

Iodonium salts in organic synthesis

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Abstract

This review summarizes the chemistry of iodonium salts with emphasis of their synthetic applications. The preparation and reactions of diaryliodonium, alkenyl(aryl)iodonium, alkynyl(aryl)iodonium, and alkyl(aryl)iodonium salts are overviewed. Application of these reagents allows mild and highly selective arylations, alkenylations, alkynylations, and alkylations of various organic and inorganic substrates in a facile and environmentally friendly manner.

Keywords: Hypervalent iodine, diaryliodonium, alkenyl(aryl)iodonium, alkynyl(aryl)iodonium, alkyl(aryl)iodonium salts

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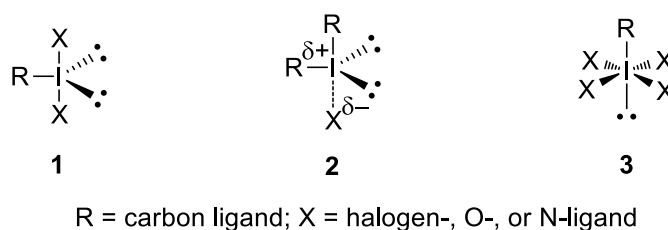
1. Introduction

Since the beginning of the 21st century, the organic chemistry of hypervalent iodine compounds has experienced an unprecedented, explosive development. Now hypervalent iodine compounds are widely used in organic synthesis as efficient reagents whose chemical properties are similar to transition metals derivatives, like mercury(II), thallium(III), lead(IV), osmium(VIII) and chromium(VI), but without the toxicity and environmental problems associated with these heavy metals. Many reviews, some comprehensive, but most dealing with specific aspects of hypervalent organoiodine chemistry, have been published just in the last ten years.¹ Particularly noteworthy was the publication of commemorative issue of *Arkivoc* honoring Prof. Anastasios Varvoglis, in which 22 research articles and accounts covered all key areas of hypervalent iodine chemistry.² More recently, a Symposium-in-Print *Tetrahedron* issue dedicated to recent advances and applications of hypervalent iodine chemistry in concert with the third International Conference on Hypervalent Iodine Chemistry (ICHCI2010) has been compiled by Quideau and Wirth.³ Previously we have published two review in *Arkivoc* summarizing synthetic applications of hypervalent iodine(V)^{4a} and hypervalent iodine(III)^{4b} compounds. The purpose of the present review is to summarize the chemistry of iodonium salts, $R_2I^+X^-$, with emphasis on recent synthetic applications, the literature coverage is through May 2011. To our knowledge, this is the first comprehensive review covering the chemistry of all classes of iodonium salts. Several earlier reviews have discussed more specific aspects of the chemistry of alkynyliodonium salts,^{5a} alkenyliodonium salts,^{5b-d} diaryliodonium salts,^{5e,f} and fluoroalkyliodonium salts.^{5g}

2. Classification and General Features of Iodonium Salts

Hypervalent iodine organic compounds belong to two general structural types: (1) iodine(III) compounds **1** and **2**, also named λ^3 -iodanes according to IUPAC recommendations, and (2) iodine(V) compounds **3**, or λ^5 -iodanes (Scheme 1). The iodine atom in λ^3 -iodanes **1** has a total 10 electrons and the overall geometry of a distorted trigonal bipyramid with two heteroatom ligands L occupying the axial positions, and the least electronegative aryl group and both electron pairs residing in equatorial positions. Iodonium salts **2**, with consideration of the closely associated anionic part of the molecule, have similar pseudo trigonal bipyramidal geometry and are generally classified as hypervalent λ^3 -iodanes with two carbon ligands (R_2IX , **2**). In the hypervalent model, bonding in R_2IX_2 uses the non-hybridized 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 λ^3 -iodanes is responsible for their high electrophilic reactivity.



Scheme 1. Common classes of hypervalent iodine compounds.

X-ray structural data for the overwhelming majority of iodonium salts R_2IX **2** show that they have structure similar to λ^3 -iodanes **1**. Their structure has trigonal bipyramidal geometry and experimentally determined bond angle R–I–R is close to 90° . X-ray data also shows the presence of significant secondary bonding between the iodine atom and the anion X with average bond distances within a range of 2.3 to 2.7 Å.

Diaryliodonium salts were discovered more than a hundred years ago and they are most investigated among iodonium salts. Their chemistry was extensively covered in previous reviews, most notably, in a recent review of Merritt and Olofsson.^{5e} Since the 1980s significant research activity has been focused on aryliodonium derivatives, $Ar(R)IX$, containing alkynyl-, alkenyl-, or fluoroalkyl groups as ligand R. These derivatives have found application as excellent reagents for the ligand R electrophilic transfer to electron-rich organic compounds. The high reactivity of aryliodonium salts, $Ar(R)IX$, in these reactions is explained by the “hyperleaving group ability” of the ArI group. For example, the leaving group ability of PhI is about 10^6 times greater than the triflate.⁶

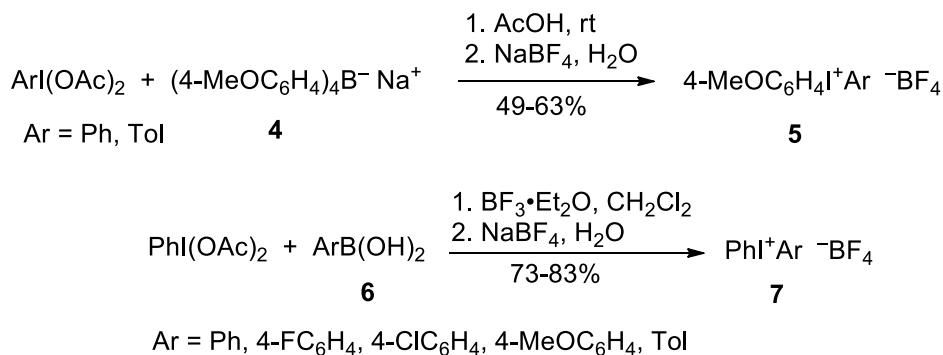
Stable iodonium salts have found numerous practical applications, such as cationic photoinitiators in polymer chemistry,⁷ and as biologically active compounds. A summary of the biological properties of iodonium salts is provided in our 1996 review.⁸ In a specific example, a study of the *in vitro* activities 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.⁹

3. Preparation of Iodonium Salts

3.1. Diaryliodonium salts

Older methods for the preparation of diaryliodonium salts are based on the reaction of arenes with iodine and potassium iodate in the presence of concentrated sulfuric acid.^{10a} Diaryliodonium tetrafluoroborates **5** and **7** can be conveniently prepared by the boron-iodine(III) exchange reaction of (diacetoxyiodo)arenes with tetraarylborates **4**^{10b} or arylboronic acids **6**^{10c,d} followed by the treatment with a saturated sodium tetrafluoroborate solution (Scheme 2). Recent

modification of this procedure involves using aryltrifluoroborates, ArBF_3K^+ , instead of tetraarylborates under mild conditions.^{11a} Likewise, fluoroorganoiodonium tetrafluoroborates $(\text{C}_6\text{F}_5)_2\text{I}^+\text{BF}_4^-$, $(4\text{-C}_5\text{F}_4\text{N})_2\text{I}^+\text{BF}_4^-$ and $[\text{C}_6\text{F}_5(4\text{-C}_5\text{F}_4\text{N})\text{I}^+\text{BF}_4^-]$ can be prepared by interaction of the appropriate (difluoroiodo)arenes with fluorinated organodifluoroboranes, Ar_fBF_2 , in dichloromethane at 0 to 20 °C.^{11b}



Scheme 2

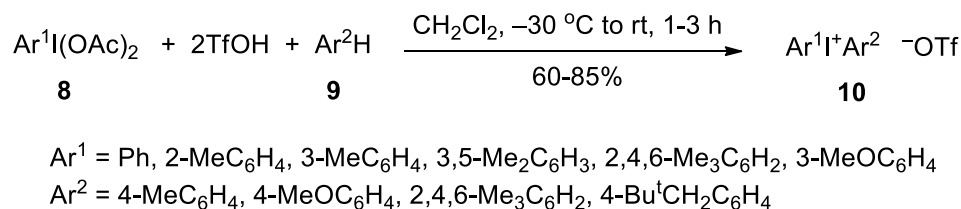
Another protocol uses a similar tin-iodine(III) and silicon-iodine(III) exchange reaction of (diacetoxyiodo)arenes or iodosylbenzene with tetraphenylstannane or trimethylsilylbenzene in the presence of boron trifluoride etherate.¹²

Frohn and co-workers reported the preparation of a perfluoroaryliodonium salt, $(\text{C}_6\text{F}_5)_2\text{I}^+\text{AsF}_6^-$, by the electrophilic arylation of $\text{C}_6\text{F}_5\text{I}$ with a stable pentafluorophenylxenonium hexafluoroarsenate, $\text{C}_6\text{F}_5\text{Xe}^+\text{AsF}_6^-$.¹³

Numerous methods for the preparation of symmetrical and unsymmetrical diaryl- and hetaryliodonium sulfates and organosulfonates have been reported. Usually unsymmetrical diaryl- and hetaryl(aryl)iodonium tosylates are obtained by reactions of [hydroxy(tosyloxy)-iodo]arenes with arenes,^{14a} aryl- or hetaryltrimethylsilanes,^{14b,c} aryltributylstannanes,^{14d-f} or arylboronic acids.^{14g} The reaction of [hydroxy(tosyloxy)iodo]benzene with arylstannanes proceeds under milder conditions compared to arylsilanes and is applicable to a wide range of arenes with electron-withdrawing substituents. Arylboronic acids in general have some advantage over arylstannanes in the case of the electron-rich heterocyclic precursors.^{14g}

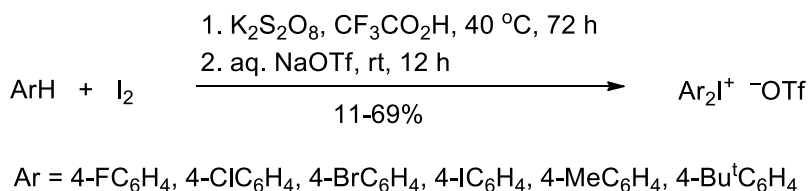
A common procedure for obtaining unsymmetrically functionalized diaryliodonium triflates **10** from iodosylbenzene^{15a} or (diacetoxyiodo)arenes **8**^{15b} in reaction with arenes **9** in trifluoromethanesulfonic acid is shown in Scheme 3. This procedure is simple and provides diaryliodonium triflates 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.^{15c} This procedure was improved to carry out the reaction more selective and under milder conditions, obtaining desired aryl(phenyl)iodonium triflates from

(diacetoxyiodo)benzene and arylboronic acids in the presence of triflic acid at $-30\text{ }^{\circ}\text{C}$ in 74-97% yields.^{14g}



Scheme 3

Several modified procedures for the preparation of diaryliodonium triflates have recently been reported.¹⁶ Kitamura and Hossain have developed a one-pot reaction to obtain symmetrical diaryliodonium triflates in good yields directly from iodoarenes and aromatic substrates using $\text{K}_2\text{S}_2\text{O}_8$ as an oxidant.^{16a} Additional improvements of this procedure consist of the reaction of arenes with elemental iodine and $\text{K}_2\text{S}_2\text{O}_8$ in trifluoroacetic acid, followed by treatment with sodium triflate (Scheme 4).^{16b,c}

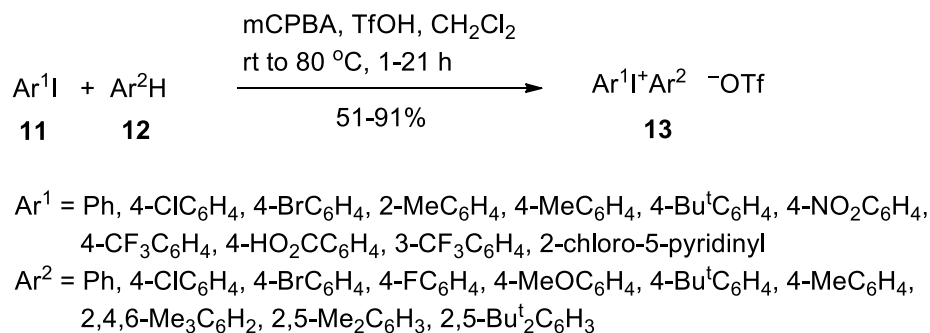


Scheme 4

Olofsson and co-workers have developed several efficient one-pot syntheses of diaryliodonium salts.^{16d-i} A general and universal procedure provides both symmetrical and unsymmetrical diaryliodonium triflates **13** from both electron-deficient and electron-rich arenes **12** and aryl iodides **11** using *m*CPBA as the oxidant and triflic acid (Scheme 5).^{16d-f} The electron-rich diaryliodonium tosylates are prepared similarly using toluenesulfonic acid instead of triflic acid as the additive.^{16f} Symmetrical diaryliodonium triflates can be synthesized by a modified one-pot procedure from iodine, arenes, *m*CPBA and triflic acid under similar conditions.^{16d,e} A similar procedure based on a one-pot reaction of arylboronic acids, aryl iodides, *m*CPBA and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ has recently been used for regioselective synthesis of unsymmetrical diaryliodonium tetrafluoroborates.^{16g,h} In a further improvement of this approach, a range of symmetrical and unsymmetrical diaryliodonium triflates were prepared employing urea- H_2O_2 as the environmentally benign oxidizing agent.¹⁶ⁱ Kita and co-workers have recently demonstrated that

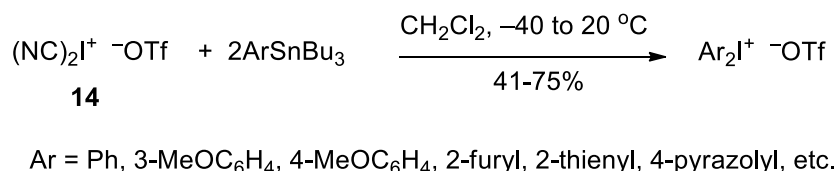
hexafluoroisopropanol (HFIP) can be used as a highly efficient solvent for the synthesis of various diaryliodonium salts.^{16j,k}

Skulski and Kraszkiwicz have also reported a new direct method for the preparation of various symmetrical diaryliodonium bromides (in 15-88% crude yields) from arenes by the reaction of ArH with NaIO₄ in sulfuric acid followed by the addition of KBr.¹⁷



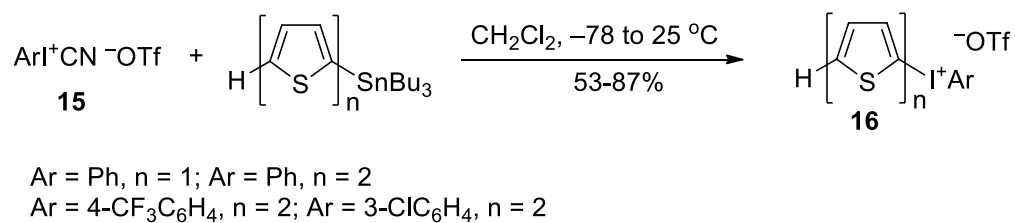
Scheme 5

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.¹⁸ Specifically, (dicyano)iodonium triflate **14**, 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 6).^{18c,d}



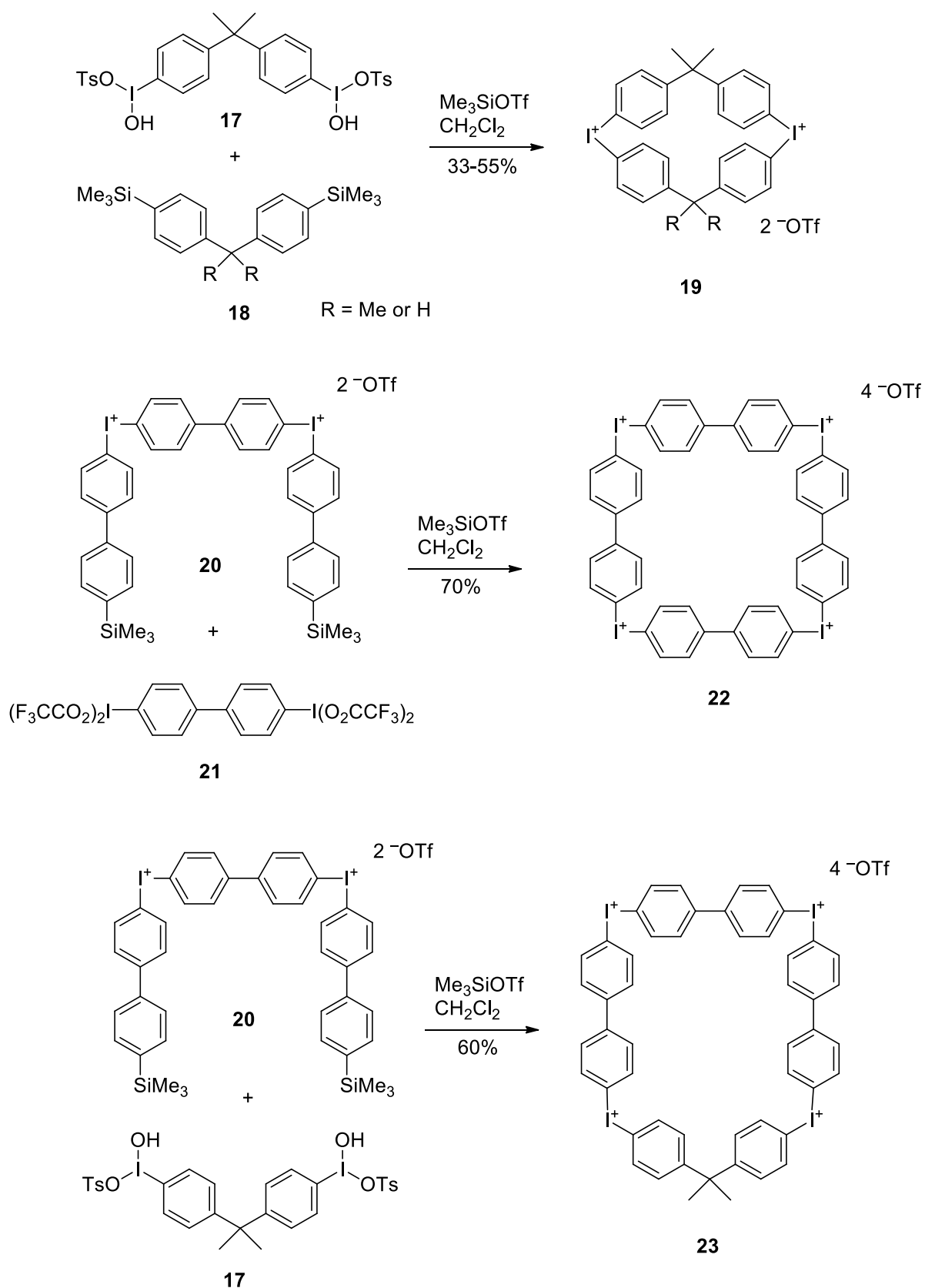
Scheme 6

Similar iodonium exchange reaction involves aryl(cyano)iodonium triflates **15** and stannylated aromatic precursors providing many kinds of diaryl or aryl(heteroaryl) iodonium salts.^{18a,b,e} Tykwinski, Hinkle and co-workers have reported an application of such iodonium transfer reaction for obtaining of a series of mono- and bithienyl(aryl)iodonium triflates **16** with increasingly electron-withdrawing substituents on the aryl moiety (Scheme 7).^{18e}



Scheme 7

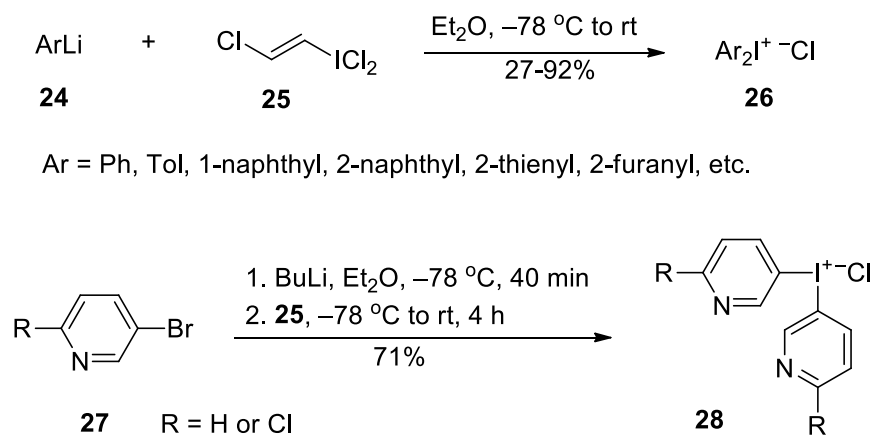
The preparation of several macrocyclic iodonium triflates, such as rhomboids **19**, a square **22**, and a pentagon **23** has been reported (Scheme 8).¹⁹ The rhomboid shaped molecules **19** were prepared by the treatment of compounds **17** and **18** with trimethylsilyl triflate.^{19a} The reaction of



Scheme 8

dication **20** with compound **21** in the presence of Me_3SiOTf gave an iodonium containing molecular square **22** in 70% yield.¹⁹ In addition, a pentagon-shaped macrocycle **23** was prepared in 60% yield from precursors **20** and **17**. 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.^{19a}

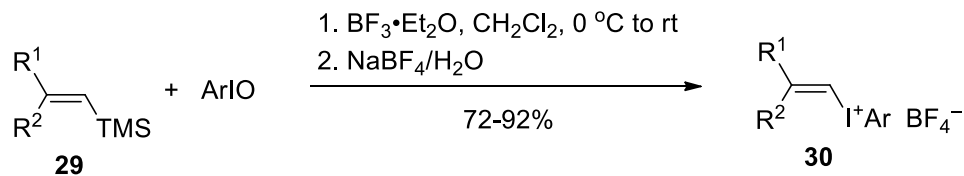
A very mild and selective approach to aryl- and hetaryliodonium chlorides **26** is based on the reaction of the appropriate aryllithium **24** (generated in situ from bromoarenes and butyllithium) with *trans*-(chlorovinyl)iodonium dichloride **25** (Scheme 9).²⁰ The iodonium transfer reagent **25** is prepared by the reaction of iodine trichloride with acetylene in concentrated hydrochloric acid;^{20c} this compound is extremely unstable and should be handled and stored with proper safety precautions.^{20b} The iodonium transfer procedure with reagent **25** is particularly useful for the preparation of bis(hetaryl)iodonium chlorides **28** from the appropriate nitrogen heterocycles **27** (Scheme 9).^{20b}



Scheme 9

3.2. Alkenyl(aryl)iodonium salts

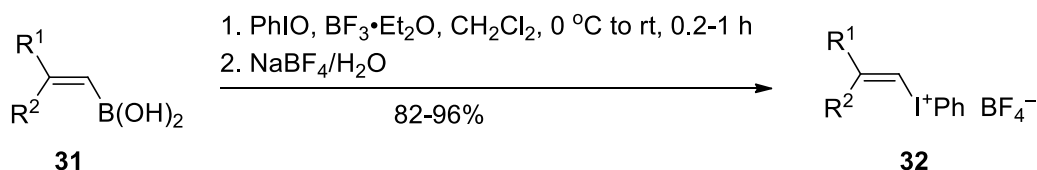
Boron trifluoride-catalyzed silicon-iodine(III) exchange reaction of organosilanes **29** with iodosylarenes followed by treatment with aqueous NaBF_4 constitutes the most general method for synthesis of alkenyl(aryl)iodonium tetrafluoroborates **30** (Scheme 10).^{10b,21} This reaction proceeds under mild conditions and in a stereospecific manner with retention of geometry of organosilanes.



$\text{R}^1 = 4\text{-BrC}_6\text{H}_4\text{OCH}_2, \text{PhCH}_2\text{CH}_2, 4\text{-ClC}_6\text{H}_4\text{OCH}_2, \text{n-C}_8\text{H}_{17}, \text{etc.}$
 $\text{R}^2 = \text{H}, \text{Me}; \text{Ar} = \text{Ph}, 2,4,6\text{-Me}_3\text{C}_6\text{H}_2, \text{etc.}$

Scheme 10

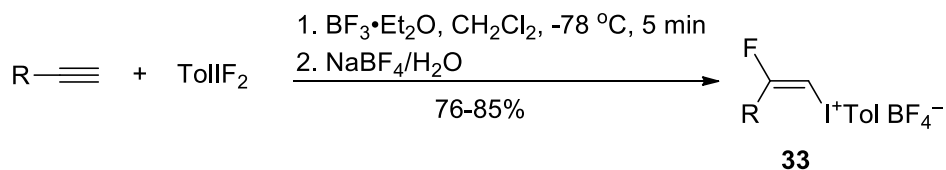
A similar borane-iodine(III) exchange of organoboronic acids **31** with iodosylbenzene or (diacetoxyiodo)benzene in the presence of boron trifluoride etherate is an efficient alternative method for a selective preparation of alkenyl(phenyl)iodonium tetrafluoroborates **32** in excellent yields (Scheme 11).²²



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

Scheme 11

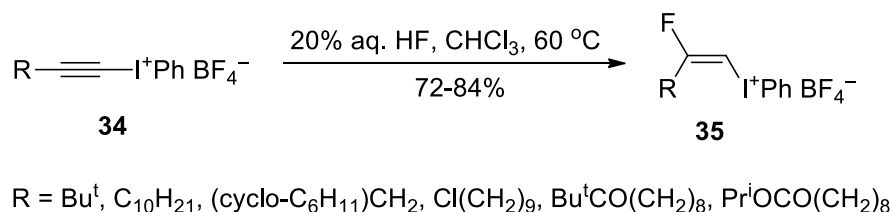
(*E*)- β -Fluoroalkenyl(tolyl)iodonium tetrafluoroborates **33** are conveniently synthesized by the treatment of terminal alkynes with 4-iodotoluene difluoride in the presence of boron trifluoride etherate (Scheme 12).^{23a} This reaction occurred instantaneously at -78°C to give fluoroalkenylidonium salts **33** in good yields with high stereoselectivity. Likewise, various alkenylidonium organosulfonates can be synthesized via electrophilic addition of the appropriate hypervalent iodine reagents to alkynes.^{23b-d}



$\text{R} = \text{AcO}(\text{CH}_2)_9, \text{Cl}(\text{CH}_2)_9, \text{MeOOC}(\text{CH}_2)_8, \text{Bu}^t\text{CO}(\text{CH}_2)_8, (\text{cyclo-C}_6\text{H}_{11})\text{CH}_2$

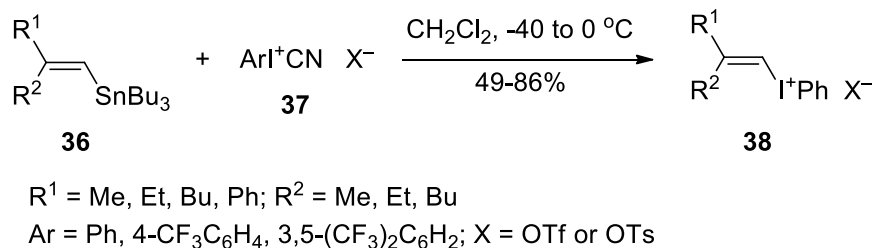
Scheme 12

(E)- β -Fluoroalkenyl(phenyl)iodonium tetrafluoroborates **35** can be stereoselectively prepared by the reaction of alkynyl(phenyl)iodonium salts **34** with aqueous HF in good yields (Scheme 13).²⁴ The method is applicable to the synthesis of fluoroalkenylidonium salts having functional groups such as ketone, ester, and chloride.

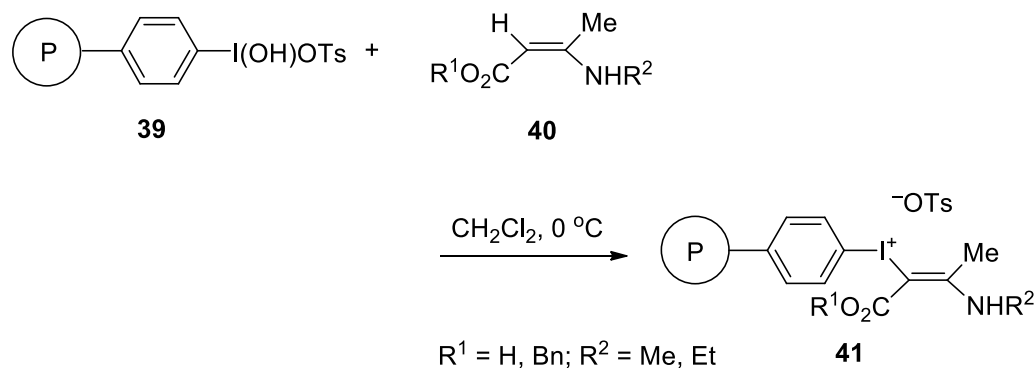


Scheme 13

A very general and mild procedure for the stereospecific synthesis of alkenylidonium organosulfonates **38** involves the reaction of aryl(cyano)iodonium triflates and tosylates **37** with stannylated alkenes **36** (Scheme 14).²⁵



Scheme 14



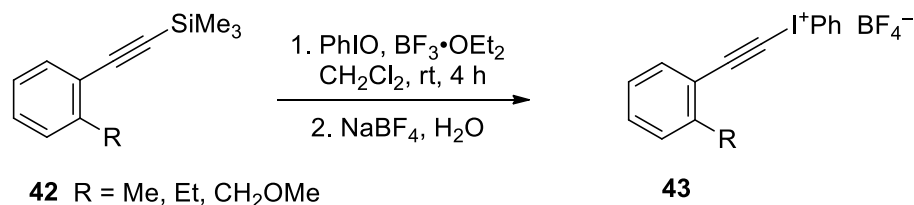
Scheme 15

The polymer-supported alkenylidonium tosylates **41** can be prepared by the treatment of polystyrene-based resin **39** with 3-aminocrotonate esters **40** (Scheme 15).^{26a} The similar

monomeric α -acyl- β -aminoalkenyl(phenyl)iodonium tosylates have been synthesized by the reaction of amino substituted α,β -unsaturated ketones with [hydroxy(tosyloxy)iodo]benzene.^{26b}

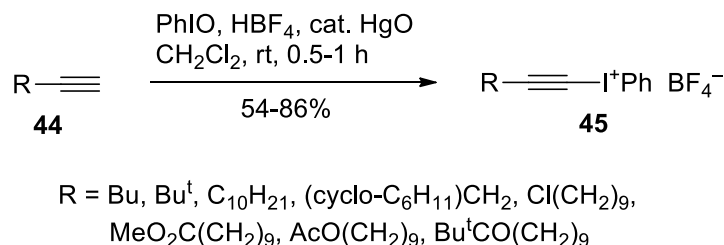
3.3. Alkynyl(aryl)iodonium salts

A widely used method for obtaining the alkynyl(phenyl)iodonium tetrafluoroborates involves the reaction of iodobenzene with alkynylsilanes and boron trifluoride etherate followed by treatment with aqueous NaBF₄.^{27a,b} Varvoglis, Koumbis and co-workers have used this procedure for the preparation of several *ortho*-substituted arylethynyl(phenyl)iodonium tetrafluoroborates **43** from alkynylsilanes **42** (Scheme 16).^{27c}



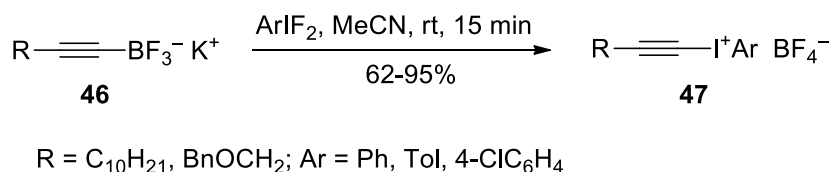
Scheme 16

A modified procedure for the synthesis of alkynyl(phenyl)iodonium tetrafluoroborates **45** reported by Hara and co-workers consists of the direct reaction of terminal alkynes **44** with iodobenzene, 42% aqueous solution of tetrafluoroboric acid, and a catalytic amount of mercury oxide (Scheme 17).^{27d}



Scheme 17

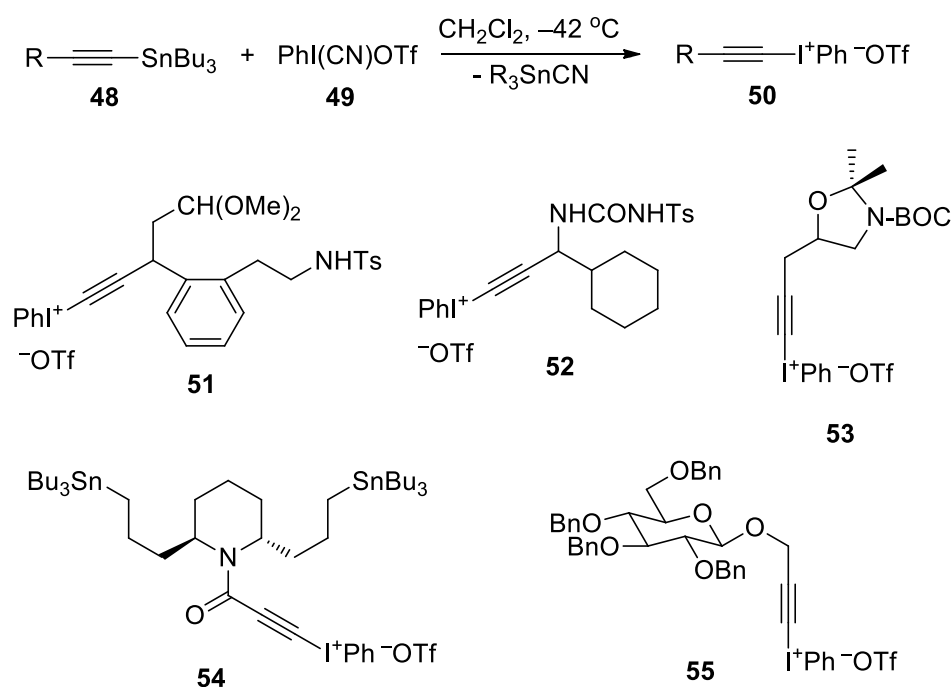
Yoshida and coauthors have reported a facile preparation of iodonium salts **47** by the reaction of potassium organotrifluoroborates **46** with (difluoroiodo)arenes under mild conditions (Scheme 18).^{11a} A similar approach to alkynyliodonium salts by the reaction of alkynyl difluoroboranes; polyfluoroorganoyliodine difluorides was developed by Frohn and Bardin.^{11c}



Scheme 18

Alkynyl(phenyl)iodonium tosylates are commonly prepared by gentle heating of [hydroxy(tosyloxy)iodo]benzene with terminal alkynes in chloroform or dichloromethane.^{27b,28} This method is also applicable to the synthesis of alkynyliodonium mesylates and 4-nitrobenzenesulfonates by the reaction of the appropriate [hydroxy(organo)sulfonyloxy]iodobenzenes with terminal alkynes under similar conditions.^{28a}

The most versatile method of preparation of alkynyl(phenyl)iodonium triflates **50** employs the iodonium transfer reaction between cyano(phenyl)iodonium triflate **49** and alkynylstannanes **48** under very mild conditions (Scheme 19).^{29a} This procedure is particularly useful for the preparation of various complex, functionalized alkynyliodonium derivatives, such as compounds **51**, **52**,^{29b} **53**,^{29c} **54**,^{29d} and **55**.^{29e} Compounds **51-55** are formed under these very mild conditions in high yields (80-90%) and can be used in subsequent transformations without additional purification.



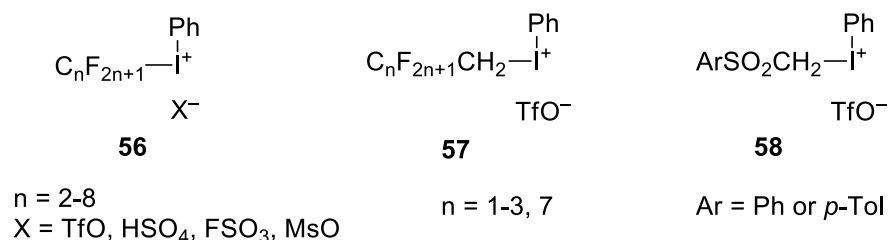
Scheme 19

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, 2PhIO•Tf₂O.^{27c,30a} This method is also applicable to the synthesis of the parent ethynyl(phenyl)iodonium triflate.^{30b}

3.4. Alkyl(aryl)iodonium salts

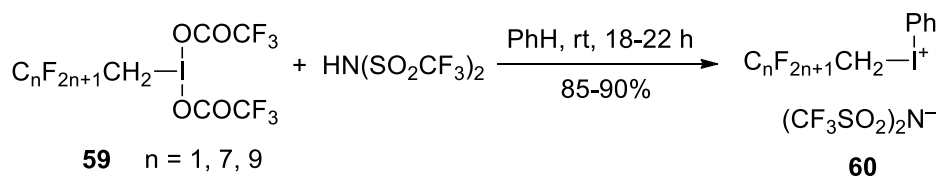
Iodonium salts with one or two aliphatic groups generally lack stability. The presence of electron-withdrawing groups in the alkyl group of iodonium salts has a pronounced stabilizing

effect. The most stable derivatives of this type are fluoroalkyl(aryl)iodonium salts **56**, **57** and (arylsulfonylmethyl)iodonium triflates **58**. Iodonium salts **56-58** are usually prepared by the reaction of the appropriate bis(trifluoroacetate) like **59** with benzene in the presence of trifluoromethanesulfonic or other strong acid. The structure of iodonium triflate **58** (Ar = Tol) was unambiguously established by a single-crystal X-ray analysis.^{31a}



Scheme 20

The preparation of fluoroalkyliodonium salts **60** by the reaction of bis(trifluoroacetates) **59** with benzene and triflimide acid was reported (Scheme 21).^{31b-d} The structure of trifluoroethyl(phenyl) iodonium salt **60** (n = 1) was established by a single-crystal X-ray analysis.^{31b} In contrast to fluoroalkyliodonium triflates **57**, compounds **60** are stable to water and can be used for fluoroalkylations in aqueous media.



Scheme 21

4. Synthetic Applications of Iodonium Salts

4.1. Arylations

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.

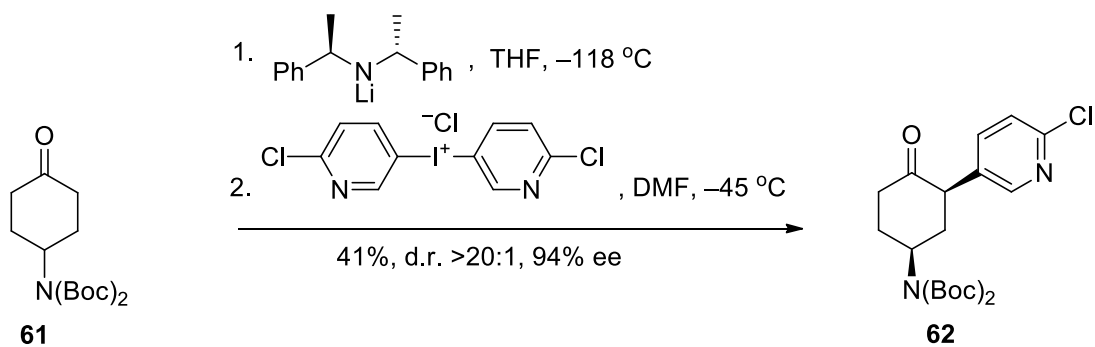
Numerous examples of the reactions of aryliodonium salts with such nucleophiles as thiosulfonate anions, fluoride anion, malonates, and silyl enol ethers under polar, non-catalytic conditions are provided in our previous reviews.^{1j,u} In more recent papers, the electrophilic arylations of sodium arenesulfonates,^{32a} potassium carbonotrithioates,^{32b} and benzazoles^{32c} using

diaryliodonium salts in ionic liquids, and the arylations of anilines,^{32d} sodium tetraphenylborate^{32e} and vinylindiums^{32f} have been reported.

The mechanism of solvolysis of methoxy-substituted diaryliodonium tetrafluoroborates, $\text{ArI}^+\text{Ph}^-\text{BF}_4$, in methanol and 2,2,2-trifluoroethanol has been investigated.^{32g} 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 and support the pathways via ligand coupling or $\text{S}_{\text{N}}\text{Ar}2$ mechanisms involving a solvent molecule as a nucleophile in the transition state.^{32g}

If the reaction is performed in inert (not nucleophilic) solvent, various nucleophiles may be involved in the reaction with iodonium salt. When diaryliodonium salt reacts with F^- anion as nucleophile there is arylfluoride among products. This reaction is widely applied for introduction ^{18}F isotope into different organic substrates to obtain labeled agents for the positron emission tomography. This topic is separately covered in Section 4.5 hereinafter due to its importance and wide usage.

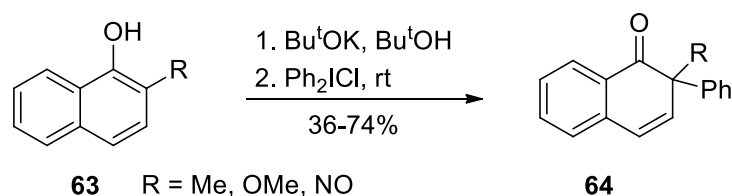
Arylations of carbon nucleophiles using aryliodonium salts are particularly important. Compounds containing an active methylene group, such as malonates, or the respective carbanions formed in situ, react smoothly with diaryliodonium salts to yield α -arylated products.^{20b,33} Aggarwal and Olofsson have developed a direct asymmetric α -arylation of prochiral ketones using chiral lithium amide bases and diaryliodonium salts.^{20b} In a specific example, the deprotonation of cyclohexanone derivative **61** using chiral Simpkins' (*R,R*)-base followed by the reaction with pyridyl iodonium salt gave the arylated product **62** in 94% enantiomeric excess (Scheme 22). This reaction (Scheme 22) has been employed in a short total synthesis of the alkaloid (-)-epibatidine.^{20b}



Scheme 22

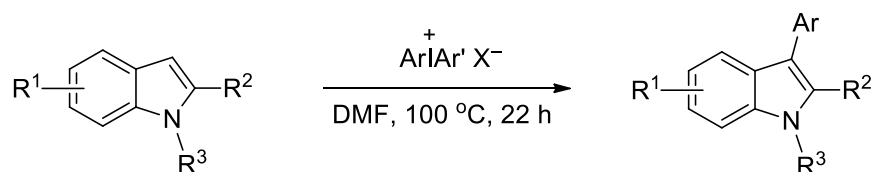
Quideau and co-workers reported a regioselective dearomatizing phenylation of phenols and naphthols using diaryliodonium salts.^{34a,b} For example, the treatment of naphthols **63** substituted at the *ortho* position by a small electron-donating group with diphenyliodonium chloride leads to their regioselective *ortho*-phenylation to give products **64** (Scheme 23). The mechanism of this

reaction involves a nonradical direct coupling of the ligands on the hypervalent iodine center.^{34a} 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.^{34a}



Scheme 23

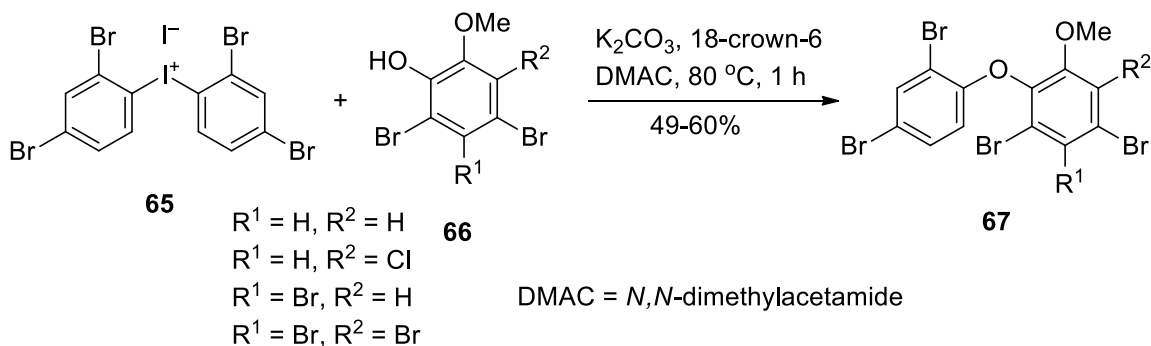
Indoles and pyrroles can be efficiently arylated by aryliodonium salts in position 3 in the absence of metal catalysts (Scheme 24).^{34c} The reaction of unsymmetrically substituted diaryliodonium salts results in the preferential transfer of the less sterically hindered aromatic moiety.



Scheme 24

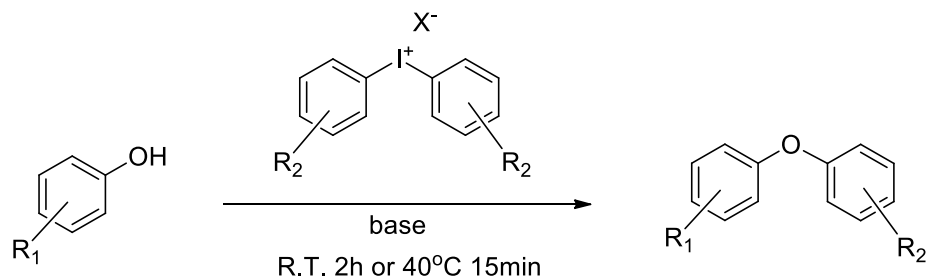
Thienyl(phenyl)iodonium salts and other heteroaryl(phenyl)iodonium salts can be used as the selective heteroaryl transfer agents in reactions with phenol ethers. These heteroarylations occur at room temperature in the hexafluoroisopropanol (HFIP) solution in the presence of TMSOTf via SET-mechanism.^{34d}

The O-arylation of the appropriate phenols using symmetrical iodonium salts has been utilized in the synthesis of hydroxylated and methoxylated polybrominated diphenyl ethers, some of which are related to natural products.^{35a,b} In particular, several polybrominated diphenyl ethers **67** were prepared by the reaction of iodonium salt **65** with phenols **66** in *N,N*-dimethylacetamide solution under basic conditions (Scheme 25).^{35a}



Scheme 25

Very recently, Olofsson and co-workers have reported a general and high-yielding synthesis of various diaryl ethers using the reaction of diaryliodonium salts with phenols under similar conditions (Scheme 26). The scope of products includes bulky ortho-substituted diaryl ethers, which are difficult to obtain by metal-catalyzed protocols.^{35c}



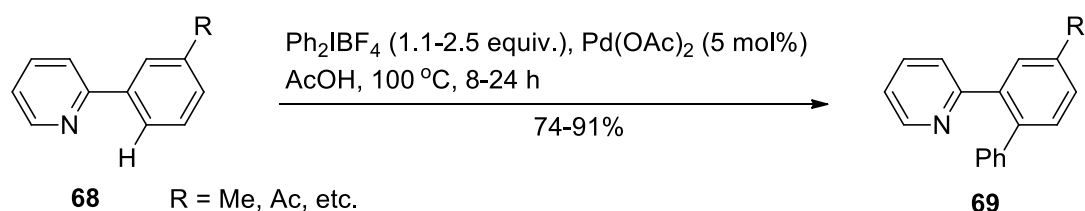
Scheme 26

Several examples of S-arylation of sulfides and P-arylation of phosphines using diaryliodonium salts were reported in the older literature.^{35d,e} These reactions generally follow a radical chain mechanism. The arylation of phosphines has been used to effect the photoinitiation of cationic polymerization.^{35f}

Aryliodonium salts have been found applicable for arylation of carbon surface.³⁶ Various iodonium salts can be used as functional groups carriers that allow covering carbon surface by wide range of functional groups, from electron-withdrawing to electron-donating. Properties of modified material are also varied widely.

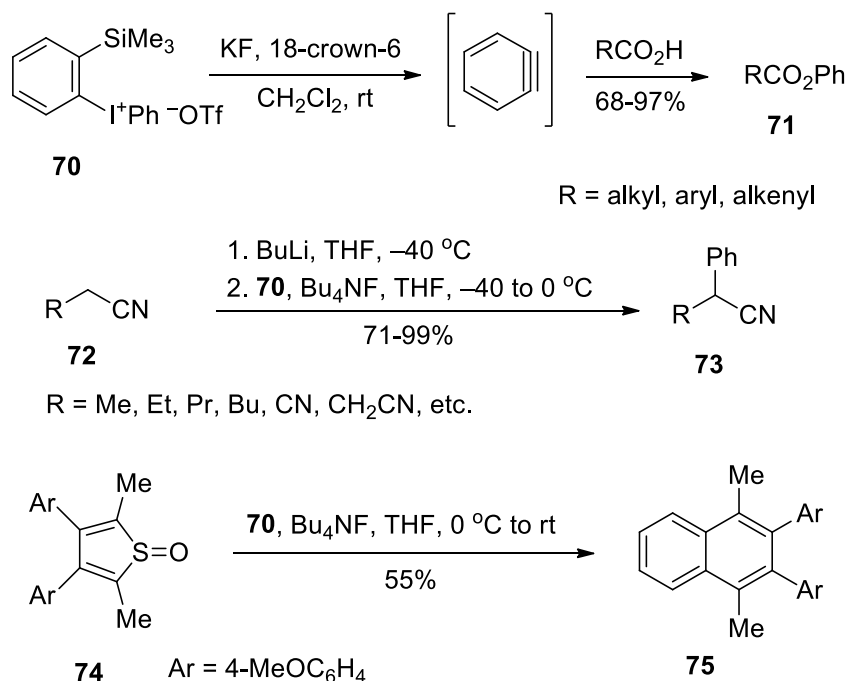
Arylations with aryliodonium salts can be effectively catalyzed by transition metals.³⁷ Aryliodonium salts can serve as efficient reagents in the copper-catalyzed arylation of lithium enolates,^{37a} thiophenes,^{37b} 5-aryl-2*H*-tetrazole,^{37c} uracil nucleosides,^{37d} aniline and phenol derivatives.^{37e} Palladium salts and complexes are efficient catalysts in the cross-coupling reactions of diaryliodonium salts with a variety of substrates,^{37f-z} such as: organoboron compounds,^{37f} organostannanes,^{37g} silanes,^{37h} organolead triacetates,³⁷ⁱ organobismuth(V) derivatives,^{37j} carbon monoxide,^{37k} allylic alcohols,^{37l} functionalized allenes,^{37n,m} Grignard

reagents,^{37o} alkenes,^{37p,q} terminal alkynes,^{37r} and arenecarboxylic acids via decarboxylative cross-coupling reaction.^{37s} Particularly interesting is the palladium-catalyzed directed C-H activation/phenylation of substituted 2-phenylpyridines and indoles with arylodonium salts reported by Sanford and co-workers.^{10c,37t} In a representative example, 2-pyridyl substituted substrates **68** are selectively phenylated to the *ortho*-position affording products **69** in good yields (Scheme 27). Preliminary mechanistic experiments have provided evidence in support of a rare Pd(II)/(IV) catalytic cycle for this transformation.^{10c} The preparation of stable triorganyl Pd(IV) complexes by the electrophilic arylation of palladium(II) bipyridine complexes using $\text{Ph}_2\text{I}^+ \text{TfO}^-$ was reported by Canty and co-workers.^{37u} Bedford and co-workers have recently demonstrated that the carbamate ($-\text{O}_2\text{CNR}_2$) function is an excellent directing group for palladium-catalyzed direct arylation reactions using diaryliodonium salts.^{37v}



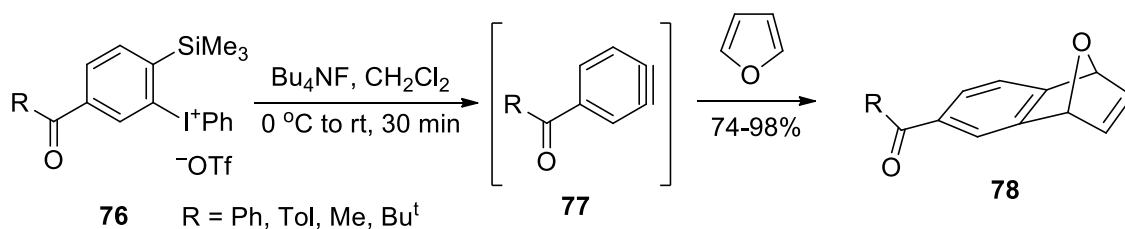
Scheme 27

Kitamura and co-workers reported the preparation and uses of several efficient benzyne precursors based on arylodonium salts.³⁸ In particular, phenyl[2-(trimethylsilyl)phenyl]iodonium triflate (**70**) is readily prepared by the reaction of 1,2-bis(trimethylsilyl)benzene with the $\text{PhI}(\text{OAc})_2/\text{TfOH}$ reagent system.^{38a} The treatment of reagent **70** 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.^{38a} Examples of synthetic application of reagent **70** as benzyne precursor include O-arylation of carboxylic acids leading to aryl esters **71**,^{39a} preparation of 2-aryl-substituted nitriles **73** by arylation of nitriles **72** via a benzyne reaction,^{39b} and cycloaddition/elimination reaction of thiophene *S*-oxide **74** with benzyne leading to product **75** (Scheme 28).^{39c} Reagent **70** 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,^{39d} 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.^{39e}



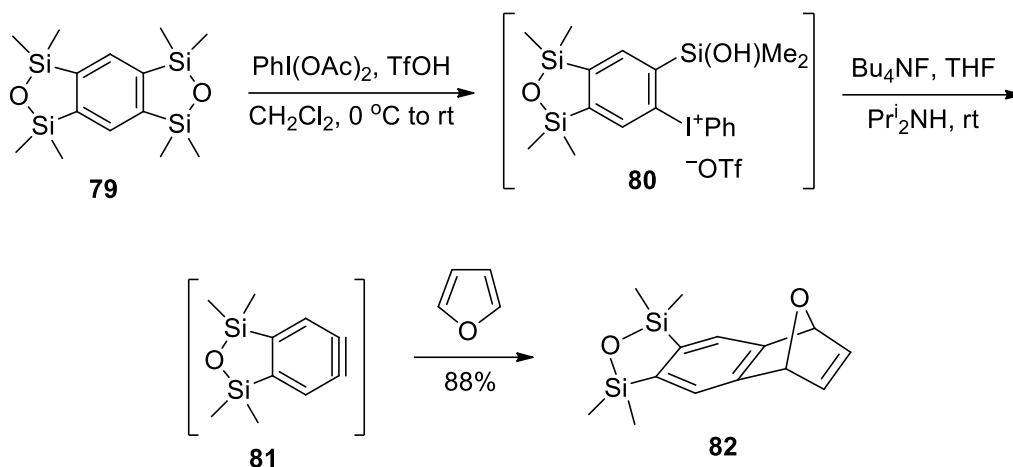
Scheme 28

The efficient acylbenzyne precursors, [5-acyl-2-(trimethylsilyl)phenyl]iodonium triflates **76** have 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 Bu₄NF in dichloromethane generates acylbenzynes **77**, which can be trapped by furan to give adducts **78** in high yield (Scheme 29).^{38d}



Scheme 29

Lee and co-workers reported the preparation of oxadisilole-substituted benzyne precursors, such as iodonium triflate **80**, from benzobisoxadisilole **79** and the PhI(OAc)₂/TfOH reagent system.^{39f} The treatment of reagent **80** with Bu₄NF in THF and diisopropylamine at room temperature generates oxadisilole-substituted benzyne **81**, which can be trapped with furan to afford adduct **82** in good yield (Scheme 30).



Scheme 30

Ko, Kang and co-workers have reported the generation and trapping of 1,2-dehydrocarborane, the carborane analog of benzyne.^{39g} 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.^{39g}

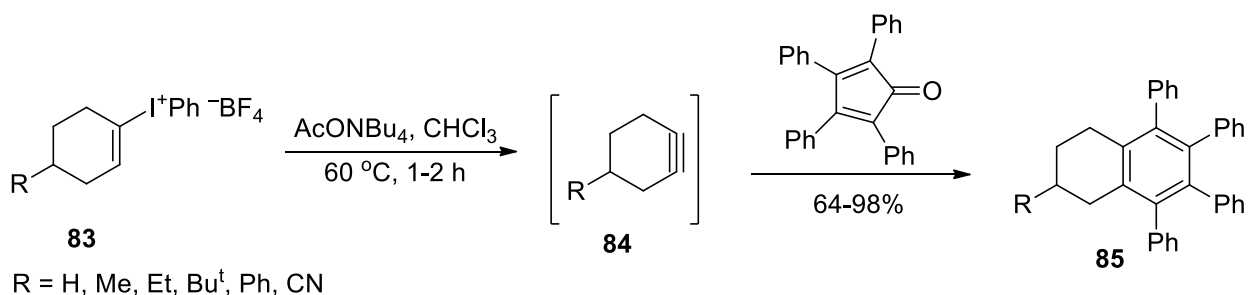
Very recently, McMillan and Allen have accomplished the enantioselective α -arylation of aldehydes using diaryliodonium salts and a combination of copper and organic amine catalysts. In a specific example, this new asymmetric protocol has been applied to the rapid synthesis of (*S*)-ketoprofen, a commercially successful oral and topical analgesic.⁴⁰

4.2. Alkenylations

Alkenyl(phenyl)iodonium salts are very reactive compounds because of the excellent leaving group ability of the phenyliodonium moiety (10^{12} times greater than for iodine itself) combined with its high electron-withdrawing properties (the Hammett substituent constant σ_m for the PhI⁺ group is 1.35).^{41a} Several research groups have been involved in the mechanistic studies of nucleophilic substitution in alkenyliodonium salts.^{41b-i} 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^{5d} and by Ochiai.^{5b}

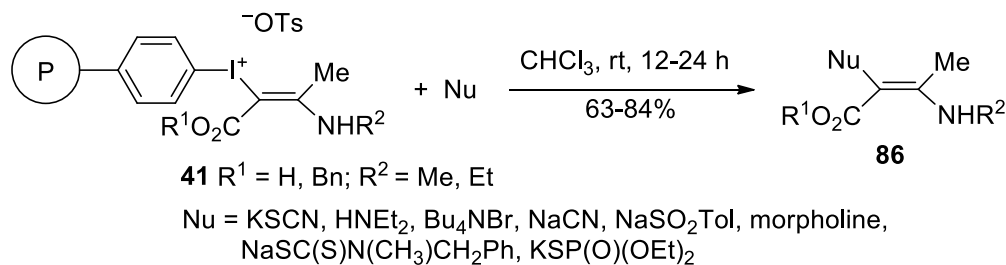
Particularly interesting is the observation of cyclohexyne intermediates **84** as products of β -elimination in the reactions of 1-cyclohexenyl(phenyl)iodonium salts **83** with mild bases such as tetrabutylammonium acetate, fluoride ion, alkoxides, and amines in aprotic solvents.^{41a,f,h} Cyclohexynes **84** could be effectively trapped with tetraphenylcyclopentadienone to give

products of [4+2] cycloaddition **85** in high yields (Scheme 31). Cycloheptyne intermediates can be generated under similar conditions from the appropriate iodonium precursors.^{41a,f,i}



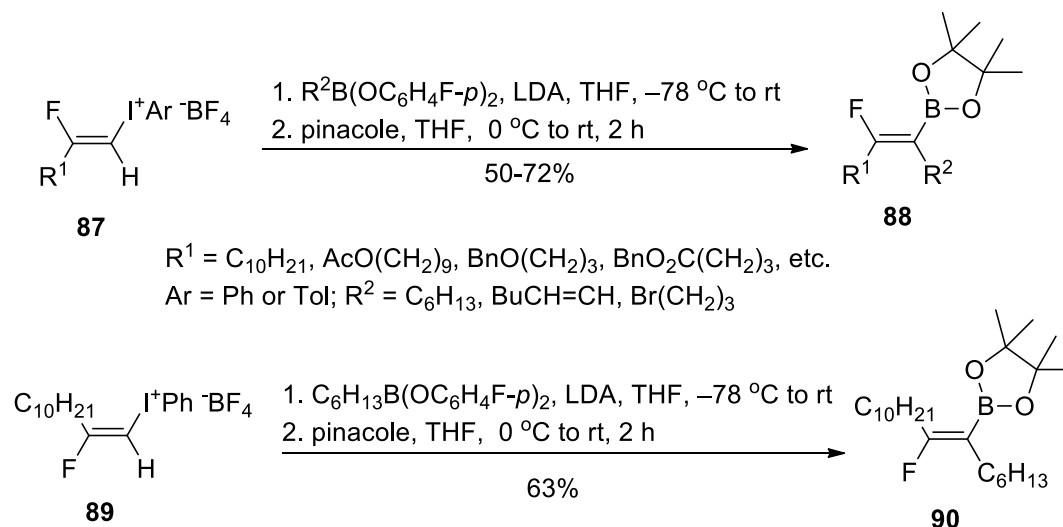
Scheme 31

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 geometry via the addition-elimination mechanism or ligand coupling on the iodine. Recent examples of alkenylations of nucleophiles under non-catalytic conditions include the stereoselective reactions of alkenyliodonium salts with sodium selenide, sodium sulfide, sodium azide, potassium thiocyanate,^{42a} and benzotriazole.^{42b} In a specific example, functionalized beta-enamines **86** have been prepared by the reaction of polymer-supported alkenyliodonium tosylates **41** with various nucleophiles at room temperature (Scheme 32).^{26a}



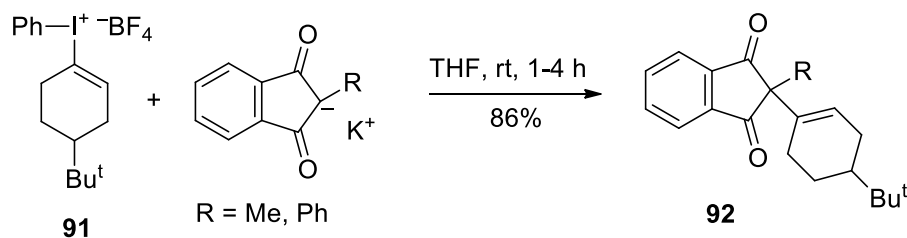
Scheme 32

(*E*)- and (*Z*)-(fluoroalkenyl)boronates **88**, **90** were prepared stereospecifically by the reaction of (*E*)- or (*Z*)-(2-fluoroalkenyl)iodonium salts **87**, **89** with di(*p*-fluorophenoxy)alkylboranes, followed by transesterification to pinacol esters (Scheme 33). 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.⁴³



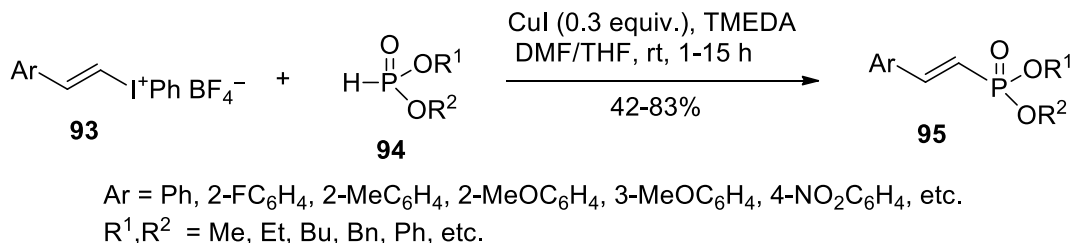
Scheme 33

Only a few examples of non-catalytic alkenylation of carbon nucleophiles are known. In particular, enolate anions derived from various 1,3-dicarbonyl compounds can be vinyliated with cyclohexenyl (**91**) and cyclopentenyl iodonium salts to afford products **92** (Scheme 34).⁴⁴



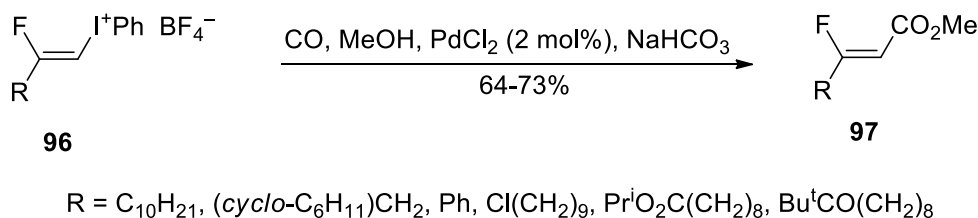
Scheme 34

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,²⁴ organoborates,^{45a} Grignard reagents,^{45b} and terminal alkynes^{45c} to afford the respective cross-coupling products in high yields with complete retention of geometry. An example of such a reaction is represented by the copper-mediated cross-coupling of H-phosphonates **94** with vinyliodonium salts **93** leading to 2-arylvinylphosphonates **95** under mild conditions (Scheme 35).^{45d}



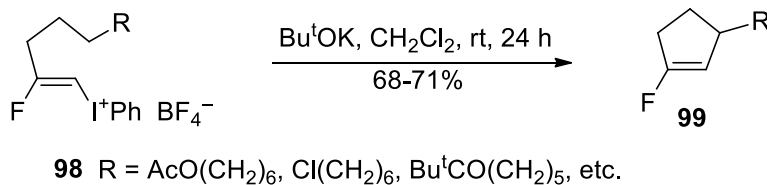
Scheme 35

Alkenyliodonium salts can be used as highly reactive reagents for Heck-type olefination,^{46a,b} Sonogashira-type coupling with alkynes,^{24a,46c} and similar palladium-catalyzed cross-coupling reactions.^{23a,24b,46d} In a specific example, (*Z*)- β -fluoro- α,β -unsaturated esters **97** were stereoselectively synthesized from (*Z*)-2-fluoro-1-alkenyliodonium salts **96** by the Pd-catalyzed methoxycarbonylation reaction (Scheme 36).^{46d} The reaction proceeded at room temperature and various functional groups on the substrate can tolerate the reaction conditions.



Scheme 36

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.⁴⁷ In a recent example, an efficient synthesis of fluorocyclopentenes **99** by the reaction of (*Z*)-(2-fluoroalkenyl)iodonium salts **98** with potassium *tert*-butoxide has been developed (Scheme 37). The mechanism of this reaction involves the initial generation of (α -fluoroalkylidene)carbenes which give fluorocyclopentenes via 1,5-C-H insertion.^{47a}

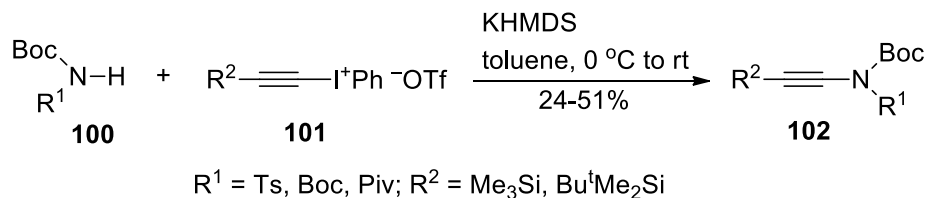


Scheme 37

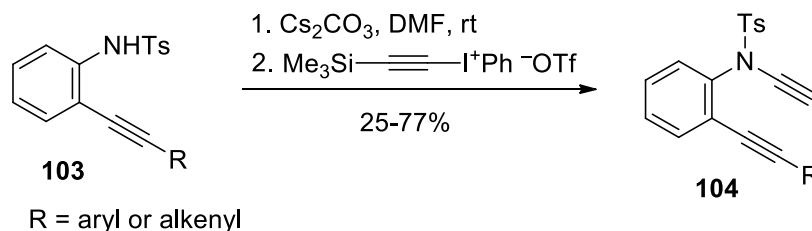
4.3. Reactions of alkynyl(aryl)iodonium salts

Reactions of alkynyliodonium salts with nucleophiles proceed via an addition-elimination mechanism involving alkylidene carbenes as key intermediates. Depending on the structure of 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.^{5a} Both of these reaction pathways have been widely utilized in organic synthesis.

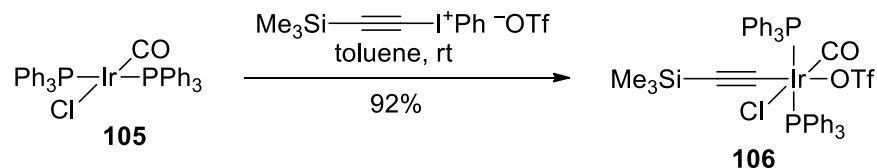
Alkynyl(phenyl)iodonium salts have found synthetic application for the preparation of various substituted alkynes by the reaction with the appropriate nucleophiles, such as: enolate anions,^{30a,48a} selenide and telluride anions,^{48b-d} dialkylphosphonate anions,^{48e} benzotriazolate anion,^{48f} imidazolate anion,^{48g} N-functionalized amide anions,^{48h-j} and transition metal complexes.^{48k-n} Specific recent examples are represented by the preparation of *N*-alkynyl carbamates **102** by alkylation of carbamates **100** using alkynyliodonium triflates **101** (Scheme 38),⁴⁸ⁱ synthesis of ynamides **104** by the alkylation/desilylation of tosylanilides **103** using trimethylsilylethynyl(phenyl)iodonium triflate (Scheme 39),^{48j} and the preparation of Ir(III) σ -acetylide complex **106** by the alkylation of Vaska's complex **105** (Scheme 40).^{48k}



Scheme 38

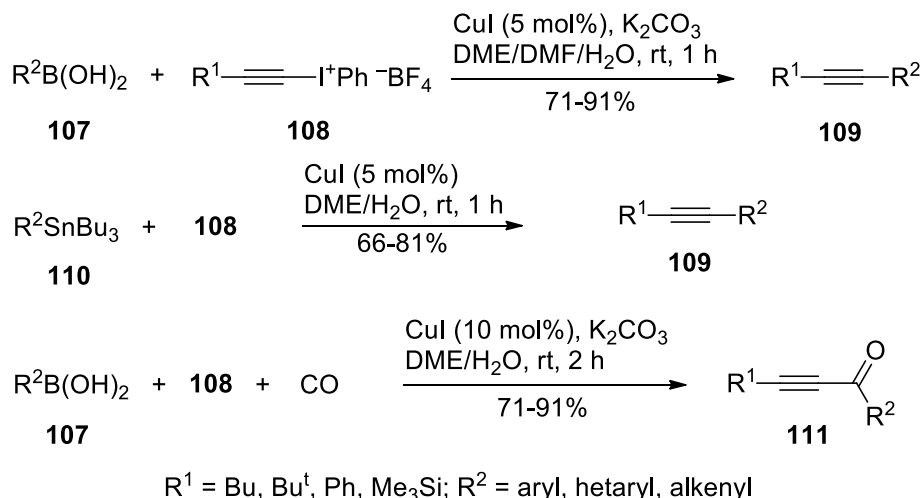


Scheme 39



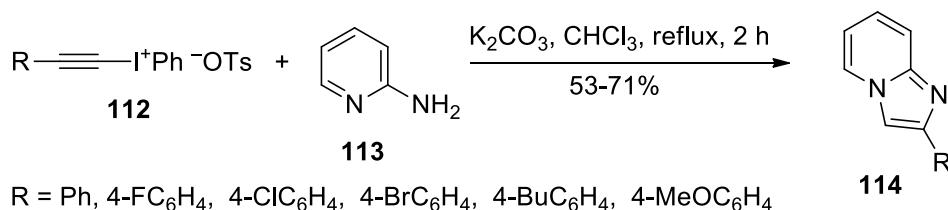
Scheme 40

Alkynyl(phenyl)iodonium salts can be efficiently coupled with organocopper reagents,^{49a} or with organoboronic acids or organostannanes in the presence of Cu(I) catalysts.^{49b,c} Specifically, the copper iodide-catalyzed cross- and carbonylative coupling reactions of alkynyliodonium salts **108** with arylboronic acids **107** or organostannanes **110** under mild conditions afford arylacetylenes **109** and aryl alkynyl ketones **111** in high yields (Scheme 41).^{49c} Interestingly, alkynyliodonium tetrafluoroborates **108** are more efficient in these coupling reactions than the corresponding iodonium triflates and tosylates.



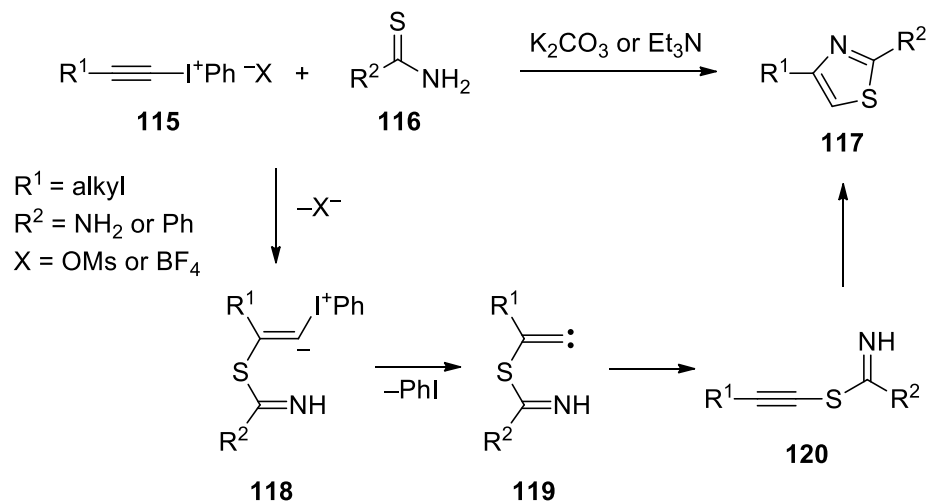
Scheme 41

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.^{5a,50a,b} The intermolecular variant of this cyclization has been utilized in the synthesis of 3-substituted-5,6-dihydroimidazo[2,1-*b*]thiazoles,^{50c} 2-substituted imidazo[1,2-*a*]pyrimidines,^{50d} and 2-substituted-imidazo[1,2-*a*]pyridines.^{50e} In a specific example, 2-substituted-imidazo[1,2-*a*]pyridines **114** were synthesized in good yield by cyclocondensation of alkynyl(phenyl)iodonium tosylates **112** with 2-aminopyridine **113** under mild conditions (Scheme 42). 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.^{50e}



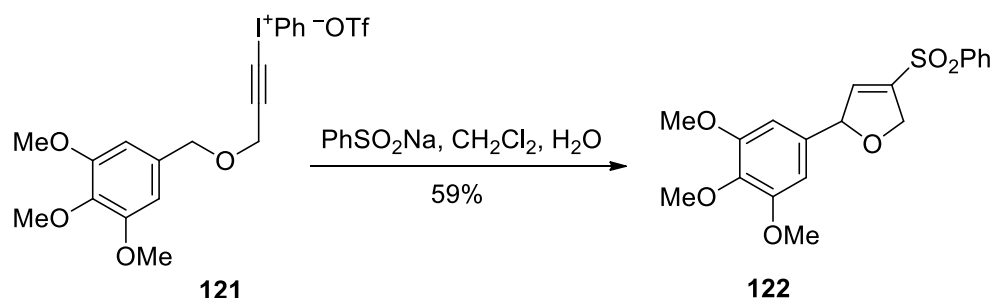
Scheme 42

Ochiai and co-workers have investigated the mechanism for the one-pot synthesis of 2,4-disubstituted thiazoles **117** by cyclocondensation of alkynyliodonium salts **115** with thioureas or thioamides **116** (Scheme 43).^{51a} This reaction was originally reported by Wipf and Venkatraman in 1996.^{51b} Ochiai and co-workers have isolated and identified by X-ray analysis intermediate products **120** (as mesylate or tetrafluoroborate salts), which suggests the mechanism involving Michael addition of sulfur nucleophile **116** to alkynyliodonium salt **115** giving intermediate ylide **118** followed by the 1,2-rearrangement of sulfenyl groups in the resulting alkylidene carbene **119** (Scheme 43).^{51a}



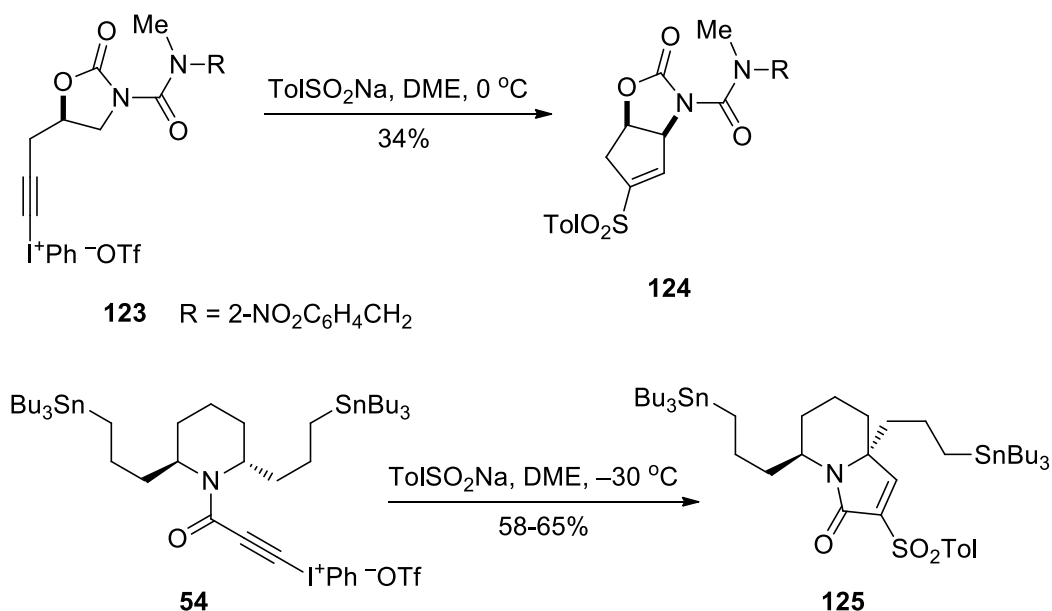
Scheme 43

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,^{29e} by the utilization of the alkylidene carbene cyclization in the total syntheses of natural products agelastatin A and agelastatin B,^{29c} and by the preparation of the tricyclic core of (\pm)-halichlorine through the use of an alkynyliodonium salt/alkylidenecarbene/1,5 C-H insertion sequence.^{29d} In particular, Wardrop and Fritz have utilized the sodium benzenesulfinate induced cyclization of the generated in situ alkynyliodonium triflate **121** leading to dihydrofuran **122** (Scheme 44), which is a key intermediate product in the total synthesis of (\pm)-magnofargesin.^{29e}



Scheme 44

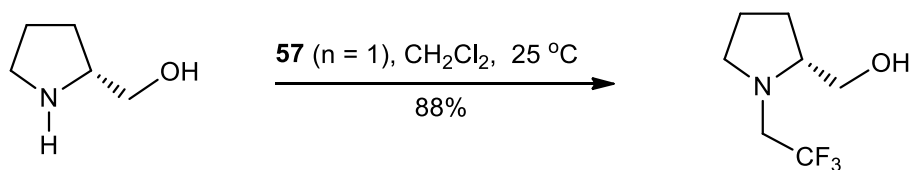
Feldman and co-workers have applied the sodium *p*-toluenesulfinate induced cyclizations of alkynyliodonium salts **123** and **54** for the preparation of compounds **124** and **125** (Scheme 45), the key intermediates in the total syntheses of agelastatins^{29c} and (±)-halichlorine, respectively.^{29d}



Scheme 45

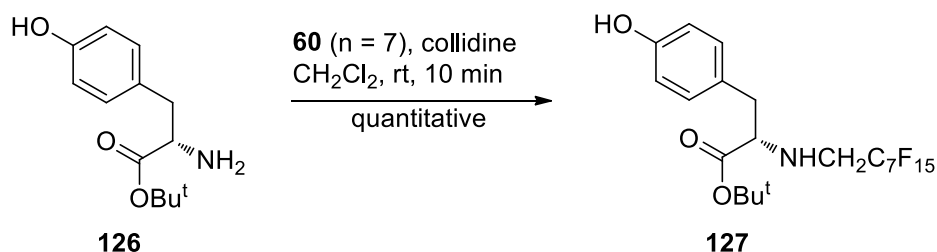
4.4. Alkylations and fluoroalkylations

Fluoroalkyl(aryl)iodonium triflates **56** and **57** (Section 3.4, Scheme 20) have found practical application as electrophilic fluoroalkylating reagents toward a variety of organic substrates, such as arenes, carbanions, alkynes, alkenes, carbonyl compounds, amines, phosphines, and sulfides.^{5g} For example, trifluoroethyl(phenyl)iodonium triflate **57** ($n = 1$) has been used for the *N*-trifluoroethylation of aminoalcohols (Scheme 46).^{52a}



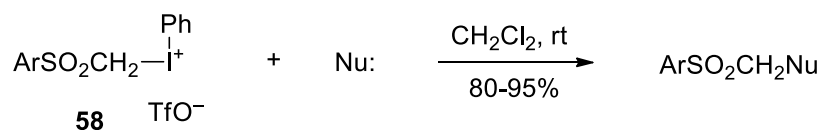
Scheme 46

Likewise, compounds **60** (Section 3.4, Scheme 21) are useful reagents for fluoroalkylation of amino acids and peptides.^{31c,d,52b-e} For example, the reaction of iodonium salt **60** ($n = 7$) with the *tert*-butyl carboxyl ester of tyrosine **126** in the presence of collidine results in quantitative formation of the monoalkylation product **127** (Scheme 47).^{31d,52d} Due to this reactivity, iodonium salts **60** can be used as fluoros capping reagents for facile purification of peptides synthesized on the solid phase.^{31d,52d} It was recently demonstrated that iodonium salts **60** are also useful for the regioselective N- or C-fluoroalkylation of imidazoles.^{52f}



Scheme 47

Similar to fluoroalkyl(aryl)iodonium salts, iodonium salts **58** are efficient electrophilic alkylating reagents towards a variety of organic nucleophiles (thiophenolate anion, amines, pyridine, triphenyl phosphine, and silyl enol ethers). All these reactions proceed under mild conditions and selectively afforded the appropriate product of alkylation along with iodobenzene as the by-product (Scheme 48).⁵³

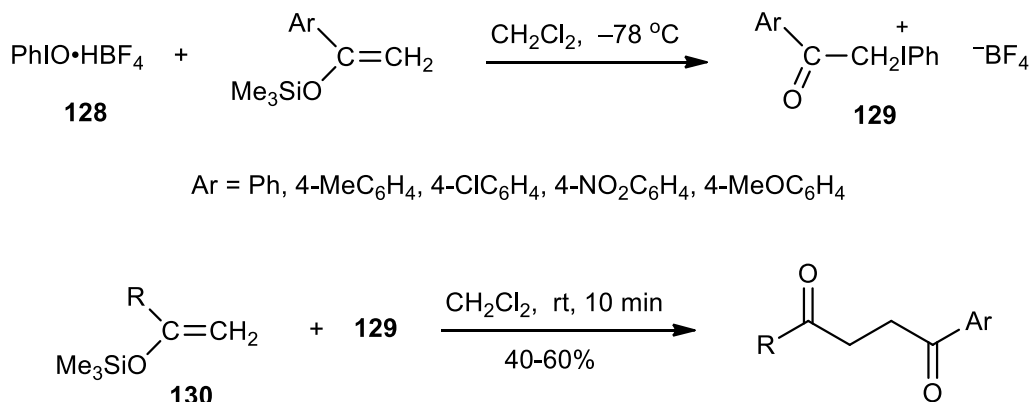


Ar = Ph or *p*-Tol; Nu: = PhS⁻, PhO⁻, R₃N, Ph₃P, silyl enols, etc.

Scheme 48

The unstable β-oxoalkyl(phenyl)iodonium salts **129** can be generated by a low temperature reaction of silyl enol ethers with reagent **128**. These species have been proposed as the reactive

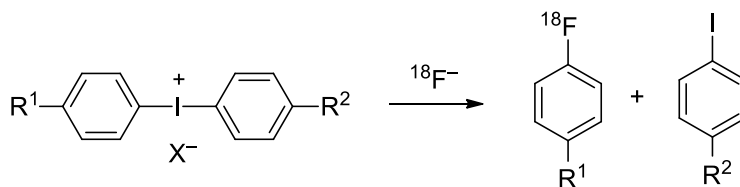
intermediates in synthetically useful carbon-carbon bond forming reactions with various silyl enol ethers **130** (Scheme 49) and other C-nucleophiles to afford the respective products of C-C bond formation.⁵⁴



Scheme 49

4.5. Introduction of fluorine and application in PET

¹⁸F-labeled imaging agents for positron emission tomography have a short lifetime (due to the short half-life of radioactive decay of ¹⁸F) and require fast and convenient methods for introduction of ¹⁸F into organic substrate molecules. Reactions of diaryliodonium salts provide such methods (Scheme 46).^{15b,55}

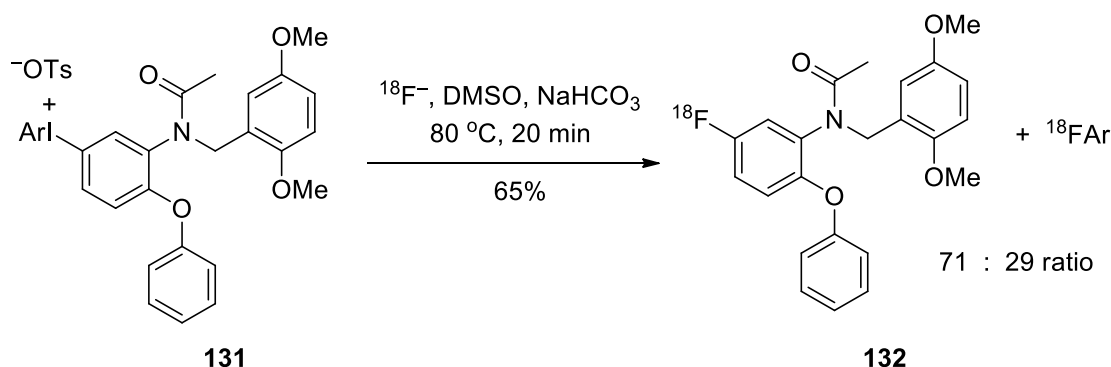


Scheme 50

In the case of reactions of symmetrical diaryliodonium salts there is no problem with selectivity, however, only half of a molecule of substrate is converted to the target product and the second half gives aryl iodide as a byproduct, which results in a low atom economy. Moreover, in this case the problem of separation of aryl iodide and aryl fluoride may take place due to their similar structure.

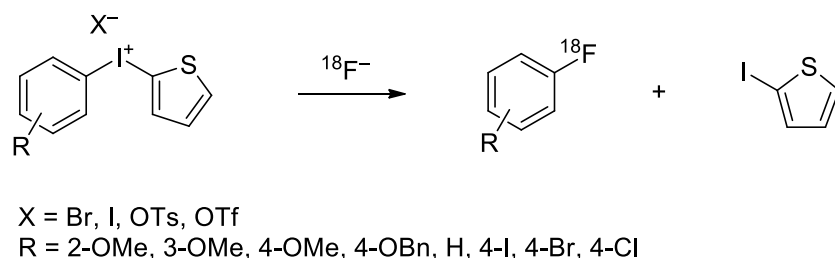
One way to eliminate this problem is by appropriate choice of R¹ and R² groups in nonsymmetrical diaryliodonium salts to make the aromatic ring with R² more electron-rich than the other aryl (Scheme 50). Zhang and coauthors reported a successful synthesis of [¹⁸F]DAA1106 (compound **132**) from diaryliodonium salt **131** with the radioactive ¹⁸F anion

(Scheme 51).^{55e} Compound **132** is used as a positron emission tomography (PET) ligand for imaging a peripheral-type benzodiazepine receptor.



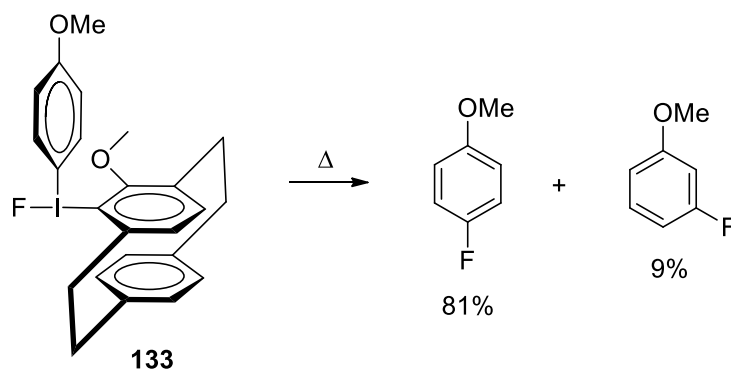
Scheme 51

Another way uses same idea to make leaving aromatic ring more electron-rich, but it is based on changing the aromatic ring nature instead of R^1 and R^2 substituents in the phenyl ring. Coenen and coauthors have developed highly efficient fluorination method using aryl-(2-thienyl)iodonium salts.^{55f} The 2-thienyl group is very electron-rich group that allows ^{18}F to be introduced directly into electron-rich arenes like anisoles (Scheme 52).^{55f}



Scheme 52

DiMugno and co-workers have recently shown that exceptionally electron-rich arene rings can be fluorinated exclusively during the reductive elimination reactions of 5-methoxy[2.2]paracyclophan-4-yl diaryliodonium salt **133** (Scheme 53).^{55g,h} Use of the sterically hindered cyclophane directing group permits a high degree of control in fluorination reactions of diaryliodonium salts.



Scheme 53

Pike and coauthors have developed a microreactor for fluorinations using diaryliodonium salts. This apparatus allows carrying out reaction between the fluoride anion and iodonium salt rapidly and efficiently.^{55b,c}

5. Conclusions and Outlook

This review demonstrates an active current interest in synthetic applications of iodonium salts. This growing interest in hypervalent iodine compounds is mainly due to their very useful reactivity, combined with benign environmental character and commercial availability. Particularly important are the applications of iodonium salts as reagents for mild and highly selective arylations, alkenylations, alkynylations, and alkylations of various organic and inorganic substrates. We anticipate that this area of hypervalent iodine chemistry will continue to attract significant research activity in the future.

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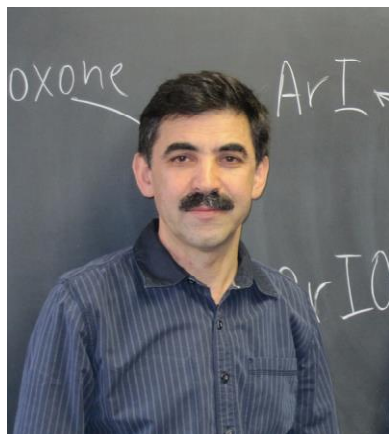
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