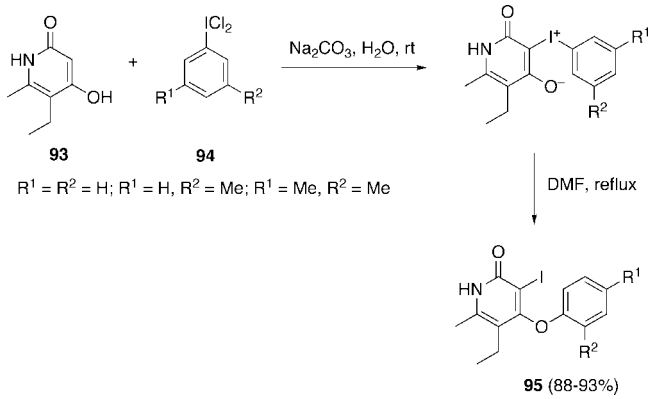
(Dichloroiodo)arenes have been applied in various oxidative transformations of organic substrates. An efficient and mild procedure has been described for the oxidation of different types of alcohols to carbonyl compounds using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as the catalyst and (dichloroiodo)benzene as a stoichiometric oxidant at 50 °C in chloroform solution in the presence of pyridine.[215] Under these conditions, 1,2-diols are oxidized to α-hydroxy ketones or α-diketones depending upon the amount of $PhICl_2$ used. A competitive study has shown that this system preferentially oxidizes aliphatic secondary alcohols over aliphatic primary alcohols.[215]

A simple and mild system using bis(dichloroiodo)biphenyl **76** in combination with tetraethylammonium bromide at room temperature has been developed for selective debenzylation of sugars. Acetates, benzoate, and sensitive glycosidic linkages are unaffected under the reaction conditions. A specific example of the debenzylation of benzyl 4-O-benzoyl 2,3-O-isopropylidene-α-L-arabinopyranoside **92** is shown in Scheme 29.[231]

An efficient route to the 3-iodo-4-aryloxypyridinones **95**, which are highly potent non-nucleoside inhibitors of HIV-1 reverse transcriptase, has been developed starting from 4-hydroxy-substituted pyridinone **93** and (dichloroiodo)arenes **94** (Scheme 30).[232,233]

Various organic substrates, such as enol silyl ethers, ketene silyl acetals, $\beta$-dicarbonyl compounds,[234] alkynes,[235] and

**Scheme 30**




*para*-unsubstituted phenols and naphthols,[236] can be effectively thiocyanated with the combination reagent $PhICl_2$/$Pb(SCN)_2$. More recently, Prakash and co-workers have reported an improved method for the thiocyanation of 2-arylindan-1,3-diones, phenols, and anilines using a reagent combination of (dichloroiodo)benzene and potassium thiocyanate in dry dichloromethane.[237] For example, the *para*-unsubstituted phenols and anilines **96** are efficiently converted under these reaction conditions to the respective *p*-thiocyanato derivatives **97** in high yields (Scheme 31).

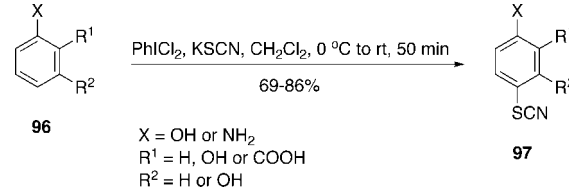
Very recently, Zhang and co-workers have reported the application of (dichloroiodo)benzene in combination with sodium azide for the effective synthesis of carbamoyl azides from aldehydes.[238]

(Dichloroiodo)benzene is commonly used as a reagent for the oxidation or chlorination of various transition metal complexes. Recent examples include the oxidation of a d8•••d10 heterobimetallic Pt(II)−Au(I) complex to give the d7−d9 Pt(III)−Au(II) complex containing a Pt(III)−Au(II) bond,[239] and oxidations or chlorinations of palladium,[240,241] cobalt,[242] vanadium,[243] and molybdenum[244] complexes. Several examples of Pd-catalyzed chlorinations of organic substrates using (dichloroiodo)benzene have also been reported.[245,246]

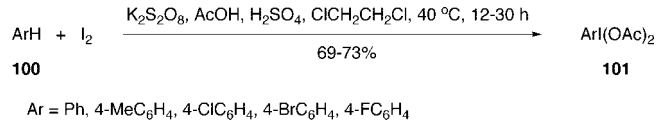
## 3.4. [Bis(acyloxy)iodo]arenes

[Bis(acyloxy)iodo]arenes, $ArI(O_2CR)_2$, are the most important, well investigated, and practically useful organic derivatives of iodine(III). Two of them, (diacetoxyiodo)benzene, commonly abbreviated as DIB, PID, PIDA (phenyliodine diacetate), IBD, or IBDA (iodosobenzene diacetate), and [bis(trifluoroacetoxy)iodo]benzene, abbreviated as BTI or PIFA [phenyliodine bis(trifluoroacetate)], are commercially available and widely used oxidizing reagents. In this review, the abbreviations DIB and BTI, originally suggested by Varvoglis,[2] will be used. Over a thousand research papers dealing mainly with various synthetic applications of DIB and BTI have been published since the year 2000. The use of [bis(acyloxy)iodo]arenes as precursors to other iodine(III) compounds and as the reagents for oxidation of alkynes, allenes, alkenes, enolizable ketones, electron-rich aromatic compounds, alcohols, organic derivatives of nitrogen, phosphorus, sulfur, selenium, tellurium, and other organic substrates has been discussed in previous reviews.[2,5,6] In this section, the preparation, structural studies, and typical recent examples of synthetic applications of [bis(acyloxy)iodo]arenes are overviewed.

**Scheme 31**

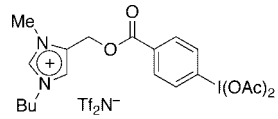



**Scheme 32**

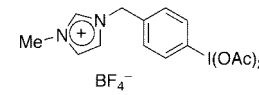



### 3.4.1. Preparation

Two general approaches are used for the preparation of [bis(acyloxy)iodo]arenes: (1) the oxidation of iodoarenes in the presence of a carboxylic acid and (2) a ligand exchange reaction of the readily available DIB with an appropriate carboxylic acid. The most common and practically important representative of [bis(acyloxy)iodo]arenes, DIB, is usually prepared by the oxidation of iodobenzene with peracetic acid in acetic acid.[247] A similar peracid oxidation of substituted iodobenzenes can be used for the preparation of other [bis(acyloxy)iodo]arenes. In particular, the polymer-supported analogues of DIB have been prepared by treatment of poly(iodostyrene) or aminomethylated poly(iodostyrene) with peracetic acid,[30,248−250] and the ion-supported [bis(acyloxy)iodo]arenes, imidazolium derivatives **98** and **99**, have been prepared by the peracetic oxidation of the appropriate aryliodides.[251,252] 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.[253−255]




98




99

A modification of this method consists of the oxidative diacetoxylation of iodoarenes in acetic or trifluoroacetic acid using appropriate oxidants, such as periodates,[256−258] sodium percarbonate,[259] *m*-chloroperoxybenzoic acid,[260−264] potassium peroxodisulfate,[265,266] $H_2O_2$−urea,[267] Selectfluor,[183] and sodium perborate.[264,268−274] The oxidation of iodoarenes with sodium perborate in acetic acid at 40 °C is the most simple and general procedure that has been used for a small scale preparation of numerous (diacetoxyiodo)-substituted arenes and hetarenes.[264,268−274] This method can be improved by performing the perborate oxidation in the presence of trifluoromethanesulfonic acid.[275] A further convenient modification of this approach employs the interaction of arenes **100** with iodine and potassium peroxodisulfate in acetic acid (Scheme 32).[276] The mechanism of this reaction probably includes the oxidative iodination of arenes, followed by diacetoxylation of ArI in situ, leading to (diacetoxyiodo)arenes **101**.

The second general approach to [bis(acyloxy)iodo]arenes is based on the ligand exchange reaction of a (diacetoxyiodo)arene (usually DIB) with the appropriate carboxylic acid. A typical procedure consists of heating DIB with a nonvolatile carboxylic acid $RCO_2H$ in the presence of a high

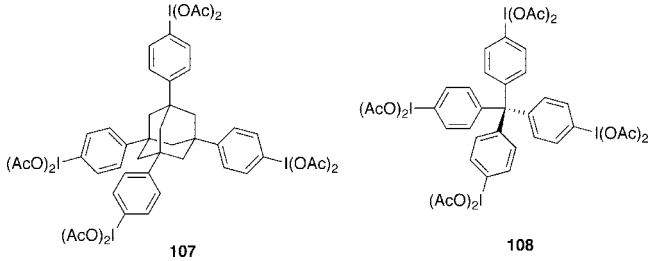
boiling solvent, such as chlorobenzene (Scheme 33).[277−282] The equilibrium in this reversible reaction can be shifted toward the synthesis of the product **102** by distillation under reduced pressure of the relatively volatile acetic acid formed during the reaction. This procedure, in particular, has recently been used for the preparation of the glutamate-derived diacyloxyiodobenzenes **103**,[278] protected amino acid derivatives **104**,[280] the cinnamate derivative **105**,[282] and 3-methylfurazan-4-carboxylic acid derivative **106**.[283]

The reactions of DIB with stronger carboxylic acids usually proceed under milder conditions at room temperature. A convenient procedure for the preparation of BTI consists of simply dissolving DIB in trifluoroacetic acid and evaporating to a small volume.[284] In a related method, used for the preparation of a series of $PhI(OCOCO_2R)_2$, DIB is treated with oxalyl chloride in the respective alcohol, ROH.[285]

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

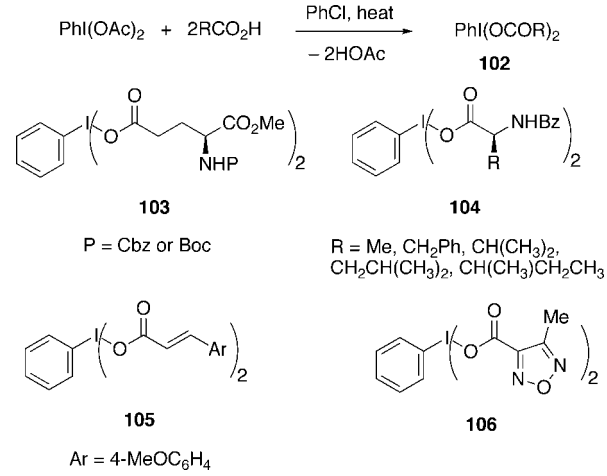
### 3.4.2. Structural Studies

Numerous structural reports on [bis(acyloxy)iodo]arenes were summarized in earlier reviews.[2,5,6] 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 I•••O interactions with the carboxylate oxygens.[286] X-ray crystal structures of four new compounds, 1,3,5,7-tetrakis[4-(diacetoxyiodo)phenyl]adamantane **107**,[260] tetrakis[4-(diacetoxyiodo)phenyl]methane **108**,[261] 3-[bis(trifluoroacetoxy)iodo]-benzoic acid **109**,[103] and 1-(diacetoxyiodo)-2-nitrobenzene **110**,[99] have been reported in the recent literature.




In the molecule of trifluoroacetate **109**, 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.[103] In addition to the five intramolecular interactions, an intermolecular coordination of the iodine atom to one of the carboxylic oxygens of the neighboring molecule is also present with a distance of 3.023 Å. It is interesting to note that the presence of the *meta*-carboxylic group does not have any noticeable effect on the molecular geometry of compound **109**, which is very similar to the X-ray crystal structure of [bis(trifluoroacetoxy)iodo]benzene.[286] The X-ray crystal structure of 1-(diacetoxyiodo)-2-nitrobenzene **110** does not show any

**Scheme 33**




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).[99]

The $^{17}O$ 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.[109,110] 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.[110]

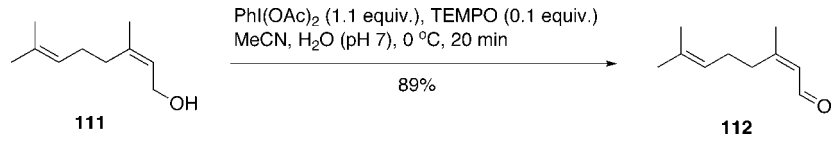
### 3.4.3. Oxidation of Alcohols

An efficient procedure for the oxidation of alcohols with DIB in the presence of catalytic amounts of TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl), originally developed by Piancatelli, Margarita, and co-workers,[287] has been frequently used in recent years.[264,288−293] An optimized protocol, published in *Organic Synthesis* for the oxidation of nerol **111** to nepal **112** (Scheme 34), consists of the treatment of the alcohol **111** solution in buffered (pH 7) aqueous acetonitrile with DIB and TEMPO (0.1 equiv) at 0 °C for 20 min.[288]

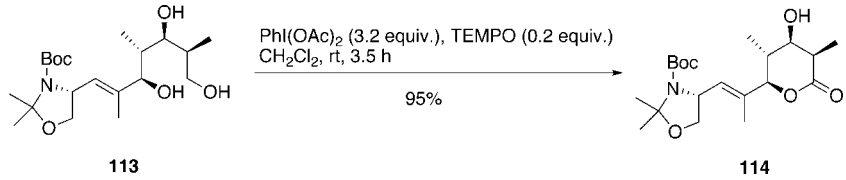
This procedure exhibits a very high degree of selectivity for the oxidation of primary alcohols to aldehydes, without any noticeable overoxidation to carboxylic acids, and a high chemoselectivity in the presence either of secondary alcohols or of other oxidizable moieties.[287] A similar oxidation procedure has been used for the oxidation of (fluoroalkyl)-alkanols, $R_F(CH_2)_nCH_2OH$, to the respective aldehydes,[289] in the one-pot selective oxidation/olefination of primary alcohols using the DIB−TEMPO system and stabilized phosphorus ylides,[290] and in the chemoenzymatic oxidation−hydrocyanation of $\gamma,\delta$-unsaturated alcohols.[291] Other [bis(acyloxy)iodo]arenes can be used instead of DIB in the TEMPO-catalyzed oxidations, such as the recyclable monomeric 1,3,5,7-tetrakis[4-(diacetoxyiodo)phenyl]adamantane **107**[260] and biphenyl- and terphenyl-based (diacetoxyiodo)arenes,[264] and the polymer-supported DIB.[292,293] Further modifications of this method include the use of polymer-supported TEMPO,[294] fluorous-tagged TEMPO,[295,296] ion-supported TEMPO,[297] and TEMPO immobilized on silica.[291]

Based on the ability of the DIB−TEMPO system to selectively oxidize primary alcohols to the corresponding aldehydes in the presence of secondary alcohols, Forsyth and co-workers have developed selective oxidative conversion

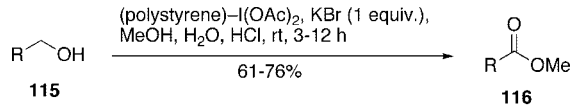
**Scheme 34**



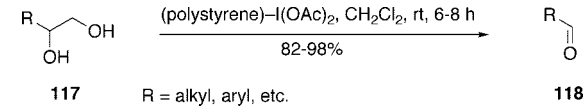

**Scheme 35**



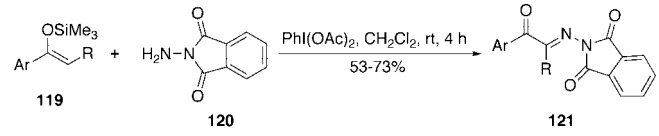

**Scheme 36**




**Scheme 37**




**Scheme 38**




Ar = Ph, 4-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$, 4-ClC$_6$H$_4$, 4-FC$_6$H$_4$, 2,4-Me$_2$C$_6$H$_3$, 2-ClC$_6$H$_4$, etc.
R = H, Me, COOEt

of a variety of highly functionalized primary and secondary 1,5-diols into the corresponding $\delta$-lactones.[298] A representative example of converting substrate **113** to the $\delta$-lactone **114** is shown in Scheme 35. Monitoring of this reaction showed the initial formation of the intermediate lactol species, which then undergoes further oxidation to the lactone.[298] A similar DIB−TEMPO-promoted $\gamma$-lactonization has recently been utilized in the asymmetric total synthesis of the antitumor (+)-eremantholide A.[299]

[Bis(acyloxy)iodo]arenes in the presence of KBr in water can oxidize primary and secondary alcohols analogously to the PhIO/KBr system.[124] The oxidation of primary alcohols affords carboxylic acids or esters,[123,300] while the oxidation of secondary alcohols under similar conditions results in the formation of the respective ketones in excellent yields.[261] In a specific example, primary alcohols **115** are readily oxidized to methyl esters **116** upon treatment with polystyrene-supported DIB in the presence of KBr in the acidic aqueous methanol solution (Scheme 36).[300] Aldehydes can be converted to methyl esters by a similar procedure using DIB and NaBr.[301]

The oxidation of various primary and secondary alcohols with the ion-supported [bis(acyloxy)iodo]arene **99** (1.4 equiv) in the ionic liquid [emim]$^+$[BF$_4$]$^-$ (1-ethyl-3-methylimidazolium tetrafluoroborate) in the presence of bromide anion selectively affords the respective carbonyl compounds without overoxidation to carboxylic acids.[251]

Molecular iodine can serve as an efficient catalyst in the oxidation of secondary alcohols to ketones and primary alcohols to carboxylic acids using DIB as an oxidant in acetonitrile solution.[302] The oxidation of primary alcohols or aldehydes with the DIB/I$_2$ system in methanol solution affords the respective methyl esters in excellent yields.[303]

Only a few examples of uncatalyzed oxidation of alcohols with [bis(acyloxy)iodo]arenes have been reported.[249,304,305] Substituted benzyl alcohols can be oxidized by BTI in aqueous acetic acid to the corresponding benzaldehydes.[304] Vicinal fullerene diol is oxidized to fullerene dione in 80% yield by DIB in benzene at 35 °C.[305] Various vicinal diols **117** (13 examples) can be oxidized to aldehydes **118** using polymer-supported DIB (Scheme 37).[249] Protecting groups such as OAc, OR, OBn, OBz, and isopropylidene in the substrates are stable under these reaction conditions. *cis*-1,2-Cyclohexandiol is converted to 1,6-hexandial in this reaction.[249]

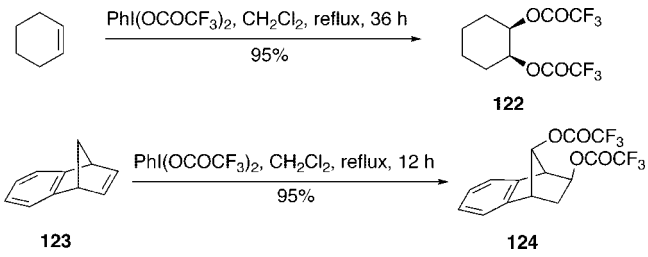
### 3.4.4. Oxidative Functionalization of Carbonyl Derivatives and Unsaturated Compounds

In the 1980s, Moriarty and co-workers have developed a particularly useful methodology for the oxidative α-functionalization of enolizable carbonyl compounds or their enol ethers using DIB or other hypervalent iodine oxidants.[306−309] The applications of this methodology in organic synthesis, especially in the chemistry of heterocyclic compounds, have been summarized in several reviews.[9,37,40,310] Ochiai and co-workers have recently reported a catalytic variant of α-acetoxylation of ketones based on the in situ generation of DIB from iodobenzene using *m*-chloroperbenzoic acid (*m*CPBA) as a terminal oxidant.[311] In a typical example, the oxidation of a ketone with *m*CPBA (2 equiv) in acetic acid in the presence of a catalytic amount of PhI (0.1 equiv), BF$_3$•OEt$_2$ (3 equiv), and water (5 equiv) at room temperature under argon affords the respective α-acetoxy ketone in 63−84% isolated yield. *p*-Methyl- and *p*-chloroiodobenzene can also serve as efficient catalysts in the α-acetoxylation of ketones using *m*CPBA as a terminal oxidant.[311]

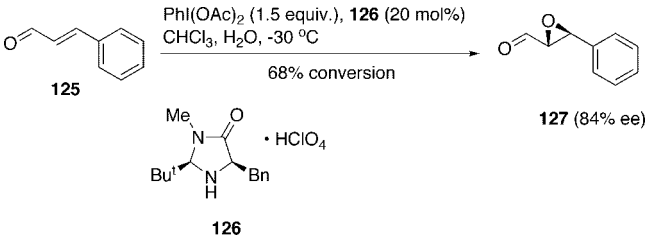
The oxidative functionalization of silyl enol ethers **119** with DIB as oxidant and *N*-aminophthalimide **120** as external nucleophile has recently been employed in the stereoselective synthesis of *trans*-α-ketohydrazones **121** in good yields under mild conditions (Scheme 38).[312] The mechanism of this reaction involves the initial formation of α-ketohydrazines, which are further oxidized by DIB to give the final ketohydrazones **121**.

Numerous recent examples of oxidative transformations of alkenes using [bis(acyloxy)iodo]arenes have been reported.[138,282,313−318] [Bis(trifluoroacetoxy)iodo]benzene re-

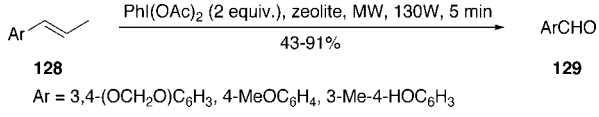
**Scheme 39**




**Scheme 40**




**Scheme 41**




acts with alkenes in the absence of any additive or catalyst, affording bis(trifluoroacetates), which can be converted into the corresponding diols or carbonyl compounds by hydrolysis.[313,319] For example, cyclohexene reacts with BTI in dichloromethane under reflux conditions to give *cis*-1,2-bis(trifluoroacetate) **122** in almost quantitative yield (Scheme 39). In the case of bicyclic alkenes, such as norbornene or benzonorbornadiene **123**, the rearranged products (e.g., **124**) are predominantly formed.[313] Similar rearranged products are formed in the reactions of alkenes with DIB in the presence of strong acids.[314]

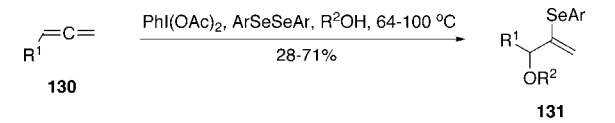
[Bis(acyloxy)iodo]arenes can be used as the oxidants in organocatalytic, asymmetric epoxidation of α,β-unsaturated aldehydes using imidazolidinone catalyst **126**.[138] In a specific example, the reaction of aldehyde **125** with DIB affords epoxide **127** with good enantioselectivity (Scheme 40).

A procedure for the preparation of aromatic aldehydes **129** from isopropenylbenzenes **128** and zeolite-supported DIB under microwave irradiation (Scheme 41) has been reported. This method was used for a clean and reproducible preparation of piperonal, vanillin, and *p*-anisaldehyde in generally high yields and selectivities.[315]

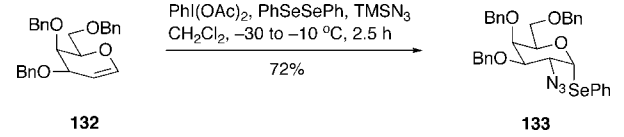
In the 1990s, Tingoli and co-workers have found a general approach to various arylselenated products by the reaction of unsaturated compounds with diaryl diselenides and DIB.[320−323] Several further modifications of this reaction have recently been reported.[282,316−318] The reaction of gem-aryl-disubstituted methylenecyclopropanes with diphenyl diselenide and DIB produced the corresponding bis-phenylselenated rearranged products in moderate yields under mild conditions.[318] A multicomponent reaction of allenes **130**, diaryl diselenides, DIB, and alcohols or acids affords 3-functionalized 2-arylselenyl-substituted allyl derivatives **131** in moderate yields (Scheme 42).[316]

Nifantiev and co-workers reported an improved preparative method for homogeneous azidophenylselenylation of glycols by the reaction with DIB, diphenyldiselenide, and trimethylsilyl azide. In a representative example, the reaction of tri-

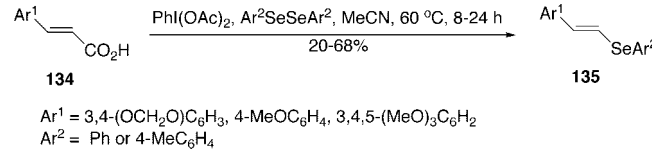
**Scheme 42**



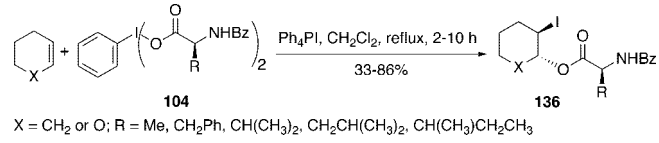

**Scheme 43**




**Scheme 44**




**Scheme 45**



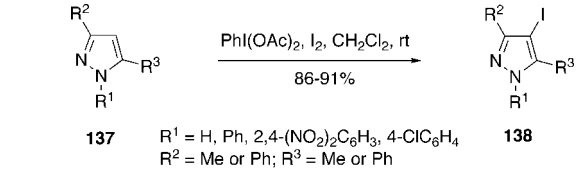

*O*-benzyl-galactal **132** with DIB/$Ph_2Se_2$/$TMSN_3$ in dichloromethane under mild conditions affords the corresponding selenoglycoside **133** in moderate yield (Scheme 43).[317] The noncarbohydrate alkenes, such as styrene and substituted cyclopentenes, can also be azidophenylselenated under these conditions.

The selenodecarboxylation of cinnamic acid derivatives **134** with diaryldiselenides promoted by DIB in acetonitrile affords vinyl selenides **135** in moderate yields (Scheme 44). A similar reaction of arylpropiolic acids gives respective alkynyl selenides in 60−90% yields.[282]

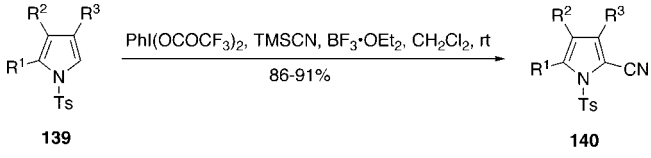
Kirschning and co-workers have developed several experimental procedures for the stereoselective bromoacetoxylation or iodoacetoxylation of alkenes based on the interaction of DIB with iodide or bromide anions.[324,325] The actual reacting electrophilic species in these reactions are the diacetylhalogen(I) anions, $(AcO)_2I^-$, and $(AcO)_2Br^-$, which can also be prepared as the polymer-supported variant.[326−328] A similar iodocarboxylation of alkenes using amino acid-derived iodobenzene dicarboxylates **104** selectively affords the respective amino acid esters **136** in moderate yields (Scheme 45).[280]

Iodine in combination with [bis(acyloxy)iodo]arenes can be used for the oxidative iodination of aromatic and heteroaromatic compounds.[6,329] A mixture of iodine and BTI in acetonitrile or methanol iodinates the aromatic ring of methoxy-substituted alkyl aryl ketones to afford the products of electrophilic monoiodination in 68−86% yield.[330] 1-Iodoalkynes can be prepared in good to excellent yields by the oxidative iodination of terminal alkynes with DIB, potassium iodide, and copper(I) iodide.[331] A solvent-free, solid state oxidative halogenation of arenes using DIB as the oxidant has recently been reported.[332] A recyclable reagent, [bis(trifluoroacetoxy)iodo]benzoic acid **109**, can also be used as the oxidant in the oxidative iodination reactions.[103,333] Substituted pyrazoles **137** can be iodinated to the corre-

**Scheme 46**




**Scheme 47**




sponding 4-iodopyrazole derivatives **138** by treatment with iodine and DIB or polymer-supported DIB at room temperature (Scheme 46).[334]

Oxidative thiocyanation of the electron-rich aromatic compounds, including phenol ethers, dimethyl aniline, thiophene, and *N*-methylindole, can be performed using ammonium thiocyanate and DIB as the oxidant at room temperature in acetonitrile solution.[335] Likewise, the direct cyanation of a wide range of electron-rich heteroaromatic compounds, such as pyrroles, thiophenes, and indoles, can be achieved under mild conditions using [bis(acyloxy)-iodo]arenes and trimethylsilyl cyanide as the cyanide source.[262,263] In a specific example, the *N*-tosylpyrroles **139** are selectively cyanated at the 2-position using [bis(trifluoroacetoxy)iodo]benzene and trimethylsilyl cyanide to afford products **140** in good yields (Scheme 47).[263]

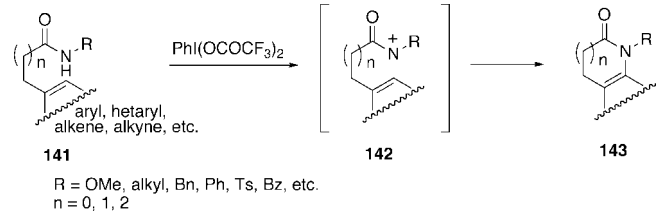
BTI in the presence of *tert*-butyl hydroperoxide can oxidize various aromatic hydrocarbons to afford the corresponding quinones.[336] For example, naphthalene is oxidized to 1,4-naphthaquinone in a moderate yield upon treatment with BTI (1.5 equiv) and *tert*-butyl hydroperoxide (5 equiv) for 3 h at −30 °C.[336] The introduction of hydroxy, alkoxy, and acetoxy groups to the activated aromatic ring using [bis(acyloxy) iodo]arenes as oxidants has also been reported. *N*-Arylamides can be hydroxylated in the *para* position by BTI in trifluoroacetic acid at room temperature.[337] The oxidation of 2,5-dihydroxyacetophenone with DIB in different alcohols leads to a regioselective alkoxylation, providing a convenient route for the synthesis of 6-alkoxy-2,5-dihydroxyacetophenones.[338] Likewise, the DIB-promoted oxidation of 6-hydroxyflavone and 6-hydroxyflavanones in acetic acid leads to regioselective acetoxylation, affording the respective 5-acetoxylated products in 53−63% yield.[339]

Applications of [bis(acyloxy)iodo]arenes in the oxidative transformations of phenolic compounds and in the biaryl coupling reaction will be discussed in sections 3.4.6 and 3.4.7.

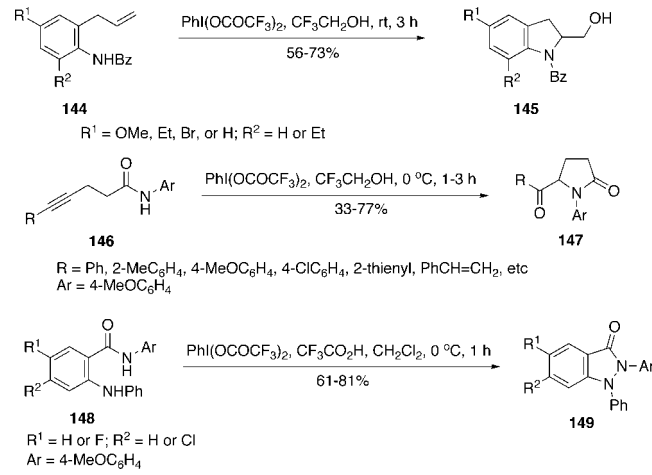
### *3.4.5. Oxidative Cationic Cyclizations, Rearrangements, and Fragmentations*

DIB and BTI are commonly used as the reagents in various cationic cyclizations, rearrangements, and fragmentations.[6] The cyclizations, induced by hypervalent iodine reagents, are particularly useful in the synthesis of heterocycles. Tellitu and Domínguez have developed a series of BTI-promoted intramolecular amidation reactions, generalized in Scheme

**Scheme 48**




**Scheme 49**

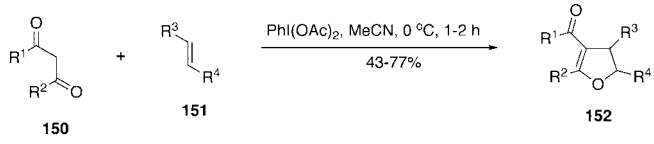



48, leading to various five-, six-, and seven-membered heterocycles **143**.[340−353] Experimental evidence supports the ionic mechanism of this reaction, involving *N*-acylnitrenium intermediates **142** generated in the initial reaction of the amide **141** with the hypervalent iodine reagent.[340]

This methodology with some variations (Scheme 48) has been utilized by Tellitu, Domínguez, and co-workers in the synthesis of the following heterocyclic systems: heterocycle-fused quinolinone derivatives,[341] 1,4-benzodiazepin-2-ones,[342] benzo-, naphtho-, and heterocycle-fused pyrrolo[2,1-*c*]-[1,4]diazepines,[343] 2,3-diarylbenzo[*b*]furans,[344] quinolinone or pyrrolidinone derivatives,[345] dibenzo[*a,c*]phenanthridines,[346] thiazolo-fused quinolinones,[347] isoindolinone and isoquinolin-2-one derivatives,[348] indoline derivatives,[349] 5-aroyl-pyrrolidinones,[350,351] and indazolone derivatives.[352,353] Recent representative examples include the preparation of indoline derivatives **145** from anilides **144**,[349] pyrrolidinones **147** from alkynylamides **146**,[350,351] and indazol-3-ones **149** from anthranilamides **148** (Scheme 49).[352,353]

Similar DIB- or BTI-induced cyclizations of the appropriate amide or amine precursors have been used in numerous useful synthetic transformations, such as the synthesis of highly substituted pyrrolin-4-ones via BTI-mediated cyclization of enaminones,[354] the synthesis of 2-substituted 4-bromopyrrolidines via DIB-induced intramolecular oxidative bromocyclization of homoallylic sulfonamides in the presence of KBr,[355] the preparation of 2-(*N*-acylaminal)-substituted tetrahydropyrans by DIB-induced oxidative cyclization of hydroxy-substituted *N*-acyl enamines,[356] the preparation of 1,2,4-thiadiazoles by the reaction of DIB or BTI with 1-monosubstituted thioureas,[357,358] the synthesis of azaspirocyclic synthetic intermediates via the BTI-induced nitrenium ion cyclizations,[359−365] the preparation of lactams and spiro-fused lactams from the reaction of *N*-acylaminophthalimides and BTI,[366] the stereocontrolled preparation of highly substituted lactams and *N*-hydroxy lactams from appropriate hydroxamates and BTI,[365] the synthesis of 1,2,4-

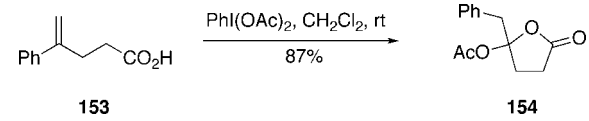
**Scheme 50**



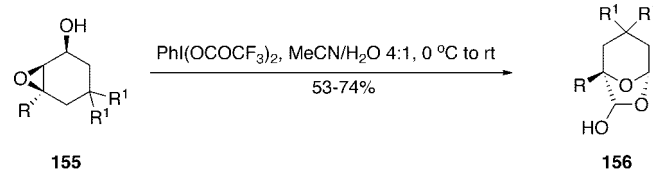

triazolo[4,3-*a*][1,8]naphthyridines using DIB-oxidation of 1,8-naphthyridin-2-ylhydrazones in the solid state,[367] the synthesis of various substituted 1,2,4-triazolo[4,3-*a*]pyrimidines by the DIB-oxidation of the appropriate 2,4-pyrimidinylhydrazones,[368−370] the preparation of thiazolo[2,3-c]-s-triazoles by the reaction of arenecarbaldehyde-4-arylthiazol-2-ylhydrazones with poly[(4-diacetoxyiodo)styrene],[371] the synthesis of pyrrolidino[60]fullerene from the DIB-promoted reaction between C60 and amino acid esters,[372] the synthesis of 1,3,4-oxadiazoles from acylhydrazones by BTI oxidation,[373−375] the synthesis of 1-aryl-4-methyl-1,2,4-triazolo[4,3-*a*]quinoxalines from arenecarboxaldehyde-3-methyl-2-quinoxalinylhydrazones,[376,377] and the synthesis of 1-benzoyltetrahydroisoquinoline derivatives using polymer-supported BTI.[378] Likewise, the preparation of benzopyrano- and furopyrano-2-isoxazoline derivatives from 2-allyloxybenzaldoximes by DIB oxidation,[379] the synthesis of various N-substituted indole derivatives via BTI-mediated intramolecular cyclization of enamines,[380] the synthesis of 2-substituted benzothiazoles via the oxidative cyclization of thiobenzamides,[381] the preparation of 2,3-diphenylquinoxaline-1-oxide from benzil-α-arylimino oximes using DIB,[382] the synthesis of 1-(5-aryl-[1,3,4]oxadiazol-2-ylmethyl)-3-(4-methoxyphenyl)-1*H*-[1,8]naphthyridin-2-ones by oxidative cyclization of [2-oxo-3-(4-methoxyphenyl)-2*H*-[1,8]naphthyridin-1-yl]acetic acid arylidenehydrazides with alumina-supported DIB under microwave irradiation,[383] the synthesis of 2,5-disubstituted-1,3,4-oxadiazoles via BTI-mediated oxidative cyclization of aldazines,[384] the preparation of 2-substituted oxazolines from aldehydes and 2-amino alcohols using DIB as an oxidant,[385] the synthesis of 3,4-bis(1-phenyl-3-arylpyrazolyl)-1,2,5-oxadiazole-*N*-oxides by the DIB oxidation of pyrazole-4-carboxaldehyde oximes,[386] the synthesis of 2-arylbenzimidazoles from phenylenediamines and aldehydes via a one-step process using DIB as an oxidant,[387] the DIB-mediated efficient synthesis of imidazoles from α-hydroxy ketones, aldehydes, and ammonium acetate,[388] the preparation of dihydrooxazole derivatives by DIB-promoted 1,3-dipolar cycloaddition reactions of phthalhydrazide,[389] and the synthesis of *seco*-psymberin/irciniastatin A via a DIB-mediated cascade cyclization reaction[390] have been demonstrated. Very recently, Togo and Moroda have reported a DIB-mediated cyclization reaction of 2-aryl-*N*-methoxyethanesulfonamides using iodobenzene as a catalyst (5−10 mol %) and *m*-chloroperoxybenzoic acid as the stoichiometric oxidant.[391]

Several examples of the DIB- or BTI-induced cyclizations of nonamine substrates have also been reported. The DIB-mediated oxidative addition of 1,3-dicarbonyl compounds **150** to various alkenes **151** allows an efficient one-pot synthesis of 2,3-dihydrofuran derivatives **152** (Scheme 50).[392] A variety of alkenes and cycloalkenes bearing electron-withdrawing or electron-donating substituents can be used in this cyclization.

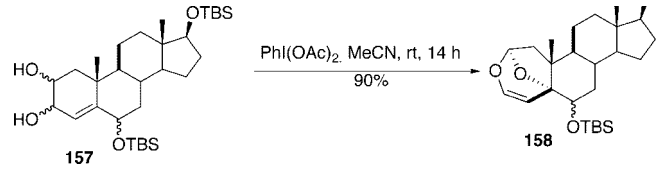
**Scheme 51**




**Scheme 52**




**Scheme 53**




Wirth and co-workers reported the lactonization of 4-phenyl-4-pentenoic acid **153** upon treatment with DIB (Scheme 51).[393] The mechanism of this reaction includes electrophilic lactonization induced by the addition of the iodine(III) electrophile to the double bond of substrate **153** followed by 1,2-phenyl migration, leading to the final rearranged lactone **154**. The same group reported a one-pot procedure for the conversion of alkenes into 1,1-dicyanocyclopropane derivatives by treatment with DIB and 1,1-dicyanopropane.[394]

Kita and co-workers developed a facile and efficient synthesis of lactols **156** via an oxidative rearrangement reaction of 2,3-epoxy alcohols **155** with BTI (Scheme 52).[395−397] This BTI-induced oxidative transformation has been utilized in the synthesis of several lactones and in the asymmetric synthesis of the marine γ-lactone metabolite (+)-tanikolide.[395,396]

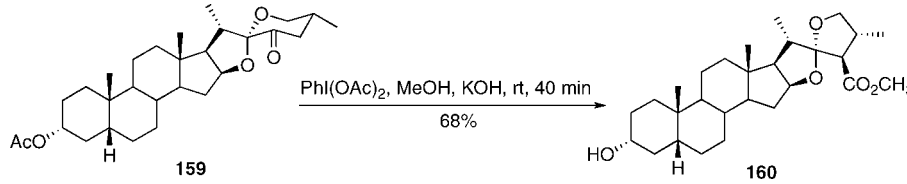
A DIB-induced domino reaction of the vicinal unsaturated diol **157** afforded cyclic ene-acetal **158** (Scheme 53), which was further utilized in the synthesis of a norsesquiterpene spirolactone/testosterone hybrid.[398]

Iglesias-Arteaga and co-workers reported several DIB-promoted oxidative transformations of steroidal substrates.[399−401] In particular, the treatment of (25*R*)-3α-acetoxy-5β-spirostan-23-one **159** with DIB in basic methanol leads to F-ring contraction via Favorskii rearrangement to afford product **160** (Scheme 54).[399]

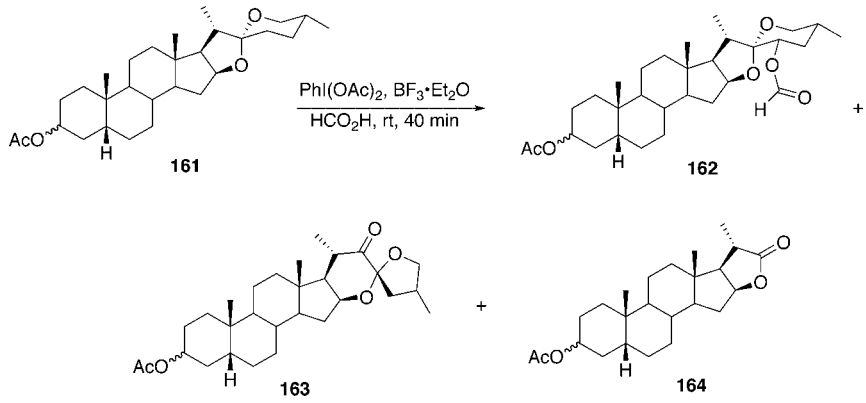
The treatment of steroidal substrate **161** with DIB and boron trifluoride etherate in acetic acid led to the introduction of an axial acetoxy group at position C-23 of the side chain,[400] while a similar reaction of the same substrate **161** with DIB and $BF_3$•$OEt_2$ in formic acid unexpectedly produced the equatorial formate **162** mixed with products of rearrangement **163** and **164** (Scheme 55).[401]

The DIB-promoted oxidative iodolactonization of pentenoic acids **165** in the presence of tetrabutylammonium iodide proceeds smoothly at room temperature to afford lactones **166** in high yields.[402] Based on this reaction, a convenient approach has been developed for the iodolactonization using iodobenzene as a catalyst (Scheme 56). In this procedure, DIB is generated in situ using a catalytic

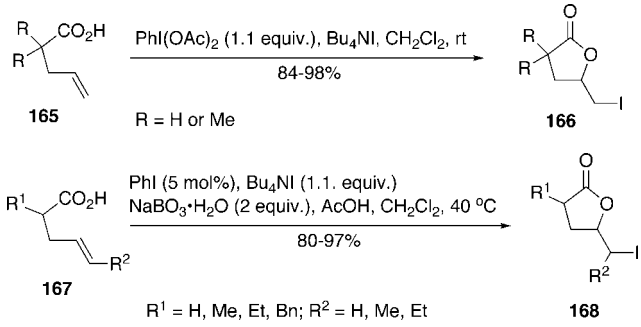
**Scheme 54**



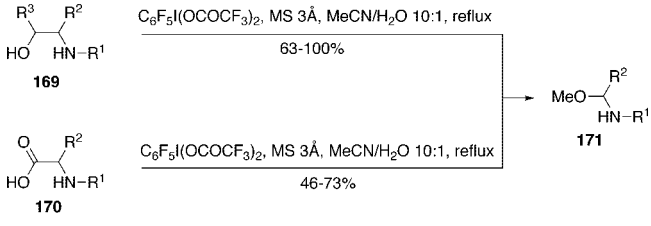

**Scheme 55**




**Scheme 56**




**Scheme 57**

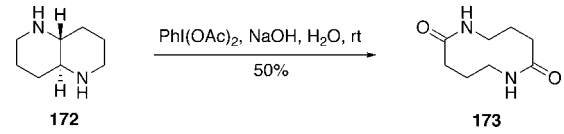



amount of iodobenzene with sodium perborate monohydrate as the stoichiometric oxidant. A variety of unsaturated acids including $\delta$-pentenoic acids **167**, $\delta$-pentynoic acids, and $\delta$-hexynoic acid gave high yields of the respective lactones (e.g., **168**) using this organocatalytic methodology (Scheme 56).[402]

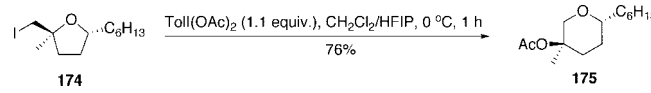
Kita and co-workers reported a mild and efficient fragmentation reaction of $\beta$-amino alcohols **169** and α-amino acids **170** upon treatment with [bis(trifluoroacetoxy)iodo]-pentafluorobenzene, leading to N,O-acetals **171** (Scheme 57). This method has been utilized in an improved synthesis of the key intermediate of discorhabdins.[403,404]

Kozlowski and co-workers reported an unusual DIB-promoted oxidative rearrangement of *cis*- and *trans*-1,5-diazadecalins. In a specific example, upon treatment with DIB in aqueous NaOH, 1,5-diaza-*trans*-decalin **172** under-

**Scheme 58**




**Scheme 59**



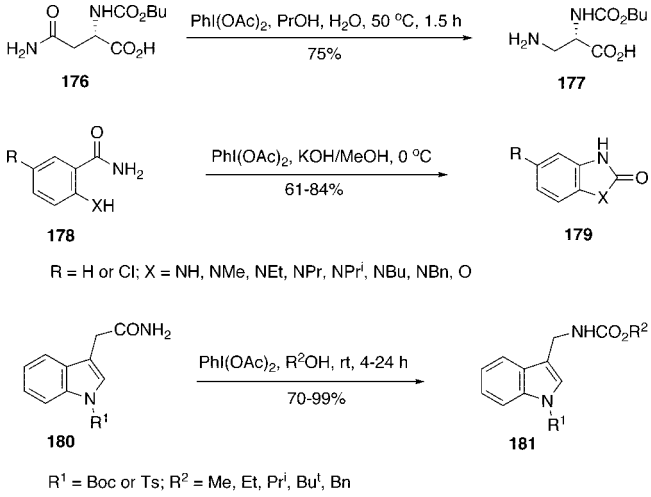

goes oxidation along with fragmentation to yield the ring-expanded bislactam **173** (Scheme 58).[405]

A stereoselective synthesis of 5−7 membered cyclic ethers can be achieved by deiodonative ring-enlargement of cyclic ethers having an iodoalkyl substituent. For example, the reaction of tetrahydrofuran derivative **174** with (diacetoxyiodo)toluene proceeds under mild conditions to afford ring-expanded product **175** (Scheme 59). The use of hexafluoroisopropanol (HFIP) as solvent in this reaction is critically important.[406]

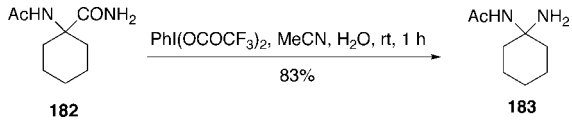
[Bis(acyloxy)iodo]arenes can serve as excellent oxidants in Hofmann-type degradation of aliphatic or aromatic carboxamides to the respective amines. DIB is a superior reagent for the Hofmann rearrangement of protected asparagines.[407] This procedure was used for the preparation of optically pure $N_\alpha$-*n*-Boc-L-α,$\beta$-diaminopropionic acid **177** from asparagine **176** in hundred kilogram quantities (Scheme 60).[408] Other examples include the oxidative rearrangement of anthranilamides or salicylamides **178** to the respective heterocycles **179**,[409] and the preparation of alkyl carbamates of 1-protected indole-3-methylamines **181** from the corresponding acetamides **180** (Scheme 60).[410]

BTI has also been used as a reagent for the Hofmann rearrangement, as illustrated by the conversion of amide **182** to the respective amine **183** (Scheme 61).[411] A similar BTI-induced Hofmann rearrangement has been used for the preparation of both enantiomers of *trans*-2-aminocyclohexanecarboxylic acid from *trans*-cyclohexane-1,2-dicarboxylic acid.[412]

**Scheme 60**




**Scheme 61**

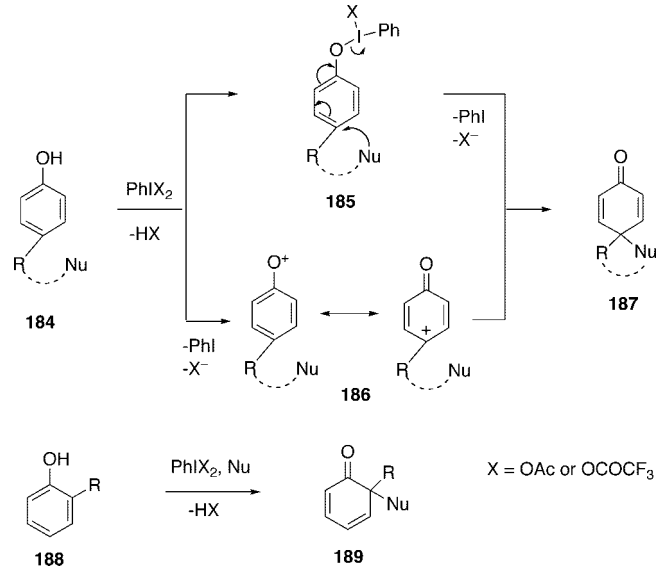



### 3.4.6. Oxidative Dearomatization of Phenolic Substrates

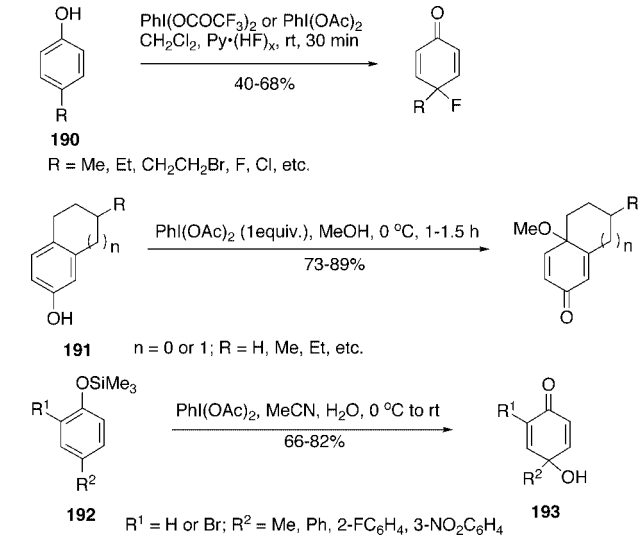
[Bis(acyloxy)iodo]arenes are commonly used as the reagents for various synthetically useful oxidative transformations of phenolic compounds.[32,34,50,51,53,60] DIB is the reagent of choice for the oxidation of various substituted *o*- and *p*-hydroquinones to the corresponding benzoquinones. The oxidation generally proceeds in methanol solution at room temperature, and the yield of benzoquinones is almost quantitative.[413] Gladysz and Rocaboy have reported the application of fluorous (diacetoxyiodo)arenes in oxidations of hydroquinones to quinones; in this procedure, the fluorous reagents can be conveniently recovered by simple liquid/liquid biphase workups.[273] Particularly useful is the oxidative dearomatization of 4- or 2-substituted phenols (e.g., **184** and **188**) with DIB or BTI in the presence of an appropriate external or internal nucleophile (Nu), leading to the respective cyclohexadienones **187** or **189** according to Scheme 62. The mechanism of this reaction most likely involves the initial formation of the phenoxyiodine(III) species **185** followed by elimination of PhI and the generation of cationic phenoxenium intermediates **186**, which finally combine with the nucleophile.[5,414]

Various nucleophiles, such as water,[415] alcohols,[76,413,416−418] fluoride ion,[419] carboxylic acids,[418,420,421] amides,[422] oximes,[423] and electron-rich aromatic rings,[424,425] have been used successfully in this reaction (Scheme 62) in either an inter- or intramolecular mode. Recent examples of this reaction in the intermolecular mode include the oxidative *ipso*-fluorination of *p*-substituted phenols **190** (or a similar *ipso*-fluorination of *p*-substituted anilines[426]) using pyridinium polyhydrogen fluoride, Py•(HF)$_x$, in combination with DIB or BTI,[427] and the methoxylation of various phenolic substrates, such as **191**, using DIB in methanol (Scheme 63).[428−430] This reaction can be further improved by using phenol trimethylsilyl ethers instead of phenols as the substrates. It was shown that the oxidation of trimethylsilyl ethers **192** affords *p*-quinols **193** in greatly improved yields due to the minimization of oligomer side products formation compared to the oxidation of free phenol.[431]

**Scheme 62**




**Scheme 63**

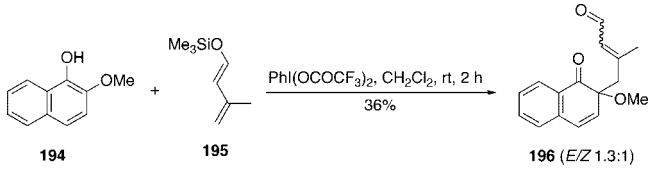



Very recently, Quideau and co-workers have reported the preparation of versatile chiral substrates for asymmetric synthesis through the DIB-induced spiroketalization of phenols with a chiral substituted ethanol unit *O*-tethered to the *ortho* position.[76] This reaction has been successfully utilized in the asymmetric total synthesis of the natural product (+)-biscarvacrol.

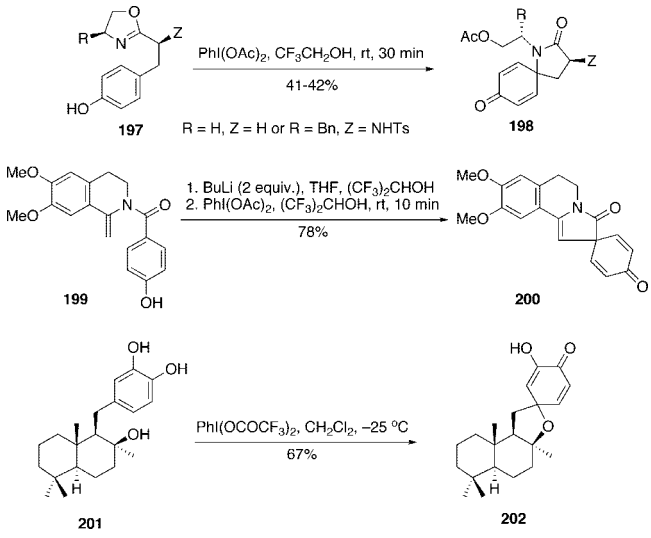
Quideau and co-workers have developed a BTI-mediated regioselective protocol for the oxidative dearomatization of 2-alkoxyarenols in the presence of external carbon-based nucleophiles.[432−435] This is a synthetically valuable process, as illustrated by the BTI-mediated oxidative nucleophilic substitution of the 2-alkoxynaphthol **194** with the silyl enol ether **195**, leading to the highly functionalized naphthoid cyclohexa-2,4-dienone **196** (Scheme 64), which is an important intermediate product in the synthesis of aquayamycin-type angucyclinones.[434,435]

The DIB- or BTI-induced phenolic oxidation in the intramolecular mode provides an efficient approach to synthetically valuable polycyclic products. Representative examples of oxidative phenolic cyclizations promoted by [bis(acyloxy)iodo]arenes are shown in Scheme 65. In particular, the oxidative cyclization of phenolic oxazolines **197**

**Scheme 64**




**Scheme 65**

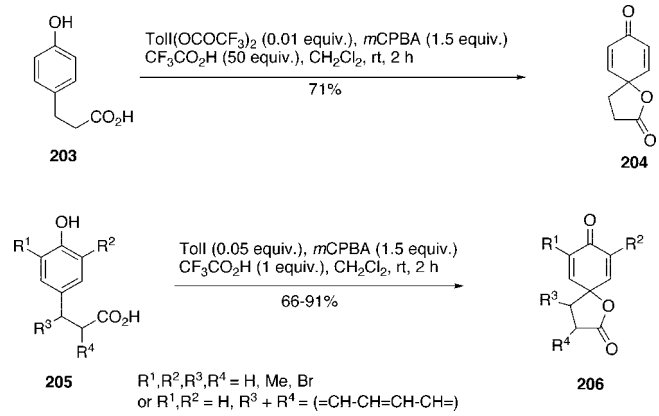



affords synthetically useful spirolactams **198**,[51,436] the oxidation of enamide **199** leads to the spiroenamide **200**, which is a key intermediate product in the total synthesis of annosqualine,[437] and the spirocyclic product **202** has been prepared by a BTI-induced oxidation of catechol **201** in a key step of the total synthesis of the marine sesquiterpene quinone (+)-puupehenone.[438]

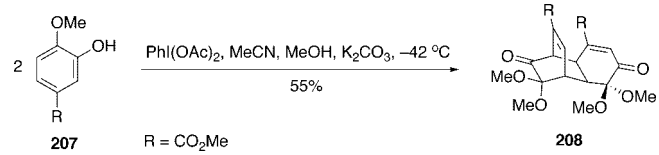
Additional examples of the DIB- or BTI-induced oxidative phenolic cyclizations include the following studies: the asymmetric total syntheses of the pentacyclic Stemona alkaloids tuberostemonine and didehydrotuberostemonine,[439] the fully stereocontrolled total syntheses of (−)-cylindricine C and (−)-2-epicylindricine C,[440,441] the asymmetric total syntheses of platensimycin,[442] the total synthesis of a potent antitumor alkaloid, discorhabdin A,[443] the total synthesis of the amaryllidaceae alkaloid (+)-plicamine using solid-supported reagents,[444] the construction of oxygenated indole, quinoline, and phenanthridine alkaloid motifs,[445] DIB-mediated regioselective aza benzannulation of nitrogen-tethered 2-methoxyphenols,[446] the investigation of oxidative dearomatization of resorcinol derivatives leading to valuable cyclohexa-2,5-dienones,[447] the development of enantioselective organocatalytic oxidative dearomatization methodology,[448] the development of a flow process for the multistep synthesis of the alkaloid natural product oxomaritidine,[449] the synthesis of carpanone using solid-supported reagents and scavengers,[450] and the studies on ring expansions of a spirocyclohexadienone system.[451]

Kita and co-workers have reported a catalytic variant of the oxidative spirocyclization reaction based on the in situ regeneration of a [bis(trifluoroacetoxy)iodo]arene from iodoarene using *m*-chloroperbenzoic acid (*m*CPBA) as a terminal oxidant.[452] In a typical example, the oxidation of the phenolic substrate **203** with *m*CPBA in dichloromethane in the presence of a catalytic amount of *p*-[bis(trifluoroacetoxy)iodo]toluene (0.01 equiv) and trifluoroacetic acid at

**Scheme 66**




**Scheme 67**



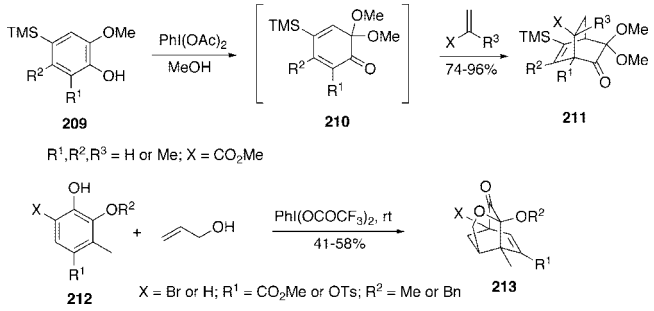

room temperature affords the respective spirolactone **204** in good yield (Scheme 66). A variety of other [bis(trifluoroacetoxy)iodo]arenes can be used as catalysts in this reaction [e.g., BTI, 4-$MeOC_6H_4I(OCOCF_3)_2$, and 2,4-$F_2C_6H_3I(OCOCF_3)_2$] and different acidic additives (acetic acid, $BF_3$•$OEt_2$, TMSOTf, molecular sieves), but the $TolI(OCOCF_3)_2$/$CF_3CO_2H$ system generally provides the best catalytic efficiency. Under these optimized conditions, a variety of phenolic substrates **205** was oxidized to spirolactones **206** in the presence of catalytic amounts of *p*-iodotoluene (Scheme 66).[452] Likewise, the amide derivatives of phenolic substrates **205** can be catalytically oxidized to the respective *N*-fused spirolactams using catalytic amounts of *p*-iodotoluene and *m*CPBA as a terminal oxidant.[453] A similar catalytic procedure has been reported for the oxidation of 4-alkoxyphenols to the corresponding 1,4-quinones using a catalytic amount of 4-iodophenoxyacetate in the presence of oxone as a co-oxidant in an aqueous acetonitrile solution.[454]

Very recently, Kita and co-workers reported the first enantioselective spirocyclization reaction of the *ortho*-substituted phenolic substrates using chiral aryliodine(III) diacetate having a rigid spirobiindane backbone.[455]

The oxidative dearomatization of substituted phenols **188** bearing electron-releasing substituents R, such as a methoxy group, at their *ortho*-position(s) leads to 6,6-disubstituted cyclohexa-2,4-dienones **189** (see Scheme 62), which can be conveniently utilized in situ as dienes in Diels−Alder reactions.[418,421,456] When the oxidation of phenols is performed in the absence of an external dienophile, a dimerization via [4 + 2] cycloaddition often occurs spontaneously at ambient temperature to afford the corresponding dimers with an extraordinary level of regioselectivity, site selectivity, and stereoselectivity. A detailed experimental and theoretical investigation of such hypervalent iodine-induced Diels−Alder cyclodimerizations has recently been published by Quideau and co-workers.[456] A representative example of an oxidative Diels−Alder cyclodimerization of a phenolic substrate **207** to the dimer **208** is shown in Scheme 67.

When the oxidation is performed in the presence of an external dienophile, the respective products of [4 + 2] cycloaddition are formed.[457−461] Typical examples are

**Scheme 68**




illustrated by a one-pot synthesis of several silyl bicyclic alkenes **211** by intermolecular Diels−Alder reactions of 4-trimethylsilyl-substituted masked *o*-benzoquinones **210** derived from the corresponding 2-methoxyphenols **209**,[457] and by the hypervalent iodine-mediated oxidative dearomatization/Diels−Alder cascade reaction of phenols **212** with allyl alcohol, affording polycyclic acetals **213** (Scheme 68).[458] The BTI-promoted tandem phenolic oxidation/Diels−Alder reaction has been utilized in the stereoselective synthesis of the bacchopetiolone carbocyclic core.[459]

A mechanistic investigation of the oxidation of 2,6-dimethylphenol using different oxidizing systems has shown that DIB is the most efficient reagent for the oxidative coupling, leading to 3,5,3′,5′-tetramethylbiphenyl-4,4′-diol. A reaction mechanism was proposed which involved an initial formation of a [bis(phenoxy)iodo]benzene intermediate followed by its radical fragmentation and then radical coupling and comproportionation/redox reaction steps.[462]

### *3.4.7. Oxidative Coupling of Electron-Rich Aromatic Substrates*

The interaction of phenol ethers **214** or other electron-rich aromatic substrates with BTI leads to the generation of cation radical intermediates **215**, which combine with external or internal nucleophiles, affording the products of dearomatization **216** or coupling **217** according to Scheme 69. Kita and co-workers have recently published a detailed mechanistic study of this process (Scheme 69) for a specific reaction of oxidative cyclization of electron-rich aromatics with the intramolecular hydroxyl group.[463] In this study, the formation of the cation radical intermediates **215** (R-Nu = $CH_2CH_2CH_2OH$) was experimentally confirmed by ESR spectroscopy, and the factors determining the ratio of products **216** and **217** and their consequent transformations were clarified.

The direct nucleophilic substitution of electron-rich phenol ethers using BTI and Lewis acid and involving aromatic cation radical intermediates was originally developed by Kita and co-workers in 1994.[464] Since then, this procedure with some variations has been extensively applied by Kita and other researchers for various oxidative transformations, such as the synthesis of biaryls,[465−472] spirodienones,[467,473−475] quinone imines,[476] sulfur-containing heterocycles,[477] and chromans.[478] Specific recent examples of the oxidative coupling of phenolic ethers include the oxidative biaryl coupling of various N-substituted 1-benzyltetrahydroisoquinolines **218** to the corresponding aporphines **219**,[468] the oxidative cyclization of 3,4-dimethoxyphenyl 3,4-dimethoxyphenylacetate **220**, leading to the seven-membered lactone **221**,[469] and the conversion of phenol ether derivatives **222** to the products of intramolecular coupling **223** using a combination of BTI and heteropoly acid (Scheme 70).[466] A similar oxidative coupling reaction of benzyltetrahydroisoquinolines (laudanosine derivatives) using BTI and heteropoly acid has been used in an efficient synthesis of morphinandienone alkaloids.[479] A catalytic version of the intermolecular oxidative coupling of phenolic ethers using BTI (0.125 equiv) as a catalyst and *m*CPBA as the stoichiometric oxidant has also been reported.[452] Very recently, Kita and co-workers have reported a new $H_2O_2$/acid anhydride system for the iodoarene-catalyzed intramolecular C−C cyclization of phenolic derivatives.[480]

The nonphenolic electron-rich aromatic substrates can also be oxidatively coupled using [bis(acyloxy)iodo]arenes. Kita and co-workers reported a facile and efficient oxidative coupling reaction of alkylarenes **224** leading to alkylbiaryls **225** using a combination of BTI and $BF_3$•$OEt_2$ (Scheme 71).[481] Similarly, multiply iodinated biaryls can be prepared in good yields by the BTI-induced direct oxidative coupling reaction of the iodinated arenes.[482]

Oxidation of N-aromatic methanesulfonamides **226** with DIB in the presence of thiophene in trifluoroethanol or hexafluoroisopropanol affords the respective coupling products **227** in good yield.[483] Likewise, the head-to-tail dimers **229** can be selectively prepared by the hypervalent iodine oxidation of 3-substituted thiophenes **228**,[484,485] and bipyrroles **231** can be regioselectively synthesized by oxidative dimerization of pyrroles **230** with BTI in the presence of bromotrimethylsilane (Scheme 72).[486]

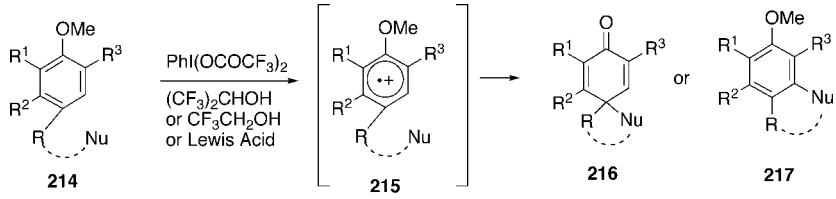
### *3.4.8. Radical Cyclizations, Rearrangements, and Fragmentations*

Useful synthetic methodologies are based on the cyclization, rearrangement, or fragmentation of the alkoxyl radicals generated in the reaction of alcohols with [bis(acyloxy)-iodo]arenes in the presence of iodine under photochemical conditions or in the absence of irradiation.[5,6] Suàrez and co-workers have applied this methodology in various useful transformations of carbohydrate derivatives, such as the synthesis of polyhydroxy piperidines and pyrrolidines related to carbohydrates,[129] the synthesis of alduronic acid lactones,[487] the syntheses of chiral dispiroacetals from carbohydrates,[488] and the synthesis of α-iodoalkyl esters from carbohydrates.[489] Recent examples include the synthesis of 1,1-difluoro-1-iodo alditols **233**,[490] 2-azido-1,2-dideoxy-1-iodo-alditols **235**,[491,492] and chiral vinyl sulfones **237**[493] by fragmentation of carbohydrate anomeric alkoxyl radicals generated from the respective carbohydrates **232**, **234**, and **236** (Scheme 73).

The intramolecular hydrogen abstraction reactions promoted by alkoxy radicals in carbohydrates are particularly useful for the stereoselective synthesis of various polycyclic oxygen-containing ring systems.[128,494−497] This reaction can be illustrated by the intramolecular 1,8-hydrogen abstraction between glucopyranose units in disaccharide **238** promoted by alkoxyl radicals and leading to the 1,3,5-trioxocane derivative **239** (Scheme 74).[494]

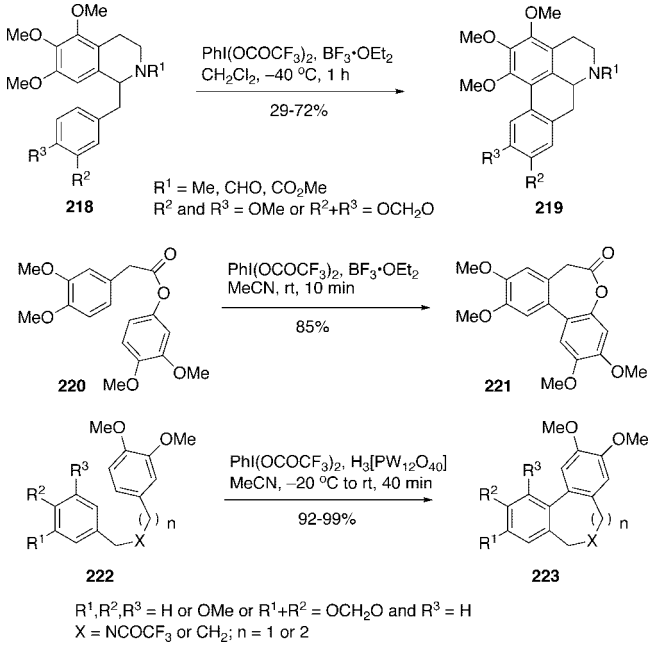
Boto and Hernandez have reported a short and efficient synthesis of chiral furyl carbinols from carbohydrates, such as **240**, based on the alkoxyl radicals fragmentation reaction leading to the intermediate product **241** (Scheme 75).[498] The same authors have developed an efficient procedure for the selective removal from carbohydrate substrates of methoxy protecting groups next to hydroxy groups by treatment with the DIB−$I_2$ system.[499]

**Scheme 69**

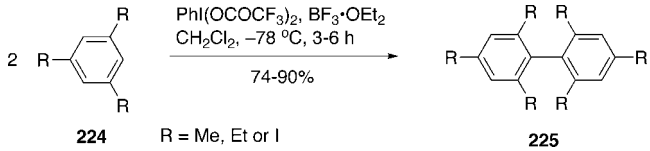



R = alkyl, alkoxy, halogen, etc.
Nu = external or internal nucleophilic group, including electron-rich aromatics

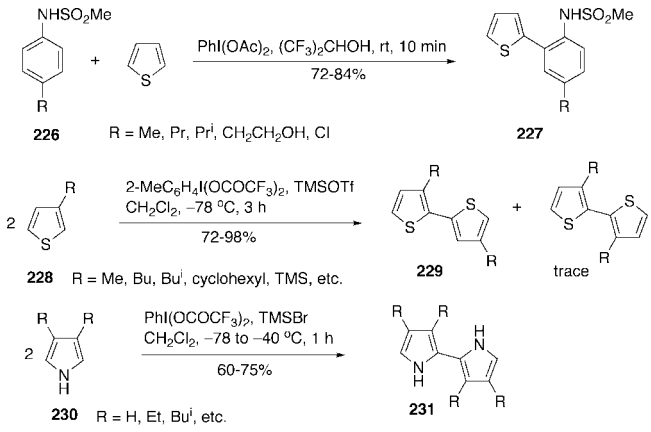
**Scheme 70**




**Scheme 71**

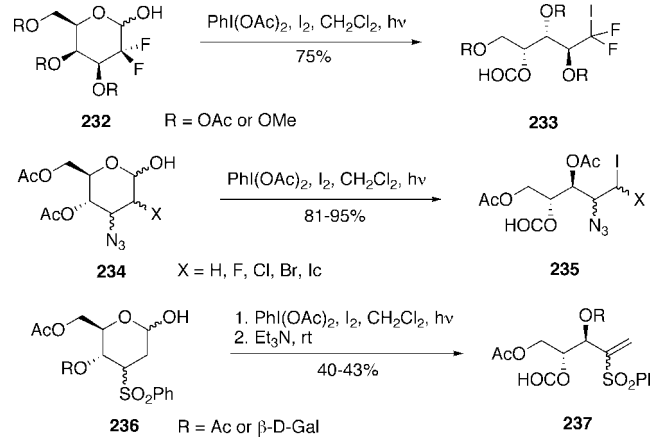



**Scheme 72**




The treatment of 1-alkynylcycloalkanols **242** with poly[styrene(iodosodiacetate)] and iodine affords (*Z*)-2-(1-iodo-1-organyl)methylenecycloalkanones **243** resulting, probably, from the alkoxyl radical-promoted ring expansion reaction (Scheme 76).[500] The mechanism of the $\beta$-scission reactions of the 1-alkylcycloalkoxyl radicals generated from alkylcycloalkanols by treatment with the DIB$-I_2$ under photochemical conditions has been investigated by Bietti and coworkers.[501]

**Scheme 73**




A mild and highly efficient one-pot synthesis of aryl glycines **245** from easily available serine derivatives **244** has been reported (Scheme 77).[502] The method is based on the $\beta$-fragmentation of a primary alkoxyl radical, generated on treatment of the serine derivative with DIB and iodine, immediately followed by the addition of the nucleophile. This methodology is also applicable to the synthesis of other uncommon amino acids.[502]

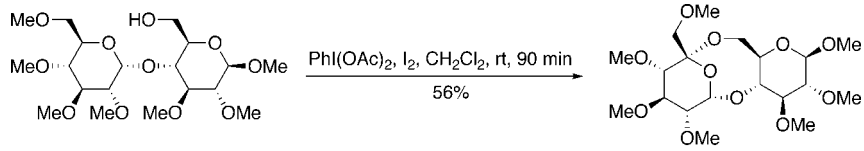
The one-pot radical fragmentation−phosphorylation reaction of α-amino acids or $\beta$-amino alcohols (e.g., **246**) affords α-amino phosphonates **247** in good yields (Scheme 78). This reaction was applied to the synthesis of potentially bioactive phosphonates.[503]

The radical decarboxylation of carboxylic acids on treatment with DIB$-I_2$ allows us to introduce iodine or other functional groups into nitrogen heterocycles under mild conditions.[504,505] For example, the decarboxylation of $\beta$- and $\gamma$-amino acids **248** under these conditions affords iodinated heterocycles **249** (Scheme 79). This reaction was applied to the synthesis of bioactive products, such as opioid analogues, imino sugars, and new antifungal agents.[504]

Kita and co-workers developed a simple and reliable method for the direct construction of biologically important aryl lactones **251** from carboxylic acids **250** using a combination of DIB with KBr (Scheme 80). The mechanism of this reaction includes the initial generation of the carbonyloxy radical followed by the intramolecular benzylic hydrogen abstraction and cyclization.[506]

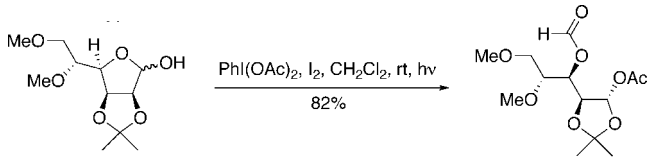
Conjugate addition of radicals generated by decarboxylative fragmentation of (diacyloxyiodo)benzene **103** to dehydroamino acid derivatives (e.g., **252**) has been used by Sutherland and Vederas in the synthesis of diaminopimelic acid analogues **253** (Scheme 81).[278]

**Scheme 74**



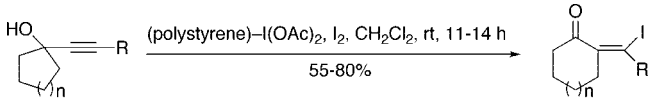

238 239

**Scheme 75**




240 241

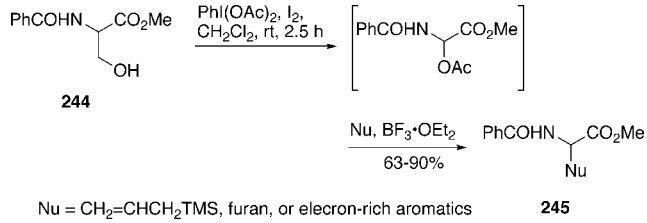
**Scheme 76**




242 243

n = 1; R = Ph, Bu, TolOCH$_2$
n = 2; R = Ph, PhCH$_2$OCH$_2$, TolOCH$_2$
n = 3; R = Ph, Bu, TolOCH$_2$, PhCH$_2$OCH$_2$

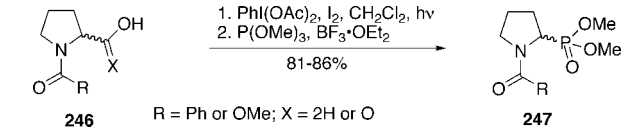
**Scheme 77**




244 245

Nu = $CH_2$=$CHCH_2$TMS, furan, or elecron-rich aromatics

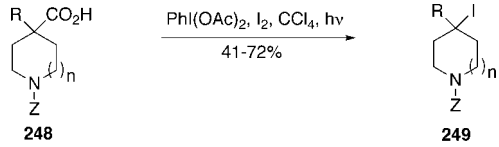
**Scheme 78**




246 247

R = Ph or OMe; X = 2H or O

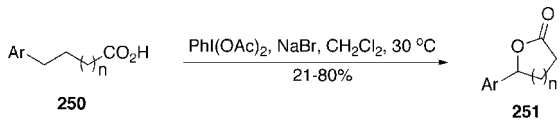
**Scheme 79**




248 249

n = 0 or 1; R = H or $CO_2$Me; Z = Boc or $CO_2$Me

**Scheme 80**

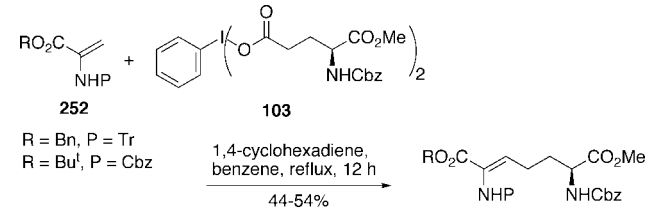



250 251

n = 1-3; Ar = Ph, 4-MeOC$_6$H$_4$, 4-NO$_2$C$_6$H$_4$, 4-FC$_6$H$_4$, etc.

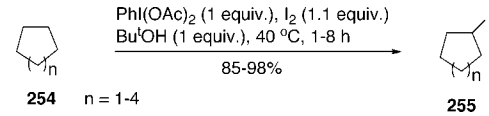
Barluenga and co-workers reported a direct iodination of alkanes **254** by the reaction with DIB−$I_2$ in the presence of *tert*-butanol under photochemical or thermal conditions (Scheme 82).[507] This reaction can be used for the preparation of alkyliodides **255** in excellent yields by direct C−H bond activations in cyclic or noncyclic alkanes and at the benzylic position. The presence of an alcohol (e.g., *tert*-butanol) is essential for an efficient alkane activation.

**Scheme 81**



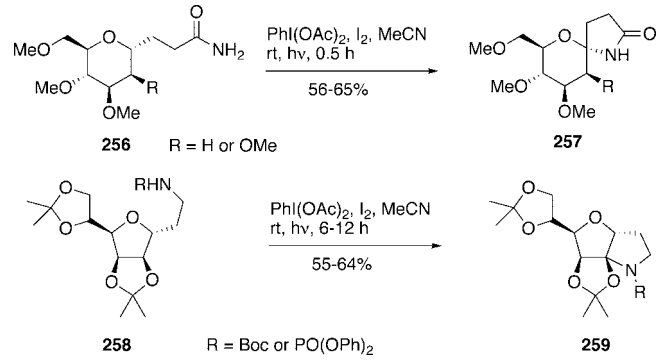

252 103 253

**Scheme 82**




254 n = 1-4 255

**Scheme 83**




256 R = H or OMe 257

258 R = Boc or PO(OPh)$_2$ 259

The alkoxy radical fragmentation with DIB in the presence of iodine was also used in a facile synthesis of (*n*+3) and (*n*+4) ring-enlarged lactones as well as of spiroketolactones from *n*-membered cycloalkanones.[508]

Useful synthetic methodologies are based on the cyclization or rearrangement of the nitrogen-centered radicals generated in the reaction of the appropriate amides with DIB in the presence of iodine.[130,509−511] Specific examples are illustrated by the synthesis of bicyclic spirolactams **257** from amides **256**,[509] and the preparation of the oxa-azabicyclic systems (e.g., **259**) by the intramolecular hydrogen atom transfer reaction promoted by carbamoyl and phosphoramidyl radicals generated from the appropriately substituted carbohydrates **258** (Scheme 83).[510]

### *3.4.9. Oxidations of Nitrogen, Phosphorus, and Sulfur Compounds*

DIB and BTI have found wide application for the oxidation of organic derivatives of such elements as nitrogen, sulfur, selenium, tellurium, and others.[5,6] The use of [bis(acyloxy) iodo]arenes for the oxidation of organonitrogen compounds leading to the generation of the N-centered cationic or radical intermediates and their subsequent cyclizations and rearrangements (e.g., Hofmann rearrangement) is discussed in previous sections of this review (see sections 3.4.5 and 3.4.8). Additional recent examples include the DIB-induced oxida-

tion of aromatic amines to imines applied for deprotection of protected amino diols,[512] the N-acylation of 1,3-disubstituted thioureas using DIB,[513] the DIB oxidation of 1,2-dicarbethoxyhydrazine to diethyl azodicarboxylate as a key step of an organocatalytic Mitsunobu reaction,[514] the BTI oxidations of phenylhydrazones leading to regeneration of the carbonyl function,[515] the low temperature generation of diazo compounds by the reaction of BTI with hydrazones,[516] the preparation of *N*-aroyl-*N*′-arylsulfonylhydrazines by oxidation of aromatic aldehyde *N*-arylsulfonylhydrazones with BTI,[517] and the conversion of oximes into nitroso compounds using *p*-bromo(diacetoxyiodo)benzene.[518]

[Bis(acyloxy)iodo]arenes have been used for the oxidation of various organosulfur compounds. Organic sulfides are selectively oxidized to the respective sulfoxides by DIB or the polymer-supported DIB in water in the presence of KBr.[519] The recyclable reagent, 3-[bis(trifluoroacetoxy)iodo-]benzoic acid **109**, can oxidize organic sulfides to the respective sulfoxides at room temperature in aqueous acetonitrile.[103] Thioacetals and thioketals are efficiently cleaved to carbonyl compounds with BTI or DIB under mild conditions. This reaction is especially useful for the selective deprotection of either thioacetals or thioketals and is compatible with a variety of other functional groups.[520−524]

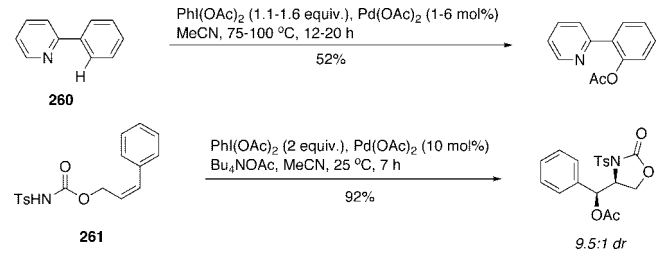
Makowiec and Rachon investigated the reactivity of DIB toward trivalent phosphorus nucleophiles. It was found that both H-phosphonates and secondary phosphine oxides react with DIB in alcohols in the presence of sodium alkoxides, yielding trialkyl phosphates and alkyl phosphinates, respectively. A mechanism of these reactions involving an initial addition of a phosphorus(III) nucleophile to the iodine(III) center has been proposed.[525]

### 3.4.10. Transition Metal-Catalyzed Reactions

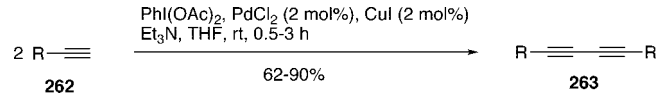
The oxidations with [bis(acyloxy)iodo]arenes can be effectively catalyzed by transition metal salts and complexes. DIB is occasionally used instead of iodosylbenzene as the terminal oxidant in biomimetic oxygenations catalyzed by metalloporphyrins and other transition metal complexes.[526−528] Primary and secondary alcohols can be selectively oxidized to the corresponding carbonyl compounds by DIB in the presence of transition metal catalysts, such as $RuCl_3$,[139,529] Ru(Pybox)(Pydic) complex,[530] polymer−micelle incarcerated ruthenium catalysts,[531] chiral Mn(salen) complexes,[532,533] Mn(TPP)CN/Im catalytic systems,[534] and (salen)Cr(III) complexes.[535] Kirschning and co-workers have recently reported the use of the recyclable reagent, phenylsulfonate-tagged DIB, in the $RuCl_3$-catalyzed oxidation of alcohols.[536] The epoxidation of alkenes, such as stilbenes, indene, and 1-methylcyclohexene, using DIB in the presence of chiral binaphthyl ruthenium(III) catalysts (5 mol %) has also been reported. The chemoselectivity and enantioselectivity of this reaction were found to be low (4% ee).[537]

The mechanisms and applications of palladium-catalyzed reactions of DIB and other hypervalent iodine reagents in synthetically useful organic transformations were recently reviewed by Deprez and Sanford.[18] Particularly useful are the Pd-catalyzed oxidation reactions, including the oxidative functionalization of C−H bonds and the 1,2-aminooxygenation of olefinic substrates.[538−552] Representative examples of these catalytic oxidations are illustrated by the selective acetoxylation of C−H bonds adjacent to coordinating functional groups (e.g., pyridine in substrate **260**)[538] and by the $Pd(OAc)_2$-catalyzed intramolecular aminoacetoxylation

**Scheme 84**




**Scheme 85**




in the reaction of $\gamma$-aminoolefins (e.g., cinnamyl alcohol derived tosyl carbamate **261**) with DIB (Scheme 84).[539] The key mechanistic step in these catalytic transformations includes the DIB-promoted oxidation of Pd(II) to the Pd(IV) species, as proved by the isolation and X-ray structural identification of stable Pd(IV) complexes prepared by the reaction of $PhI(O_2CPh)_2$ with Pd(II) complexes containing chelating 2-phenylpyridine ligands.[553]

Yan and co-workers have developed an efficient procedure for synthesis of symmetrical conjugated diynes **263** from terminal alkynes **262** using DIB as oxidant under palladium-catalyzed conditions (Scheme 85).[554,555]

## 3.5. Organosulfonates

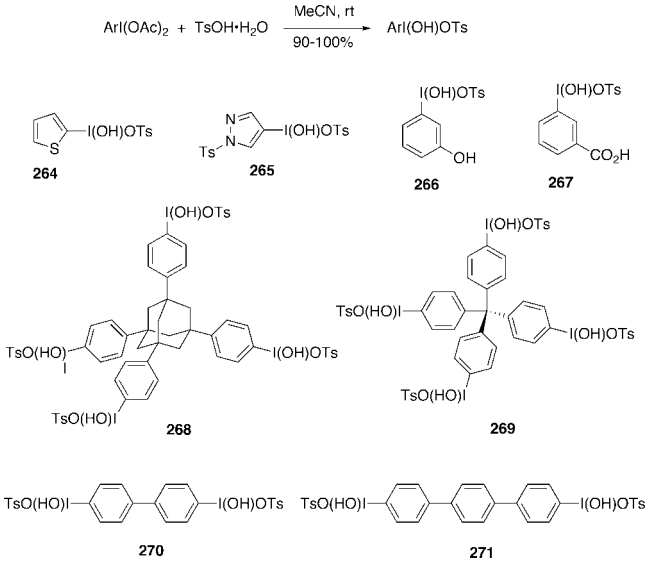
A detailed discussion of the literature on the preparation, structural studies, and synthetic applications of aryliodine(III) compounds derived from strong inorganic acids can be found in our previous reviews.[5,6] The aryliodine(III) compounds $ArI(OX)_2$ that are derived from strong acids HOX, such as $H_2SO_4$, $HNO_3$, $HClO_4$, $CF_3SO_3H$, $HSbF_6$ and $HPF_6$, usually lack stability and can only be generated at low temperature, under absolutely dry conditions. Traces of moisture immediately convert these compounds into $\mu$-oxo-bridged derivatives or more complex polymeric structures (see structures **8** and **9** in section 3.1.2). For example, the unstable and extremely hygroscopic phenyliodine(III) sulfates $PhIO•SO_3$ and $(PhIO)_2•SO_3$ can be generated from PhIO and $SO_3$ or $Me_3SiOSO_2Cl$ under absolutely dry conditions,[556−558] while the partially hydrolyzed, stable oligomeric sulfate $(PhIO)_3•SO_3$ (structure **8**) is conveniently prepared by the treatment of $PhI(OAc)_2$ with aqueous $NaHSO_4$.[88]

[Hydroxy(organosulfonyloxy)iodo]arenes, $ArI(OH)OSO_2R$, are the most common, well investigated, and practically useful aryliodine(III) derivatives of strong acids. The most important of them, [hydroxy(tosyloxy)iodo]-benzene (HTIB or Koser's reagent), is commercially available and is commonly used as an oxidizing reagent in organic synthesis.[41] In this section, the preparation, structural studies, and recent examples of synthetic applications of [hydroxy-(organosulfonyloxy)iodo]arenes are overviewed.

### 3.5.1. Preparation

Various [hydroxy(tosyloxy)iodo]arenes are readily prepared by a ligand exchange reaction of (diacetoxyiodo)arenes with *p*-toluenesulfonic acid monohydrate in acetonitrile (Scheme 86).[75,103,257,260,261,559,560] This method has recently been applied to the synthesis of [hydroxy(tosyloxy)iodo]het-

**Scheme 86**




eroaromatic derivatives (e.g., **264** and **265**),[560] the derivatives with various substituted aromatic groups (e.g., **266** and **267**),[103,257,560] and the recyclable hypervalent iodine reagents **268** and **269**.[260,261] A convenient modified procedure for the preparation of various [hydroxy(sulfonyloxy)iodo]arenes consists of the one-pot reaction of iodoarenes and *m*CPBA in the presence of sulfonic acids in a small amount of chloroform at room temperature.[561] This modified procedure was recently used for the preparation of new biphenyl- and terphenyl-based recyclable organic trivalent iodine reagents **270** and **271**.[264]

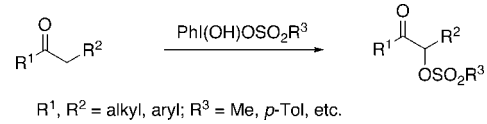
A similar procedure using 4-nitrobenzenesulfonic acid, methanesulfonic acid, or 10-camphorsulfonic acid leads to the corresponding organosulfonyloxy analogues.[559,562] A solvent-free, solid-state version of this reaction is carried out by simple grinding of $ArI(OAc)_2$ with the appropriate sulfonic acid in an agate mortar followed by washing the solid residue with diethyl ether.[563] 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[(diacetoxy)-iodo]styrene with *p*-toluenesulfonic acid monohydrate in chloroform at room temperature.[564,565]

The highly electrophilic phenyliodine(III) trifluoromethanesulfonate $(PhIO)_2•Tf_2O$, which is also known as Zefirov's reagent, may be prepared either by the exchange reaction of (diacetoxy)iodobenzene with trifluoromethanesulfonic acid[566] or by the combination of 2 equiv of iodosobenzene with 1 equiv of triflic anhydride.[567] This triflate has an oxo-bridged structure and is isolated as a relatively stable yellow microcrystalline solid that can be handled for brief periods in air and stored under a nitrogen atmosphere. It can be conveniently generated in situ from PhIO and triflic anhydride or trimethylsilyl triflate and immediately used in the subsequent reactions;[568] the extended storage of this reagent in the presence of trifluoromethanesulfonic acid results in self-condensation with the formation of oligomeric products.[569]

### 3.5.2. Structural Studies

Single-crystal X-ray structural data for HTIB 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).[570] The presence of a substituent in the phenyl ring does not have any noticeable effect on the molecular geometry of [hydroxy(tosyloxy)iodo]arenes. The recently reported X-ray structure of 3-[hydroxy(tosyloxy)iodo]benzoic acid **267** is very similar to the structure of HTIB. The I−OTs bond distance in tosylate **267** (2.437 Å) is significantly longer than the I−OH bond distance of 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 the 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 a *meta* carboxylic group is present in molecule **267**.[103]

**Scheme 87**

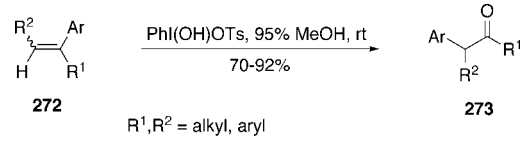



The solution studies of HTIB in water by spectroscopic measurements and potentiometric titrations indicate complete ionization to a hydroxy(phenyl)iodonium cation ($PhI^+OH$ in hydrated form) and tosylate anion.[111]

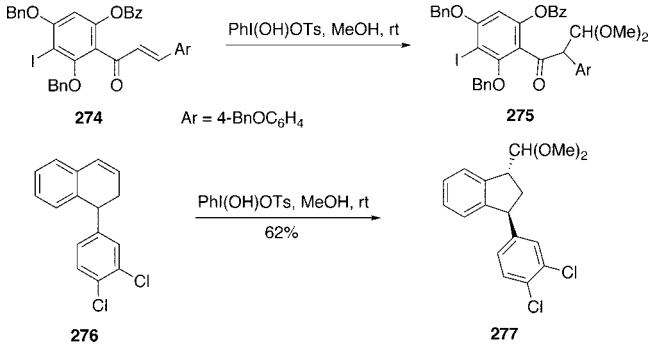
### 3.5.3. Reactions

The functionalization of carbonyl compounds at an α-carbon represents the most typical reaction of [hydroxy-(organosulfonyloxy)iodo]arenes (Scheme 87).[41] Recent examples of synthetic application of this procedure include the following: the preparation of α-mesyloxyketones for the photochemical synthesis of highly functionalized cyclopropyl ketones,[571] the one-step conversion of ketones into α-azidoketones using HTIB and sodium azide,[572,573] the one-pot conversion of ketones into *β*-keto sulfones using HTIB and sodium arene sulfinate under solvent-free conditions,[574] the solvent-free synthesis of α-tosyloxy *β*-keto sulfones using HTIB,[575] direct α-hydroxylation of ketones using HTIB or polymer-supported HTIB in dimethyl sulfoxide−water,[576,577] the use of HTIB in the synthesis of 1,4-diaryl-2-(arylamino)-but-2-ene-1,4-diones,[578] the high yield preparation of dicarboxylic acid dimethyl esters from cycloalkanones using [hydroxy(2,4-dinitrobenzenesulfonyloxy)iodo]benzene,[579] the ionic liquid-accelerated one-pot synthesis of 2-arylimidazo[1,2-*a*]pyrimidines,[580] the HTIB mediated stereoselective synthesis of bicyclic ketones,[581] the HTIB-promoted synthesis of 6-arylimidazo[2,1-*b*]thiazoles,[582] the synthesis of thiazole-2(3*H*)-thiones through [hydroxy(tosyloxy)iodo]benzene,[583] the HTIB-promoted synthesis of 2-substituted 4,5-diphenyloxazoles under solvent-free microwave irradiation conditions,[584] the preparation of oxazoles from ketones and amides using [hydroxy(2,4-dinitrobenzenesulfonyloxy)iodo]-benzene,[585] the one-pot preparation of 2,4,5-trisubstituted oxazoles from ketones, nitriles, and aryliodine(III) triflates generated in situ from iodoarene, *m*CPBA, and triflic acid,[586] the preparation of flavones from flavanones using HTIB,[587] the synthesis of isoflavones from 2′-benzoyloxychalcones using polymer-supported HTIB,[588] the preparation of 3-tosyloxychromanones by the reaction of HTIB with chromanone and 2-methylchromanone,[589] the HTIB-promoted one-pot synthesis of 3-carbomethoxy-4-arylfuran-2-(5*H*)-ones from ketones,[590] the HTIB mediated synthesis of 2-aryl-7-cyano(ethoxycarbonyl)-6-methylthio-1*H*-imidazo[1,2-*b*]pyra-

**Scheme 88**




**Scheme 89**




zoles from 5-amino-4-cyano(ethoxycarbonyl)-3-methylthio-1*H*-pyrazole and acetophenones,[591,592] the synthesis of imidazo[2,1-*a*]isoquinolines using [hydroxy(2,4-dinitrobenzenesulfonyloxy)iodo]benzene,[593] and the microwave-promoted solvent-free oxidation of α-methylene ketones to α-diketones.[594]

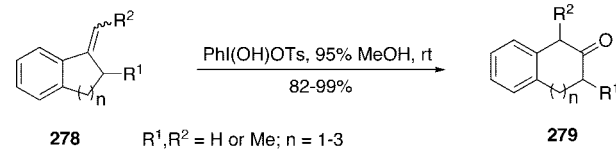
Recent modifications of this procedure (Scheme 87) include the use of solvent-free reaction conditions,[563,575] application of ionic liquids as solvents,[595−597] the use of recyclable reagents **267**−**271**,[103,260,261,264] the use of heterocycle-based reagents **264** and **265**,[560] and the catalytic α-oxytosylation of ketones using *m*CPBA as stoichiometric oxidant and iodoarenes as catalysts in the presence of *p*-toluenesulfonic acid.[598−601]

HTIB has been used in various oxidative rearrangements and fragmentations. Justik and Koser have reported a study of an oxidative rearrangement that occurs upon the treatment of arylalkenes **272** with HTIB in 95% methanol, affording the corresponding α-aryl ketones **273** in generally high yields (Scheme 88). This oxidative rearrangement is general for acyclic and cyclic arylalkenes and permits the regioselective syntheses of isomeric α-phenyl ketone pairs.[602]

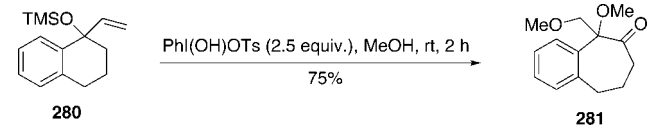
A similar HTIB-induced oxidative rearrangement has recently been utilized in the regioselective synthesis of 6-prenylpolyhydroxyisoflavone (wighteone)[603] and in a diastereoselective total synthesis of (±)-indatraline.[604] In particular, the key intermediate product **275** in the synthesis of wighteone was prepared by the oxidative rearrangement of 3′-iodotetraalkoxychalcone **274**,[603] and the key step in the synthesis of (±)-indatraline involved the HTIB-promoted diastereoselective ring contraction of a 1,2-dihydronaphthalene **276** to construct the indane ring system **277** (Scheme 89).[604] A similar oxidative rearrangement of 3-cinnamoyl-4-hydroxy-6-methyl-2*H*-pyran-2-ones with HTIB in dichloromethane followed by cyclization was used by Prakash and co-workers for the direct conversion of *o*-hydroxychalcones into isoflavone derivatives.[605]

The HTIB-induced oxidative rearrangement of alkenes can be effectively used in ring expansion reactions. Justik and Koser have investigated the oxidative ring expansions of alkylidenebenzocycloalkenes **278** to β-benzocycloalkenones **279** using HTIB in 95% methanol (Scheme 90).[606] This reaction allows the efficient conversion of alkenes **278**, which can be conveniently prepared from the respective α-benzocycloalkenones by Wittig olefination, to the homologous β-benzocycloalkenones **279** containing six-, seven-, and eight-membered rings.

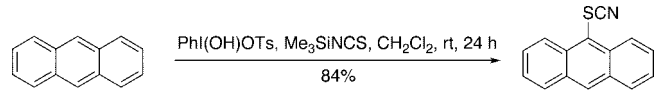
**Scheme 90**



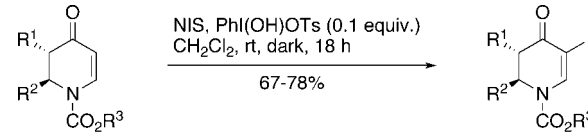

**Scheme 91**




**Scheme 92**




**Scheme 93**




$R^1$ = H or OAc
$R^2$ = Ph or $CH_2$=CH
$R^3$ = Ph or Bn

Silva and co-workers reported a similar HTIB-promoted ring expansion of 1-vinylcycloalkanol derivatives leading to seven- or eight-membered rings. In a specific example, the reaction of the unsaturated TMS ether **280** with excess HTIB affords benzocycloheptanone derivative **281** in high yield (Scheme 91).[607]

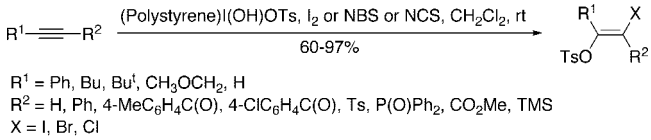
HTIB is commonly used for the oxidative functionalization of arenes, alkenes, and alkynes. Koser, Telu, and Laali investigated the oxidative substitution reactions of polycyclic aromatic hydrocarbons with iodine(III) sulfonate reagents.[608] Various polycyclic arenes, such as pyrene, anthracene, phenanthrene, perylene, and others, undergo regioselective oxidative substitution reactions with iodine(III) sulfonate reagents in dichloromethane at room temperature to give the corresponding aryl sulfonate esters in moderate to good yields. The reaction of polycyclic aromatic hydrocarbons with HTIB in the presence of trimethylsilyl isothiocyanate leads to the regioselective thiocyanation of the PAH nucleus, as illustrated by the reaction of anthracene shown in Scheme 92.[608]

Dihydropyridone derivatives **282** can be efficiently iodinated to afford products **283** by the treatment with *N*-iodosuccinimide (NIS) in the presence of HTIB (Scheme 93).[609]

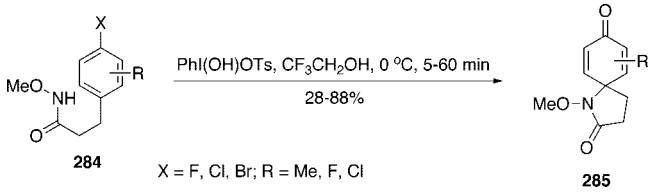
Poly[4-(hydroxy)(tosyloxy)iodo]styrene can be used in the halotosyloxylation reaction of alkynes with iodine or *N*-bromosuccinimide (NBS) or *N*-chlorosuccinimide (NCS) (Scheme 94).[610] The polymer reagent can be regenerated and reused.

HTIB can also be used in the oxidative rearrangements and fragmentations of various nitrogen-containing compounds. Similar to [bis(trifluoroacetoxy)iodo]benzene, HTIB can be applied in the intramolecular cyclization reactions

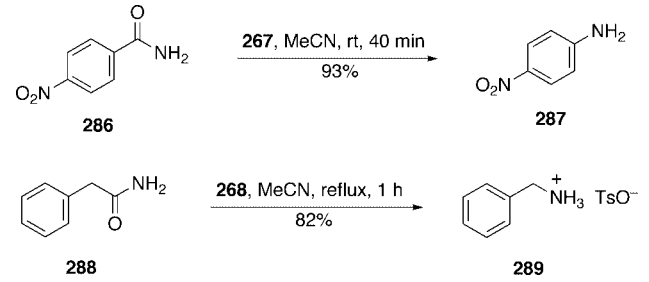
**Scheme 94**



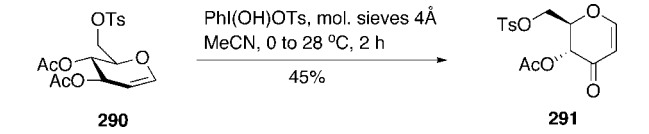

**Scheme 95**




**Scheme 96**




**Scheme 97**



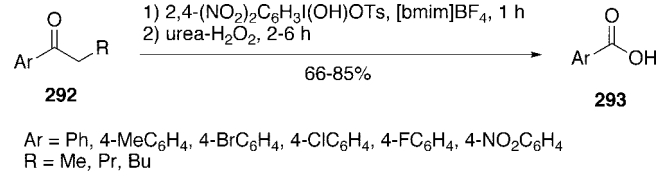

involving *N*-acylnitrenium intermediates **142** (see Scheme 48 in section 3.4.5).[366,611] For example, spirodienones **285** bearing the 1-azaspiro[4.5]decane ring system were synthesized from *N*-methoxy-3-(4-halophenyl)propanamides **284** via the intramolecular *ipso*-cyclization of a nitrenium ion generated with HTIB in trifluoroethanol (Scheme 95).[611] The HTIB-promoted cyclizations of the appropriate amides were also utilized in the preparation of 2,1-benzothiazine derivatives from sulfonamides[612] and in the synthesis of (−)-lapatin B via oxidative cyclization of *N,N*-diacetylglyantrypine.[613]

Similar to [bis(acyloxy)iodo]arenes (see section 3.4.5), HTIB can serve as an excellent oxidant in Hofmann-type degradation of carboxamides to the respective amines.[614−616] In a recent example, primary alkyl- and benzylcarboxamides were converted to the corresponding alkylammonium tosylates with poly[4-hydroxy(tosyloxy)iodo]styrene in acetonitrile at reflux in yields ranging from 60% to 90%.[617] Likewise, the recyclable reagents **267**[103] and **268**[260] (see section 3.5.1) have been used to convert *p*-nitrobenzamide **286** and phenylacetamide **288** to the respective aniline **287** and benzylammonium tosylate **289** in good yields under mild reaction conditions (Scheme 96).[103,260]

Benzylic alcohols can be oxidized with HTIB under solvent-free microwave irradiation conditions to afford the corresponding aldehydes or ketones in excellent yields.[618] The glucal derivative **290** was oxidized to the enone **291** by treatment with HTIB in acetonitrile (Scheme 97).[619]

Aryl ketones **292** can be converted to the corresponding substituted benzoic acids **293** by sequential treatment with

**Scheme 98**




[hydroxy(2,4-dinitrobenzenesulfonyloxy)iodo]benzene and urea−hydrogen peroxide in [bmim]$BF_4$ ionic liquid (Scheme 98).[620]

Yan and co-workers reported a catalyst- and base-free Suzuki-type coupling reaction of sodium tetraphenylborate with HTIB or other $\lambda^3$-iodanes. This noncatalytic coupling affords the respective biaryls in good yields in water solution or solvent-free conditions under microwave irradiation.[621−623]

HTIB and other sulfonate derivatives of iodosylbenzene have also found wide application for the preparation of various iodonium salts.

## 3.6. Nitrogen-Substituted $\lambda^3$-Iodanes

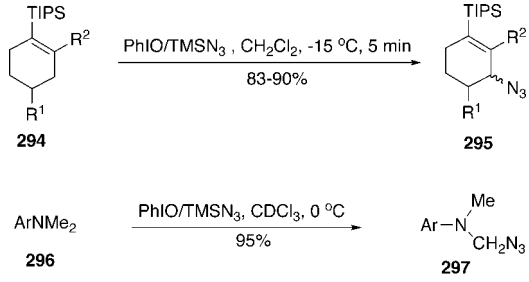
The noncyclic aryliodine(III) derivatives with an iodine nitrogen bond usually lack stability and, with a few exceptions, cannot be isolated as individual compounds. The chemistry of these compounds was discussed in our previous reviews.[5,6] In particular, several examples of aryliodine(III) amides, ArI(NHCOR)$_2$, derived from phthalimide, succinimide, glutarimide, and saccharine have been reported by Varvoglis and co-workers.[624−626] Aryliodine(III) amides ArI(NHCOR)OAc and ArI(NHCOR)OTs bearing one N-ligand at iodine 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.

The noncyclic azidoiodanes, PhI($N_3$)X (X = OAc, Cl, OTMS, etc.) or PhI($N_3$)$_2$, were proposed as reactive intermediates in the widely used azidation reactions involving the combination of iodosylbenzene or (diacetoxy)iodobenzene with trimethylsilyl azide or sodium azide.[5] Attempts to isolate these intermediates always resulted in fast decomposition at −25 to 0 °C with the formation of iodobenzene and dinitrogen; however, low-temperature spectroscopy and the subsequent chemical reactions in situ provided some experimental evidence toward the existence of these species. The final proof for the existence of azidoiodanes was provided by the preparation and the single-crystal X-ray structure determination of stable azidobenziodoxoles.[627]

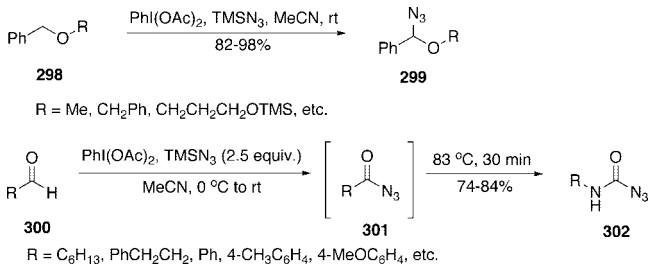
(Diazidoiodo)benzene, PhI($N_3$)$_2$, generated in situ from PhIO/$TMSN_3$, has found some practical application as an efficient reagent for the introduction of the azido function into organic molecules.[6] Magnus and co-workers reported the synthetically useful azidation of triisopropylsilyl enol ethers **294**, affording $\beta$-azido adducts **295** and the azidation of *N,N*-dimethylarylamines **296** to give *N*-azidomethyl derivatives **297** in excellent yields (Scheme 99).[628−630]

More recently, Bols and co-workers have found that the PhI(OAc)$_2$/$TMSN_3$ system is similar in reactivity to $IN_3$ and can promote high-yield azidations of ethers, aldehydes, and benzal acetals at 0 °C to room temperature in acetonitrile.[631] For example, the azidation of ethers **298** under these conditions leads to benzylic azides **299**, while the aldehydes **300** initially afford the unstable acyl azides **301**, which are

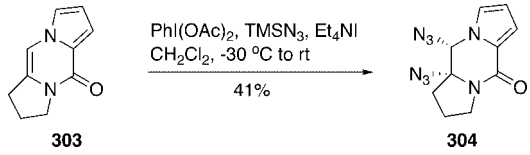
**Scheme 99**




**Scheme 100**




**Scheme 101**

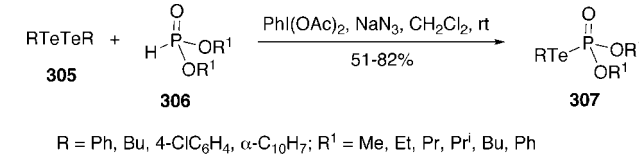



converted to carbamoyl azides **302** via the Curtius rearrangement upon heating with an excess of $TMSN_3$ (Scheme 100). These azidations proceed through a radical mechanism and involve the initial generation of $PhI(N_3)_2$. It is essential for the reaction that $TMSN_3$ is added subsequent to the mixture of $PhI(OAc)_2$ and the substrate; mixing of $TMSN_3$ and $PhI(OAc)_2$ before adding the substrate completely fails to produce any azidation products, presumably because the generated intermediate azidoiodane species decompose before the reaction.[631]

Austin and co-workers utilized the $PhI(N_3)_2$ mediated vicinal diazidation of a double bond in the key step of the total synthesis of (±)-dibromophakellstatin. The key *syn*-diazide **304** was prepared by the treatment of pyrazinone **303** with the $PhI(OAc)_2/TMSN_3$ system followed by the addition of tetraethylammonium iodide (Scheme 101).[632] Under these conditions, the initially generated $PhI(N_3)_2$ further reacts with the iodide anion, leading to the in situ formation of the diazido iodate anion, $(N_3)_2I^-$,[633] which serves as the actual azidating species in this reaction.

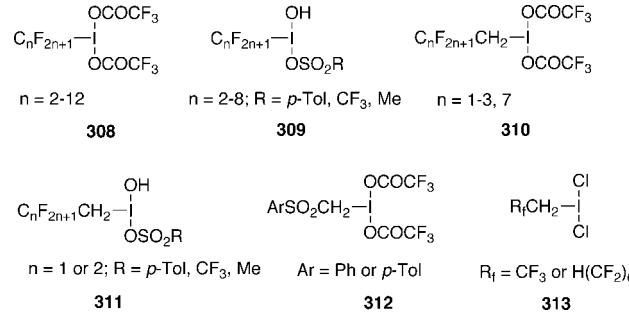
The interaction of the $PhI(OAc)_2/NaN_3$ system with organic ditellurides can be used for the generation of the organotellurenyl radicals. This reaction has been utilized in the synthesis of organyltellurophosphates **307** by the treatment of diorganyl phosphites **306** and diorganyl ditellurides **305** with (diacetoxyiodo)benzene and sodium azide in dichloromethane at room temperature (Scheme 102).[634]

**Scheme 102**




## 3.7. Stabilized Alkyl-Substituted $\lambda^3$-Iodanes

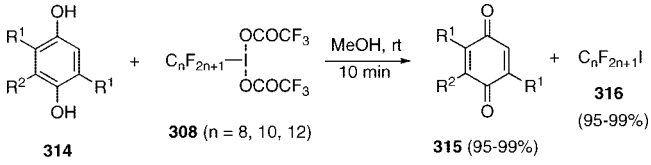
Alkyl-substituted $\lambda^3$-iodanes, $RIX_2$, in general lack stability and can exist only as short-lived reactive intermediates in the oxidations of alkyliodides.[5,6] The thermal stability of alkyliodosyl derivatives can be substantially increased by steric or electronic modification of the alkyl moiety, preventing decomposition of the molecule by either elimination or nucleophilic substitution pathways. Most commonly, such a stabilization is achieved by the introduction of electron-withdrawing substituents, such as fluorine atoms or a sulfonyl group, into the alkyl moiety. Especially well-investigated and important representatives of stabilized alkyl-substituted $\lambda^3$-iodanes are [bis(trifluoroacetoxy)iodo]perfluoroalkanes **308**,[44,417,635−639] [hydroxy(sulfonyloxy)iodo]perfluoroalkanes **309**,[640,641] 1-[bis(trifluoroacetoxy)iodo]-1*H*,1*H*-perfluoroalkanes **310**,[642] 1-[hydroxy(sulfonyloxy)iodo]-1*H*,1*H*-perfluoroalkanes **311**,[643,644] [bis(trifluoroacetoxy)iodo](arylsulfonyl)-methane derivatives **312**,[645] and fluoroalkyliododichlorides **313**.[225]




The trifluoroacetate derivatives **308**, **310**, and **312** are usually prepared by the oxidation of appropriate iodides with 80% hydrogen peroxide and trifluoroacetic anhydride followed by removal of the volatile products in vacuum (yield 97−98%).[637,638,640] A convenient procedure for the preparation of [bis(trifluoroacetoxy)iodo]perfluoroalkanes **308** by the oxidation of commercial perfluoroalkyl iodides using a urea−hydrogen peroxide complex in a mixture of trifluoroacetic anhydride and trifluoroacetic acid at −5 to 0 °C was recently reported.[417] Trifluoroacetates **308** and **310** can be converted to sulfonates **309** and **311** by treatment with the appropriate sulfonic acid.[640,644] In contrast to the starting trifluoroacetates **308** and **310**, sulfonates **309** and **311** have a substantially higher thermal stability and are not water sensitive; they can be purified by crystallization from acetonitrile, and can be stored for several months in a refrigerator.

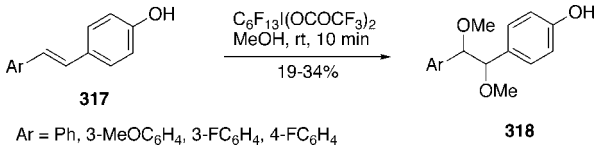
Single crystal X-ray diffraction studies of several representatives of stabilized alkyl-substituted $\lambda^3$-iodanes have previously been reported, namely, trifluoromethyliodine(III) difluoride, $CF_3IF_2$ (see section 3.2.2),[190] trifluoromethyliodine(III) dichloride, $CF_3ICl_2$,[646] trifluoromethyliodine(III) chloride fluoride, $CF_3I(Cl)F$,[647] [bis(trifluoroacetoxy)iodo]trifluoromethane, $CF_3I(OCOCF_3)_2$,[648] trifluoromethyliodine(III) chloride trifluoroacetate, $CF_3I(Cl)OCOCF_3$,[649] [bis(methoxy)iodo]trifluoromethane, $CF_3I(OMe)_2$,[650] methoxy(trifluoromethyl)iodine(III) chloride, $CF_3I(Cl)OMe$,[650] fluoroalkyliododichlorides **313** (see section 3.3.2),[225] and the bis(trifluoroacetate) $CF_3CH_2I(OCOCF_3)_2$.[651] In particular, the bis(trifluoroacetate) $CF_3CH_2I(OCOCF_3)_2$ has a distorted T-shaped coordination similar to that of other known dicarboxylates but forms a

**Scheme 103**




$R^1/R^2$ = H/H, Me/Me, Bu$^t$/H, Cl/H

**Scheme 104**




Ar = Ph, 3-MeOC$_6$H$_4$, 3-FC$_6$H$_4$, 4-FC$_6$H$_4$

previously unknown tetrameric array of molecules due to strong intermolecular I•••O contacts.[651]

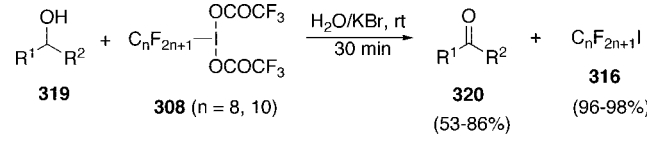
[Bis(trifluoroacetoxy)iodo]perfluoroalkanes **308** are the most practically useful representatives of stabilized alkyl-substituted $\lambda^3$-iodanes. Trifluoroacetates **308** have found practical application as starting compounds for the preparation of (perfluoroalkyl)aryliodonium salts, which are useful electrophilic perfluoroalkylating reagents.[44] Recently, Tesevic and Gladysz have demostrated the utility of [bis(trifluoroacetoxy)iodo]perfluoroalkanes **308** with a long fluorous alkyl chain ($n$=7−12) as convenient recyclable oxidants.[637,638] Similarly to [bis(trifluoroacetoxy)iodo]benzene and (diacetoxyiodo)benzene (see section 3.4.6), [bis(trifluoroacetoxy)iodo]-perfluoroalkanes can serve as excellent reagents for the oxidation of phenolic substrates. The reduced form of the reagent, the respective iodoperfluoroalkane, can be efficiently separated from the reaction mixture using fluorous techniques and reused. In a specific example, reagents **308** ($n$ = 8, 10, 12) can rapidly oxidize 1,4-hydroquinones **314** to the respective quinones **315** in methanol at room temperature (Scheme 103). Subsequent addition of a fluorous solvent, such as perfluoro(methylcyclohexane), results in a liquid/liquid biphase system. The product quinones **315** are generally isolated in about 95% yields from the methanol phase, and iodoperfluoroalkanes **316** are isolated in 98−99% yields from the fluorous phase. The recovered iodoperfluoroalkanes **316** may be reoxidized to the initial reagents **308** in 97% yield and reused.[637]

Westwell and co-workers investigated the oxidation of hydroxylated stilbenes **317** using [bis(trifluoroacetoxy)iodo]perfluorohexane (Scheme 104).[417] Instead of the expected products of the phenolic oxidation, diaryl-1,2-dimethoxyethanes **318** as mixtures of diastereoisomers were isolated in moderate yields from this reaction. The perfluorohexyl iodide byproduct (bp 140 °C) could be removed simply by evaporation of the reaction mixture under reduced pressure.[417]

[Bis(trifluoroacetoxy)iodo]perfluoroalkanes **308** ($n$ = 7, 8, 10, 12) are effective and easily recyclable reagents for the oxidation of aliphatic and benzylic secondary alcohols **319** to ketones **320** in the presence of aqueous KBr and the absence of organic or fluorous solvents (Scheme 105).[638] The reduced form of the reagent, the respective iodoperfluoroalkane **316**, can be efficiently isolated from the reaction mixture in 96−98% yield by adding 3−5 volumes of methanol and separating the resulting fluorous/methanolic liquid/liquid biphase system. The recovered iodoperfluoroalkane **316** can be reoxidized to reagent **308** and reused.[638]

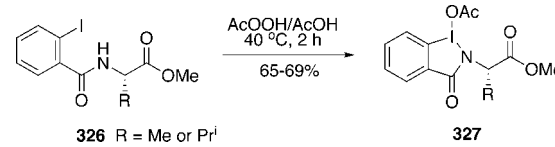
It is noteworthy that the fluorous reagents **308** oxidize secondary alcohols in the presence of bromide ions much

**Scheme 105**




$R^1/R^2$ = Ph/Et, Ph/Me, Me/C$_6$H$_{13}$, –(CH$_2$)$_7$–, menthol

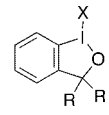
**Scheme 106**




more rapidly than other iodine(III) compounds (e.g., iodosylbenzene or DIB) under similar conditions. The higher reactivity may in part be ascribed to the directly bound electron-withdrawing perfluoroalkyl substituent in compounds **308**, which enhances its oxidizing strength.[638]

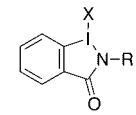
## 3.8. Iodine(III) Heterocycles

The most important iodine(III) heterocycles are represented by various derivatives of benziodoxole **321** and benziodazole **322**.[24] The collective name "benziodoxoles" is commonly used for heterocycles **321** with iodine and oxygen incorporated in the five-membered ring and various substituents X attached to iodine. The first derivatives of benziodoxole, 1-hydroxy-1,2-benziodoxol-3-(1*H*)-one (**321**, X = OH, 2R = O)[652] and 1-chloro-1,2-benziodoxol-3-(1*H*)-one (**321**, X = Cl, 2R = O),[653] were prepared over 100 years ago by oxidation or chlorination of 2-iodobenzoic acid. In the mid-1980s, 1-hydroxybenziodoxoles have attracted considerable interest and research activity, mainly due to their excellent catalytic activity in the cleavage of reactive phosphate esters.[33] More recently, various new benziodoxole derivatives were synthesized and their usefulness as reagents for organic synthesis was demonstrated.[24] In contrast to benziodoxoles, the analogous five-membered iodine−nitrogen heterocycles, benziodazoles **322**, have received much less attention and, moreover, their structural assignment in some cases was not reliable. The most important and readily available derivative of benziodazole, 1-acetoxybenziodazole (**322**; X = OAc, R = H), was first prepared in 1965 by the peracetic oxidation of 2-iodobenzamide,[654] and the correct structure of this compound was reported in 1997.[655]



**321**

R = alkyl or 2R = O,
X = OH, Cl, Br, OTs, OAc, CN, N$_3$, etc.

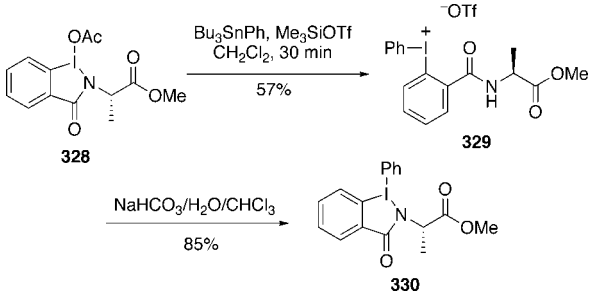


**322**

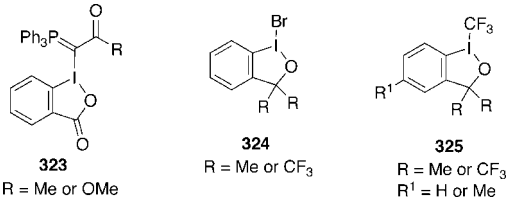
R = H or alkyl; X = Cl, OAc, etc.

X-ray molecular structures were reported for numerous benziodoxole derivatives **321**.[100,101,627,656−668] In general, the five-membered ring in benziodoxole is highly distorted with almost linear alignment of the two electronegative ligands. The I−O bond length in benziodoxolones (**321**, 2R = O) varies in a wide range from 2.11 Å in carboxylates (**321**; X = $m$-ClC$_6$H$_4$CO$_2$)[661] to 2.48 Å in the phenyl derivative (**321**, X = Ph),[100] 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

**Scheme 107**




the expected angle of 90° for the normal T-shaped geometry of hypervalent iodine. The examples of recently reported X-ray structures of benziodoxoles include phosphoranyl-derived benziodoxoles **323**,[101] 1-bromobenziodoxoles **324**,[666] and 1-trifluoromethylbenziodoxoles **325**.[667,668] Benziodoxoles **323** and **325** were prepared by a standard ligand exchange procedure starting from the appropriate 1-acetoxybenziodoxole and a phosphonium ylide or $CF_3SiMe_3$, respectively,[101,667,668] while 1-bromobenziodoxoles **324** were synthesized in 56−60% yield by oxidative bromination of the appropriate iodoarenes with *N*-bromosuccinimide.[666]

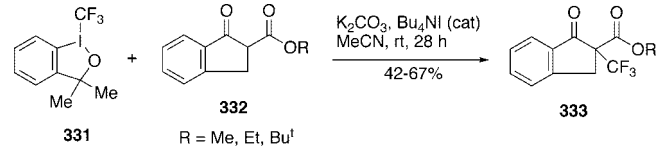



The structural parameters of benziodazoles (**322**, X = OAc or Ph) in general are similar to those of benziodoxoles.[74,102,655] The synthesis and structural studies of N-functionalized benziodazoles were recently reported.[102] 1-Acetoxybenziodazoles **327** were prepared by the peracetic oxidation of 2-iodobenzamides **326** derived from alanine or valine (Scheme 106).[102]

The alanine derivative **328** was further converted to phenyliodonium salt **329**, which, according to X-ray data, has a pseudocyclic structure with an I•••O distance of 2.56 Å in the benziodoxole ring.[102] The treatment of pseudobenziodoxole **329** with sodium bicarbonate affords 1-phenylbenziodazole **330** (Scheme 107), whose structural parameters are very similar to the structure of the previously reported 1-phenylbenziodoxole (**321**, X = Ph). In particular, the benziodazole ring system in compound **330** is essentially planar and has a relatively long I−N bond of 2.445 Å. This structural study of benziodazole-based phenyliodonium derivatives **329** and **330** provides insight into facile interchange between benziodazole and benziodoxole ring systems under acidic or basic conditions.[102]

The distinctive feature of heterocyclic $\lambda^3$-iodanes is the considerably higher stability than that of their acyclic analogues. This stabilization is usually explained by the bridging of the apical and the equatorial positions by a five-membered ring and also by the better overlap of the lone pair electrons on the iodine atom with the $\pi$-orbitals of the benzene ring.[656,669] The greater stability of benziodoxoles enabled the preparation and isolation of otherwise unstable iodine(III) derivatives with I−Br,[656,666] I−OOR,[670−674] I−$N_3$,[627,675,676] I−CN,[664,665,677] and I−$CF_3$ bonds.[667,668] These various benziodoxole derivatives have found practical application as the reagents for oxidative functionalization of

**Scheme 108**




organic substrates. For example, the stable 1-azidobenziodoxoles (**321**, X = $N_3$) can be used as efficient reagents for direct azidation of an unactivated C−H bond in alkanes,[627,675,676] while 1-*tert*-butylperoxy-1,2-benziodoxol-3(1H)-one (**321**, X = $OOBu^t$) is a useful oxidant with numerous synthetic applications.[670−674] Ochiai and co-workers have recently demonstrated that 1-*tert*-butylperoxy-1,2-benziodoxol-3(1H)-one is a particularly useful radical reagent for the generation of α-oxy carbon-centered radicals from cyclic ethers and acetals.[674,678]

Togni and co-workers have found that 1-trifluoromethylbenziodoxole **331** is a useful reagent for electrophilic trifluoromethylation of nucleophilic substrates. This reagent, in particular, reacts with $\beta$-ketoesters **332** under mild conditions in the presence of potassium carbonate, affording α-trifluoromethylated product **333** in good yield (Scheme 108).[667,668] Likewise, this mild electrophilic trifluoromethylation reagent can be used to transfer a $CF_3$ group to other C-centered nucleophiles, such as α-nitro esters, to S-centered nucleophiles,[668] and to secondary or primary aryl- and alkylphosphines.[679]

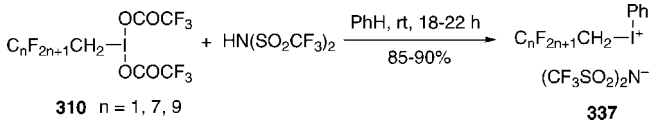
Very recently, Hu and co-workers have reported the preparation of the reagent's **331** analogue bearing a $PhSO_2CF_2$-substituent on the iodine atom. This new benziodoxole derivative was found to act as the electrophilic (phenylsulfonyl)difluoromethylating reagent for a variety of S-nucleophiles under mild reaction conditions.[680]

## 3.9. Iodonium Salts

Iodonium salts, $R_2I^+ X^-$, are defined as positively charged 8-I-2 species with two carbon ligands and a negatively charged counterion. X-ray structural data for the overwhelming majority of iodonium salts show a significant secondary bonding between the iodine atom and the anion, with average bond distances within a range of 2.3−2.7 Å, which results in a pseudo-trigonal bipyramidal geometry similar to that for $\lambda^3$-iodanes with one carbon ligand. In agreement with this model, the experimentally determined bond angle R−I−R in iodonium salts is close to 90°.[6] The most common and well investigated class of these compounds are diaryliodonium salts, known for over 100 years and extensively covered in previous reviews. In the 1980s and 1990s, significant research activity was focused on aryliodonium derivatives, $Ar(R)I^+ X^-$, bearing alkynyl, alkenyl, or fluoroalkyl groups as ligand R. These aryl-substituted iodonium salts are particularly useful reagents for the electrophilic transfer of ligand R to electron-rich organic substrates. The high reactivity of phenyliodonium salts, $Ph(R)I^+ X^-$, in these reactions is explained by the "hyperleaving group ability" of the PhI group, which has a leaving group ability about $10^6$ times greater than that of triflate.[681]

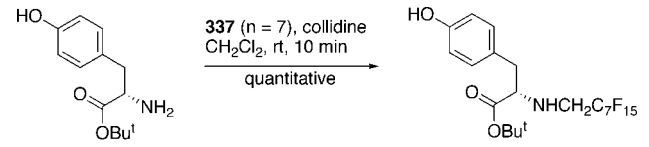
Stable iodonium salts have found numerous practical applications, such as as cationic photoinitiators in polymer chemistry[682−685] and as biologically active compounds. A summary of the biological properties of iodonium salts is provided in our 1996 review.[5] In a specific example, a recent

**Scheme 109**




**310** n = 1, 7, 9 **337**

**Scheme 110**



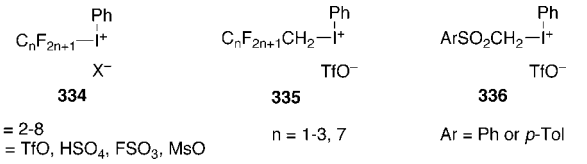

**338** **339**

study of the in vitro activities of several iodonium salts against oral and dental anaerobes has demonstrated that their activities are comparable to that of chlorhexidine and these compounds may be suitable for incorporation into an oral mouthwash.[686]

In this section, the preparation and chemistry of iodonium salts will be discussed with emphasis on recent synthetic applications.

### 3.9.1. Alkyl- and Fluoroalkyliodonium Salts

Similar to the alkyl-substituted $\lambda^3$-iodanes (see section 3.7), iodonium salts with one or two aliphatic groups generally lack stability.[6] The presence of electron-withdrawing groups in the alkyl group of iodonium salts has a pronounced stabilizing effect. The most stable derivatives of this type are fluoroalkyl(aryl)iodonium salts **334** and **335** and (arylsulfonylmethyl)iodonium triflates **336**. The preparation of fluoroalkyl(aryl)iodonium salts and their application as electrophilic fluoroalkylating reagents was reviewed by Umemoto.[44] Iodonium salts **334**−**336** are usually prepared by the reaction of the appropriate bis(trifluoroacetates) **308**, **310**, and **312** (section 3.7) with benzene in the presence of trifluoromethanesulfonic or another strong acid.[6] The structure of iodonium triflate **336** (Ar = Tol) was unambiguously established by a single-crystal X-ray analysis.[645]




**334** **335** **336**

n = 2-8
X = TfO, $HSO_4$, $FSO_3$, MsO

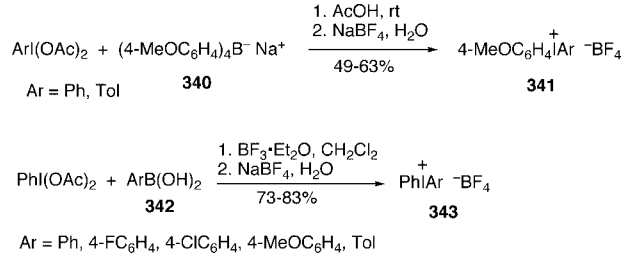
n = 1-3, 7

Ar = Ph or *p*-Tol

The preparation of fluoroalkyliodonium salts **337** by the reaction of bis(trifluoroacetates) **310** with benzene and triflimide acid was recently reported (Scheme 109).[225,651,687] The structure of trifluoroethyl(phenyl) iodonium salt **337** ($n$ = 1) was established by a single-crystal X-ray analysis.[225] In contrast to fluoroalkyliodonium triflates **335**, compounds **337** are stable to water and can be used for fluoroalkylations in aqueous media.

Compounds **337** are especially useful as reagents for fluoroalkylation of amino acids and peptides.[651,687−691] For example, the reaction of iodonium salt **337** ($n$ = 7) with the *tert*-butyl carboxyl ester of tyrosine **338** in the presence of collidine results in quantitative formation of the monoalkylation product **339** (Scheme 110).[687,690] Due to this reactivity, iodonium salts **337** can be used as fluorous capping reagents for facile purification of peptides synthesized on the solid phase.[687,691]

**Scheme 111**




### 3.9.2. Aryl- and Heteroaryliodonium Salts

Diaryliodonium salts belong to the most common and well investigated class of iodine(III) compounds, and the chemistry of these compounds has been extensively covered in previous reviews.[5,6] In this section, the preparative methods and recent examples of synthetic applications of diaryliodonium and heteroaryliodonium salts, $Ar_2I^+X^-$, are overviewed. Numerous X-ray structures of aryliodonium salts have been reported in the older literature. The more recent structural studies include the X-ray structure reports on (2-methoxy-5-methylphenyl)(4-methoxy-2-methylphenyl)iodonium trifluoroacetate,[692] diaryl zwitterionic iodonium compound $PhI^+C_6H_4$-4-$SO_2N^-Tf$,[693] 1-naphthylphenyliodonium tetrafluoroborate, and 1-naphthylphenyliodonium tetrakis(pentafluorophenyl)gallate[694] and the study of the structural and electronic characteristics of thienyl(aryl)iodonium triflates.[695]

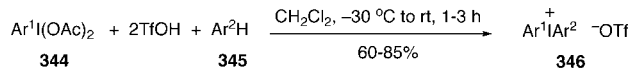
**3.9.2.1. Preparation of Aryliodonium Salts.** Diaryliodonium tetrafluoroborates **341** and **343** can be conveniently prepared by the boron−iodine(III) exchange reaction of (diacetoxyiodo)arenes with tetraarylborates **340**[696] or arylboronic acids **342**[697,698] followed by the treatment with a saturated sodium tetrafluoroborate solution (Scheme 111). Recent modification of this procedure consists of the treatment of aryltrifluoroborates, $ArBF_3^-K^+$, with (difluoroiodo)arenes under mild conditions.[205] Likewise, fluoroorganoiodonium tetrafluoroborates $(C_6F_5)_2I^+BF_4^-$, $(4\text{-}C_5F_4N)_2I^+BF_4^-$, and $[C_6F_5(4\text{-}C_5F_4N)I^+BF_4^-$ can be prepared by interaction of the appropriate (difluoroiodo)arenes with fluorinated organodifluoroboranes, $Ar_fBF_2$, in dichloromethane at 0 to 20 °C.[178]

An alternative procedure consists of a similar tin−iodine(III) and silicon−iodine(III) exchange reaction of (diacetoxyiodo)arenes or iodosylbenzene with tetraphenylstannane[699] or trimethylsilylbenzene[699] in the presence of boron trifluoride etherate.

Frohn and co-workers reported the preparation of a perfluoroaryliodonium salt, $(C_6F_5)_2I^+$ $AsF_6^-$, by the electrophilic arylation of $C_6F_5I$ with a stable pentafluorophenylxenonium hexafluoroarsenate, $C_6F_5Xe^+AsF_6^-$.[700]

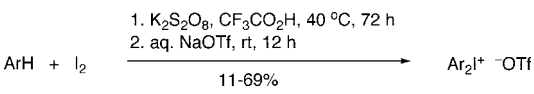
Numerous experimental procedures for the preparation of symmetrical and unsymmetrical diaryl- and hetaryliodonium sulfates and organosulfonates have been reported.[3,5,6] The most common synthetic approach to unsymmetric diaryl- and hetaryl(aryl)iodonium tosylates is based on the reactions of [hydroxy(tosyloxy)iodo]arenes with arenes,[701] aryl- or hetaryltrimethylsilanes,[702,703] aryltributylstannanes,[257,704,705] or arylboronic acids.[706] The reaction of HTIB with arylstannanes proceeds under milder conditions compared to those needed for reaction with arylsilanes and is applicable to a wide range of arenes with electron-withdrawing substituents. Arylboronic acids in general have some advantage over

**Scheme 112**



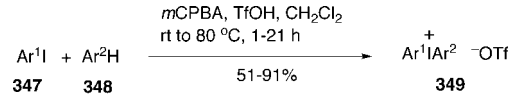

$Ar^1$ = Ph, 2-$MeC_6H_4$, 3-$MeC_6H_4$, 2,4,6-$Me_3C_6H_2$, 3,5-$Me_2C_6H_3$, 3-$MeOC_6H_4$
$Ar^2$ = 4-$MeC_6H_4$, 4-$MeOC_6H_4$, 2,4,6-$Me_3C_6H_2$, 4-$Bu^tCH_2C_6H_4$

**Scheme 113**




Ar = 4-$ClC_6H_4$, 4-$BrC_6H_4$, 4-$FC_6H_4$, 4-$IC_6H_4$, 4-$MeC_6H_4$, 4-$Bu^tC_6H_4$

**Scheme 114**




$Ar^1$ = Ph, 4-$ClC_6H_4$, 4-$BrC_6H_4$, 2-$MeC_6H_4$, 4-$MeC_6H_4$, 4-$Bu^tC_6H_4$, 4-$NO_2C_6H_4$, 4-$CF_3C_6H_4$, 4-$HO_2CC_6H_4$, 3-$CF_3C_6H_4$, 2-chloro-5-pyridinyl
$Ar^2$ = Ph, 4-$ClC_6H_4$, 4-$BrC_6H_4$, 4-$FC_6H_4$, 4-$MeOC_6H_4$, 4-$Bu^tC_6H_4$, 4-$MeC_6H_4$, 2,4,6-$Me_3C_6H_2$, 2,5-$Me_2C_6H_3$, 2,5-$Bu^t_2C_6H_3$

arylstannanes in the case of the electron-rich heterocyclic precursors.[706]

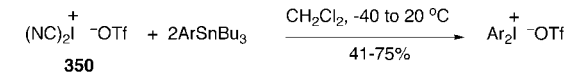
Various unsymmetrically functionalized diaryliodonium triflates **346** can be synthesized by the reaction of iodosylbenzene[707] or (diacetoxyiodo)arenes **344**[708] with arenes **345** in trifluoromethanesulfonic acid (Scheme 112).[708] This simple procedure affords diaryliodonium triflates in relatively high yields, but it is limited to aromatic substrates that are not sensitive to strong acids. Moreover, the formation of the *p*-phenylene type oligomeric iodonium salts as side products may occur upon the reaction of (diacetoxyiodo)benzene with trifluoromethanesulfonic acid.[569] In a milder and a 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.[706]

Several modified procedures for the preparation of diaryliodonium triflates have recently been reported. Kitamura and Hossain have developed a direct preparation of diaryliodonium triflates in good yields from iodoarenes and aromatic substrates using $K_2S_2O_8$ as an oxidant in a one-pot reaction.[709] Further modification of this procedure involves the reaction of arenes with elemental iodine and $K_2S_2O_8$ in trifluoroacetic acid, followed by treatment with sodium triflate (Scheme 113).[710,711]

Olofsson and co-workers have developed a general and efficient one-pot synthesis of symmetrical and unsymmetrical diaryliodonium triflates **349** from both electron-deficient and electron-rich arenes **348** and aryl iodides **347** using *m*CPBA as the oxidant and triflic acid (Scheme 114).[712−714] The electron-rich diaryliodonium tosylates are prepared similarly using toluenesulfonic acid instead of triflic acid as the additive.[714] Symmetrical diaryliodonium triflates can be synthesized by a modified one-pot procedure from iodine, arenes, *m*CPBA, and triflic acid under similar conditions.[712,713] A similar procedure based on a one-pot reaction of arylboronic acids, aryl iodides, *m*CPBA, and $BF_3$•$Et_2O$ has recently been used for regioselective synthesis of unsymmetrical diaryliodonium tetrafluoroborates.[715]

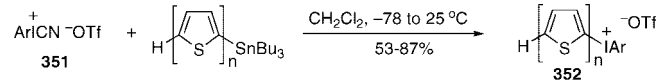
Skulski and Kraszkiewicz have recently reported a new method for the preparation of various symmetrical diaryliodonium bromides (in 15−88% crude yields) directly from arenes by the reaction of ArH with $NaIO_4$ in sulfuric acid followed by the addition of KBr.[716]

**Scheme 115**




Ar = Ph, 3-$MeOC_6H_4$, 4-$MeOC_6H_4$, 2-furyl, 2-thienyl, 4-pyrazolyl, etc.

**Scheme 116**




Ar = Ph, n = 1; Ar = Ph, n = 2
Ar = 4-$CF_3C_6H_4$, n = 2; Ar = 3-$ClC_6H_4$, n = 2

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.[253,255,717,718] Specifically, (dicyano)iodonium triflate **350**, generated in situ from iodosyl triflate and TMSCN, reacts with tributyltin derivatives of aromatic and heteroaromatic compounds, affording the corresponding symmetrical iodonium salts under very mild conditions (Scheme 115).[717,718]

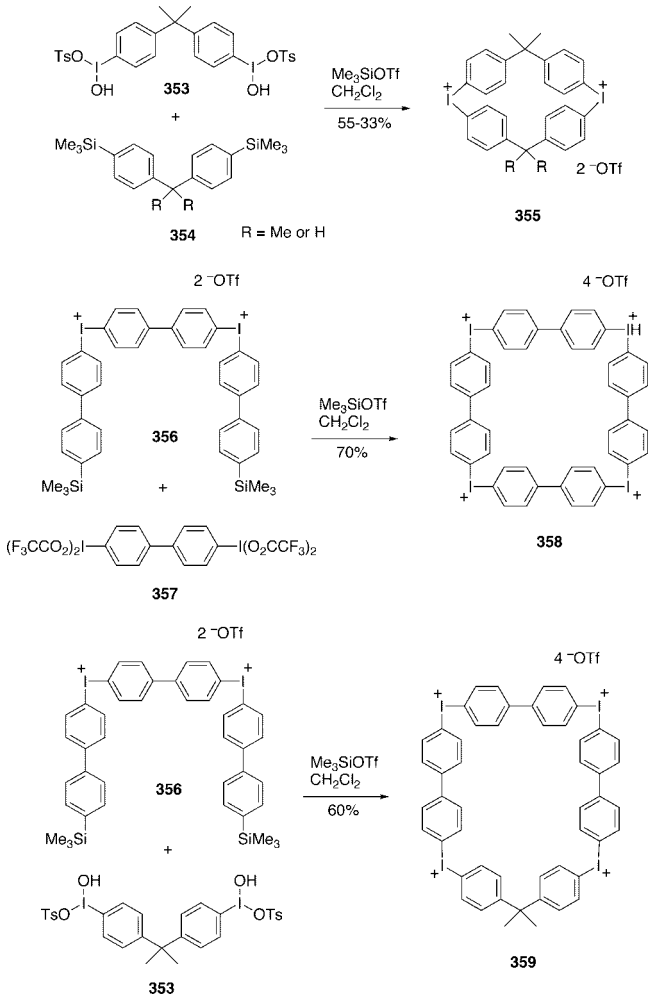
Aryl(cyano)iodonium triflates (e.g., **351**) can be used in a similar iodonium exchange with stannylated aromatic precursors, affording various mixed diaryl or aryl(heteroaryl) iodonium salts.[253,255,695] In a recent study, Tykwinski, Hinkle, and co-workers have utilized this iodonium transfer reaction in the preparation of a series of mono- and bithienyl(aryl)iodonium triflates **352** with increasingly electron-withdrawing substituents on the aryl moiety (Scheme 116).[695]

The preparation of several macrocyclic iodonium triflates, such as rhomboids **355**, a square **358**, and a pentagon **359**, was recently reported (Scheme 117).[719] The rhomboid shaped molecules **355** were prepared by the treatment of compounds **353** and **354** with trimethylsilyl triflate. The reaction of dication **356** with compound **357** in the presence of $Me_3SiOTf$ gave an iodonium containing molecular square **358** in 70% yield.[254,719] In addition, a pentagon-shaped macrocycle **359** was prepared in 60% yield from precursors **356** and **353**. The 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.[719]

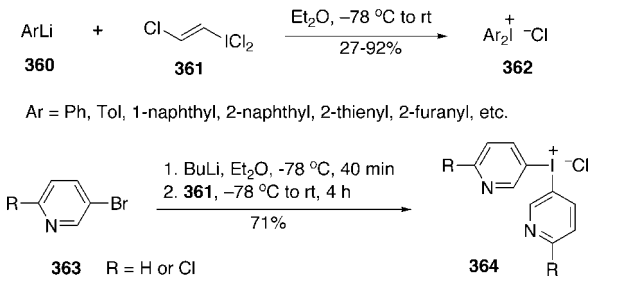
A very mild and selective approach to aryl- and hetaryliodonium chlorides **362** is based on the reaction of the appropriate aryllithium **360** (generated in situ from bromoarenes and butyllithium) with *trans*-(chlorovinyl)iodonium dichloride **361** (Scheme 118).[720−724] The iodonium transfer reagent **361** is prepared by the reaction of iodine trichloride with acetylene in concentrated hydrochloric acid;[722] this compound is extremely unstable and should be handled and stored with proper safety precautions.[721] The iodonium transfer procedure with reagent **361** is particularly useful for the preparation of bis(hetaryl)iodonium chlorides **364** from the appropriate nitrogen heterocycles **363** (Scheme 118).[721]

**3.9.2.2. Reactions of Aryliodonium Salts.** The most important and synthetically useful reactions of aryliodonium salts include the direct electrophilic arylations of various nucleophiles, the transition metal mediated cross-coupling reactions, and the reactions involving the generation and trapping of the benzyne intermediates.

**Scheme 117**



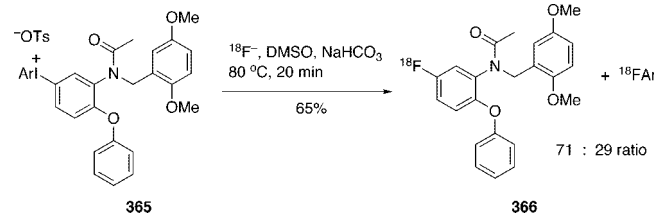

**Scheme 118**



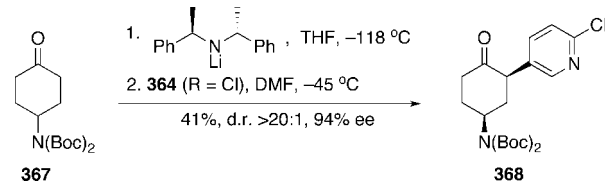

Numerous examples of the reactions of aryliodonium salts with such nucleophiles as thiosulfonate anions, fluoride anion, malonates, and silyl enol ethers under polar, noncatalytic conditions are provided in our previous reviews.[5,6] In more recent papers, the electrophilic arylations of sodium arenesulfinates,[725] potassium carbonotrithioates,[726] and benzazoles[727] using diaryliodonium salts in ionic liquids, and the arylations of anilines,[728] sodium tetraphenylborate,[729] and vinylindiums[730] have been reported.

The mechanism of solvolysis of methoxy-substituted diaryliodonium tetrafluoroborates, $ArI^{+}Ph\ {}^{-}BF_4$, in methanol and 2,2,2-trifluoroethanol has recently been investigated.[731] The solvolysis products include alkoxide substitution products (ArOR and PhOR) as well as iodoarenes (PhI and ArI). The ratios of products, ArOR/PhOR, range from 8/2 to 4/6. The results of this study provide experimental evidence against the formation of aryl cation under these conditions

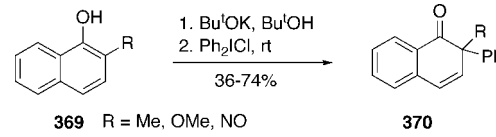
**Scheme 119**




**Scheme 120**




**Scheme 121**




and support the pathways via ligand coupling or $S_NAr2$ mechanisms involving a solvent molecule as a nucleophile in the transition state.[731]

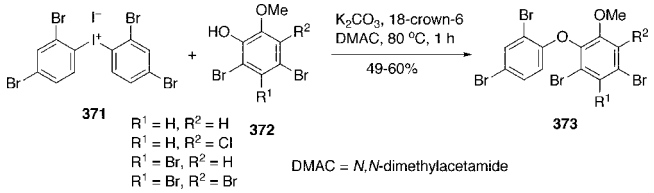
The reactions of aryliodonium salts with fluoride anion have recently been used for the preparation of fluorine-18 labeled aromatic compounds.[258,705,732] In a specific example, the $^{18}F$ labeled compound **366** was prepared by the reaction of diaryliodonium salt **365** with the radioactive $^{18}F$ anion (Scheme 119). Compound **366** is used as a positron emission tomography (PET) ligand for imaging peripheral-type benzodiazepine receptor.[705]

Reactions of arylation of carbon nucleophiles using aryliodonium salts are particularly important. Compounds containing an active methylene group, such as malonates, or the respective carbanions formed in situ, react smoothly with diaryliodonium salts to yield α-arylated products.[733,734] Aggarwal and Olofsson have developed a direct asymmetric α-arylation of prochiral ketones using chiral lithium amide bases and diaryliodonium salts.[721] In a specific example, the deprotonation of cyclohexanone derivative **367** using chiral Simpkins' (*R,R*)-base followed by the reaction with pyridyl iodonium salt **364** gave the arylated product **368** in 94% enantiomeric excess (Scheme 120). This reaction (Scheme 120) has been employed in a short total synthesis of the alkaloid (−)-epibatidine.[721]

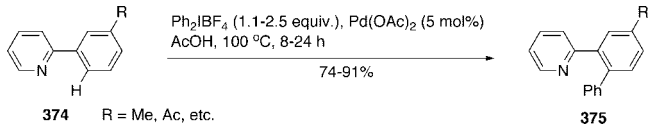
Ozanne-Beaudenon and Quideau reported a regioselective dearomatizing phenylation of phenols and naphthols using diaryliodonium salts.[735,736] For example, the treatment of naphthols **369** substituted at the *ortho* position by a small electron-donating group with diphenyliodonium chloride leads to their regioselective *ortho*-phenylation to give products **370** (Scheme 121). The mechanism of this reaction involves a nonradical direct coupling of the ligands on the hypervalent iodine center.[735] The formation of phenol ethers due to the O-phenylation can also occur when the reaction of phenolate anion with diphenyliodonium chloride is carried out in a polar aprotic solvent such as dimethylformamide.[735]

The O-arylation of the appropriate phenols using symmetrical iodonium salts has been utilized in the synthesis of hydroxylated and methoxylated polybrominated diphenyl

**Scheme 122**




**Scheme 123**



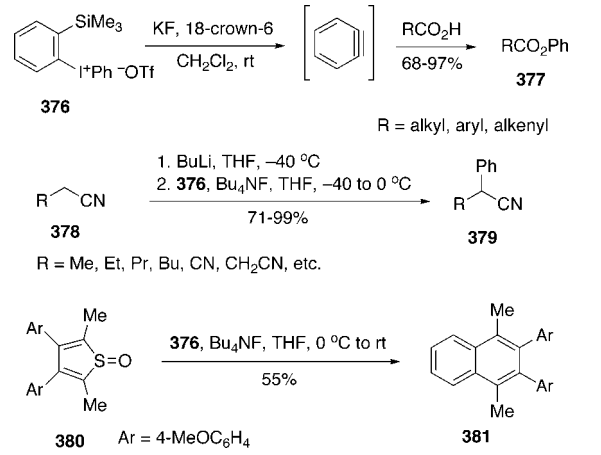

ethers, some of which are related to natural products.[737,738] In particular, several polybrominated diphenyl ethers **373** were prepared by the reaction of iodonium salt **371** with phenols **372** in *N,N*-dimethylacetamide solution under basic conditions (Scheme 122).[737]

Arylations with aryliodonium salts can be effectively catalyzed by transition metals. Aryliodonium salts can serve as efficient reagents in the copper-catalyzed arylation of lithium enolates,[739] thiophenes,[740] 5-aryl-2*H*-tetrazole,[741] and uracil nucleosides.[742]

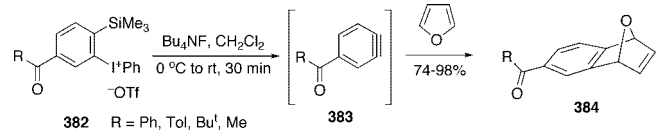
Palladium salts and complexes are efficient catalysts in the cross-coupling reactions of diaryliodonium salts with organoboron compounds,[743,744] organostannanes,[745] silanes,[746] organolead triacetates,[747] organobismuth(V) derivatives,[748] carbon monoxide,[749] allylic alcohols,[750] functionalized allenes,[751,752] Grignard reagents,[753] alkenes,[754,755] terminal alkynes,[756] and arenecarboxylic acids via decarboxylative cross-coupling reaction.[757] Particularly interesting is the palladium-catalyzed directed C−H activation/phenylation of substituted 2-phenylpyridines and indoles with aryliodonium salts recently reported by Sanford and co-workers.[698,758] In a representative example, 2-pyridyl-substituted substrates **374** are selectively phenylated to the *ortho*-position, affording products **375** in good yields (Scheme 123). Preliminary mechanistic experiments have provided evidence in support of a rare Pd(II)/(IV) catalytic cycle for this transformation.[698] The preparation of stable triorganyl Pd(IV) complexes by the electrophilic arylation of palladium(II) bipyridine complexes using $Ph_2I^+$ $TfO^-$ was reported by Canty and co-workers.[759]

Kitamura and co-workers reported the preparation and uses of several efficient benzyne precursors based on aryliodonium salts.[760−764] In particular, phenyl[2-(trimethylsilyl)phenyl]iodonium triflate (**376**) is readily prepared by the reaction of 1,2-bis(trimethylsilyl)benzene with the $PhI(OAc)_2$/TfOH reagent system.[760] The treatment of reagent **376** with tetrabutylammonium fluoride in dichloromethane at room temperature generates benzyne, which can be trapped with a diene to afford the respective benzyne adducts in high yields.[760] Recent examples of synthetic application of reagent **376** as benzyne precursor include *O*-arylation of carboxylic acids leading to aryl esters **377**,[765] preparation of 2-aryl-substituted nitriles **379** by arylation of nitriles **378** via a benzyne reaction,[766] and cycloaddition/elimination reaction of thiophene *S*-oxide **380** with benzyne leading to product **381** (Scheme 124).[767] Reagent **376** was also used in the synthesis of spiro(imidazolidine-2,3′-benzo[*b*]thiophene) by a one-pot reaction of benzyne, aryl isothiocyanates, and *N*-heterocyclic carbenes,[768] and for the preparation of benzo[*b*]seleno[2,3-*b*]pyridines by the reaction of acetic acid 2-selenoxo-2*H*-pyridin-1-yl esters with benzyne.[769]

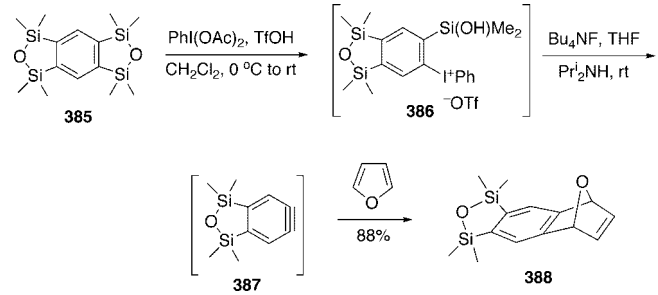
**Scheme 124**




**Scheme 125**




**Scheme 126**

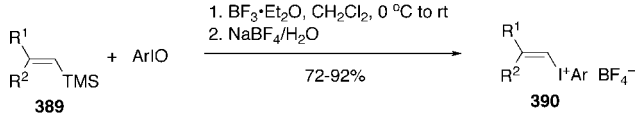



The efficient acylbenzyne precursors [5-acyl-2-(trimethylsilyl)phenyl]iodonium triflates **382** have recently been prepared by the reaction of the appropriate 1,2-bis(trimethylsilyl)benzenes with $PhI(OAc)_2$ in the presence of trifluoromethanesulfonic acid in dichloromethane at room temperature. Treatment of these reagents with $Bu_4NF$ in dichloromethane generates acylbenzynes **383**, which can be trapped by furan to give adducts **384** in high yield (Scheme 125).[763]

Lee and co-workers reported the preparation of oxadisilole-substituted benzyne precursors, such as iodonium triflate **386**, from benzobisoxadisilole **385** and the $PhI(OAc)_2$/TfOH reagent system.[770] The treatment of reagent **386** with $Bu_4NF$ in THF and diisopropylamine at room temperature generates oxadisilole-substituted benzyne **387**, which can be trapped with furan to afford adduct **388** in good yield (Scheme 126).

Ko, Kang, and co-workers have reported the generation and trapping of 1,2-dehydrocarborane, the carborane analogue of benzyne.[771] The 1,2-dehydrocarborane precursor, phenyl[*o*-(trimethylsilyl)carboranyl]iodonium acetate, was readily prepared by the reaction of [*o*-(trimethylsilyl)carboranyl]lithium and $PhI(OAc)_2$. 1,2-Dehydrocarborane was efficiently generated from phenyl[*o*-(trimethylsilyl)carboranyl]iodonium acetate by treatment with CsF in ether and trapped with dienes such as anthracene, naphthalene, norbornadiene, and 2,5-dimethylfuran to give the respective 1,2-dehydrocarborane adducts in high yield.[771]

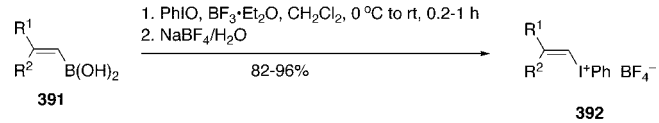
**Scheme 127**




389 390

$R^1$ = 4-$BrC_6H_4OCH_2$, $PhCH_2CH_2$, 4-$ClC_6H_4OCH_2$, n-$C_8H_{17}$, etc.
$R^2$ = H, Me; Ar = Ph, 2,4,6-$Me_3C_6H_2$, etc.

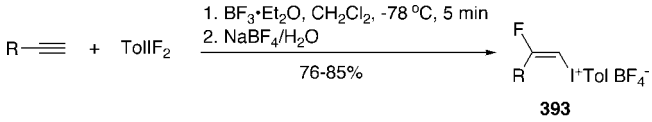
**Scheme 128**




391 392

$R^1$ = Bu, Bu$^t$, $Ph(CH_2)_3$, $(CH_3)_2CH(CH_2)_2$, etc.; $R^2$ = H, Me

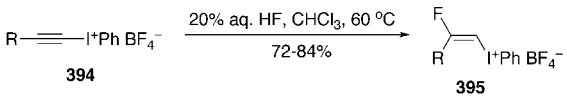
**Scheme 129**




393

R = $AcO(CH_2)_9$, $Cl(CH_2)_9$, $MeOOC(CH_2)_8$, Bu$^t$CO$(CH_2)_8$, (*cyclo*-$C_6H_{11}$)$CH_2$

**Scheme 130**




394 395

R = $C_{10}H_{21}$, Bu$^t$, (*cyclo*-$C_6H_{11}$)$CH_2$, $Cl(CH_2)_9$, Bu$^t$CO$(CH_2)_8$, Pr$^i$OCO$(CH_2)_8$

### *3.9.3. Alkenyliodonium Salts*

The chemistry of alkenyliodonium salts was extensively covered in several recent reviews by Ochiai,[36,38] Okuyama,[47,54,55] and Zefirov and coauthors.[46] This section of our review will summarize the important recent developments in the preparation and synthetic application of alkenyliodonium salts.

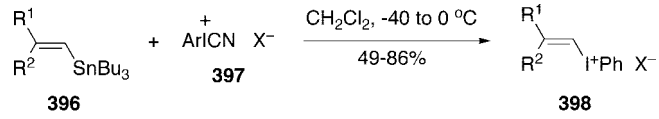
**3.9.3.1. Preparation of Alkenyliodonium Salts.** The boron trifluoride-catalyzed silicon−iodine(III) exchange reaction of organosilanes **389** with iodosylarenes followed by treatment with aqueous $NaBF_4$ constitutes the most general method for synthesis of alkenyl(aryl)iodonium tetrafluoroborates **390** (Scheme 127).[697,772,773] This reaction proceeds under mild conditions and in a stereospecific manner with retention of configuration of organosilanes.

A similar borane−iodine(III) exchange of organoboronic acids **391** 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 **392** in excellent yields (Scheme 128).[774,775]

(*E*)-$\beta$-Fluoroalkenyl(tolyl)iodonium tetrafluoroborates **393** are conveniently synthesized by the treatment of terminal alkynes with 4-iodotoluene difluoride in the presence of boron trifluoride etherate (Scheme 129).[206] This reaction occurred instantaneously at −78 °C to give fluoroalkenyliodonium salts **393** in good yields with high stereoselectivity. Likewise, various alkenyliodonium organosulfonates can be synthesized via electrophilic addition of the appropriate hypervalent iodine reagents to alkynes.[184,776,777]

(E)-$\beta$-Fluoroalkenyl(phenyl)iodonium tetrafluoroborates **395** can be stereoselectively prepared by the reaction of alkynyl(phenyl)iodonium salts **394** with aqueous HF in good yields (Scheme 130).[778,779] The method is applicable to the synthesis of fluoroalkenyliodonium salts having functional groups such as ketone, ester, and chloride.

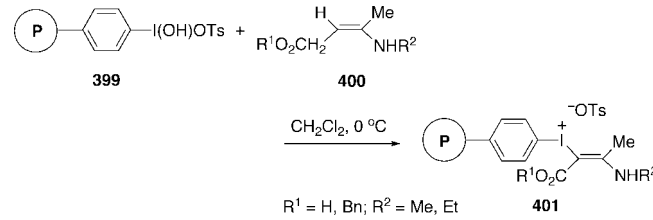
**Scheme 131**




396 397 398

$R^1$ = Me, Et, Bu, Ph; $R^2$ = Me, Et, Bu
Ar = Ph, 4-$CF_3C_6H_4$, 3,5-$(CF_3)_2C_6H_2$; X = OTf or OTs

**Scheme 132**




399 400 401

$R^1$ = H, Bn; $R^2$ = Me, Et

A very general and mild procedure for the stereospecific synthesis of alkenyliodonium organosulfonates **398** involves the reaction of aryl(cyano)iodonium triflates and tosylates **397** with stannylated alkenes **396** (Scheme 131).[780,781]

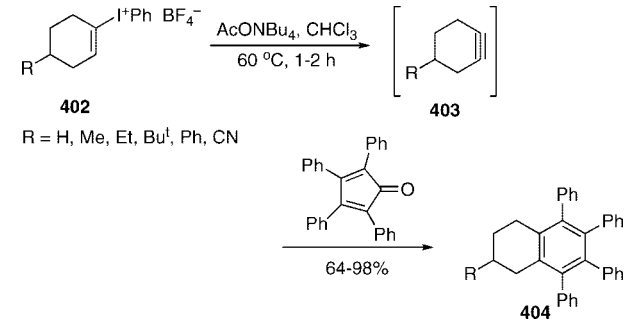
The polymer-supported alkenyliodonium tosylates **401** can be prepared by the treatment of polystyrene-based resin **399** with 3-aminocrotonate esters **400** (Scheme 132).[782] The similar monomeric $\alpha$-acyl-$\beta$-aminoalkenyl(phenyl)iodonium tosylates have been synthesized by the reaction of amino-substituted $\alpha,\beta$-unsaturated ketones with [hydroxy(tosyloxy)-iodo]benzene.[783]

**3.9.3.2. Reactions of Alkenyliodonium Salts.** Alkenyl(phenyl)iodonium salts are very reactive compounds because of the excellent leaving group ability of the phenyliodonium moiety ($10^{12}$ times greater than that for iodine itself) combined with its high electron-withdrawing properties (the Hammett substituent constant $\sigma_m$ for the $PhI^+$ group is 1.35).[784] Several research groups have recently been involved in the mechanistic studies of nucleophilic substitution in alkenyliodonium salts.[785−790] Various mechanisms, including $S_N1$, $S_N2$, ligand coupling, and Michael addition−elimination, have been observed in these reactions. The mechanistic aspects of the reactions of vinylic iodonium salts with nucleophiles have been reviewed by Okuyama[47,791] and by Ochiai.[36,38]

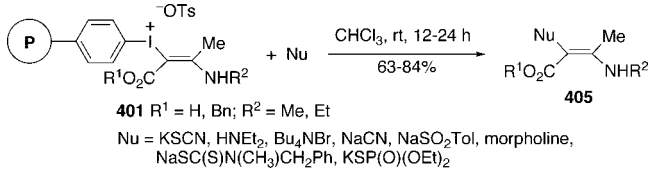
Particularly interesting is the recently reported observation of cyclohexyne intermediates **403** as products of $\beta$-elimination in the reactions of 1-cyclohexenyl(phenyl)iodonium salts **402** with mild bases such as tetrabutylammonium acetate, fluoride ion, alkoxides, and amines in aprotic solvents.[784,785,792] Cyclohexynes **403** could be effectively trapped with tetraphenylcyclopentadienone to give products of [4 + 2] cycloaddition **404** in high yields (Scheme 133). Cycloheptyne intermediates can be generated under similar conditions from the appropriate iodonium precursors.[784,789,793]

Alkenyl(phenyl)iodonium salts have found synthetic application as alkenylating reagents in the reactions with various nucleophilic substrates. In most cases, these reactions proceed with predominant retention of configuration via the addition−elimination mechanism or ligand coupling on the iodine. Recent examples of alkenylations of nucleophiles under noncatalytic conditions include the stereoselective reactions of alkenyliodonium salts with sodium selenide, sodium sulfide, sodium azide, potassium thiocyanate,[794] and

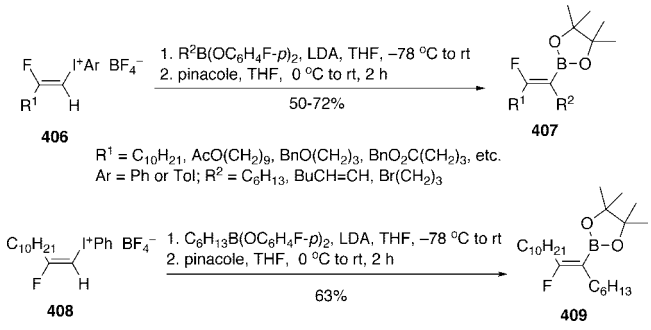
**Scheme 133**



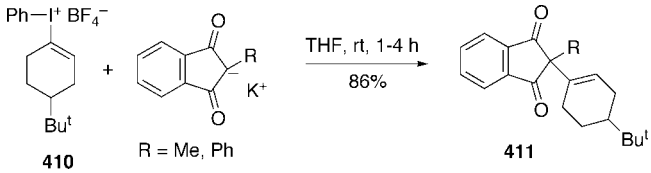

**Scheme 134**




**Scheme 135**




**Scheme 136**



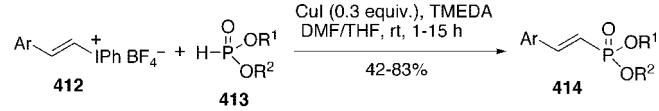

benzotriazole.[795] In a specific example, functionalized $\beta$-enamines **405** have been prepared by the reaction of polymer-supported alkenyliodonium tosylates **401** with various nucleophiles at room temperature (Scheme 134).[782]

(*E*)- and (*Z*)-(fluoroalkenyl)boronates **407** and **409** were prepared stereospecifically by the reaction of (*E*)- or (*Z*)-(2-fluoroalkenyl)iodonium salts **406** and **408** with di(*p*-fluorophenoxy)alkylboranes, followed by transesterification to pinacol esters (Scheme 135). The mechanism of this reaction involves the initial generation of 2-fluoroalkylideneiodonium ylide by the α-deprotonation of iodonium salts with LDA followed by its reaction with di(*p*-fluorophenoxy)alkylboranes.[796,797]

Only a few examples of noncatalytic alkenylation of carbon nucleophiles are known. In particular, enolate anions derived from various 1,3-dicarbonyl compounds can be vinylated with cyclohexenyl (**410**) and cyclopentenyl iodonium salts to afford products **411** (Scheme 136).[798]

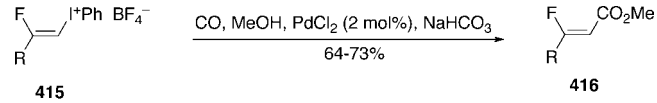
The selectivity of the alkenylation reactions and the yields of products can be dramatically improved by carrying out the reaction of alkenyliodonium salts with carbon nucleophiles in the presence of transition metal compounds in stoichiometric or catalytic amounts. In the presence of a copper(I) catalyst, iodonium salts selectively react with iodide anion,[778,779] organoborates,[799] Grignard reagents,[800] and terminal alkynes[801] to afford the respective cross-coupling products in high yields with complete retention of configuration. A recent example of such a reaction is represented by the copper-mediated cross-coupling of H-phosphonates **413** with vinyliodonium salts **412**, leading to 2-arylvinylphosphonates **414** under mild conditions (Scheme 137).[802]

**Scheme 137**



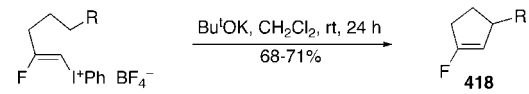

Ar = Ph, 2-FC$_6$H$_4$, 2-MeC$_6$H$_4$, 2-MeOC$_6$H$_4$, 3-MeOC$_6$H$_4$, 4-NO$_2$C$_6$H$_4$, etc.
R$^1$,R$^2$ = Me, Et, Bu, Bn, Ph, etc.

**Scheme 138**




R = C$_{10}$H$_{21}$, (*cyclo*-C$_6$H$_{11}$)CH$_2$, Ph, Cl(CH$_2$)$_9$, Pr$^i$O$_2$C(CH$_2$)$_8$, Bu$^t$CO(CH$_2$)$_8$

**Scheme 139**




**417** R = AcO(CH$_2$)$_6$, Cl(CH$_2$)$_6$, Bu$^t$CO(CH$_2$)$_5$, etc.

Alkenyliodonium salts can be used as highly reactive reagents for Heck-type olefination,[803,804] Sonogashira-type coupling with alkynes,[778,805] and similar palladium-catalyzed cross-coupling reactions.[206,779,806] In a specific example, (*Z*)-$\beta$-fluoro-α,$\beta$-unsaturated esters **416** were stereoselectively synthesized from (*Z*)-2-fluoro-1-alkenyliodonium salts **415** by the Pd-catalyzed methoxycarbonylation reaction (Scheme 138).[806] The reaction proceeded at room temperature, and various functional groups on the substrate can tolerate the reaction conditions.

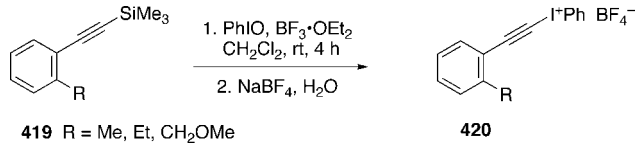
Reactions of alkenyliodonium salts with strong bases may lead to the generation of an alkylidenecarbene via a base-induced α-elimination. Alkylidenecarbenes generated by this method can undergo a 1,5-carbon−hydrogen insertion, providing a useful route for the construction of substituted cyclopentenes.[807−809] In a recent example, an efficient synthesis of fluorocyclopentenes **418** by the reaction of (*Z*)-(2-fluoroalkenyl)iodonium salts **417** with potassium *tert*-butoxide has been developed (Scheme 139). The mechanism of this reaction involves the initial generation of (α-fluoroalkylidene)carbenes, which give fluorocyclopentenes via 1,5-C−H insertion.[807]

### *3.9.4. Alkynyliodonium Salts*

The chemistry of alkynyliodonium salts was exhaustively covered in several previous reviews.[29,42,810] Therefore, this section will only summarize the important recent developments in the preparation and synthetic application of alkynyliodonium salts.

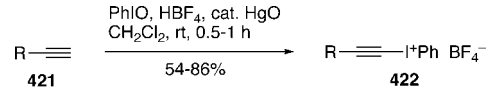
**3.9.4.1. Preparation of Alkynyliodonium Salts.** The most common approach to alkynyl(phenyl)iodonium tetrafluoroborates employs the reaction of iodosylbenzene with alkynylsilanes in the presence of boron trifluoride etherate

**Scheme 140**




**419** R = Me, Et, $CH_2OMe$ **420**

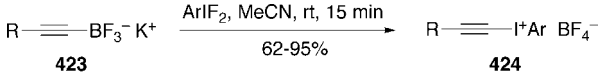
**Scheme 141**




**421** **422**

R = Bu, Bu$^t$, $C_{10}H_{21}$, (*cyclo*-$C_6H_{11}$)$CH_2$, $Cl(CH_2)_9$
$Bu^tCO(CH_2)_9$, $MeO_2C(CH_2)_9$, $AcO(CH_2)_9$

**Scheme 142**




**423** **424**

R = $C_{10}H_{21}$, $BnOCH_2$; Ar = Tol, Ph, 4-$ClC_6H_4$

followed by treatment with aqueous $NaBF_4$.[811,812] Varvoglis, Koumbis, and co-workers have recently used this procedure for the preparation of several *ortho*-substituted arylethynyl(phenyl)iodonium terafluoroborates **420** from alkynylsilanes **419** (Scheme 140).[813]

A modified procedure for the synthesis of alkynyl(phenyl)iodonium tetrafluoroborates **422** reported by Hara and co-workers consists of the direct reaction of terminal alkynes **421** with iodosylbenzene, a 42% aqueous solution of tetrafluoroboric acid, and a catalytic amount of mercury oxide (Scheme 141).[814]

Yoshida and coauthors have reported a facile preparation of iodonium salts **424** by the reaction of potassium organotrifluoroborates **423** with (difluoroiodo)arenes under mild conditions (Scheme 142).[205]

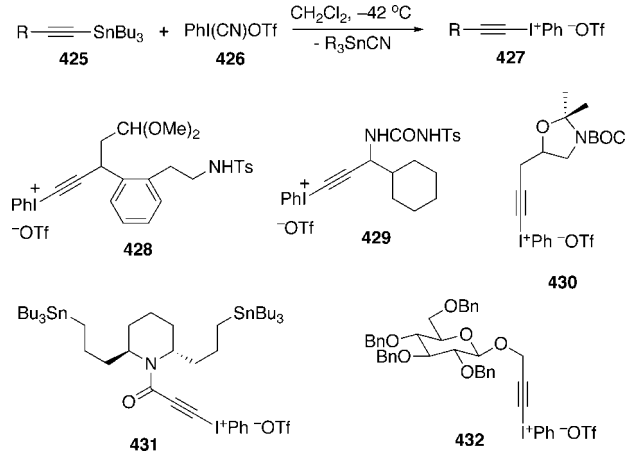
Alkynyl(phenyl)iodonium tosylates are commonly prepared by gentle heating of [hydroxy(tosyloxy)iodo]benzene with terminal alkynes in chloroform or dichloromethane.[812,815,816] This method is also applicable to the synthesis of alkynyliodonium mesylates and 4-nitrobenzenesulfonates by the reaction of the appropriate [hydroxy(organosulfonyloxy)iodo]benzenes with terminal alkynes under similar conditions.[815]

The most versatile method of preparation of alkynyl(phenyl)iodonium triflates **427** employs the iodonium transfer reaction between cyano(phenyl)iodonium triflate **426** and alkynylstannanes **425** under very mild conditions (Scheme 143).[817] This procedure is particularly useful for the preparation of various complex, functionalized alkynyliodonium derivatives, such as compounds **428**, **429**,[818] **430**,[819] **431**,[820] and **432**.[821] Compounds **428**−**432** are formed under these very mild conditions in high yields (80−90%) and can be used in subsequent transformations without additional purification.

An alternative general procedure for the selective preparation of alkynyl(phenyl)iodonium triflates in moderate yields employs the reaction of alkynylsilanes or alkynylstannanes with Zefirov's reagent (see section 3.5.1).[813,822] This method is also applicable to the synthesis of the parent ethynyl(phenyl)iodonium triflate.[823]

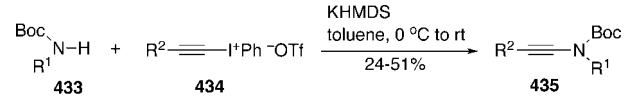
**3.9.3.2. Reactions of Alkynyliodonium Salts.** Reactions of alkynyliodonium salts with nucleophiles proceed via an addition−elimination mechanism involving alkylidene carbenes as key intermediates. Depending on the structure of

**Scheme 143**




**425** **426** **427** **428** **429** **430** **431** **432**

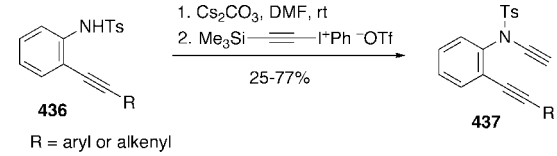
**Scheme 144**




**433** **434** **435**

$R^1$ = Ts, Boc, Piv; $R^2$ = $Me_3Si$, $Bu^tMe_2Si$

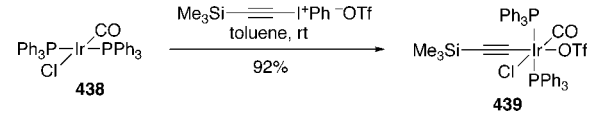
**Scheme 145**




**436** **437**

R = aryl or alkenyl

**Scheme 146**



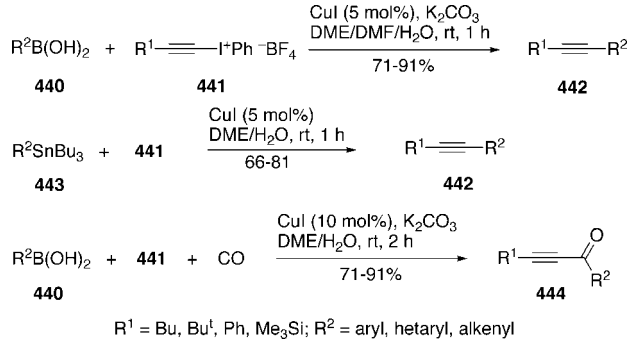

**438** **439**

the alkynyliodonium salt, specific reaction conditions, and the nucleophile employed, this process can lead to a substituted alkyne due to the carbene rearrangement or to a cyclic product via intramolecular 1,5-carbene insertion.[42] Both of these reaction pathways have been widely utilized in organic synthesis.

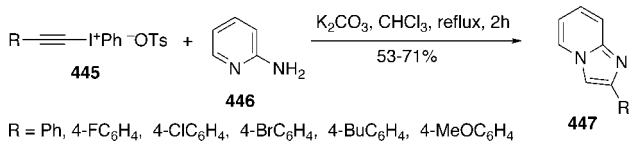
Alkynyl(phenyl)iodonium salts have found synthetic application for the preparation of various substituted alkynes by the reaction with the appropriate nucleophiles, such as enolate anions,[822,824] selenide and telluride anions,[825−827] dialkylphosphonate anions,[828] benzotriazolate anion,[829] imidazolate anion,[830] N-functionalized amide anions,[831−833] and transition metal complexes.[834−838] Specific recent examples are represented by the preparation of *N*-alkynyl carbamates **435** by alkynylation of carbamates **433** using alkynyliodonium triflates **434** (Scheme 144),[832] the synthesis of ynamides **437** by the alkynylation/desilylation of tosylanilides **436** using trimethylsilylethynyl(phenyl)iodonium triflate (Scheme 145),[833] and the preparation of Ir(III) $\sigma$-acetylide complex **439** by the alkynylation of Vaska's complex **438** (Scheme 146).[834]

Alkynyl(phenyl)iodonium salts can be efficiently coupled with organocopper reagents[839] or with organoboronic acids or organostannanes in the presence of Cu(I) catalysts.[840,841] Specifically, the copper iodide-catalyzed cross-coupling and carbonylative coupling reactions of alkynyliodonium salts **441** with arylboronic acids **440** or organostannanes **443** under

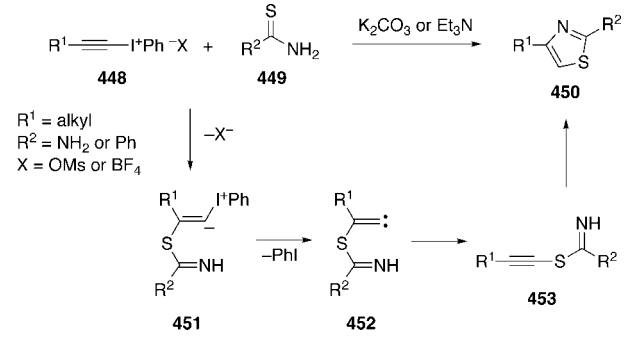
**Scheme 147**




**Scheme 148**




**Scheme 149**

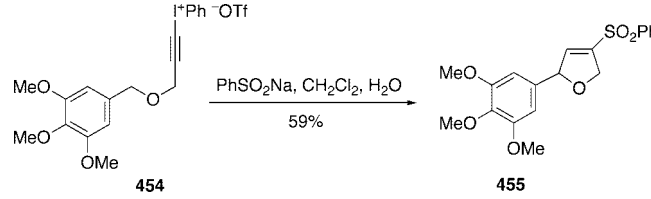



mild conditions afford arylacetylenes **442** and aryl alkynyl ketones **444** in high yields (Scheme 147).[841] Interestingly, alkynyliodonium tetrafluoroborates **441** are more efficient in these coupling reactions than the corresponding iodonium triflates and tosylates.

A variety of five-membered heterocycles can be prepared efficiently by inter- or intramolecular addition/cyclizations of appropriate nucleophiles with alkynyliodonium salts via alkylidene carbene intermediates.[29,42,810] The intermolecular variant of this cyclization has recently been utilized in the synthesis of 3-substituted 5,6-dihydroimidazo[2,1-*b*]thiazoles,[842] 2-substituted imidazo[1,2-*a*]pyrimidines,[843] and 2-substituted imidazo[1,2-*a*]pyridines.[844] In a specific example, 2-substituted imidazo[1,2-*a*]pyridines **447** were synthesized in good yield by cyclocondensation of alkynyl(phenyl)iodonium tosylates **445** with 2-aminopyridine **446** under mild conditions (Scheme 148). The mechanism of this cyclization involves initial nucleophilic addition of the amino group of 2-aminopyridine to the triple bond of the alkynyliodonium salt followed by generation and subsequent cyclization of the intermediate alkylidene carbene. [844]

Ochiai and co-workers have investigated the mechanism for the one-pot synthesis of 2,4-disubstituted thiazoles **450** by cyclocondensation of alkynyliodonium salts **448** with thioureas or thioamides **449** (Scheme 149).[845] This reaction was originally reported by Wipf and Venkatraman in 1996.[846] Ochiai and co-workers have isolated and identified by X-ray analysis intermediate products **453** (as mesylate or tetrafluoroborate salts), which suggests the mechanism involving Michael addition of sulfur nucleophile **449** to alkynyliodonium salt **448**, giving intermediate ylide **451** followed by the 1,2-rearrangement of sulfenyl groups in the resulting alkylidene carbene **452** (Scheme 149).[845]

**Scheme 150**




The intramolecular variant of the alkylidene carbene cyclization is achieved by the treatment of functionalized alkynyliodonium salts with the appropriate nucleophile. Recent examples are represented by the preparation of various functionalized 2,5-dihydrofurans by treatment of 3-alkoxy-1-alkynyl(phenyl)iodonium triflates with sodium benzenesulfinate,[821] by the utilization of the alkylidene carbene cyclization in the total syntheses of the natural products agelastatin A and agelastatin B,[819] and by the preparation of the tricyclic core of (±)-halichlorine through the use of an alkynyliodonium salt/alkylidenecarbene/1,5-C−H insertion sequence.[820] In particular, Wardrop and Fritz have utilized the sodium benzenesulfinate-induced cyclization of the generated in situ alkynyliodonium triflate **454**, leading to dihydrofuran **455** (Scheme 150), which is a key intermediate product in the total synthesis of (±)-magnofargesin.[821]

Feldman and co-workers have applied the sodium *p*-toluenesulfinate-induced cyclizations of alkynyliodonium salts **456** and **431** for the preparation of compounds **457** and **458** (Scheme 151), the key intermediates in the total syntheses of agelastatins[819] and (±)-halichlorine, respectively.[820]

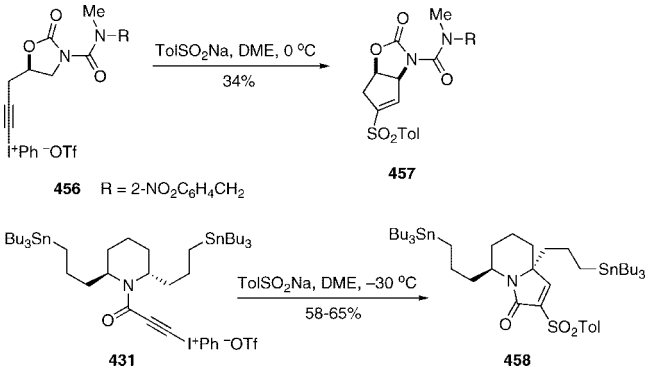
## 3.10. Iodonium Ylides

The first preparation of an iodonium ylide by the reaction of dimedone and (difluoroiodo)benzene was reported by Neiland and co-workers in 1957.[847] Since then, a large number of stable iodonium ylides have been prepared, and many synthetic applications have emerged. The chemistry of iodonium ylides was overviewed in several reviews devoted to the reactions of carbenes.[56−58] This section will summarize the preparation and structural studies of iodonium ylides and important recent developments in their synthetic applications.

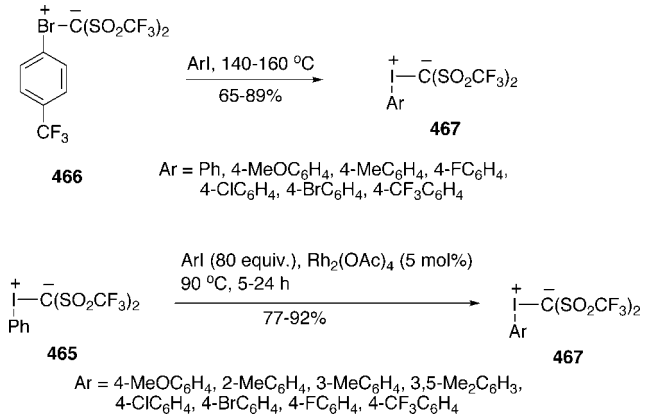
### *3.10.1. Preparation and Structure*

The most common and relatively stable structural types of iodonium ylides, namely phenyliodonium bis(organosulfonyl)methides, $PhIC(SO_2R)_2$, and the dicarbonyl derivatives $PhIC(COR)_2$, are generally prepared by a reaction of (diacetoxyiodo)benzene with the appropriate disulfone or dicarbonyl compound under basic conditions.[848−850] The vast majority of iodonium ylides have low thermal stability and can be handled only at low temperature or generated and used in situ. Several structural types of ylides, however, are sufficiently stable for X-ray structural analysis. Single crystal X-ray structural parameters have been reported for 3-phenyliodonio-1,2,4-trioxo-1,2,3,4-tetrahydronaphthalenide **459**,[851] 3-phenyliodonio-2,4-dioxo-1,2,3,4-tetrahydro-1-oxanaphthalenide **460**,[851] mixed phosphonium iodonium ylides **461**[852] and **462**,[853] mixed arsonium iodonium ylides **463**,[854]

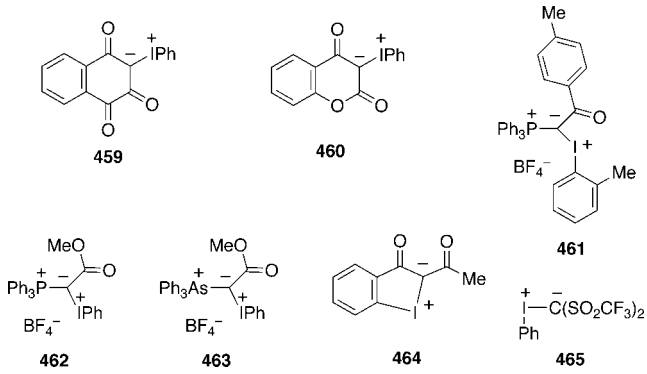
**Scheme 151**




**Scheme 152**

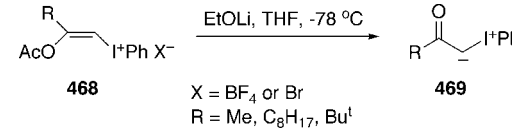



cyclic iodonium ylide **464**,[855] and phenyliodonium bis(trifluoromethanesulfonyl)methide **465**.[856] In particular, the X-ray structural analysis for phenyliodonium bis(trifluoromethanesulfonyl)methide **465** shows a geometry typical for an iodonium ylide with the I−C ylide bond length of about 1.9 Å and an C−I−C bond angle of 98°.[856]

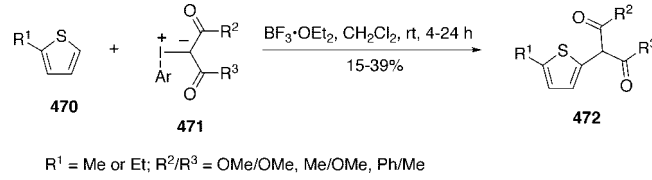



Ochiai and co-workers have recently reported the intermolecular transylidation reactions between halonium ylides under thermal or catalytic conditions, which allow us to synthesize a variety of iodonium ylides **467** (Scheme 152). The transylidations of bromonium **466** to iodonium **467** ylides proceed under thermal conditions and probably involve generation of a reactive carbene intermediate.[857] The heating of phenyliodonium bis(trifluoromethylsulfonyl)methylide **465** in a large amount of an iodoarene in the presence of 5 mol % of rhodium(II) acetate as a catalyst results in the transfer of the bis(trifluoromethylsulfonyl)methylidene group to the iodine(I) atom to afford a substituted aryliodonium ylide **467** in a good yield. The reversible nature of the catalytic intermolecular transylidation makes it possible to evaluate the thermodynamic stability of aryliodonium ylides.[858]

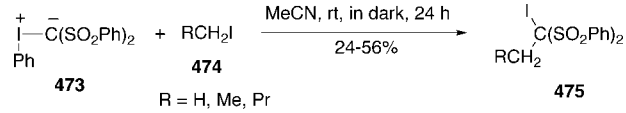
**Scheme 153**




**Scheme 154**




**Scheme 155**




A mechanistic study of 1,4 alkyl group migration in hypervalent halonium ylides was recently reported by Moriarty and coauthors. In particular, it was found that the rhodium(II)-acetate-catalyzed decomposion of either 1,3-cyclohexanedione phenyliodonium ylide or 5,5-dimethyl-1,3-cyclohexanedione phenyliodonium ylide in the presence of alkyl halides yields the corresponding 3-alkoxy-2-halocyclohex-2-enones via a 1,4 alkyl group migration shown to be concerted and intramolecular.[859]

The monocarbonyl iodonium ylides **469** can be quantitatively generated in situ from the (*Z*)-(2-acetoxyvinyl)iodonium salts **468** via an ester exchange reaction with ethoxylithium in THF at −78 °C (Scheme 153). $^1$H NMR measurements indicate that ylides **469** are stable up to −30 °C, and they can be conveniently used in the subsequent transformations without isolation.[860−862]

The unstable ylides PhIC(H)$NO_2$[863,864] and PhIC($CO_2$Me)$NO_2$[865,866] can be generated in situ from nitromethane and methyl nitroacetate, respectively, and used in the rhodium(II) carbenoid reactions without isolation.

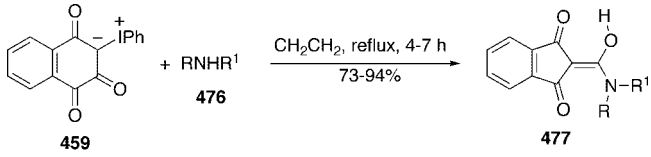
### *3.10.2. Reactions*

Iodonium ylides can serve as convenient precursors to the respective carbene intermediates under thermal, photochemical, or catalytic conditions. A detailed discussion of the reaction mechanisms and synthetic applications of iodonium ylides as carbene precursors can be found in the 2004 review of Muller.[58]

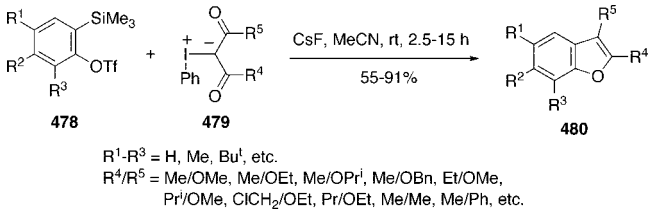
Several new uncatalyzed reactions of iodonium ylides have recently been reported.[867−873] Koser and co-workers have found that the treatment of electron-rich aromatic substrates, such as anthracene, pyrene, 2-alkylthiophenes, and 1,4-dimethoxybenzene with phenyliodonium bis(carbonyl)methylides in the presence of $BF_3$•$Et_2O$ leads to bis(carbonyl)alkylation of the aromatic nucleus.[867] For example, the reactions of 2-alkylthiophenes **470** with ylides **471** afford products **472** in 15−39% isolated yield (Scheme 154).

The reaction of disulfonyl iodonium ylide **473** with alkyl iodides **474** affords functionalized iodides **475** in moderate yield (Scheme 155). The mechanism of this reaction most likely involves the initial transylidation with the formation of unstable alkyliodonium ylides, $RCH_2I{=}C(SO_2Ph)_2$, which then undergo the intramolecular Stevens rearrangement, forming iodides **475**.[868]

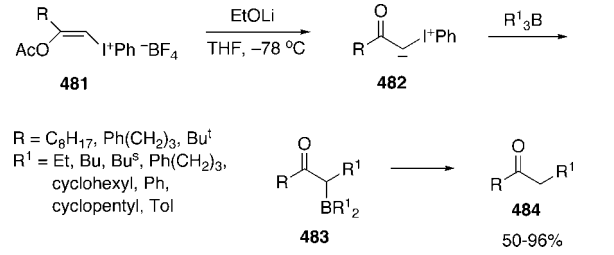
**Scheme 156**




**Scheme 157**




**Scheme 158**



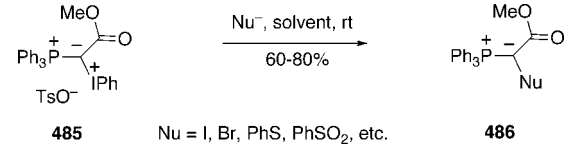

Spyroudis and co-workers have reported the reaction of the phenyliodonium ylide of 2-hydroxy-1,4-naphthoquinone **459** with amines **476** in refluxing dichloromethane to afford good yields of the indanedione 2-carboxamides **477** (Scheme 156). This reaction proceeds through initial carbene formation, followed by a ring-contraction, leading to an intermediate α,α′-dioxoketene,[874] which reacts with amines **476** to afford the final amides **477**.[869] The analogous products are formed when ylide **459** is reacted with amino esters, ureas, amino alcohols, aminophenols, and indole derivatives under thermal conditions.[870,871]

Li and co-workers have developed a mild and general synthesis of substituted benzofurans by the cycloaddition of iodonium ylides with arynes generated from 2-(trimethylsilyl)aryl triflates and CsF. In a specific example, 2-(trimethylsilyl)aryl triflates **478** smoothly react with iodonium ylides **479** in the presence of CsF at room temperature, giving benzofurans **480** in moderate to good yields (Scheme 157).[872]

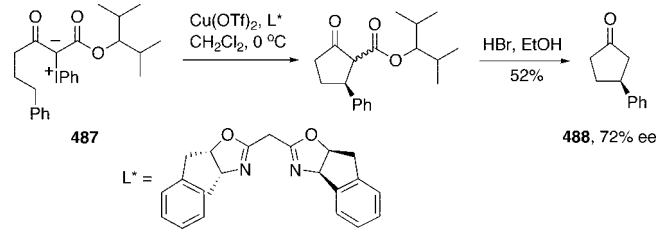
Ochiai and co-workers have found that the interaction of monocarbonyl iodonium ylides **482**, generated by the ester exchange of (*Z*)-(2-acetoxyvinyl)iodonium salts **481** with EtOLi, with organoboranes results in the formation of ketones **484**, probably via the intermediate formation of the hitherto unknown α-boryl ketones **483** (Scheme 158).[861]

The mixed phosphonium−iodonium ylides, such as the tosylate **485**, represent a potentially useful class of reagents that combine in one molecule the synthetic advantages of a phosphonium ylide and an iodonium salt.[854,875−878] Specifically, phosphorane-derived phenyliodonium tosylate **485** can react with soft nucleophiles, such as iodide, bromide, benzenesulfinate, and thiophenolate anions, with a selective formation of the respective α-functionalized phosphonium ylides **486** (Scheme 159), which can be further converted to alkenes by the Wittig reaction with aldehydes.[875,876] The

**Scheme 159**




**Scheme 160**



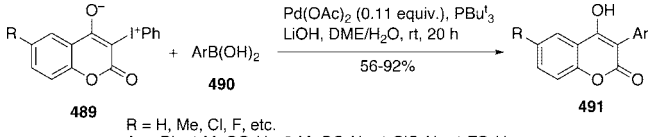

analogous arsonium−iodonium ylides (e.g., **463**) have a similar reactivity toward nucleophiles.[854,877,879]

The carbenoid reactions of iodonium ylides can be effectively catalyzed by rhodium(II) or copper complexes.[56−58] The product composition in the rhodium(II)-catalyzed reactions of iodonium ylides was found to be identical to that of the corresponding diazo compounds, which indicates that the mechanisms of both processes are similar and involve metallocarbenes as key intermediates, as has been unequivocally established for the diazo decomposition.[849] Recent examples of the transition metal-catalyzed carbenoid reactions of iodonium ylides are represented by the following publications: Rh(II)- or Cu(I)-catalyzed cyclopropanation reactions using the unstable ylides $PhIC(H)NO_2$[863] and $PhIC(CO_2Me)NO_2$[865,866] generated in situ from nitromethane and methyl nitroacetate; Rh(II)-catalyzed three-component coupling of an ether with a nitromethane-derived carbenoid generated from $PhIC(H)NO_2$;[864] Rh(II)- or Cu(II)-catalyzed insertion of carbene into the alkenyl C−H bond in pyrroles,[880] flavones,[881] and highly phenylated ethylenes;[882] Rh(II)-catalyzed reaction of iodonium ylides with conjugated compounds, leading to efficient synthesis of dihydrofurans, oxazoles, and dihydrooxepines;[883] synthesis of various heterocycles by Rh(II)-catalyzed reactions of iodonium ylides with vinyl ethers, carbon disulfide, alkynes, and nitriles;[884] Rh(II)-catalyzed reaction of iodonium ylides with electron-deficient and conjugated alkynes, leading to substituted furans;[885] efficient synthesis of β-substituted α-haloenones by Rh(II)-catalyzed reactions of iodonium ylides with benzyl halides and acid halides;[886] Rh(II)- or Cu(II)-catalyzed generation/rearrangement of onium ylides of allyl and benzyl ethers via iodonium ylides;[887] and Rh(II)- or Cu(II)-catalyzed stereoselective cycloaddition of disulfonyl iodonium ylides with alkenes, leading to 1,2,3-trisubstituted benzocyclopentenes[888] or functionalized indanes.[889−891]

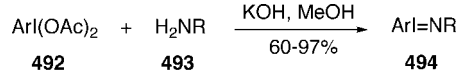
The metal-catalyzed carbenoid decomposition of iodonium ylides can be applied in asymmetric reactions.[865,892−894] For example, the copper(II)-catalyzed intramolecular C−H insertion of phenyliodonium ylide **487** in the presence of chiral ligands followed by hydrolysis and decarboxylation affords product **488** in moderate yield with up to 72% ee (Scheme 160).[894]

A palladium-catalyzed coupling reaction of iodonium ylides **489** with aryl boronic acids **490** was reported. The mild reaction conditions and convenient synthetic accessibility of iodonium ylides **489** make this method a valuable tool for the preparation of diversified 3-aryl-4-hydroxycoumarins **491** (Scheme 161).[895]

**Scheme 161**

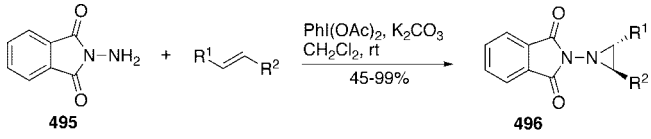



**Scheme 162**




Ar = Ph, 3-$MeC_6H_4$, 2,4,6-$Me_3C_6H_2$, etc.
R = Ts, 4-$MeOC_6H_4SO_2$, 4-$CF_3C_6H_4SO_2$, 4-$NO_2C_6H_4SO_2$, 2-$NO_2C_6H_4SO_2$, 4-$FC_6H_4SO_2$, 4-$IC_6H_4SO_2$, $PhSO_2$, $MeSO_2$, $CF_3CO$, etc.

**Scheme 163**




$R^1/R^2$ = Ph/H, 4-$CF_3C_6H_4$/H, 4-$FC_6H_4$/H, 4-$MeC_6H_4$/H, Ph/Me, Ph/$CO_2$Me, etc.

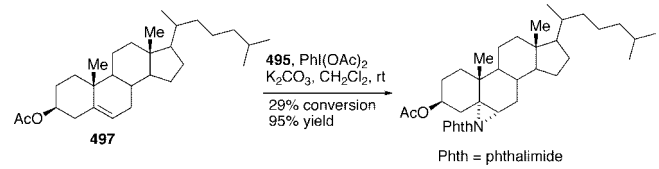
## 3.11. Iodonium Imides

The chemistry of iodonium imides (also known as iminoiodanes) has been reviewed by Dauban and Dodd in 2003.[28] Aryliodonium imides **494** are best prepared by the reaction of (diacetoxyiodo)arenes **492** with the respective amides **493** under basic conditions (Scheme 162).[28,73,222,896−900] Most iodonium imides are stable at room temperature, but their storage under an inert atmosphere at low temperature is recommended. They are thermally sensitive, and some of them are even claimed to be explosive. Violent decomposition frequently occurs at the melting point.[28]

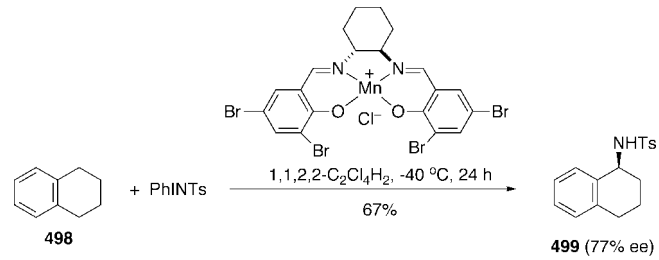
Single-crystal X-ray structural data have been reported for several *N*-tosyliminoiodanes, namely, PhI=NTs,[222,901] 2,4,6-$Me_3C_6H_2$I=NTs,[222] and 2-$MeC_6H_4$I=NTs.[898] Similar to iodosylarenes (see section 3.1.2), iminoiodanes have a linear polymeric, asymmetrically bridged structure with the T-shaped geometry around the iodine centers. In the case of PhI=NTs, the monomeric units are bridged by I−N interactions, while, in the more sterically hindered 2,4,6-$Me_3C_6H_2$I=NTs, the bridging atom is the oxygen of the tosyl group.[222] Protasiewicz and co-workers have reported the preparation and X-ray structure of highly soluble, *ortho*-sulfonyl-substituted aryliodonium imide 2-$Bu^tSO_2C_6H_4$I=NTs, in which the intramolecular secondary I•••O bond replaces the intermolecular interactions that are typical of the other iminoiodanes.[90]

Aryliodonium imides have found synthetic applications as useful nitrene precursors under thermal or catalytic conditions in amidation and imidation reactions of various organic substrates and in the aziridination of alkenes.[28] Only a few examples of the reactions of aryliodonium imides in the absence of transition metal catalysts have been published in the recent literature. Che and co-workers have reported the aziridination of alkenes with phenyliodonium imides generated in situ from N-substituted hydrazines **495** and (diacetoxyiodo)benzene under mild conditions (Scheme 163).[902] This reaction affords aziridines **496** in good to excellent yields (up to 99%) and conversions. The practicality and simplicity of this C−N bond formation protocol were exemplified by its application to the aziridination of cholesteryl acetate **497** in a stereoselective manner (Scheme 164).[902] A similar reaction of the $PhI(OAc)_2$/N-substituted hydrazine **495** system has been used in the nitrene mediated metal-free ring expansions of alkylidenecyclopropanes and alkylidenecyclobutanes.[903]

**Scheme 164**




**Scheme 165**

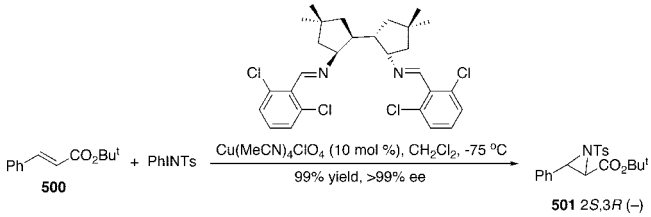



Wirth, Desaize, and Richardson have published a detailed study of the aziridination of alkenes with the $PhI(OAc)_2$/N-substituted hydrazine **495** system and, in particular, reported tentative evidence that this reaction (Scheme 163) proceeds through the formation of an aminoiodane that reacts directly with the alkene.[904] Furthermore, the authors of this publication[904] have analyzed the requirements to make this reaction catalytic in iodoarene. This reaction requires an oxidant that will oxidize iodoarenes but that does not oxidize alkenes, and it is possible that no such oxidant actually exists. However, a method in which the hypervalent iodine reagent can be recycled without the need for reisolation is possible.[904]

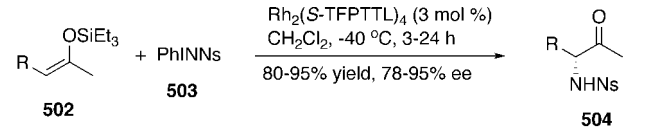
The transition metal-catalyzed amidation of C−H bonds in saturated or unsaturated substrates represents one of the most common reactions of aryliodonium imides.[6,28] Recent examples of this reaction using PhI=NTs as the nitrene precursor are represented by the following publications: the highly efficient Ru(II) porphyrin-catalyzed C−H bond amidation of aldehydes,[905] the aromatic C−H amidation mediated by a diiron complex,[906] the $AuCl_3$-catalyzed nitrene insertion into aromatic and benzylic C−H bonds,[907] the silver-catalyzed intermolecular and intramolecular amidation of the C−H bond in saturated hydrocarbons,[908,909] the α-amidation of cyclic ethers catalyzed by $Cu(OTf)_2$,[910] the mechanistic study of catalytic intermolecular amination of C−H bonds,[911] the nitrene insertion into the $sp^3$ C−H bonds of alkylarenes and cyclic ethers or the $sp^2$ C−H bonds of benzene using a copper-homoscorpionate complex,[912] the Co(II)-catalyzed allylic amidation reactions,[913] the Ru(II) porphyrin-catalyzed amidation of aromatic heterocycles,[914] and the nonheme iron-catalyzed amidation of aromatic substrates.[915] The enantioselective amidation of a C−H bond can also be achieved in the presence of the chiral (salen)-manganese(III) complexes. For example, the amidation of substrate **498** occurs at the benzylic C−H bond to afford product **499** with good enantioselectivity (Scheme 165).[916]

Aryliodonium imides are efficient nitrene precursors in the transition metal-catalyzed aziridination of alkenes.[6,28] Particularly important is the application of PhINTs in the asymmetric aziridination of alkenes using copper catalysts with chiral dinitrogen ligands.[917−924] In a specific example,

**Scheme 166**

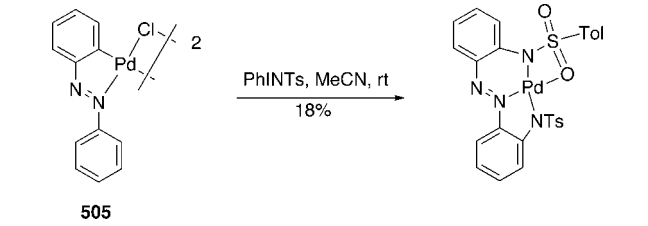



**Scheme 167**




R = Ph, 4-ClC$_6$H$_4$, 4-MeOC$_6$H$_4$, PhCH$_2$, 4-ClC$_6$H$_4$CH$_2$, 4-MeOC$_6$H$_4$CH$_2$, etc.
Ns = 2-NO$_2$C$_6$H$_4$SO$_2$

**Scheme 168**



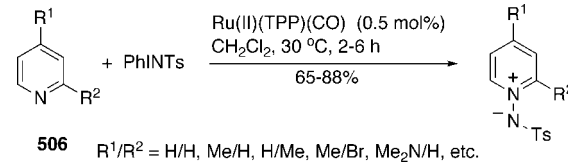

the PhINTs-promoted asymmetric aziridination of alkene **500** affords chiral aziridine **501** in over 99% ee (Scheme 166).[921]

The aziridination and amidation reactions of aryliodonium imides can be efficiently catalyzed by the Rh(II) complexes.[925−930] Dirhodium(II) tetrakis[*N*-tetrafluorophthaloyl-(*S*)-*tert*-leucinate], Rh$_2$(*S*-TFPTTL)$_4$, is an exceptionally efficient catalyst for enantioselective aminations of silyl enol ethers **502** with iodonium imide **503**, providing α-amido ketones **504** in high yields and with enantioselectivities of up to 95% ee (Scheme 167). The effectiveness of this catalytic protocol has been demonstrated by an asymmetric formal synthesis of (−)-metazocine.[925] The same catalyst has also been used for the asymmetric synthesis of phenylglycine derivatives by enantioselective amidation of silylketene acetals with aryliodonium imides.[926]

Sanford and co-workers have recently reported the carbon−nitrogen bond-forming reactions of palladacycles with aryliodonium imides.[931] In particular, palladium(II) complexes (e.g., **505**) containing bidentate cyclometalated chelating ligands react with PhINTs at room temperature to insert the tosylimino group into the Pd−C bond (Scheme 168). This tosylimino insertion reaction has been applied to palladacyclic complexes of azobenzene, benzo[*h*]quinoline, and 8-ethylquinoline. The newly aminated organic ligands can be liberated from the metal center by protonolysis with a strong acid.[931]

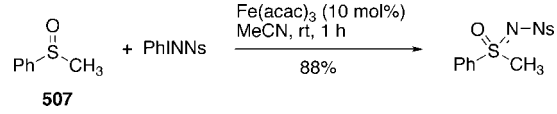
The imido group can be efficiently transferred to the sulfur atom in organic sulfides or sulfoxides,[932−935] or the nitrogen atom in aromatic nitrogen heterocycles using aryliodonium imides in the presence of copper, ruthenium, or iron complexes.[936,937] Specific examples are represented by the selective N-imidation of aromatic nitrogen heterocycles (e.g., **506**) catalyzed by carbonyl[*meso*-tetrakis(*p*-tolyl)porphyrinato]ruthenium(II) [Ru(II)(TPP)(CO)] (Scheme 169),[936] and the iron-catalyzed imination of sulfoxides (e.g., **507**) and sulfides (Scheme 170).[932]

**Scheme 169**




$R^1/R^2$ = H/H, Me/H, H/Me, Me/Br, Me$_2$N/H, etc.

**Scheme 170**



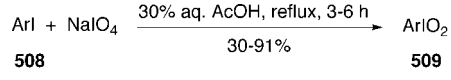

## 4. Iodine(V) Compounds

The chemistry of organic iodine(V) compounds, or $\lambda^5$-iodanes according to the IUPAC nomenclature, in general has been less developed in comparison with that of the $\lambda^3$-iodanes.[6] The first comprehensive review on the synthetic applications of hypervalent iodine(V) reagents appeared in 2006,[22] and a specialized review on iodoxybenzoic acid (IBX) was published by Wirth in 2001.[938] There has been very significant recent interest in the cyclic $\lambda^5$-iodanes, mainly IBX 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.[938] Despite their importance, IBX and DMP are not perfect reagents and have some disadvantages. IBX is potentially explosive and is insoluble in common organic solvents due to the strong intermolecular secondary bonding creating a three-dimensional polymeric structure, while DMP is highly sensitive to moisture. Several IBX derivatives and analogues with improved properties have been developed in the last 5−6 years and utilized in organic synthesis. In particular, the highly soluble and nonexplosive pseudocyclic derivatives of IBX, as well as their polymer-supported analogues, have been introduced. This section of our review will summarize the preparation and structure of $\lambda^5$-iodanes and overview important recent developments in their synthetic applications.

### 4.1. Noncyclic and Pseudocyclic Iodylarenes

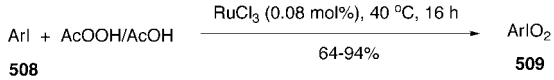
Iodylarenes, ArIO$_2$, which are also known as iodoxy compounds, are commonly prepared by direct oxidation of iodoarenes with strong oxidants or by disproportionation of iodosylarenes. It is assumed that the initial oxidation of ArI usually leads to iodosylarenes, ArIO, which then slowly disproportionate to ArI and ArIO$_2$ upon gentle heating or even at room temperature.[92,256,939] The most common oxidizing reagents that are used for the preparation of iodylarenes from iodoarenes include sodium hypochlorite, sodium periodate, dimethyldioxirane, and oxone. In particular, Skulski and Kraszkiewicz reported an improved method for the preparation of various iodylarenes **509** from the corresponding iodoarenes **508** using sodium periodate as the oxidant dissolved in boiling 30% aqueous acetic acid (Scheme 171).[939] Iodylarenes **509** usually precipitate from the reaction mixture and can be additionally purified by recrystallization from hot water or other solvents. Dry iodylarenes are potentially hazardous compounds, which may explode upon impact, scratching with a spatula, or heating, and therefore, they should be handled with appropriate precautions.

**Scheme 171**



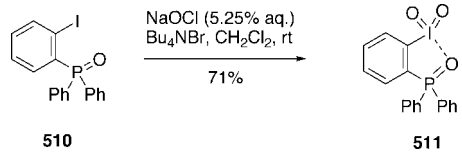

Ar = Ph, 4-$MeC_6H_4$, 3-$MeC_6H_4$, 2-$MeC_6H_4$, 4-$FC_6H_4$, 3-$FC_6H_4$, 4-$ClC_6H_4$, 3-$ClC_6H_4$, 2-$ClC_6H_4$, 4-$BrC_6H_4$, 3-$NO_2C_6H_4$, 2-$NO_2C_6H_4$, 4-$NO_2C_6H_4$, 2,4-$Me_2C_6H_3$, 2,4-$Cl_2C_6H_3$

**Scheme 172**




R = H, 4-$MeC_6H_4$, 2-$MeC_6H_4$, 2-$ClC_6H_4$, 3-$ClC_6H_4$, 4-$ClC_6H_4$, 4-$BrC_6H_4$, 4-$C_6H_4F$, 4-$CF_3C_6H_4$, 3,5-$CF_3C_6H_3$, etc.

**Scheme 173**




A new facile methodolology for the preparation of noncyclic iodylarenes using peracetic acid as an oxidant in the presence of catalytic amounts of ruthenium trichloride has recently been reported.[529,940] This new procedure allows the preparation of several previously unknown iodylarenes **509** bearing strongly electron-withdrawing $CF_3$ groups in the aromatic ring[940] (Scheme 172).

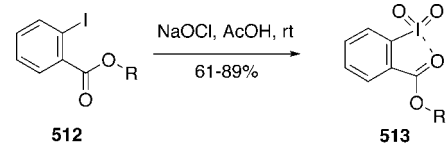
Iodylbenzene, $PhIO_2$, has a polymeric structure, which makes it insoluble in the majority of organic solvents, with the exception of DMSO. X-ray crystal structural investigations of $PhIO_2$ revealed infinite polymeric chains with strong I•••O secondary intermolecular interactions.[941] Iodylbenzene and other noncyclic iodylarenes in general have found only very limited practical application due to their low stability and explosive properties.[22]

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.[89,91]

Protasiewicz and co-workers have recently reported the preparation of a soluble *ortho*-phosphoryl stabilized aryliodyl derivative **511**, which was obtained by the hypochlorite oxidation of the appropriate aryliodide **510** (Scheme 173).[92] Single crystal X-ray analysis of compound **511** 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 aryliodide **510**.[92]

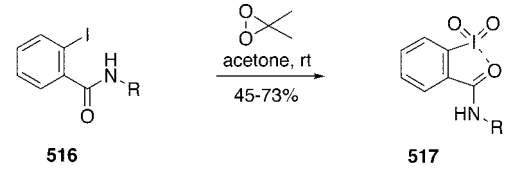
The previously unknown esters of 2-iodoxybenzoic acid (IBX-esters, **513**) were prepared by the hypochlorite oxidation of the readily available esters of 2-iodobenzoic acid **512** (Scheme 174) and isolated in the form of stable microcrystalline solids.[95,96] This procedure allows for the preparation of products **513** derived from various types of alcohols, such as primary, secondary, and tertiary alcohols, adamantanols, optically active menthols, and borneol. X-ray data on products **513** revealed a pseudobenziodoxole structure in

**Scheme 174**




R = Me, Et, Pr$^i$, (-)-menthyl, (+)-menthyl, (±)-menthyl, [(1*S*)-endo]-(–)-bornyl, 2-adamantyl, 1-adamantyl, Bu$^t$

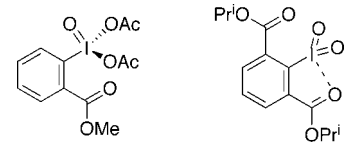
**Scheme 175**




R = (*S*)-$CH(CH_3)CO_2CH_3$, (*R*)-$CH(CH_3)CO_2CH_3$, (*S*)-$CH(CH_2Ph)CO_2CH_3$, (*S*)-$CH(Bu^i)CO_2CH_3$, $CH_2CH_2CO_2H$, $CH(CH_3)CH_2CO_2H$, (*R*)-$CH(Ph)CH_3$

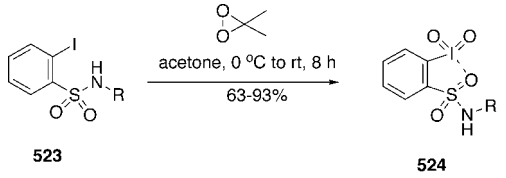
which the intramolecular I•••O secondary bonds partially replace the intermolecular I•••O secondary bonds disrupting the polymeric structure characteristic of $PhIO_2$[941] and other previously reported iodylarenes.[96] This structural feature substantially increases the solubility of these compounds in comparison to other iodine(V) reagents and affects their oxidizing reactivity. IBX-esters can oxidize alcohols to the respective aldehydes or ketones in the presence of trifluoroacetic acid or boron trifluoride etherate.[96] Isopropyl 2-iodoxybenzoate **513** (R = Pr$^i$) is a particularly useful reagent for the clean and selective oxidation of organic sulfides to sulfoxides.[942] This reaction proceeds without overoxidation to sulfones and is compatible with the presence of the hydroxy group, double bond, phenol ether, benzylic carbon, and various substituted phenyl rings in the molecule of organic sulfide.

Methyl 2-iodoxybenzoate **513** (R = Me) can be further converted to the diacetate **514** or a similar bis(trifluoroacetate) derivative by treatment with acetic anhydride or trifluoroacetic anhydride, respectively. Single crystal X-ray diffraction analysis of methyl 2-[(diacetoxy)iodosyl]benzoate **514** revealed a pseudobenziodoxole structure with three relatively weak intramolecular I•••O interactions. The dimethyl and diisopropyl esters of 2-iodoxyisophthalic acid were prepared by oxidation of the respective iodoarenes with dimethyldioxirane. Single crystal X-ray diffraction analysis of diisopropyl 2-iodoxyisophthalate **515** showed intramolecular I•••O interaction with the carbonyl oxygen of only one of the two carboxylic groups, while NMR spectra in solution indicated equivalency of both ester groups.[96]




The amides of 2-iodoxybenzoic acid (IBX-amides, **517**) were prepared by the dioxirane oxidation of the appropriate derivatives of 2-iodobenzoic acid **516** (Scheme 175) in the form of stable, microcrystalline solids moderately soluble in dichloromethane and chloroform.[94] This procedure (Scheme 175) can be used for the preparation of products **517** derived

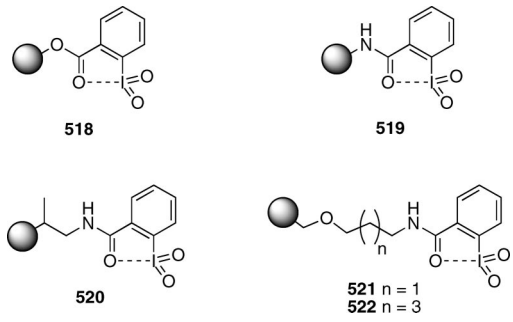
**Scheme 176**




from numerous types of amino compounds, such as esters of α-amino acids, esters of β-amino acids, and (*R*)-1-phenylethylamine. Single crystal X-ray analysis of the phenylalanine derivative (**517**, R = (*S*)-CH(CH$_2$Ph)CO$_2$Me) 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, enforcing a planar geometry of the resulting five-membered ring, a geometry that is analogous to that observed for IBX and other benziodoxoles.[94]

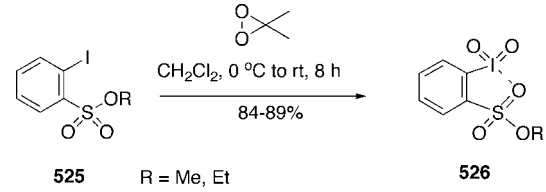
2-Iodoxybenzamides **517** are useful oxidizing reagents toward alcohols with a reactivity pattern similar to that of IBX. A wide range of primary and secondary alcohols can be oxidized by these reagents to the respective carbonyl compounds in excellent yields under mild conditions in chloroform.[94,943] Oxidative kinetic resolution of racemic *sec*-phenethyl alcohol using reagents **517** has showed very low enantioselectivity (1−6% ee).[943]

Lee and co-workers have synthesized the polymer-supported IBX-ester **518** and IBX-amides **519** and **520** starting from the commercially available hydroxy or amino polystyrene in two steps.[944] The oxidant resins **518**−**520** were prepared with loadings of 0.65−1.08 mmol/g and were evaluated with a series of alcohol substrates. The polymer supported IBX-amide **520** exhibited particularly fast and efficient oxidative activities toward a series of alcohols under mild reaction conditions.[944] IBX-amide resin **520** is also an efficient oxidant for oxidative bromination of activated aromatic compounds using tetraethylammonium bromide.[945] Linclau and co-workers reported an improved synthesis of solid-supported IBX-amide resins **521** and **522** using inexpensive and commercially available 2-iodobenzoic acid chloride and Merrifield resin.[946] Oxidation of a range of alcohols to the corresponding carbonyl compounds can be accomplished using 1.2 equiv of the resins **521** and **522**. Recycling of the resin was also possible with minimal loss of activity after two reoxidations.[946]



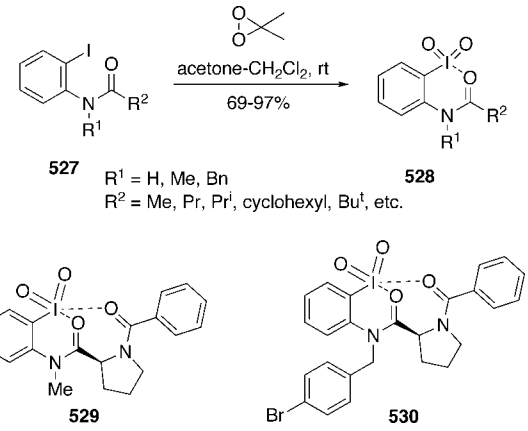

Amides of 2-iodoxybenzenesulfonic acid **524** were prepared by the dioxirane oxidation of the corresponding 2-iodobenzenesulfamides **523** and isolated as stable, microcrystalline products (Scheme 176).[947] Single crystal X-ray structures of 2-iodylbenzenesulfonamides **524** reveal a combination of intra- and intermolecular I•••O interactions, leading to a unique heptacoordinated iodine(V) center in the alanine derivative **524** (R = (*S*)-CH(CH$_3$)CO$_2$Me).[93]

**Scheme 177**




Likewise, esters of 2-iodoxybenzenesulfonic acid **526** were prepared by the dioxirane oxidation in dichloromethane of the respective monovalent iodine derivatives **525** (Scheme 177). These new pseudocyclic hypervalent iodine reagents can selectively oxidize benzyl alcohols to aldehydes, secondary amines to imines, and sulfides to sulfoxides.[948]

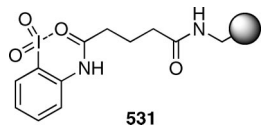
**Scheme 178**




The soluble and stable IBX analogues having pseudobenziodoxazine structure, *N*-(2-iodylphenyl)acylamides (NIPA) **528**, were prepared in good yields by the oxidation of 2-iodoaniline derivatives **527** with 3,3-dimethyldioxirane under mild conditions (Scheme 178). X-ray data on compounds **528** revealed a unique pseudobenziodoxazine structure with intramolecular secondary I•••O (2.647 Å) bonding, which is the first reported example of a six-membered pseudocyclic scaffold for iodine(V). NIPA reagents **528** are able to selectively oxidize either alcohols or sulfides, with the reactivity depending largely on the substitution pattern on the amide group adjacent to the iodyl moiety.[97] The synthesis of chiral NIPA reagents **529** and **530** has been carried out based on inexpensive and readily available (*S*)-proline.[949] The evaluation of these compounds as stereoselective oxidizing reagents toward a racemic alcohol, mesodiol, and a sulfide was performed, and moderate enantioselectivities of 29−41% were achieved. These preliminary results indicate that the NIPA scaffold is a promising structure for further elaboration of chiral iodine(V) oxidants.[949]

As a further expansion of this work, a polymer-supported version of *N*-(2-iodylphenyl)acylamides (NIPA resin) **531** has been prepared in three simple steps. The synthesis employs commercially available aminomethylated polystyrene and affords resin **531** with a good loading of 0.70−0.80 mmol g$^{-1}$. This convenient, recyclable reagent was shown to effect smooth and efficient oxidation of a broad variety of alcohols.[950]

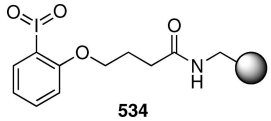
2-Iodylphenol ethers **533** were prepared by the dioxirane oxidation of the corresponding 2-iodophenol ethers **532**



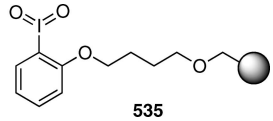
531

(Scheme 179) and isolated as chemically stable, microcrystalline products.[98] Single-crystal X-ray diffraction analysis of 1-iodyl-2-isopropoxybenzene and 1-iodyl-2-butoxybenzene revealed pseudopolymeric arrangements in the solid state formed by intermolecular interactions between the $IO_2$ groups of different molecules. 2-Iodylphenol ethers **533** can selectively oxidize sulfides to sulfoxides and alcohols to the respective aldehydes or ketones.[98]

The polymer-supported analogues of 2-iodylphenol ethers **534** and **535** based on the commercially available aminomethylated polystyrene or Merrifield resin have also been reported. These polymer-supported reagents effect clean and efficient conversion of a wide range of alcohols, including heteroatomic and unsaturated structures, to the corresponding carbonyl compounds. Recycling of the resins is possible with minimal loss of activity after several reoxidations.[951]



534



535

## 4.2. Iodine(V) Heterocycles

### *4.2.1. 2-Iodoxybenzoic Acid (IBX) and Analogues*

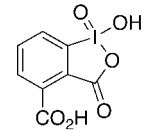
**4.2.1.1. Preparation, Structure, and Properties.** The most important representative of pentavalent iodine heterocycles, 2-iodoxybenzoic acid (IBX, **537**), was first prepared in 1893 by Hartman and Meyer.[952] IBX has the structure of the cyclic benziodoxole oxide (1-hydroxy-1-oxo-1*H*-1$\lambda^5$-benzo[*d*][1,2]iodoxol-3-one, according to IUPAC nomenclature), as determined by X-ray structural analysis.[107,953,954] Most commonly, IBX is prepared by the oxidation of 2-iodobenzoic acid with potassium bromate in an aqueous solution of sulfuric acid.[955] IBX was reported to be explosive under excessive heating or impact, and Dess and Martin attributed the explosive properties of some samples to the presence of bromate impurities.[106] A convenient procedure for the preparation of IBX **537** which involves oxidation of 2-iodobenzoic acid **536** with oxone (Scheme 180) was reported by Santagostino and co-workers.[956] This protocol substantially reduced the amount of explosive impurities in the prepared IBX samples.

IBX samples, prepared by the oxidation of 2-iodobenzoic acid with potassium bromate, usually contain a mixture of the powder and the macrocrystalline forms. A detailed X-ray diffraction study of both forms of IBX was published by Stevenson and co-workers.[107] 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. Treatment of the macrocrystalline IBX with aqueous sodium hydroxide and then with HCl can be used to convert it to the more reactive powder form.[107]

The theoretical and experimental study of the p$K_a$ value and proton affinity of IBX has been published by Williams and co-workers.[957] Solution-phase acidity determinations were performed in both aqueous media and DMSO. In particular, the aqueous p$K_a$ value of 2.40 for IBX was obtained by using standard potentiometric titration methods. The relatively high acidity of IBX should be taken into consideration while using this important reagent in the oxidation of complex organic molecules. Very recently, O'Hair and coauthors reported the gas phase proton affinities of the anions of IBX ($1300 \pm 25$ mol$^{-1}$) and 2-iodosylbenzoic acid ($1390 \pm 10$ kJ mol$^{-1}$) using mass spectrometry-based experiments.[958] The experimental results were supported by theoretical calculations, which yielded proton affinities of 1336 and 1392 kJ mol$^{-1}$ for $IBX^-$ and $IBA^-$, respectively, at the B3LYP/aug-cc-PVDZ level of theory.

A nonexplosive formulation of IBX (SIBX), consisting of IBX, benzoic acid, and isophthalic acid, has been introduced by Quideau and co-workers.[959] The synthetic utility of SIBX has been demonstrated on the reactions of hydroxylative phenol dearomatization,[418,960,961] oxidation of sulfides into sulfoxides,[962] oxidative demethylation of phenolic methyl aryl ethers,[959] and other useful oxidative transformations.[959]

Several analogues of IBX have been reported in the literature. Vinod and co-workers have developed the water-soluble analogues of IBX, *m*-iodoxyphthalic acid (mIBX) **538**,[963] and a similar derivative of terephthalic acid,[964] which can oxidize benzylic and allylic alcohols to carbonyl compounds in water. Martin and co-workers first introduced bis(trifluoromethyl)benziodoxole oxides **539** and **540**, which are stable and nonexplosive oxidizing reagents soluble in a wide range of organic solvents.[106,965] Wirth and co-workers have recently reported the preparation of the tetrafluoro IBX derivative (FIBX, **541**), which is more soluble and has a higher reactivity than its nonfluorinated counterpart.[966] Moorthy and co-workers have developed *o*-methyl-substituted IBX (Me-IBX, **542**), which is the first modified analogue of IBX that oxidizes alcohols in common organic solvents at room temperature due to the hypervalent twisting-promoted rate enhancement.[967]



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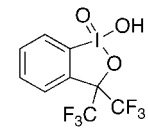

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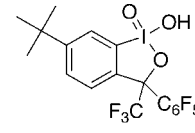
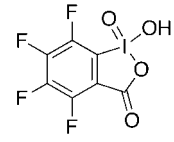
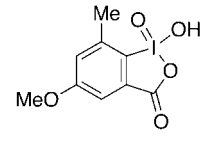


540



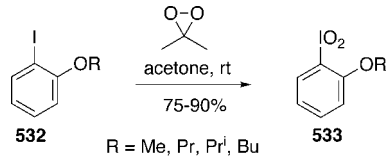
541



542

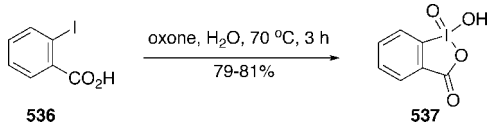
2-Iodoxybenzenesulfonic acid **545** (in a cyclic tautomeric form of 1-hydroxy-1*H*-1,2,3-benziodoxathiole 1,3,3-trioxide), a thia-analogue of IBX and a powerful oxidizing reagent, was prepared by two different pathways: hydrolysis of the methyl ester of 2-iodylbenzenesulfonic acid **543** or direct oxidation of 2-iodobenzenesulfonic acid **544** (Scheme 181).[104] The resulting 1-hydroxy-1*H*-1,2,3-benziodoxathiole 1,3,3-trioxide **545** was found to be thermally unstable and highly reactive toward organic solvents. The structure of its reductive decomposition product, 1-hydroxy-1*H*-1,2,3-benziodoxathiole 3,3-dioxide (the cyclic tautomeric form of 2-iodosylbenzenesulfonic acid), was established by single-crystal X-ray diffraction.[104]

**Scheme 179**



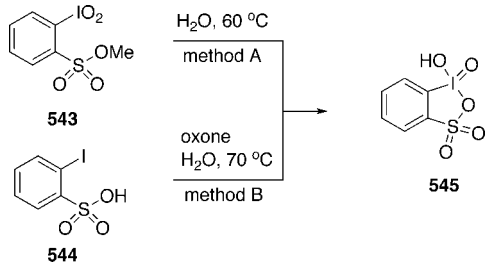

532 533

**Scheme 180**



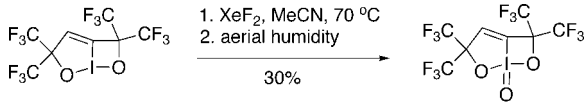

536 537

**Scheme 181**




543 544 545

**Scheme 182**

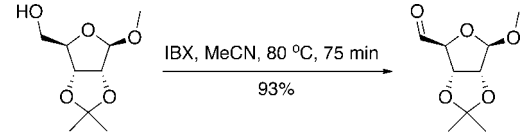



546 547

Kawashima and co-workers reported the preparation and oxidative properties of aliphatic iodoxole oxide **547**, which is the first example of this class of iodine(V) compounds. The tetracoordinate 1,2-iodoxetane **547** was prepared by the fluorination of a tricoordinate 1,2-iodoxetane **546** with xenon difluoride followed by hydrolysis (Scheme 182).[968] Compound **547** oxidizes alcohols and sulfides to the corresponding carbonyl compounds and sulfoxides, respectively, in good yields under mild conditions.[968]

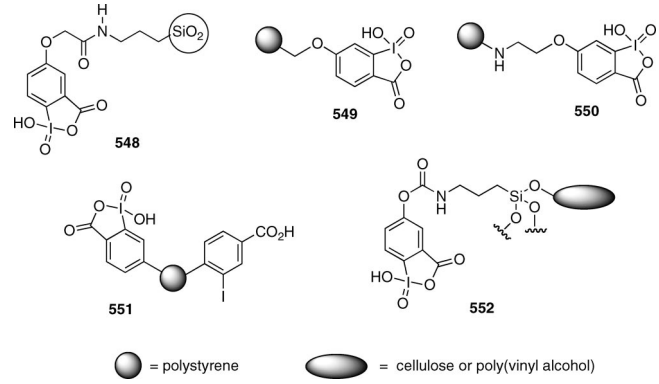
The preparation and oxidative reactivity of several polymer-supported analogues of IBX have been reported. Giannis and Mülbaier have developed the aminopropylsilica gel-based reagent **548**, which can oxidize various primary and secondary alcohols to the respective carbonyl compounds in excellent yields at room temperature in THF under heterogeneous conditions and can be regenerated by oxidation with oxone without any loss of activity.[969] Rademann and co-workers prepared the polystyrene-based polymeric analogue of IBX **549**, which was characterized by IR spectroscopy, elemental analysis, and MAS NMR spectroscopy.[970] Reagent **549** oxidizes various primary, secondary, benzylic, allylic, and terpene alcohols, and the carbamate-protected amino alcohols to afford the respective aldehydes or ketones in excellent yields, and it can be recycled by repeated oxidation after extensive washings. Lei and co-workers have developed a polymer-supported IBX derivative **550**, which has the advantages of a simplified preparation method and a high oxidation activity of 1.5 mmol $g^{-1}$.[971] A conceptually different approach was used by Sutherland and co-workers for the preparation of the polystyrene-based reagent **551**; in this procedure, the iodobenzoic acid moiety was introduced directly to the resin backbone by the iodination/oxidation sequence.[972] Very recently, the preparation of functional

**Scheme 183**




553

organic−inorganic colloids modified by IBX **552** has been reported by Hatton and co-workers.[973]



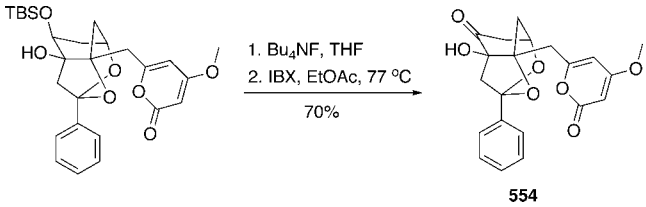

548 549 550 551 552

**4.2.1.2. Synthetic Applications of IBX.** IBX has attracted significant interest as a mild and selective oxidizing reagent. IBX is a particularly useful oxidant for the selective oxidation of alcohols to carbonyl compounds, even in complex molecules in the presence of other functional groups.[974−976] Recently, this oxidative methodology has been utilized in numerous syntheses, such as the total synthesis of (+)-wailupemycin B,[977] the total synthesis of (−)-decarbamoyloxysaxitoxin,[978] the total synthesis of abyssomicin C and atrop-abyssomicin C,[979] the stereoselective synthesis of pachastrissamine (jaspine B),[980] the syntheses of (±)-pterocarpans and isoflavones,[981] the total synthesis of (±)-nitidanin,[982] the total synthesis of lagunamycin,[983] the synthesis of (−)-agelastatin,[984] the syntheses of heliannuols B and D,[985] the synthesis of the C1−C15 fragment of dolabelide C,[986] the total syntheses of (−)-subincanadines A and B,[987] the synthesis of the spiro fused $\beta$-lactone-$\gamma$-lactam segment of oxazolomycin,[988] the synthesis of marine sponge metabolite spiculoic acid A,[989] the synthesis of optically pure highly functionalized tetrahydro-isoquinolines,[990] the preparation of Fmoc-protected amino aldehydes from the corresponding alcohols,[991] and the selective oxidation of hydroxyl-substituted organotrifluoroborates to the respective carbonyl compounds.[992]

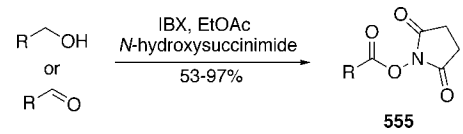
The synthetic usefulness of IBX in general is significantly restricted by its low solubility in most organic solvents, with the exception of DMSO. However, in several recent reports it has been shown that IBX can be used as an effective oxidant in other than DMSO solvents.[993−996] More and Finney have found that primary and secondary alcohols can be oxidized into the corresponding aldehydes or ketones in excellent yields (90−100%) by heating a mixture of the alcohol and IBX in common organic solvents.[993] All reaction byproducts can be completely removed by filtration. This method was used for the efficient preparation of the ribosyl aldehyde **553** (Scheme 183), the key intermediate in the stereoselective synthesis of the core structure of the polyoxin and nikkomycin antibiotics.[994]

Kuhakarn and co-workers have recently found that IBX can be used for the oxidation of alcohols in a 1:1 water/

**Scheme 184**




**Scheme 185**




dichloromethane mixture in the presence of tetrabutylammonium bromide.[996]

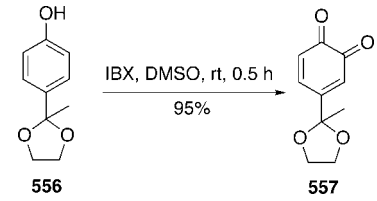
IBX is especially useful for the oxidation of 1,2-diols. Moorthy and co-workers have investigated the reactions of IBX with various vicinal diols and found that the oxidative cleavage of the C−C bond, as well as the previously known oxidation to α-ketols or α-diketones, can occur in these reactions.[997] In DMSO solutions, IBX oxidatively cleaves strained and sterically hindered syn 1,2-diols, while the nonhindered secondary glycols are oxidized to α-ketols or α-diketones. The use of trifluoroacetic acid as a solvent leads to efficient oxidative fragmentation of 1,2-diols of all types.[997] The oxidation of 1,2-diols using IBX in DMSO has been utilized for the synthesis of α-ketols[977,998,999] or α-diketones.[1000] For example, in the key step of the total synthesis of the streptomyces maritimus metabolite, wailupemycin B, IBX oxidation led to the desired hydroxyketone **554** without any cleavage of the glycol C−C bond (Scheme 184).[977]

An interesting IBX-mediated oxidation of primary alcohols or aldehydes to *N*-hydroxysuccinimide esters **555** was developed by Giannis and Schulze.[1001] The generality of this procedure was demonstrated on a variety of aliphatic, allylic, and benzylic alcohols (Scheme 185).

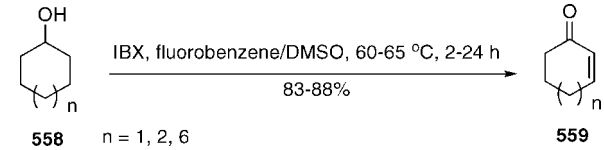
Chen and co-workers reported a mild, efficient, and environmentally benign protocol for the oxidation of alcohols with IBX in the ionic liquid 1-butyl-3-methylimidazolium chloride and water.[995] Stirring a solution of the alcohol and IBX in 1-butyl-3-methyl-imidazolium chloride followed by removal of water at room temperature and subsequent extraction with ether or ethyl acetate gives excellent yields (88−99%) of the corresponding carbonyl compounds. No overoxidation to acids was observed in the case of aldehyde products, and various functionalities such as methoxy and nitro groups, double bonds, and a furan ring could be tolerated. The oxidation of glycols under these conditions, depending of the amount of IBX used, affords α-ketols or α-diketones.[995]

Catalytic IBX-based procedures for the oxidation of alcohols have been reported by Giannis and Schulze,[1002] by Vinod and co-workers,[1003] and by Page et al.[1004] In particular, the oxidation of primary or secondary alcohols using catalytic amounts (20−30 mol %) of IBX or 2-iodobenzoic acid (IBA) in the presence of oxone as a stoichiometric oxidant in aqueous acetonitrile at 70 °C affords the corresponding carboxylic acids or ketones in 74−97% yield.[1003] A further modification of this procedure employs tetraphenylphosphonium monoperoxysulfate as the oxidant in the presence of catalytic 2-iodobenzoic acid; in this case,

**Scheme 186**




**Scheme 187**




primary alcohols are oxidized to aldehydes without overoxidation to carboxylic acids.[1004]

IBX in DMF has been shown to be an excellent reagent for the oxidation of various phenols to *o*-quinones.[1005] This procedure was used for the oxidation of phenol **556** to quinone **557** (Scheme 186), the key intermediate in the total synthesis of a novel cyclooxygenase inhibitor (±)-aiphanol.[1006] The same protocol was recently utilized in the synthesis of (±)-brazilin, a tinctorial compound found in the alcoholic extracts of trees collectively referred to as Brazil wood, by Pettus et al.[1007]

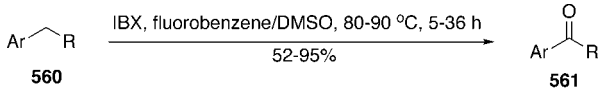
Quideau and co-workers have recently utilized the nonexplosive formulation of IBX (SIBX) in the total synthesis of the bissesquiterpene (+)-aquaticol by biomimetic oxidative dearomatization of the appropriate phenolic substrate via an orthoquinol intermediate.[961]

The practical value of IBX as a reagent was recently extended to a variety of other synthetically useful oxidative transformations, such as the one-step synthesis of α,β-unsaturated carbonyl systems from saturated alcohols and carbonyl compounds,[1008] the selective oxidation of the benzylic carbon,[1009,1010] the oxidation of amines to imines[1011,1012] and nitriles,[1013−1017] the oxidative deprotection of dithianes[1011] and 1,3-oxathiolanes,[1018] the oxidation of indoles into 3-hydroxyoxindoles and isatins in the presence of $InCl_3$ or $CeCl_3$,[1019,1020] the aromatization of 1,4-dihydropyridines,[1021] the α-hydroxylation of the α-alkynyl carbonyl systems leading to the corresponding tertiary alcohols[1022] or (*Z*)-enediones,[1023] the synthesis of β-(hetero)aryl-α-nitro-α,β-enals,[1024] the synthesis of quinoxaline derivatives from 1,2-diketones and *o*-phenylenediamines,[1025] the oxidative cyclization of anilides and related compounds leading to various heterocyclic systems,[1026] the generation of alkoxyamidyl radicals from the corresponding acylated alkoxyamines,[1027] the preparation of nitrile oxides from aldoximes,[1028] and various multicomponent oxidative transformations.[1029−1032] Several specific examples of these reactions are discussed below.

Nicolaou and co-workers reported a one-pot procedure for the oxidation of alcohols, ketones, and aldehydes to the corresponding α,β-unsaturated species using IBX under mild conditions. For example, cycloalkanols **558** react with 2 equiv of IBX in a 2:1 mixture of either fluorobenzene or toluene and DMSO at gentle heating to afford the corresponding α,β-unsaturated ketones **559** in good yields (Scheme 187).[1008]

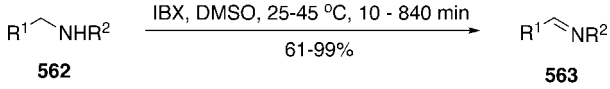
IBX is an efficient and selective reagent for the oxidation of alkyl-substituted aromatic compounds **560** at the benzylic

**Scheme 188**



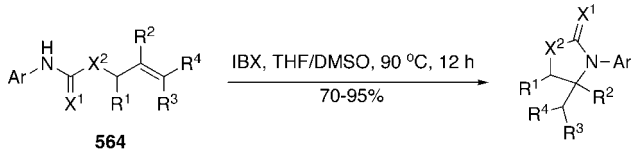

Ar = Ph, 4-Bu$^t$C$_6$H$_4$, 2-MeC$_6$H$_4$, 3-IC$_6$H$_4$, 4-BrC$_6$H$_4$, 3,4-(MeO)$_2$C$_6$H$_3$, 2-PhC$_6$H$_4$, 4-(4-pyridyl)C$_6$H$_4$, etc.
R = H, C$_3$H$_7$, etc.

**Scheme 189**



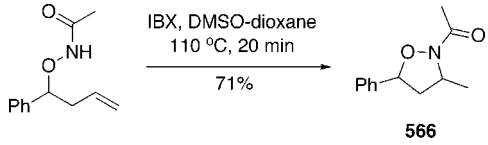

R$^1$ = Ph, 4-BrC$_6$H$_4$, 4-MeOC$_6$H$_4$, etc.
R$^2$ = 4-BrC$_6$H$_4$, 4-MeOC$_6$H$_4$, CH$_3$, OH, OBn, etc.

**Scheme 190**




X$^1$ = O, S; X$^2$ = CH$_2$, O, N
Ar = Ph, 3-EtC$_6$H$_4$, 3-BrC$_6$H$_4$, 3-FC$_6$H$_4$, 4-EtC$_6$H$_4$, etc.
R$^1$ - R$^4$ = H, alkyl, cycloalkyl, etc.

**Scheme 191**




position to the corresponding carbonyl derivatives **561** (Scheme 188). This reaction is quite general and can tolerate a variety of substituents within the aromatic ring. Overoxidation to the corresponding carboxylic acids is not observed even in the presence of electron-rich substituents.[1009]

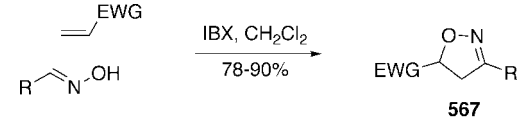
Similar to the oxidation of alcohols, secondary amines **562** can be oxidized with IBX in DMSO to yield the corresponding imines **563** in good to excellent yields (Scheme 189).[1011]

A variety of new heterocycles **565** can be synthesized by the treatment of unsaturated aryl amides, carbamates, thiocarbamates, and ureas **564** with IBX (Scheme 190).[1026,1033] The mechanism of this reaction has been investigated in detail.[1034] On the basis of solvent effects and D-labeling studies, it was proposed that the IBX-mediated cyclization of anilides in THF involves an initial single electron transfer (SET) to a THF-IBX complex followed by deprotonation, radical cyclization, and concluding termination by hydrogen abstraction from THF.[1034] A similar IBX-mediated cyclization was applied in the synthetic protocol for the stereoselective preparation of amino sugars.[1035]

Studer and Janza reported a method for the generation of alkoxyamidyl radicals starting from the corresponding acylated alkoxyamines using IBX as a single electron transfer (SET) oxidant. Stereoselective 5-exo and 6-exo reactions with these N-heteroatom-centered radicals lead to isoxazolidines and [1,2]oxazinanes (e.g., **566**) (Scheme 191).[1027]

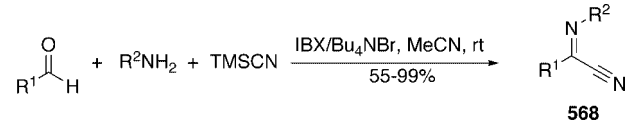
IBX has also been used for the preparation of the 3,5-disubstituted isoxazolines **567**. SET oxidation of substituted aldoximes with IBX in dichloromethane produces the respective nitrile oxide, which then undergoes 1,3-dipolar addition with an alkene component (Scheme 192).[1028]

**Scheme 192**



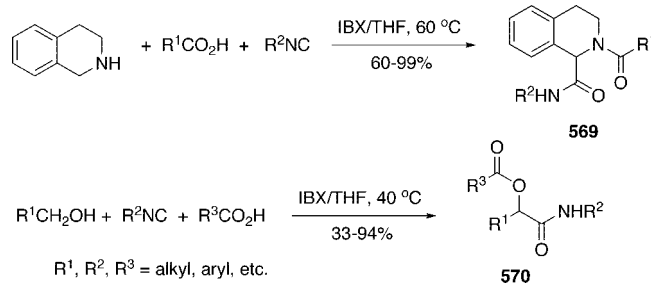

EWG = electron withdrawing group

**Scheme 193**



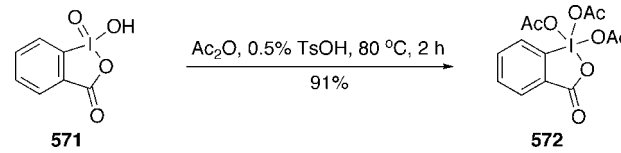

R$^1$ = Ph, 4-MeOC$_6$H$_4$, 2,6-Cl$_2$C$_6$H$_3$, PhC=CH, Ph(CH$_2$)$_2$, Pr$^i$, etc.
R$^2$ = Ph(CH$_2$)$_2$, Bu$^t$, 4-MeOC$_6$H$_4$, Ph, etc.

**Scheme 194**




R$^1$, R$^2$, R$^3$ = alkyl, aryl, etc.

**Scheme 195**




A one-pot, three-component synthesis of α-iminonitriles **568** by IBX/tetrabutylammonium bromide-mediated oxidative Strecker reaction (Scheme 193) was reported by Zhu, Masson, and co-workers.[1032] This methodology was applied to a two-step synthesis of indolizidine via a microwave-assisted intramolecular cycloaddition of α-iminonitrile.

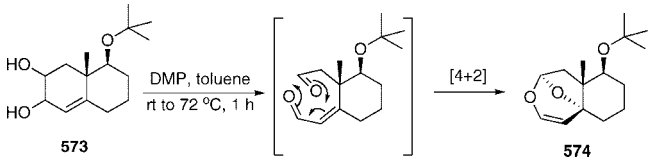
The IBX-mediated oxidative Ugi-type multicomponent reaction of tetrahydroisoquinoline with isocyanides and carboxylic acids affords the N and C1 functionalized tetrahydroisoquinolines **569** in good to excellent yields.[1031] Likewise, the three-component Passerini reaction of an alcohol, a carboxylic acid, and an isonitrile in the presence of IBX affords the corresponding α-acyloxy carboxamides **570** in generally high yields (Scheme 194).[1030]

### *4.2.2. Dess−Martin Periodinane (DMP)*

Dess−Martin periodinane (DMP, **572**) was originally introduced in 1984[1036] and since then has emerged as the reagent of choice for the oxidation of primary and secondary alcohols to aldehydes and ketones, respectively.[22,59] DMP is best prepared by the reaction of IBX **571** with acetic anhydride in the presence of *p*-toluenesulfonic acid (Scheme 195).[1037]

Due to the mild reaction conditions (room temperature, absence of acidic or basic additives) and high chemoselectivity, DMP is especially suitable for the oxidation of alcohols containing sensitive functional groups, such as unsaturated moieties, amino groups, silyl ethers, phosphine oxides, sulfides, selenides, etc. In the case of epimerization sensitive

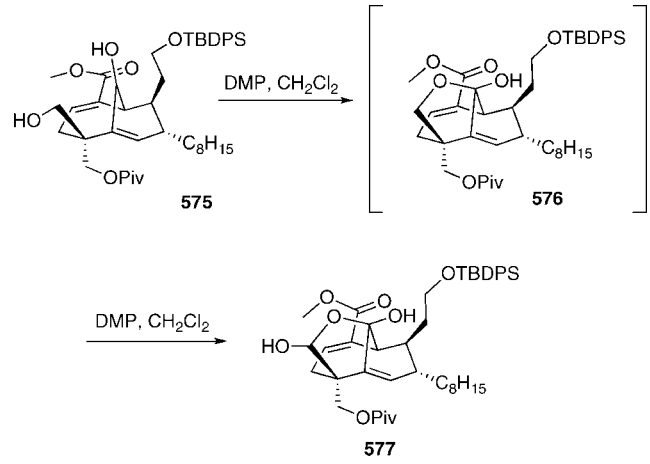
**Scheme 196**



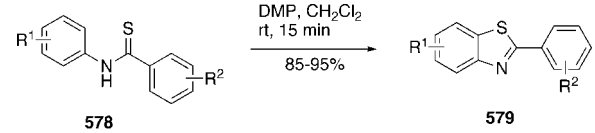

substrates, DMP allows clean oxidation with virtually no loss of enantiomeric excess. Thus, the oxidation of N-protected $\beta$-amino alcohols with DMP afforded the respective aldehydes with 99% ee and excellent chemical yields, while Swern oxidation gave unsatisfactory results (50−68% ee).[1038] The DMP oxidation is accelerated by the addition of water to the reaction mixture immediately before or during the reaction.[1039] Silyl ethers can be effectively used instead of alcohols in the DMP oxidations, affording the corresponding carbonyl compounds in excellent yields.[1040] The DMP oxidation of 1,2-diols generally cleaves the glycol C−C bond, as illustrated by the synthesis of tricyclic enol ether **574** from diol **573** via tandem 1,2-diol cleavage−intramolecular cycloaddition (Scheme 196).[1041]

Because of the unique oxidizing properties and convenience of use, DMP is widely employed in the synthesis of biologically important natural products. Recently, DMP has been used in the key oxidation steps of the following synthetic works: the preparation of 2-alkynyl acroleins,[1042] the oxidation of α-diazo-$\beta$-hydroxyesters to α-diazo-$\beta$-ketoesters,[1043] the scale-up syntheses of (−)-epicatechin-(4$\beta$,8)-(+)-catechin and (−)-epicatechin-3-*O*-galloyl-(4$\beta$,8)-(−)-epicatechin-3-*O*-gallate,[1044] the synthesis of a potent antitumor therapeutic 7-Epi (+)-FR900482,[1045] the formal total synthesis of (±)-platensimycin,[1046] the total synthesis of several members of the vinca and tacaman classes of indole alkaloids,[1047] the oxidation of the appropriately functionalized hydroxyporphyrins to chlorin-α-diones and bacteriochlorin-tetraones,[1048] the synthesis of an *N*-mesityl-substituted chiral imidazolium salt, the N-heterocyclic carbene precursor,[1049] the synthesis of new lavendamycin analogues,[1050] the synthetic studies toward the total synthesis of providencin,[1051] the stereocontrolled synthesis of prelasalocid,[1052] the total synthesis of (*R*,*R*,*R*)-α-tocopherol,[1053] the stereoselective total syntheses of lycopodium alkaloids,[1054] the synthetic studies toward bridgehead diprenyl-substituted bicyclo[3.3.1]nonane-2,9-diones,[1055] the total synthesis of (−)-pseudolaric acid B,[1056] the synthesis of azadirachtin,[1057] the total synthesis of (±)-phomactin B2,[1058] the stereoselective total synthesis of arenastatin A,[1059] the stereoselective formal total synthesis of (+)-hyperaspine,[1060] the asymmetric synthesis of salvinorin A,[1061] the asymmetric syntheses of heliannuols B and D,[985] the total synthesis of C16 analogues of (−)-dictyostatin,[1062] the total synthesis of racemic clusianone and a formal synthesis of racemic garsubellin A,[1063] the synthesis of 2,6-disubstituted dihydropyranones,[1064] the enantioselective synthesis of hydrobenzofuranones,[1065] the synthesis of di- and trisaccharide mimetics with nonglycosidic amino bridges,[1066] the total synthesis of (4*R*,5*S*)-melithiazole C and (3*R*,4*S*)-cystothiazole E,[1067] the synthesis of trifluoromethylated cyclodextrin derivatives,[1068] the asymmetric total syntheses of ecteinascidin 597 and ecteinascidin 583,[1069] the enantioselective total synthesis of (−)-erinacine B,[1070] the synthesis of the C31−C67 fragment of amphidinol 3,[1071] the total synthesis of (−)-himgaline,[1072] the total synthesis of pseudolaric acid A,[1073] and the total synthesis of (−)-sarain A.[1074]

**Scheme 197**




**Scheme 198**




R1,R2 = alkyl, acyl, aryl, etc.

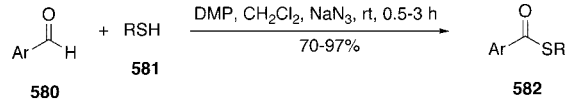
The unique oxidizing properties of DMP can be illustrated by its application in the total synthesis of the CP-molecules, lead structures for cardiovascular and anticancer drugs, published by Nicolaou and co-workers.[1075−1077] In this synthetic investigation, a hindered secondary alcohol **575** was oxidized with DMP to the stable diol **577** through intermediate hemiketal **576** (Scheme 197).

The practical value of DMP as a reagent was recently extended to a variety of other synthetically useful oxidative transformations, such as the synthesis of various polycyclic heterocycles via the oxidative cascade cyclization of anilides with pendant double bonds,[1078] the oxidative aromatization of 1,4-dihydropyridines,[1079] the one-pot oxidative allylation of Morita−Baylis−Hillman adducts with allyltrimethylsilane promoted by DMP/$BF_3$•$OEt_2$,[1080] the DMP-promoted oxidative coupling of Baylis−Hillman adducts with silyl enol ethers,[1081] the synthesis of 2-amino-1,4-benzoquinone-4-phenylimides from anilines via DMP oxidation,[1082] the α-bromination of 1,3-dicarbonyl compounds using DMP and tetraethylammonium bromide,[1083] the decarboxylative bromination of α,$\beta$-unsaturated carboxylic acids with DMP and tetraethylammonium bromide,[1084] the α-tosyloxylation of ketones using DMP and *p*-toluenesulfonic acid,[1085] the solvent-free synthesis of 1-(*p*-toluenesulfonyloxy)-1,2-benziodoxol-3(1*H*)-one from DMP and *p*-toluenesulfonic acid and its subsequent utilitization for α-tosyloxylation of ketones,[1086] the synthesis of 2-substituted benzothiazoles **579** via oxidative cyclization of thioformanilides **578** (Scheme 198),[381] the synthesis of thioesters **582** from the corresponding aldehydes **580** and thiols **581** under mild conditions (Scheme 199),[1087] and the synthesis of imides (e.g., **583**), *N*-acyl vinylogous carbamates and ureas, and nitriles by the oxidation of amides and amines with DMP (Scheme 200).[1088]

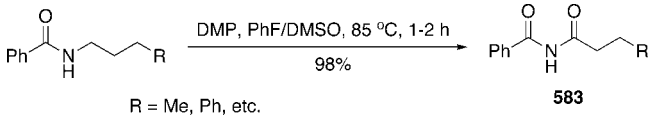
## 5. Conclusions

The preceding survey of the recent developments in the chemistry of polyvalent iodine compounds reflects an active current interest in this highly versatile class of valuable reagents. From the practical point of view, especially

**Scheme 199**




**Scheme 200**




important are the simplest, traditional reagents, such as (diacetoxyiodo)benzene and iodosylbenzene, which have been increasingly employed in organic synthesis. This growing interest in iodine(III) compounds is mainly due to their very useful oxidizing properties, combined with their benign environmental character and commercial availability.

There has been a major surge of activity in several areas of organic polyvalent iodine chemistry. These areas include the synthetic applications of IBX and similar oxidizing reagents based on the iodine(V) derivatives, the development and synthetic use of polymer-supported and recyclable polyvalent iodine reagents, structural studies of complexes and supramolecular assemblies of polyvalent iodine compounds, the catalytic applications of organoiodine compounds, and the transition metal-catalyzed reactions of various hypervalent iodine reagents.

We hope and anticipate that this review will provide additional stimulus for the further development of the chemistry of polyvalent iodine compounds.

## 6. Acknowledgments

Our own work described here was supported by the National Science Foundation (NSF/CHE-0702734) at Minnesota and by the National Institute of Health (Grant GM-57052) at Utah.

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