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Iodonium imides in organic synthesis

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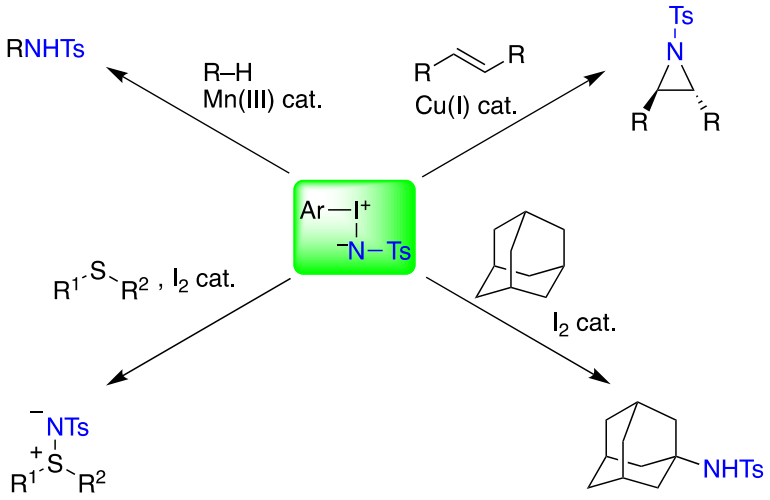
Abstract

Iodonium imides (ArINR) represent an important class of hypervalent iodine(III) compounds recently emerging as versatile, efficient and environmentally friendly synthetic reagents with numerous applications in academic and industrial research. Iodonium imides, which are also known as iminoiodanes, are widely used in organic synthesis as common nitrene precursors in the aziridination of alkenes and the amidation reactions of various organic substrates. In the present review, the preparation and structural features of iminoiodanes are discussed, and recent developments in their synthetic applications are summarized.



Keywords: Iminoiodanes, iodonium imides, nitrenes, aziridination, amidation

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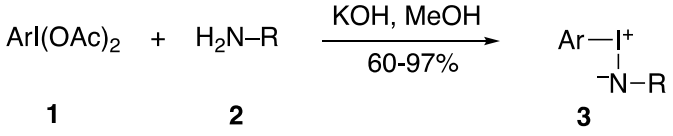
Introduction

Hypervalent iodine compounds have emerged as versatile and sustainable synthetic reagents with numerous applications in academic and industrial research.[1-10] The reactivity pattern of hypervalent iodine reagents in many aspects is similar to that of the heavy metal derivatives, but without the toxicity and environmental problems associated with these metals. Previously we have published several reviews in Arkivoc summarizing synthetic applications of hypervalent iodine reagents,[11-13] aryliodonium salts,[14] and aryliodonium ylides.[15] Iodonium imides (ArINR) are considered as the I–N analogues of iodonium ylides ($ArICR_2$) and are also known under the name of iminoiodanes. Iodonium imides represent an important class of iodonium compounds with numerous applications in organic synthesis. In general literature, iodonium imides are commonly shown as compounds with a double bond (ArI=NR); however in fact the iodine-nitrogen bond in these compounds is of a dative 2c-2e nature ($ArI^{+}–^{-}NR$) as demonstrated by adaptive natural density partitioning (AdNDP) computational studies.[16] The most important iodonium imide is *N*-tosyliminophenyliodane (PhINTs) which is widely used as a nitrene precursor in the aziridination of alkenes and the amidation reactions of various organic substrates. The chemistry of iodonium imides was previously overviewed by Dodd and coauthors in 2003 and 2011,[17,18] and their application as efficient nitrene precursors has been summarized in several general reviews on metal-catalyzed aminations.[19-21] In the present review, the preparation and structural features of iminoiodanes are discussed, and recent developments in their synthetic applications are presented. The literature coverage is through Spring 2019.

2. Preparation of Iodonium Imides

Iodonium imides **3** are generally synthesized by the interaction of (diacetoxyiodo)arenes **1** with the respective amides **2** under basic conditions (Scheme 1). Some iodonium imides are relatively unstable at room temperature, and low temperature storage is recommended. Exothermic decomposition frequently occurs at the melting point of imides, and some of them are considered to be explosive.[17] The parent iodonium imide, PhINH, is unknown and probably unstable; however, according to mechanistic studies,[22] it can be generated *in situ* from $PhI(OAc)_2$ and ammonium carbamate and used as a valuable electrophilic NH precursor.[22-27]



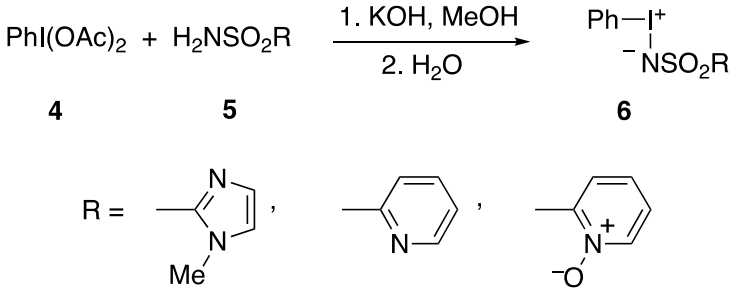
1 **2** **3**

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 1

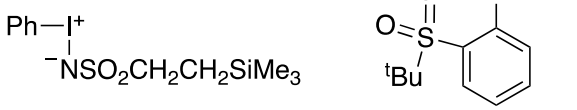
Examples of known iodonium imides **3** include *N*-tosyl-,[28] *N*-methanesulfonyl,[29] *N*-triflyl,[30,31] and *N*-trifluoroacetyl derivatives.[32,33] *N*-(Trifluoroacetyl) and *N*-(methanesulfonyl) iodonium imides are relatively unstable, while the arenesulfonyl derivatives are stable, crystalline compounds which can be stored for extended periods. Various arenesulfonyl phenyliodonium imides, $PhINSO_2Ar$ (Ar = Ph, 4-MeC_6H_4, 4-$NO_2C_6H_4$, 4-$MeOC_6H_4$, 4-$CF_3C_6H_4$, 2-$NO_2C_6H_4$, 4-FC_6H_4, 4-BrC_6H_4, and 4-IC_6H_4), have been prepared from (diacetoxyiodo)-benzene and the appropriate sulfonylamides under basic conditions as shown in Scheme 1.[34,35]

Several phenyliodonium imides **6** derived from heteroarenesulfonylamides and other precursors have been synthesized from (diacetoxyiodo)benzene **4** and the respective amides **5** (Scheme 2). Imides **6** can be used as sources of the corresponding heterocycle-containing nitrenes in copper-catalyzed aziridination and sulfimidization reactions.[36]



4 **5** **6**

R =



7

8

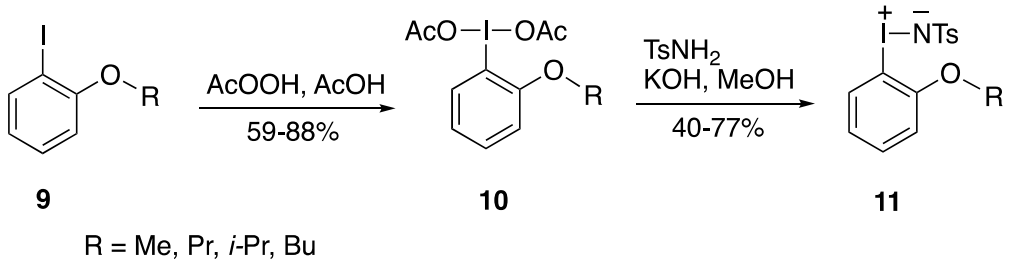
Scheme 2

Iodonium imide **7** [PhINSes, where Ses = 2-(trimethylsilyl)ethanesulfonyl] was prepared by a similar procedure from (diacetoxyiodo)benzene and the respective sulfonamide.[37] This reagent is useful for the copper-catalyzed aziridination of olefins leading to the synthetically versatile Ses-protected aziridines.

Protasiewicz and co-workers reported the preparation and X-ray crystallographic analysis of a highly soluble nitrene precursor **8**, in which the intramolecular secondary I---O bond replaces intermolecular interactions that are typical for iodonium imides.[38] Iodonium imide **8** is highly soluble in organic solvents (up to 0.14 M in chloroform, which is a 50-fold increase over PhINTs), and it can be analyzed by NMR in solution.

Solubilization of various imides ArINTs in organic solvents can also be achieved by the addition of organic N-oxides, such as Me_3NO.[39]

The highly soluble iodonium imides **11**, which are derived from *ortho*-alkoxyiodobenzenes, were synthesized in two simple steps starting from readily available 2-iodophenol ethers **9** (Scheme 3).[40] In the first step, iodides **9** were oxidized by peracetic acid to form diacetoxyiodo derivatives **10**; the structures of two products **10** (R = Me and Bu) were established by X-ray analysis. In the second step, diacetates **10** were converted to iminoiodanes **11** by treatment with tosylamide under basic conditions in methanol. Compounds **11** are relatively stable at room temperature and can be stored for several weeks in a refrigerator. Products **11** have good solubility in dichloromethane, chloroform, and acetonitrile (e.g., the solubility of **10**, R = Bu in dichloromethane is 0.25 g/mL).



9 **10** **11**

R = Me, Pr, *i*-Pr, Bu

Scheme 3

3. Structural Studies

Single crystal X-ray structural data have been reported for the following iodonium imides presented in Figure 1: phenyl(*N*-tosylimino)iodane **12**,[28] mesityl(*N*-tosylimino)iodane **13**,[28] *o*-tolyl(*N*-tosylimino)iodane **14**,[41] *ortho*-sulfonyl substituted phenyliodonium imide **8**,[39] *ortho*-methoxy substituted phenyliodonium imide **15**,[40] *ortho*-methoxymethyl substituted iodonium imides **16**,[42] **17**,[33] and **18**,[33] nitro substituted phenyliodonium imides **19** and **20**,[35] and (*N*-triflylimino)iodane **21**.[30]

Aryl(*N*-tosylimino)iodanes in general have a linear polymeric, asymmetrically bridged structure with the T-shaped geometry around the iodine centers. In the case of PhINTs **12**, the monomeric units are bridged by I–N interactions, while in the more sterically hindered MesINTs **13** the bridging atom is the oxygen of the tosyl group (Figure 2).[28] The structure of 2-TolINTs **14** is intermediate between the structures **12** and **13**: it can form two different polymorphic modifications, one with nitrogen and the second with oxygen as the bridging atom in the polymeric chain.[41] A polymeric, nitrogen-bridged structure was determined for 4-MeC_6H_4INTs by X-ray powder diffraction and EXAFS analyses.[43] The intramolecular I–N distance of 2.01-2.04 Å in *N*-tosyliminoiodanes is consistent with a single bond and the positive charge at iodine and the negative charge delocalized at the nitrogen and oxygen atoms of the tosylimino group.

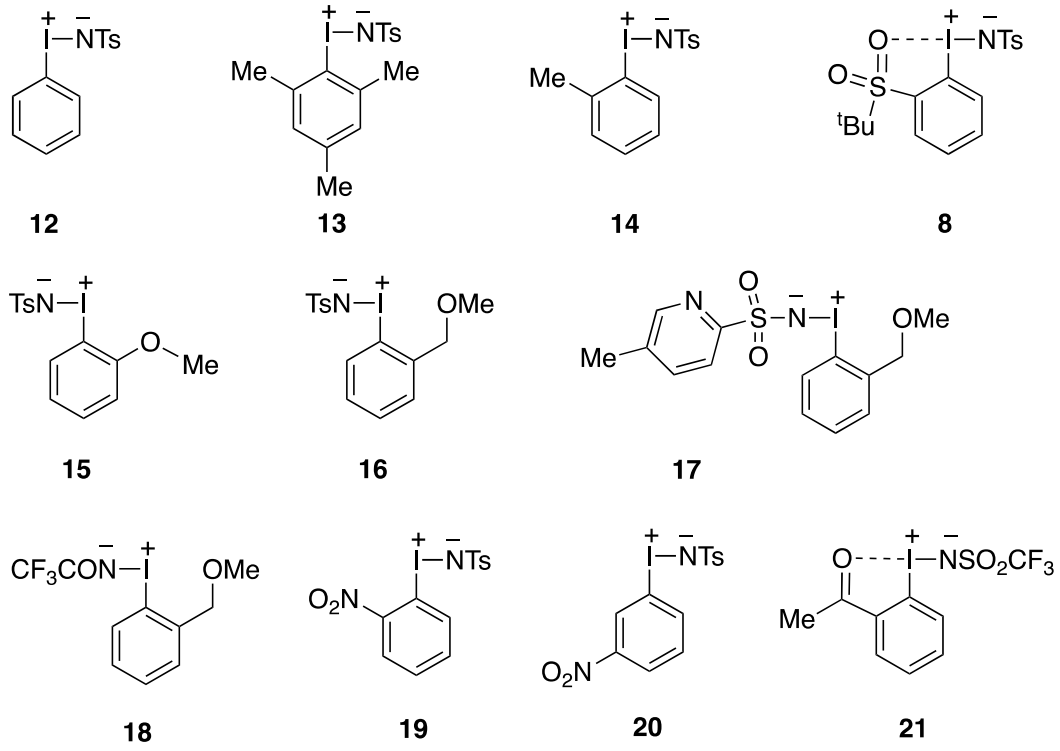


Figure 1. Iminoiodanes analyzed by a single crystal X-ray diffraction.

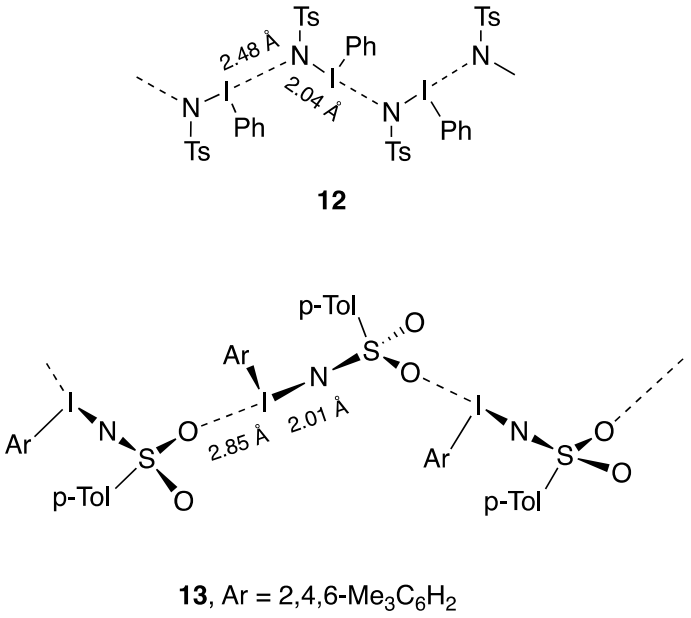


Figure 2. Primary and secondary bonding pattern in single crystal X-ray structures of iminoiodanes **12** and **13**.

A single crystal X-ray analysis of *ortho*-sulfonyl substituted phenyliodonium imide **8** showed a structure of loosely associated centrosymmetric dimers with a long-range intramolecular I–N and I–O distance of more than 3.0 Å, quite unlike the infinite polymeric chains adopted in the solid state for PhINTs.[44] One of the sulfonyl oxygen atoms forms a short intramolecular I–O secondary bond to the iodine atom with a bond length

of 2.667 Å. Because of the non-polymeric structure, imide **8** has excellent solubility in common organic solvents.

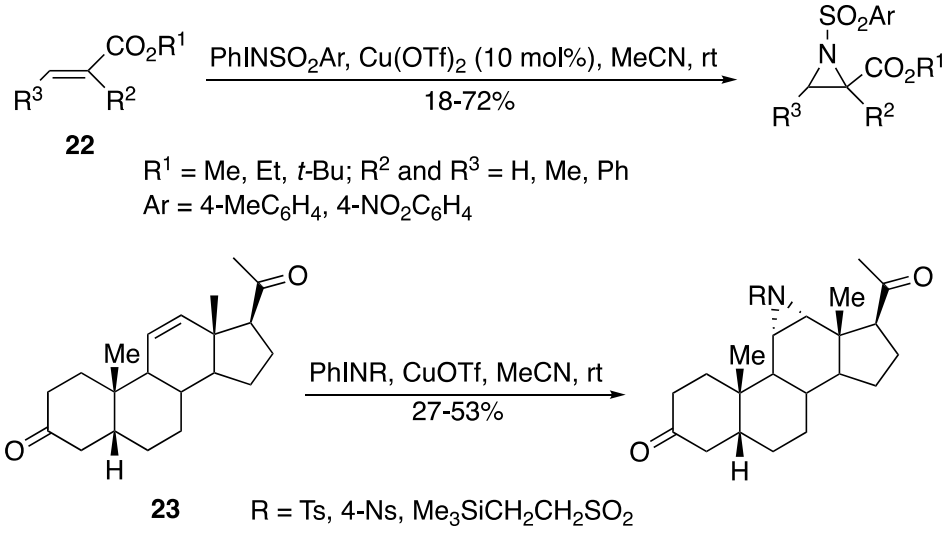
Similar to the structure of PhINTs **12** (Figure 2), molecules of *ortho*-methoxy substituted phenyliodonium imide **15**,[40] have a polymeric, asymmetrically bridged structure with a T-shaped geometry around the iodine centers formed by two iodine–nitrogen bonds and one iodine–carbon bond. However, in contrast to PhINTs, compound **15** has two additional weak intra- and intermolecular I•••O contacts between the iodine center and the oxygen atoms of the alkoxy and sulfonyl groups. These weak interactions lead to an elongation of the I•••N intermolecular bond in **15** (2.735 Å) compared with that observed in PhINTs (2.482 Å). As a result, the polymeric structure of **15** is weakened and the solubility is significantly increased.[40]

4. Applications in Organic Synthesis

4.1. Transition metal catalyzed aziridinations and amidations

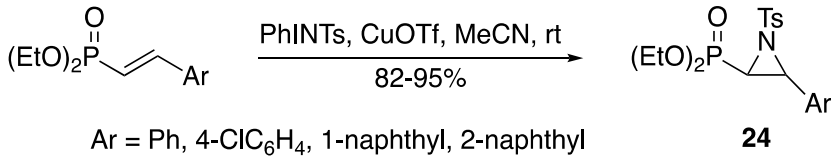
Iminoiodanes, and especially *N*-tosyliminoiodanes, ArINTs, have found wide synthetic application as nitrene precursors in transion metal-catalyzed aziridination of alkenes and amidation of various organic substrates.[17,18,45] Aziridination of alkenes with tosyliminoiodane PhINTs in the presence of iron- or manganese porphyrins was first reported in 1984.[32] This reaction involves a metal-nitrene complex as the initial reactive species and has a mechanism similar to the metal-catalyzed oxygenation reactions with iodosylbenzene. A detailed investigation of copper- or silver-catalyzed alkene aziridination reactions was recently published by Pérez and coauthors.[46,47]

Current interest in the transition metal-catalyzed reactions of iminoiodanes was initiated in the 1990s by the groundbreaking works of Evans[48,49] and Jacobsen[50,51] on the asymmetric aziridination of alkenes using PhINTs as the nitrene precursor in the presence of copper catalysts and chiral N,N-ligands. In the following works, the copper-catalyzed aziridination of alkenes was utilized in numerous syntheses. For example, Dodd and co-workers applied the Evans aziridination procedure to the aziridination of 2-substituted acrylates and cinnamates **22**[52] and to steroid **23** (Scheme 4).[53]



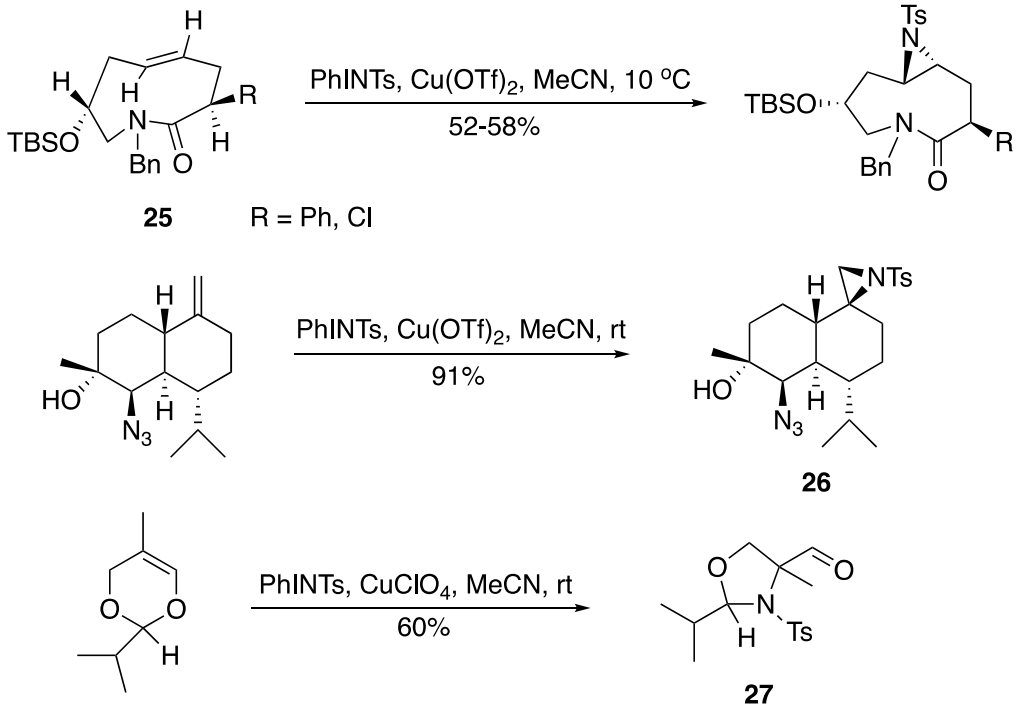
Scheme 4

Copper-catalyzed aziridination of the corresponding unsaturated substrates was employed in the preparation of various 2-acylaziridines[54,55] and aziridinylphosphonates **24** (Scheme 5).[56]



Scheme 5

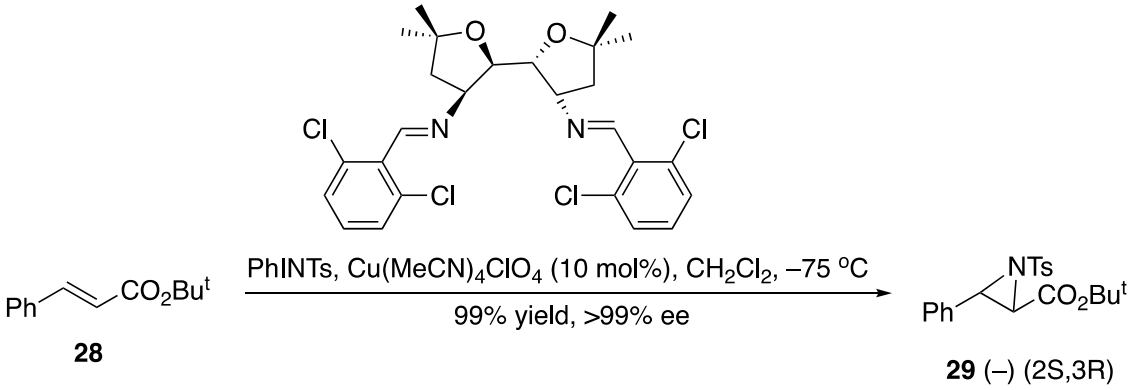
A similar catalytic aziridination was used for the functionalization of the optically active azoninones **25**,[57] in the preparation of a key intermediate **26** in the total synthesis of kalihinane diterpenoids,[58] in the synthesis of α-methylserinal derivatives **27** (Scheme 6),[59] in the preparation of 2,4-disubstituted *N*-tosylpyrrolidines,[60] in the synthesis of nosylaziridines,[61] and in the synthesis of β-alkoxy-*N*-protected phenethylamines via one-pot copper-catalyzed aziridination and ring opening.[62]



Scheme 6

Alkenes can be efficiently aziridinated using highly soluble iminoiodanes **11** in the presence of copper catalysts under continuous flow conditions.[63] This approach can be used to synthesize and use in subsequent reactions aziridines that are difficult to isolate and purify because of their high reactivity.

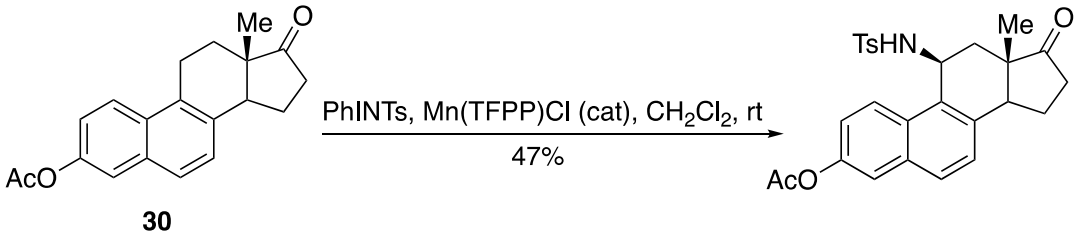
Particularly important are enantioselective aziridinations of alkenes using PhINTs and copper catalysts with chiral dinitrogen ligands.[64-68] In a representative example, the PhINTs-promoted asymmetric aziridination of alkene **28** affords the chiral aziridine **29** with excellent enantioselectivity (Scheme 7).[64]



Scheme 7

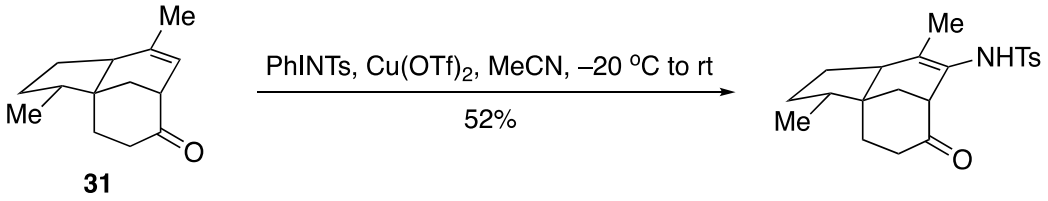
A variety of chiral ligands or counteranions, or complexes of other transition metals than copper, have been evaluated in these reactions. High enantioselectivity in the copper-catalyzed aziridination of styrene derivatives was observed in the presence of chiral biaryldiamines,[69] chiral C_2-symmetric bisferrocenyl-diamines,[70] chiral borate counteranion,[71] a phosphoramidite derived from (–)-(a*R*)-[1,1′-binaphthalene]-8,8′-diol,[72] bis(oxazolines) on zeolite Y,[73,74] chiral tartrate–derived bis-oxazoline ligands,[75] and C_2-symmetric bis(aziridine) ligands.[76] Highly enantioselective catalytic aziridinations of styrenes were realized by using (salen)manganese(III) complexes,[77] manganese and iron tetramethylchiroporphyrins,[78] and chiral rhodium(II) complexes.[79-81] An enhanced reactivity of PhINTs in the olefin aziridination reaction under achiral conditions was observed in the presence of the copper(II) complexes of pyridyl–appended diazacycloalkanes,[82,83] poly(pyrazolyl)borate–copper complexes,[84] the copper(II) complexes of 1,4,7-triisopropyl-1,4,7-triazacyclo-nonane,[85] a Cu(I) complex of ferrocenyldiimine,[86] bis(tosyl)imidoruthenium(VI) porphyrin complexes,[87] and methyltrioxorhenium.[88] Mechanistic studies of copper-catalyzed aziridinations have demonstrated that copper nitrene species are the key intermediates in these reactions.[89-91]

N-Tosyliminoiodanes, ArINTs have found synthetic application as useful nitrene precursors in transition metal-catalyzed amidation of saturated C–H bonds in various organic substrates. Breslow and co-workers have developed the regioselective amidation of steroids catalyzed by metalloporphyrins.[92,93] Specifically, the aromatic steroid equilenin acetate **30** undergoes regioselective and stereoselective amidation catalyzed by a manganese porphyrin using PhINTs as the nitrene donor (Scheme 8).[92]



Scheme 8

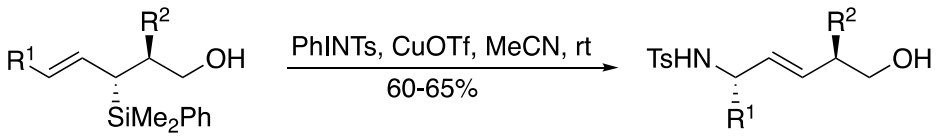
Overman and Tomasi utilized the copper-catalyzed amidation of compound **31** (Scheme 9) in the key step of the enantioselective total synthesis of the natural tetracyclic spermidine alkaloid (–)-hispidospermidin.[94]



31

Scheme 9

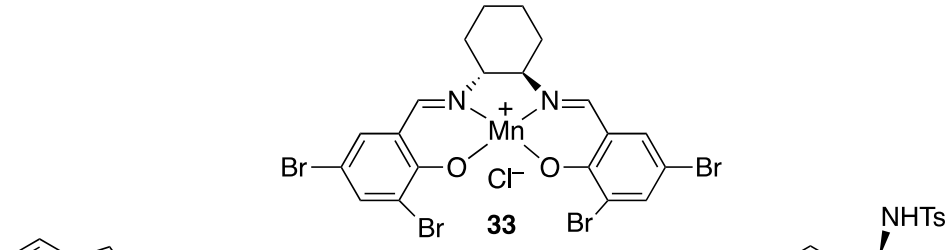
Allylic silanes can be converted into allylic tosylamides by the reaction with PhINTs in the presence of copper salts. In particular, the copper(I)–catalyzed enantioselective amidation of the chiral (*E*)-crotylsilanes **32** (Scheme 10) was used in the asymmetric synthesis of (*E*)-olefin dipeptide isosteres.[95]



32 R^1 = Me, *i*-Pr; R^2 = H, Me, OMe

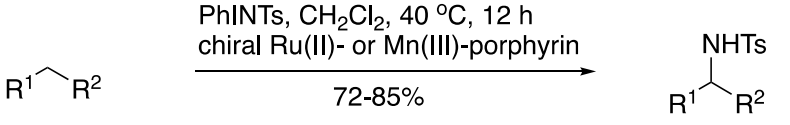
Scheme 10

The amidation of saturated C–H bonds can be effectively catalyzed by ruthenium or manganese complexes. Unfunctionalized hydrocarbons, such as adamantane, cyclohexene, ethylbenzene, cumene, indane, tetralin, diphenylmethane and others, are selectively amidated with PhINTs in the presence of ruthenium or manganese porphyrins or the ruthenium cyclic amine complexes to afford N-substituted sulfonamides in 80–93% yields with high selectivity.[96] The enantioselective amidation of a C–H bond can be catalyzed by chiral (salen)manganese(III) complexes (e.g., **33**),[97] or by chiral ruthenium(II) and manganese(III) porphyrins (Scheme 11).[98]



n = 1, 2; R = H or Me

77-89% ee

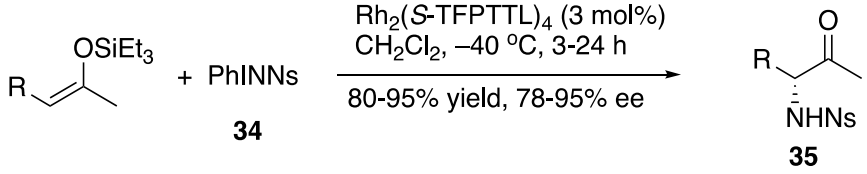


R^1 = Ph, 4-$MeOC_6H_4$, 2-naphthyl, 1-naphthyl
R^2 = alkyl

26-53% ee

Scheme 11

The aziridination and amidation reactions of iminoiodanes can be efficiently catalyzed by Rh(II) complexes.[99-104] Dirhodium(II) tetrakis[*N*-tetrafluorophthaloyl-(*S*)-*tert*-leucinate], Rh_2(*S*-TFPTTL)$_4$, has been found to be an exceptionally efficient catalyst for enantioselective aminations of silyl enol ethers with iminoiodane **34** affording α-amido ketones **35** in high yields and with enantioselectivities of up to 95% ee (Scheme 12). The effectiveness of this catalytic protocol has been demonstrated by an asymmetric formal synthesis of (–)-metazocine.[99] This catalyst has also been used for the asymmetric synthesis of phenylglycine derivatives by enantioselective amidation of silylketene acetals with PhINTs.[100]

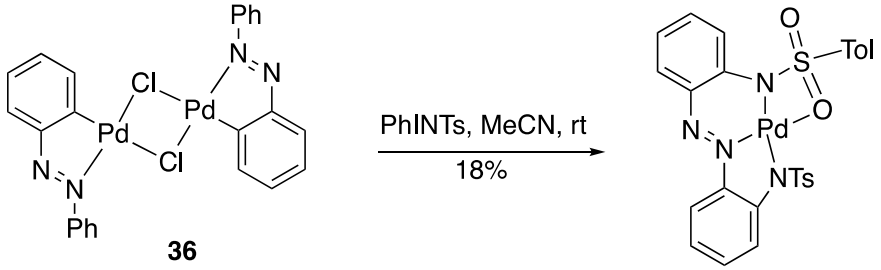


R = Ph, 4-ClC_6H_4, 4-$MeOC_6H_4$, $PhCH_2$, 4-$ClC_6H_4CH_2$, 4-$MeOC_6H_4CH_2$, etc.
Ns = 2-$NO_2C_6H_4SO_2$

Scheme 12

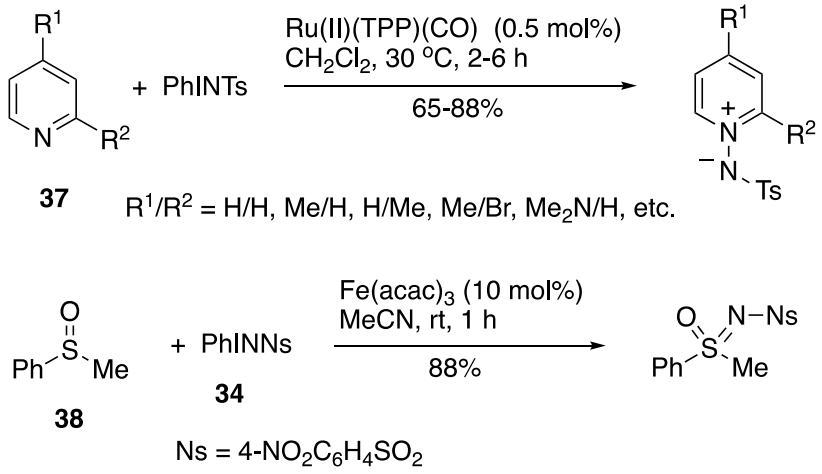
Additional examples of C–H amidations using PhINTs as the nitrene precursor are represented by the following publications: highly efficient Ru(II) porphyrin catalyzed C–H bond amidation of aldehydes,[105,106] chemoselective copper-catalyzed α-amidation of acylpyrazoles,[107] aromatic C–H amidation mediated by a diiron complex,[108] gold-catalyzed nitrene insertion into aromatic and benzylic C–H bonds,[109,110] silver-catalyzed intermolecular and intramolecular amidation of C–H bond in saturated hydrocarbons,[111,112] α-amidation of cyclic ethers catalyzed by $Cu(OTf)_2$,[113] mechanistic study of catalytic intermolecular amination of C–H bonds,[114] 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,[115] Co(II)-catalyzed allylic amidation reactions,[116] the Ru(II) porphyrin–catalyzed amidation of aromatic heterocycles,[117] non-heme iron-catalyzed amidation of aromatic substrates,[118] and by the efficient stereoselective allylic C−H amination of terpenes and enol ethers involving the combination of a chiral aminating agent with a chiral rhodium catalyst.[119]

Sanford and co-workers have investigated the carbon-nitrogen bond-forming reactions of palladacycles with aryliodonium imides.[120] In particular, palladium(II) complexes (e.g., **36**) containing bidentate cyclometalated chelating ligands react with PhINTs at room temperature to give products of insertion of the tosylimino group into the Pd–C bond (Scheme 13). 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.[120]



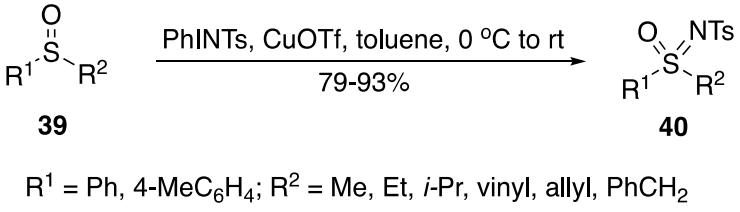
Scheme 13

Iminoiodanes can be used for the transfer of the imido group to other elements under catalytic conditions. The imido group can be efficiently transferred to the sulfur atom in organic sulfides and sulfoxides,[40,121-125] or the nitrogen atom in amines[126,127] and aromatic nitrogen heterocycles using aryliodonium imides in the presence of copper, ruthenium, or iron complexes.[128,129] Specific examples are illustrated by the selective N-imidation of aromatic nitrogen heterocycles (e.g., **37**) catalyzed by carbonyl[*meso*-tetrakis(*p*-tolyl)-porphyrinato]ruthenium(II) [Ru(II)(TPP)(CO)],[128] and the iron-catalyzed imidation of sulfoxides (e.g., **38**) and sulfides using iminoiodane **34** (Scheme 14).[121]



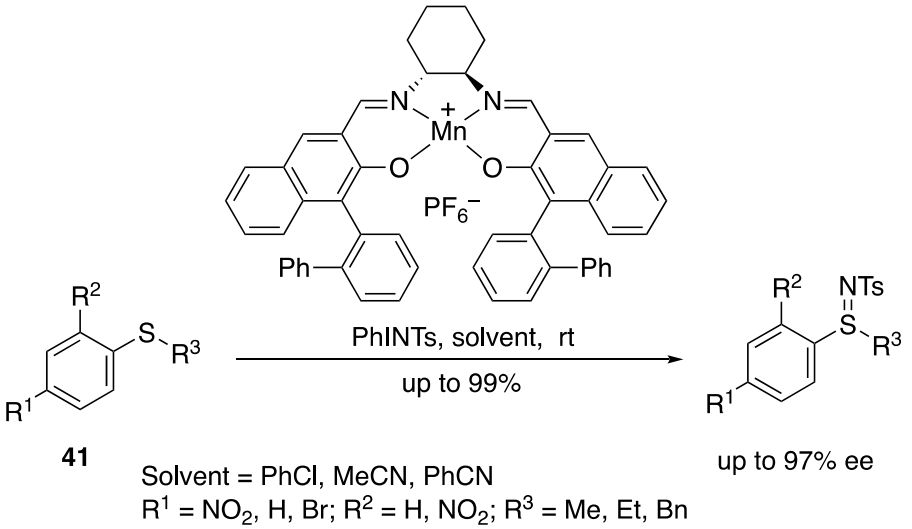
Scheme 14

Similarly, the reaction of PhINTs with sulfoxides **39** in the presence of catalytic amounts of copper(I) triflate affords the corresponding *N*-tosylsulfoximides **40** in high yield (Scheme 15).[125] The imidation of enantiomerically pure sulfoxides **39** allows stereoselective access to *N*-tosylsulfoximides **40** with complete retention of configuration at sulfur. A similar imidation procedure has been used for the preparation of the chiral ferrocenylsulfoximides.[130,131]



Scheme 15

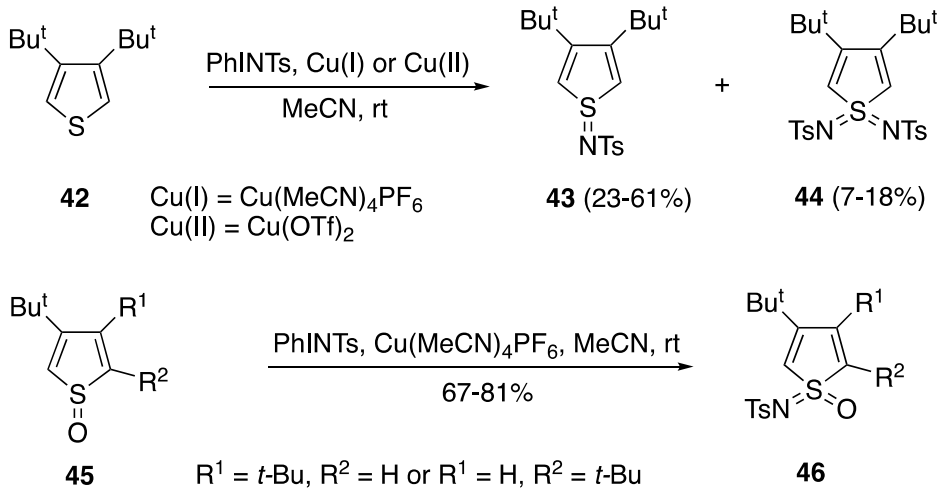
Enantioselective imidation of alkyl aryl sulfides **41** can be achieved by using the chiral manganese(salen) complex as a catalyst (Scheme 16).[132,133] Bolm and coworkers reported a similar enantioselective imidation of sulfides catalyzed by a chiral iron complex.[134]



Scheme 16

Similarly, a direct catalytic sulfimidation of sulfides or 1,3-dithianes with PhINTs using a catalytic amount of copper(I) triflate and a chiral 4,4'-disubstituted bis(oxazoline) as ligand affords the respective chiral monosulfimides in good yield and with moderate enantioselectivity of up to 40–71% ee.[135,136] Under similar conditions, prochiral selenides react with PhINTs in the presence of CuOTf and the chiral 4,4'-disubstituted 2,2'-bis(oxazoline) ligands to give the corresponding chiral selenimides with up to 64% yield and 36% ee.[137,138]

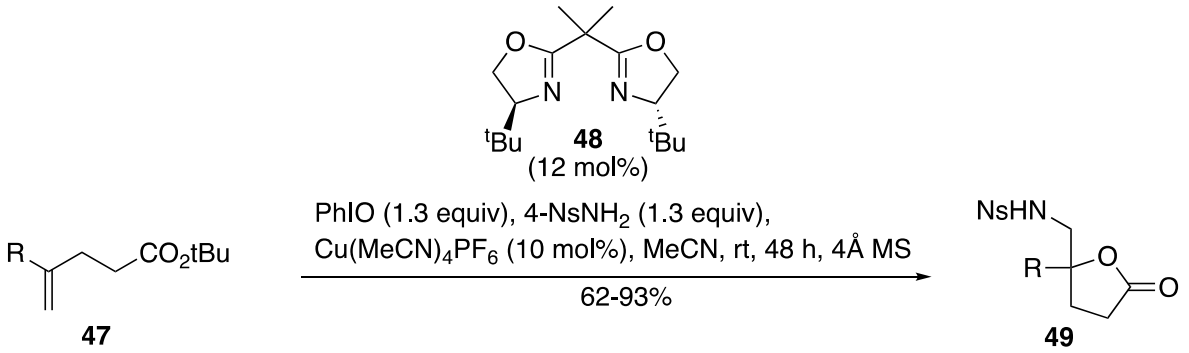
The reaction of 3,4-di-*tert*-butylthiophene **42** with PhINTs in the presence of copper(I) or copper(II) catalysts affords a mixture of imide **43** and diimide **44** as principal products (Scheme 17).[139-141] The imidation of thiophene 1-oxides **45** under similar conditions gives imides **46** in good yield.[142]



Scheme 17

The reaction of PhINTs with complexes of ruthenium(II),[87] osmium(II),[143,144] and cobalt(III)[145] results in the imidation at the metal center with the formation of the respective tosylimidometal complexes. X-Ray crystal structures were determined for several bis(tosylimido)ruthenium(VI) and bis(tosylimido)osmium(VI) porphyrin complexes.[87,143,144] The reactivity of a cobalt(II) iminoiodane complex in hydrogen atom abstraction reactions has been investigated by Kundu and coauthors.[146]

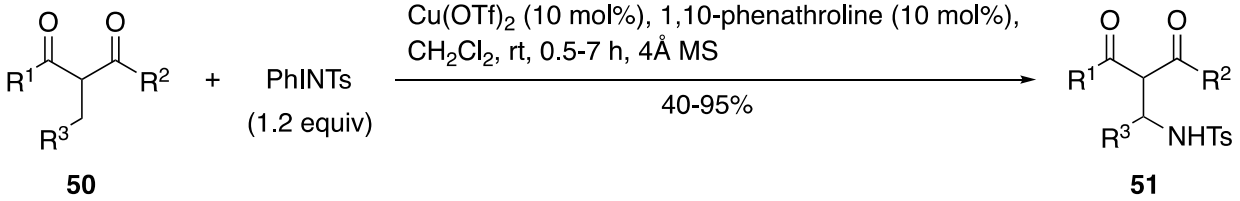
The *in situ* generated aziridine products can be easily transformed to heterocyclic compounds. Dodd's group has developed the synthesis of 5,5-disubstituted butyrolactones **49** from corresponding alkenes **47** and the *in situ* generated nosyliminoiodane in the presence of a copper source and ligand **48** (Scheme 18). This reaction presumably involves initial formation of aziridine intermediates followed by aminolactonization to give the final products. The obtained products **47** can be further transformed into novel highly functionalized spiro-heterocyclic compounds.[147]



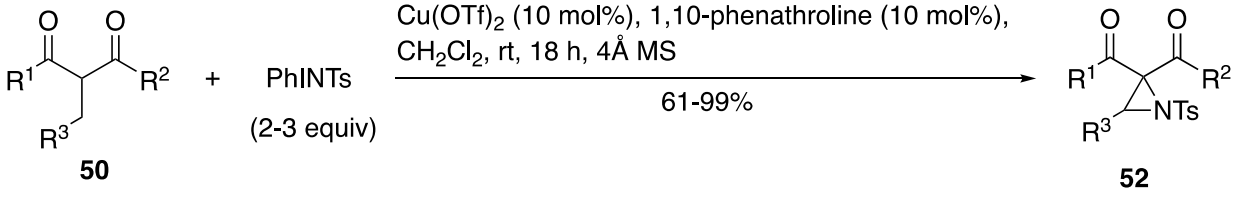
R = 2-$MeOC_6H_4$, 3-$MeOC_6H_4$, 4-$MeOC_6H_4$, 3,4,5-$(MeO)_3C_6H_2$, 2-$CO_2MeC_6H_4$, 2-FC_6H_4, 3-furyl, 3-thienyl, etc.

Scheme 18

Amidation of the allylic C-H bond of enolic form of dicarbonyl compound **50** affords the corresponding α-acyl-β-amino derivatives in good yields. This reaction can give amination products **51**, or the same reaction with increased amounts of iminoiodane **34** can selectively afford 2,2-diacyl aziridine derivatives **52** (Scheme 19).[148] A similar aziridination can be also achieved under Brønsted base conditions (DBU or potassium carbonate) in the absence of copper catalyst.[149]



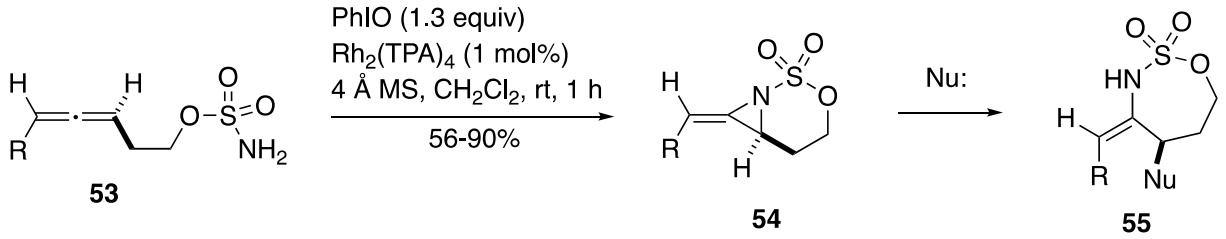
R^1 = Me, ^{i}Pr, *c*-C_3H_5, OMe, OEt, OBn; R^2 = OMe, OEt; R^3 = Me, Et, $(CH_2)_2Cl$



R^1 = Me, *i*-Pr, *c*-C_3H_5, Ph, 4-MeC_6H_4, 4-FC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 4-IC_6H_4, OMe, OEt, OBn
R^2 = Me, OMe, OEt, OBn
R^3 = H, Me, Et, Bu, $(CH_2)_2Cl$, CO_2Et, CH_2CO_2Et

Scheme 19

Schomaker's group utilized intramolecular aziridination reactions of appropriate amide precursors and PhIO in the presence of transition metal catalysts in numerous syntheses of stereochemically complex products.[150,151] For example, intramolecular aziridination of homoallenic sulfamates **53** (Scheme 20) using a dinuclear Rh(II) catalyst, such as $Rh_2(TPA)_4$ (TPA = triphenylacetate), yielded exocyclic methyleneaziridines **54** with excellent chemo-, regio-, and stereoselectivity.[150,152] This aziridination was followed by immediate ring-opening of the initially formed labile intermediate **54** to afford enesulfamates **55** in good yield and excellent stereoselectivity in favor of the *E* isomer.[152] Most likely, the mechanism of these reactions involves intermediate formation of iodonium imides *in situ*.

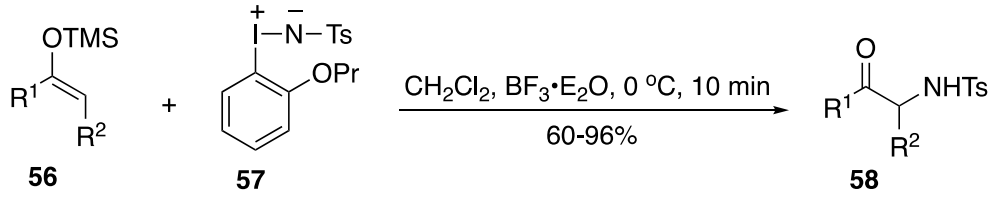


Nu: = AcOH, MeOH, H_2O, TMSCl, PhSH, $PhNH_2$, R_2NH, $HF{\bullet}Et_3N$, etc.
R = alkyl

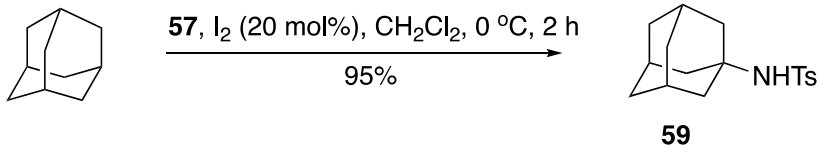
Scheme 20

4.2. Metal-free reactions of aminoiodanes

Iminoiodanes ArINTs can be used for various amidations under metal-free conditions. In particular, *o*-alkoxyphenyliminoiodane **57** readily reacts with silyl enol ethers **56** in the presence of BF_3-etherate giving products of α-tosylamination **58** in good yields (Scheme 21).[40] Furthermore, reagent **57** in the presence of catalytic amounts of iodine readily reacts with adamantane to give product of tosylamination **59** in excellent yield under very mild conditions. By comparison, PhINTs reacts with adamantane and iodine (0.2 equiv) in dichloromethane at room temperature in 2 h to afford 1-tosylaminoadamantane **59** in only 63% yield.[153]

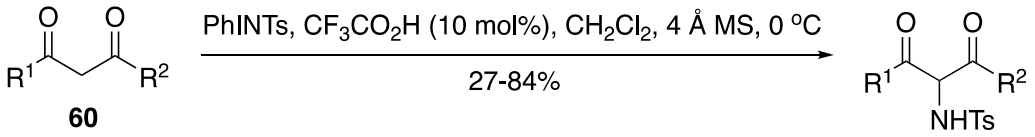


R^1 = Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-BrC_6H_4, 2-ClC_6H_4 and R^2 = H;
or R^1 = Pr and R^2 = Et; or $R^1 + R^2 = (CH_2)_4$



Scheme 21

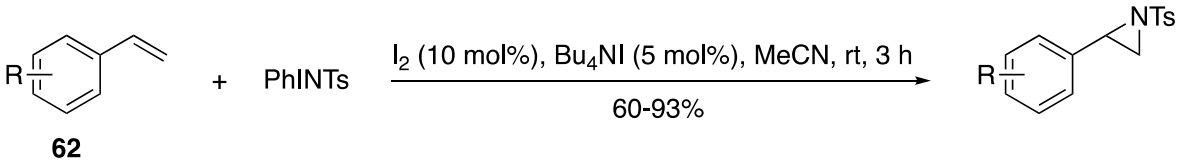
Various 1,3-dicarbonyl compounds **60** can be amidated with PhINTs using Bronsted acid catalysis (Scheme 22).[154] This method is applicable to β-keto esters and phosphonates as well as 1,3-diones, providing the corresponding α,α-acylamino acid derivatives **61** in moderate to excellent yields.



60 **61**

Scheme 22

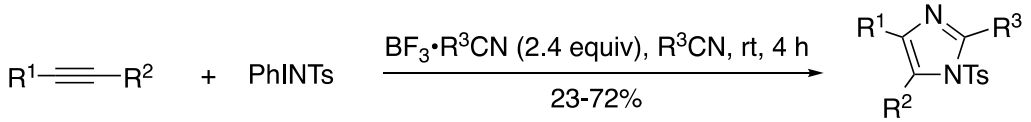
Numerous examples of inter- or intra-molecular aziridination reactions using iminoiodanes under metal-free conditions have recently been reported by several groups.[40,46,47,112,147,155-166] For example, Minakata and co-workers have reported a metal-free aziridination of styrene derivatives **62** with PhINTs in the presence of a combination of elemental iodine and tetrabutylammonium iodide (TBAI) (Scheme 23).[163] This aziridination reaction probably has a radical mechanism, and $TBAI_3$ (generated from I_2 and TBAI) acts as the actual catalyst in this reaction. A photo-induced aziridination of alkenes with ArINTs was also reported.[167]



62

Scheme 23

Saito and co-workers have developed a metal-free [2+2+1] annulation reaction of alkynes **63** with PhINTs in nitrile solvents to give the highly substituted *N*-tosylimidazoles **64** with high regioselectivities (Scheme 24).[168] The *N*-tosyl group in products **64** can be deprotected by treatment with trifluoroacetic anhydride and pyridine to afford the *N*-unsubstituted imidazole. This reaction has been used in the synthesis of catharsitoxin E, a natural product isolated from the Chinese remedy *qiung laug*.



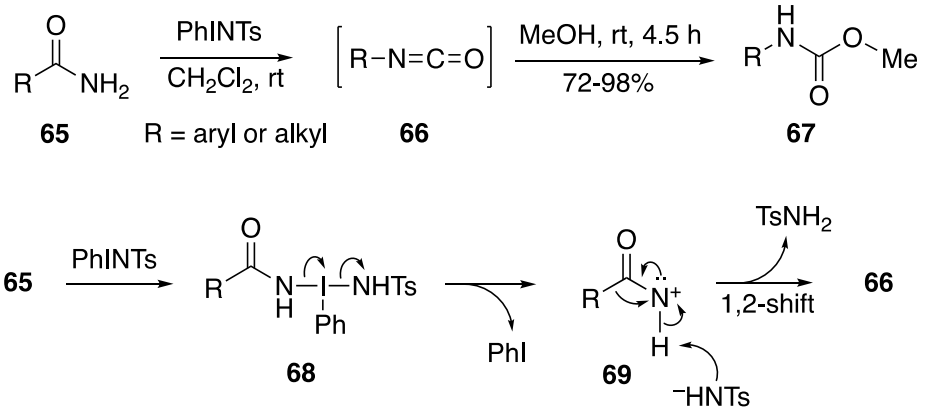
63 **64**

R^1 = Ph, Ph$(CH_2)_2$, *n*-Pr, *i*-Pr, *n*-C_6H_{13}; R^2 = H, Me, *n*-Pr; R^3 = Me, Et, *i*-Bu, Ph

Scheme 24

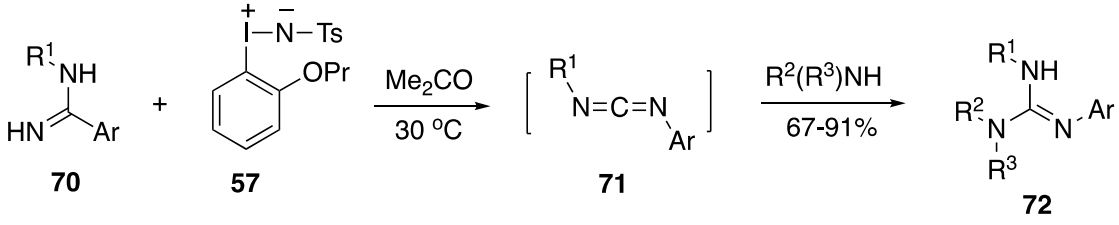
A very mild procedure for the Hofmann reaction of aromatic and aliphatic carboxamides **65** is based on the use of PhINTs as the oxidant (Scheme 25).[169] Due to the mild reaction conditions, this method is particularly useful for the Hofmann reaction of substituted benzamides **65** (R = aryl), which usually afford

complex reaction mixtures with other hypervalent iodine oxidants. The mild reaction conditions and high selectivity in the reaction of carboxamides with PhINTs allow the isolation of the initially formed labile isocyanates **66**, or their subsequent conversion to stable carbamates **67** by treatment with alcohols. Based on the previously reported mechanistic studies of Hofmann rearrangements using other hypervalent iodine reagents,[170-172] it is assumed that this reaction starts from the formation of amidoiodane **68** (Scheme 25). Subsequently, the reductive elimination of iodobenzene and the 1,2-alkyl or -aryl shift to the electron–deficient nitrenium nitrogen atom in the intermediate **67** afford isocyanate **64**. Subsequent addition of an alcohol to isocyanate **66** gives the final carbamate **67**.[169]



Scheme 25

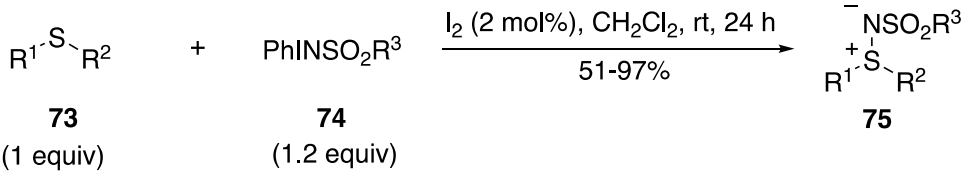
Baeten and Maes have reported the preparation of various guanidines **72** via oxidative rearrangement of amidines **70** with reagent **57** into carbodiimides **671**, followed by *in situ* reaction with amines (Scheme 26).[173] The conditions for this reaction are mild and involve the use of a "green" solvent (dimethyl carbonate) and a recyclable oxidant (the reduced form of reagent **57**, 2-$PrOC_6H_4I$, can be isolated and recycled). The amine scope is broad, including sterically hindered, oxidation-sensitive and chiral amines. This method was used to prepare the antihypertensive drug Pinacidil in increased yield relative to the previous route.



Scheme 26

A practical metal-free procedure for the imidation of sulfides with aryliodonium imides was recently reported.[174] In particular, the reaction of various sulfides **73** with ArINTs **74** in the presence of a catalytic amount of iodine under mild conditions affords the corresponding *N*-tosylsulfilimines **75** in moderate to good yields (Scheme 27). This facile transfer procedure of sulfonylimino group can also be applied to

triphenylphosphine to produce the respective iminotriphenylphosphoranes in high yields. According to the reaction mechanism studies, the process of the sulfonylimino group transfer from PhINTs to sulfide involves radical steps.

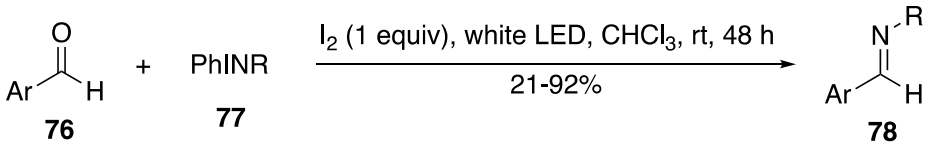


73 (1 equiv) **74** (1.2 equiv) **75**

R^1 and R^2 = alkyl or aryl
R^3 = 4-$CH_3C_6H_4$, 4-$NO_2C_6H_4$, 2-$NO_2C_6H_4$, Ph

Scheme 27

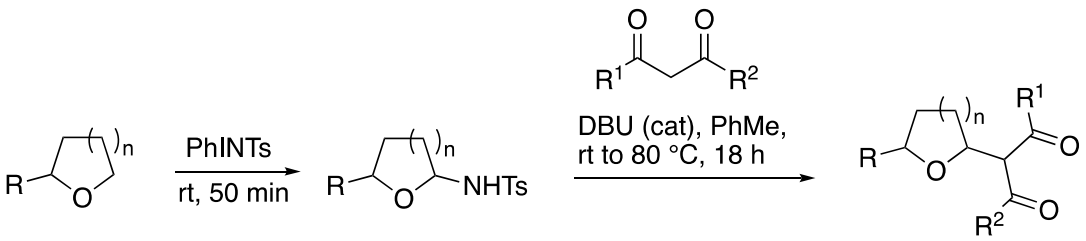
Additional recent examples of metal-free amidation reactions with aryliodonium imides include the following: preparation of *N*-sulfonylimines **78** from a range of aryl aldehydes **76** by reaction with imino-iodinanes **77** and iodine (Scheme 28),[175] amidation of cyclic ethers **79** followed by substitution with 1,3-dicarbonyl compounds (Scheme 29),[176] and organocatalytic C-H amidation reaction using a trifluoromethyl iminium salt **80** as the catalyst (Scheme 30).[177]



76 **77** **78**

R = 4-$CH_3C_6H_4SO_2$, 4-$NO_2C_6H_4SO_2$, 4-$ClC_6H_4SO_2$

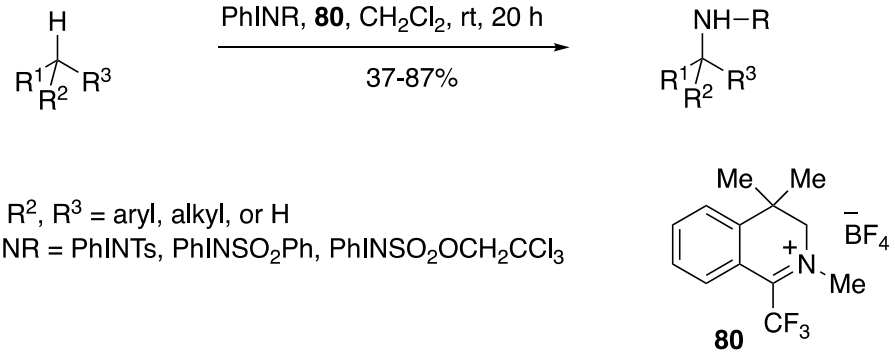
Scheme 28



79

n = 1, 2; R = H or Me; R^1 and R^2 = alkyl, aryl, or alkoxy

Scheme 29



Scheme 30

5. Conclusions

This review reveals the active current interest in synthetic applications of iodonium imides. Iodonium imides represent an important class of hypervalent iodine(III) compounds, emerging as versatile, efficient and environmentally friendly synthetic reagents with numerous applications in academic and industrial research. Iminoiodanes are widely used in organic synthesis as common nitrene precursors in the aziridination of alkenes and the amidation reactions of various organic substrates. In the present review, the preparation and structural features iminoiodanes are discussed, and recent developments in their synthetic applications are summarized. We anticipate that this area of hypervalent iodine chemistry will continue to attract significant research activity in the future.

6. Acknowledgements

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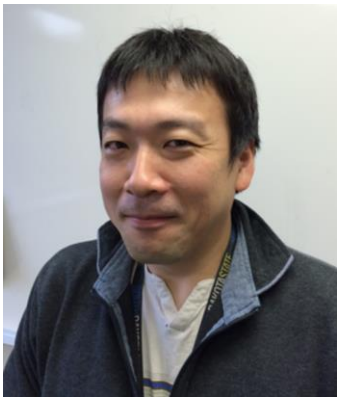
Authors' Biographies



Akira Yoshimura, a native of Osaka, Japan, received his M.S. in 2007 and Ph.D. in 2010, both from Tokushima University, under the supervision of Professor Masahito Ochiai. During 2010-2015 he carried his postdoctoral work with Professor Viktor Zhdankin at University of Minnesota Duluth. In 2016-2017 he was a Visiting Research Assistant Professor in Southern Methodist University, USA. Since 2019 he is a Researcher 5 at

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