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Review article

Iodine catalysis: A green alternative to transition metals in organic chemistry and technology

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Abstract

Iodine and compounds of iodine in higher oxidation states have emerged as versatile and environmentally benign reagents for organic chemistry. One of the most impressive recent achievements in this area has been the discovery of catalytic activity of iodine in numerous oxidative transformations leading to the formation of new C—O, C—N, and C—C bonds in organic compounds. These catalytic transformations in many cases are very similar to the transition metal-catalyzed reactions, but have the advantage of environmental sustainability and efficient utilization of natural resources. Iodine is an environmentally friendly and a relatively inexpensive element, which is currently underutilized in industrial applications. One of the main goals of this review is presenting to industrial researchers the benefits of using catalytic iodine in chemical technology as an environmentally sustainable alternative to transition metals. The present review summarizes catalytic applications of iodine and compounds of iodine in organic synthesis. The material is organized according to the nature of active catalytic species (hypoiodite, trivalent, or pentavalent hypervalent iodine species) generated in these reactions from appropriate pre-catalysts. Numerous synthetic procedures based on iodine(III) or iodine(V) catalytic species in the presence of hydrogen peroxide, Oxone, peroxyacids or other stoichiometric oxidants are summarized. A detailed discussion of catalytic cycles involving hypervalent iodine, hypoiodites, and other active intermediates is presented.

Keywords: Hypervalent catalysis; Iodine catalysis; Hypoiodite catalysis; Hypervalent iodine

1. Introduction

Iodine is one of the heaviest non-radioactive elements in the Periodic Table classified as a non-metal, and it is the largest, the least electronegative, and the most polarizable of the halogens. Iodine can form inorganic and organic derivatives in various oxidation states (−1, 0, +1, +3, +5, +7) and structural features and reactivity pattern of iodine compounds in many aspects are similar to the derivatives of heavy transition metals. Reactions of iodine compounds are commonly discussed in terms of oxidative addition, ligand exchange, reductive elimination, and ligand coupling, which are typical of the transition metal chemistry [1]. In contrast to the heavy metals, iodine is an environmentally friendly and a relatively inexpensive element; iodine bulk price in the last 10 years was within the range of $20–100 per kg, which is orders of magnitude cheaper than platinum, palladium, or osmium. Iodine annual production is about 30,000 tons with estimated world's total reserves of 15 million metric tons located mainly in Chile and Japan [2].

Compounds of iodine have found some industrial application. About 16% of iodine world production is utilized in industrial catalysis. Hydroiodic acid is used as a co-catalyst for the production of acetic acid by the Monsanto and Cativa processes. In this technology, which is the main industrial process for the production of acetic acid, hydroiodic acid converts the methanol feedstock into methyl iodide, which then undergoes Rh-catalyzed carbonylation. Hydrolysis of the resulting acetyl iodide regenerates hydroiodic acid and gives acetic acid. Other practical applications of iodine compounds include the use in polymer industry, in liquid-crystal display polarizers, and also numerous applications in food industry, medicine, and pharmaceuticals [3].

In recent years, organic derivatives of polyvalent iodine (which are known under common name of "hypervalent" iodine compounds) have attracted significant research activity as versatile

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and environmentally benign reagents for organic synthesis [1,4,5]. One of the most impressive recent achievements in this area has been the discovery of catalytic activity of iodine in numerous oxidative transformations leading to the formation of new C—O, C—N, and C—C bonds in organic compounds. These catalytic transformations in many cases are very similar to the transition metal-catalyzed reactions, but have the advantage of environmental sustainability and efficient utilization of natural resources.

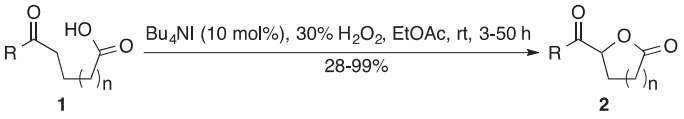
In the present review, we summarize catalytic applications of iodine and compounds of iodine in organic synthesis. The material is organized according to the nature of active catalytic species (hypoiodite, trivalent, or pentavalent iodine species) generated in these reactions from appropriate pre-catalysts. One of the main goals of this review was to attract attention of the industrial researchers to the benefits of using catalytic iodine in chemical technology as an environmentally sustainable alternative to transition metals.

2. Catalytic cycles involving elemental iodine or iodide anion as pre-catalysts

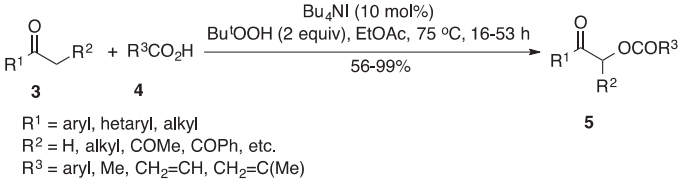
Catalytic reactions, utilizing iodide anion or elemental iodine as the pre-catalysts, usually involve the iodine cation, hypoiodic acid, or inorganic iodine(III) species as active oxidants. There has been significant recent interest in these reactions since 2010, when first examples of such reactions were reported. The oxidative catalytic reactions utilizing iodide anion or elemental iodine as a catalyst or pre-catalyst have been summarized in several reviews [6–9].

In 2010, Ishihara and co-workers have first reported that tetrabutylammonium iodide can be used as a highly effective pre-catalyst for the oxylactonization of oxocarboxylic acids **1** with aqueous hydrogen peroxide at room temperature (Scheme 1) [10]. Importantly, no Baeyer–Villiger products were obtained under these reaction conditions. Both γ-aryl- and γ-heteroarylcarbonyl-γ-butyrolactones **2** (R = aryl or heteroaryl, n = 1) were obtained in excellent yields, and γ-alkylcarbonyl-γ-butyrolactones **2** (R = alkyl, n = 1) and δ-valerolactones **2** (n = 2), in moderate yields. Lactones are important intermediate products in organic synthesis and in the manufacturing of polyesters, therefore, this simple and environmentally friendly procedure represents interest to industrial chemists.

This catalytic procedure has been further applied to the oxidative coupling of carbonyl compounds with carboxylic acids using Bu_4NI as catalyst and *tert*-butyl hydroperoxide (TBHP) as the terminal oxidant [10]. Various ketones **3** as well as 1,3-dicarbonyl compounds as substrates react with carboxylic



Scheme 1. Tetrabutylammonium iodide as a pre-catalyst for the oxylactonization of oxocarboxylic acids.



Scheme 2. Tetrabutylammonium iodide-catalyzed oxidative coupling of carbonyl compounds with carboxylic acids.

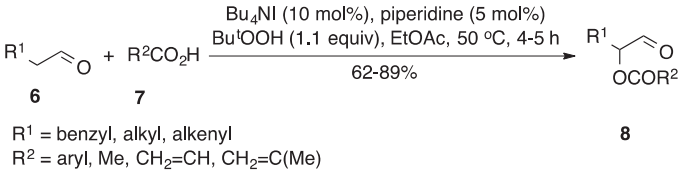
acids **4** under these conditions to give the corresponding α-acyloxy ketones **5** in good to excellent yields (Scheme 2) [10]. A similar TBAI-catalyzed oxidative coupling of β-ketoesters with carboxylic acid has been reported in a more recent work [11].

Aldehydes can be α-oxyacylated under similar conditions in the presence of piperidine [10]. Thus, aldehydes **6** and acids **7** react upon mild heating in the presence of catalytic amounts of Bu_4NI and piperidine and TBHP as the terminal oxidant in ethyl acetate to afford α-acyloxy aldehydes **8** in high yields (Scheme 3). Various functional groups such as terminal or internal alkenyl, benzyloxy, silyloxy, acetal, halogen, and ester are stable under these conditions.

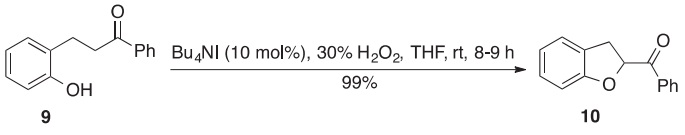
The Bu_4NI/TBHP catalytic system has also been applied toward the α-oxyacylation of ethers with carboxylic acids in ethyl acetate at 80 °C [12], possibly, via a radical mechanism.

During their studies on the oxylactonization of oxocarboxylic acids **1** (Scheme 1), Ishihara and co-workers discovered that the catalytic oxidative system Bu_4NI/H_2O_2 could be used for the oxidative cycloetherification of oxo-substituted phenols [6]. For example, the oxidation of phenolic substrate **9** with two equivalents of 30% aqueous H_2O_2 in the presence of Bu_4NI as a catalyst in THF or ether at room temperature selectively afforded the corresponding 2-acyldihydrobenzofurane **10** in excellent yield and (Scheme 4).

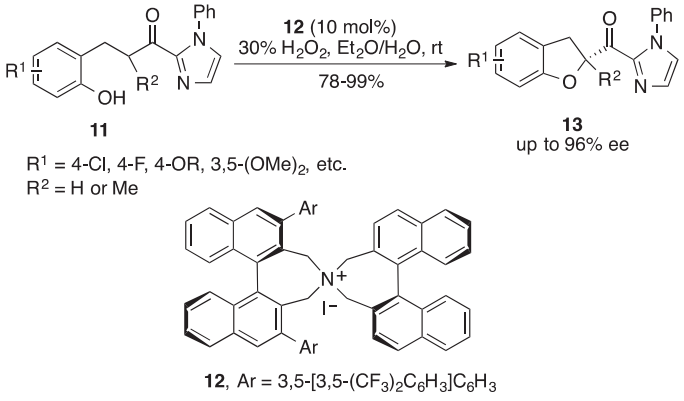
Based on this reaction (Scheme 4), Ishihara and co-workers have developed a highly enantioselective oxidative cycloetherification of substrates **11** using hydrogen peroxide as the oxidant in the presence of the chiral quaternary ammonium iodide catalyst **12** (Scheme 5) [13]. This cycloetherification leads to the chiral 2-acyl-2,3-dihydrobenzofuran skeleton **13**, which is a key structural unit in numerous biologically active compounds, for example, entremirol and entremiridol.



Scheme 3. Catalytic α-acyloxylation of aldehydes.



Scheme 4. Catalytic oxidative cycloetherification of phenolic substrates.



Scheme 5. Enantioselective catalytic cyclization of phenolic substrates.

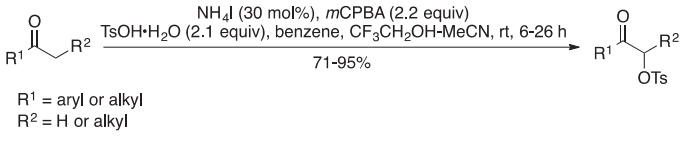
In the more recent works by Li and co-workers, the Ishihara's catalytic cycloetherification has been employed in the synthesis of bisbenzannelated spiro [5], ketals [14], and also used in a new synthetic approach to γ-rubromycin [15].

Several control experiments supported that either tetrabutylammonium hypoiodite ($Bu_4N^+IO^-$) or iodite ($Bu_4N^+IO_2^-$), which are generated *in situ* from tetrabutylammonium iodide and hydrogen peroxide, are the active species in these oxidations (Schemes 1–5) [10]. The presence of highly unstable iodite anions (IO_2^-) in the reaction mixtures containing Bu_4NI/H_2O_2 was confirmed by the negative ion ESI–MS analysis [16]. Hypoiodite (IO^-) species were also detected in this experiment.

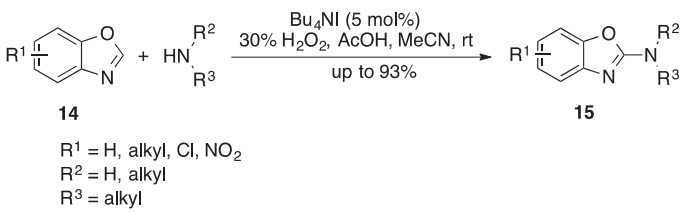
A procedure for the α-tosyloxylation of ketones by the reaction with *m*CPBA and TsOH•H_2O in the presence of catalytic amounts of NH_4I and benzene in a mixture of MeCN and trifluoroethanol (8:2) has been reported (Scheme 6) [17]. This method has the advantages of mild reaction conditions with a simple procedure, and it is suitable for preparing various α-sulfonyloxy ketones. It has been suggested that [hydroxyl(tosyloxy)iodo]benzene, generated by the reaction of iodide anion with *m*CPBA, benzene, and TsOH, is the active oxidant in this reaction [17].

First examples of a hypoiodite-catalyzed oxidative C—N coupling reaction were independently reported by Nachtsheim [18] and Yu and Han [19] in 2011. Natchtsheim and co-workers have found that the reaction of benzoxazoles **14** with various amines in the presence of Bu_4NI as a catalyst and 30% aqueous H_2O_2 or 70% aqueous TBHP as a terminal oxidant afforded the products of C—N coupling (**15**) in moderate to high yields (Scheme 7) [18]. The reaction was generally faster and the yield of the products was higher when TBHP was used as an oxidant. The authors suggested that the *in situ*-generated acetyl hypoiodite is the actual oxidant in this reaction [18].

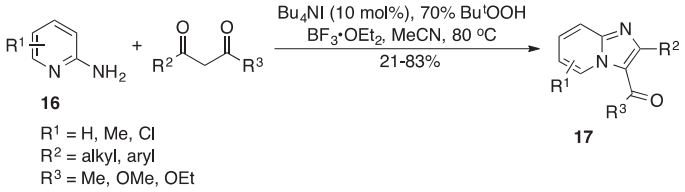
Yu and co-workers reported the oxidative coupling of 2-aminopyridines **16** with β-ketoesters or 1,3-diones in the



Scheme 6. Catalytic α-tosyloxylation of ketones.



Scheme 7. Tetrabutylammonium iodide-catalyzed C—N coupling reaction.

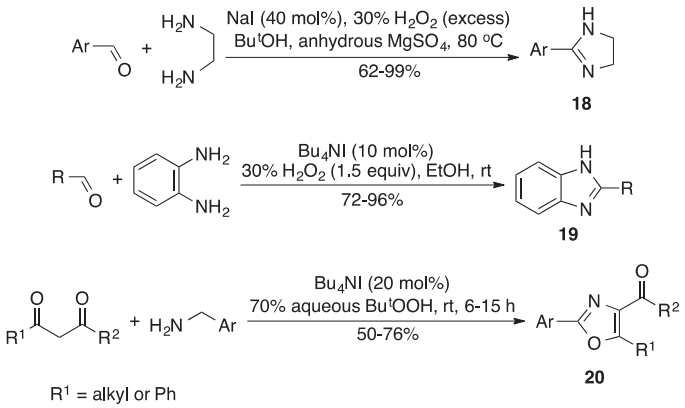


Scheme 8. Catalytic oxidative coupling of 2-aminopyridines with β-ketoesters or 1,3-diones.

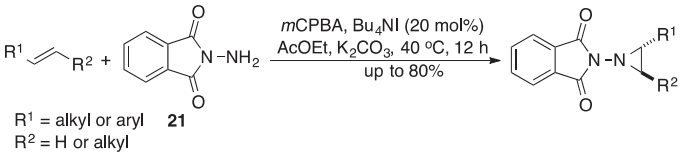
presence of 10 mol% of Bu_4NI, BF_3-etherate and two equivalents of 70% aqueous TBHP in acetonitrile (Scheme 8) [19]. The corresponding imidazo[1,2-*a*]pyridines **17** were obtained as final products in moderate to high yields. The *in situ*-generated hypoiodite or iodite species are the actual oxidants in this reaction.

The catalytic system I^-/oxidant has also been used for the synthesis of the following heterocycles: (i) 2-imidazolines **18** by the oxidative coupling of benzaldehydes with ethylenediamines [20], (ii) benzimidazoles **19** by a similar oxidative coupling reaction of phenylenediamines with aromatic or aliphatic aldehydes [16], and (iii) oxazole derivatives **20** by the oxidative coupling of β-ketoesters with benzylamines (Scheme 9) [21]. This simple approach to the preparation of oxazoles and imidazoles represents a potentially important new experimental method that can find practical application in the synthesis of heterocyclic compounds.

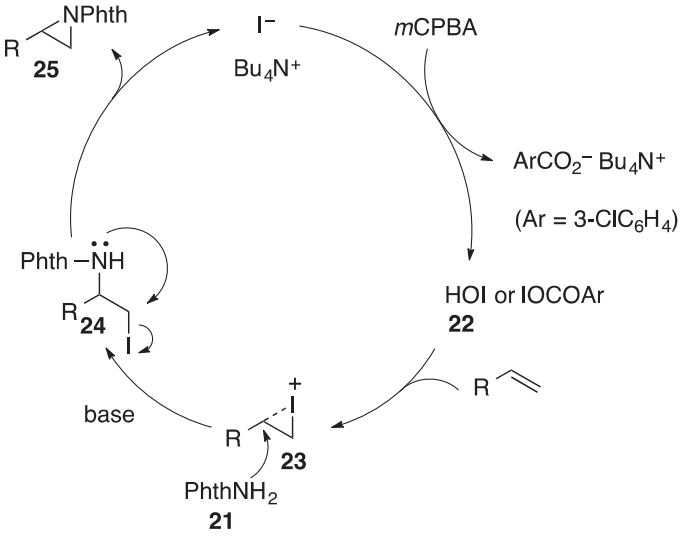
Yoshimura and coauthors developed an efficient metal-free catalytic procedure for aziridination of alkenes using tetrabutylammonium iodide as a catalyst, *m*-chloroperoxybenzoic



Scheme 9. Synthesis of oxazole derivatives by catalytic oxidative coupling of β-ketoesters with benzylamines.



Scheme 10. Metal-free catalytic aziridination of alkenes.

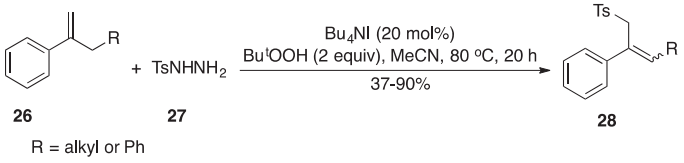


Scheme 11. Mechanism of tetrabutylammonium iodide-catalyzed aziridination of alkenes.

acid as the terminal oxidant, and *N*-aminophthalimide **21** as a nitrenium precursor (Scheme 10) [22].

The proposed mechanism of this catalytic aziridination is outlined in Scheme 11 [22]. The active species, hypoiodous acid **22** (or iodine 3-chlorobenzoate, IOCOAr), generated from Bu_4NI and *m*CPBA, further react with alkene to give the iodonium ion **23**, which is then opened at the benzylic position by *N*-aminophthalimide **21** (or the corresponding potassium salt, PhthNHK, formed from **21** in the presence of K_2CO_3). This sequence of reactions gives β-iodo-*N*-aminophthalimide **24**, cyclization of which affords the aziridine product **25** and iodide anion. The regenerated iodide anion continues the catalytic cycle [22].

Li and co-workers reported Bu_4NI-catalyzed allylic sulfonylation of α-methyl styrene derivatives with sulfonylhydrazides **27** using TBHP as the terminal oxidant (Scheme 12) [23]. The mechanism of this reaction involves the generation of sulfonyl radicals, Ts˙, from sulfonylhydrazides **27** by the Bu_4NI/TBHP catalytic system, followed by the addition of Ts˙ to α-methyl styrene derivatives **26** to give the corresponding allylic sulfones **28**.

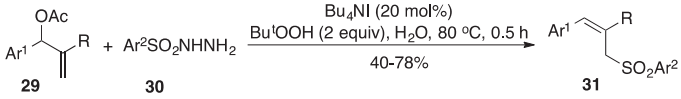


Scheme 12. Tetrabutylammonium iodide-catalyzed allylic sulfonylation of α-methyl styrene derivatives.

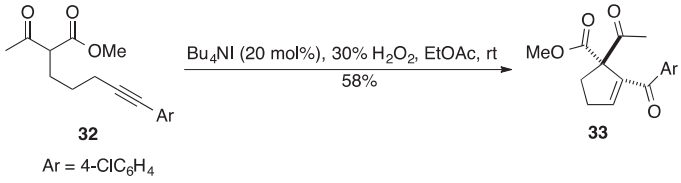
This reaction has been further extended to a catalytic procedure for the synthesis of allyl aryl sulfone derivatives **31** from Baylis–Hillman acetates **29** and sulfonylhydrazides **30** using Bu_4NI as the catalyst and TBHP as an oxidation agent in water (Scheme 13) [24].

Only few examples of the C—C bond forming Bu_4NI-catalyzed reactions have been reported. In 2011, during their studies on the hypervalent iodine-catalyzed oxidative cyclization of δ-alkynyl β-ketoesters with *m*CPBA, Moran and co-workers found that treatment of starting material **32** with a catalytic amount of Bu_4NI and 30% aqueous H_2O_2 gave product **33** in moderate yield (Scheme 14) [25]. Although the mechanism is not clear, this is the first example of the hypoiodite-catalyzed C—C coupling reaction. This unique cyclization opens a new approach to 1,3- and 1,4-dicarbonyl compounds, which are useful building blocks in total synthesis.

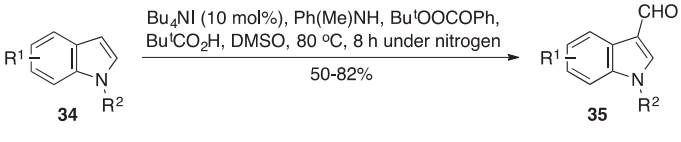
Another example of the hypoiodite-catalyzed C—C coupling reaction is represented by the C3-selective formylation of indoles **34** to products **35** by using *N*-methylaniline as a formylating reagent in the presence of catalytic Bu_4NI and *tert*-butyl peroxybenzoate as the terminal oxidant (Scheme 15) [26]. Pivalic acid is used as an additive since it has been shown to suppress decomposition of indoles under oxidative conditions. This reaction probably proceeds via a free radical process [26]. The β-formylation of indole (Scheme 15) opens a new approach to a broad range of important for pharmaceutical industry indole derivatives, including serotonin.



Scheme 13. Catalytic procedure for the synthesis of allyl aryl sulfone derivatives.



Scheme 14. Catalytic oxidative cyclization of δ-alkynyl β-ketoesters.



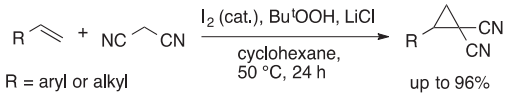
Scheme 15. C3-selective catalytic formylation of indoles.

Several oxidative catalytic systems utilizing elemental iodine as the catalyst have been developed. Recently, we have reported an efficient synthetic procedure for dicyano cyclopropanation of alkenes using catalytic amounts of molecular iodine as a precatalyst and *tert*-butyl hydroperoxide (TBHP) as a terminal oxidant under mild conditions (Scheme 16) [27]. This catalytic reaction works especially well for the aryl-substituted double bond affording products of cyclopropanation in high yields. A catalytic cycle based on the generated *in situ* hypoiodite species has been proposed for this reaction [27].

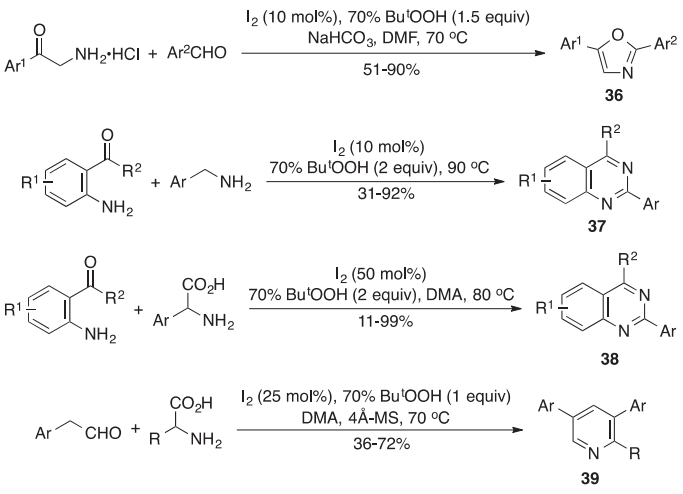
Wang and co-workers have reported several tandem oxidative cyclization reactions using I_2 as a catalyst and 70% aqueous TBHP as a stoichiometric oxidant (Scheme 17) [28–31]. Heteroaromatic compounds such as oxazoles **36**, quinazolines **37**, and pyridine derivatives **38** and **39** were synthesized in moderate to high yields under these catalytic conditions. The authors suggested that the I_2/I^- catalytic cycle might play an important role in the radical mechanism under these conditions [31]. This simple synthesis of 5- and 6-membered heterocycles from readily available precursors is potentially useful for the development of new resource efficient technologies in chemical industry.

A highly efficient α-amination of various aldehydes **40** using secondary amines **41** as nitrogen source, iodine as the pre-catalyst, and sodium percarbonate as an environmentally benign co-oxidant has been reported (Scheme 18) [32]. This reaction affords synthetically useful α-amino acetals **42** in good yields and tolerates a wide range of functional groups, such as benzyl, allyl, or ester groups, as well as bulky aldehydes and secondary amine derivatives.

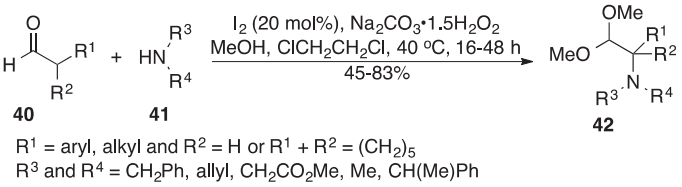
Based on control experiments, a mechanism for the α-amination of aldehydes catalyzed by the *in situ* generated hypoiodite has been proposed (Scheme 19) [32]. In the first step, the active cationic iodine species, hypoiodite acid, which is thought



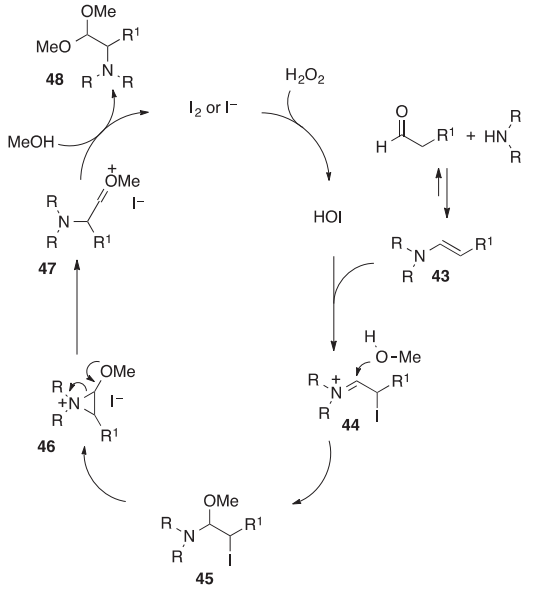
Scheme 16. Catalytic dicyano cyclopropanation of alkenes.



Scheme 17. Catalytic oxidative cyclization reactions using iodine as a catalyst.



Scheme 18. Catalytic oxidative α-amination of aldehydes using secondary amines.



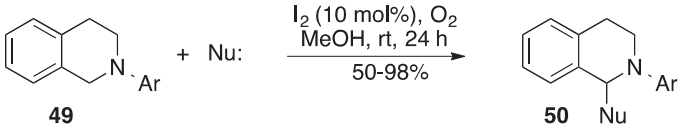
Scheme 19. Mechanism of hypoiodite-catalyzed α-amination of aldehydes.

to function as a one-electron oxidizing reagent or electrophilic reagent, is formed by oxidation of iodine (I_2) or iodide (I^-) with hydrogen peroxide. In the second step, hypoiodite reacts with enamine **43** to provide iminium ion **44**, the existence of which was confirmed by a control experiment, in which the hydrolysis of this intermediate led to the corresponding α-iodoaldehyde. In the third step, methanol attacks iminium ion **44** to give the iodo-substituted intermediate **45**, which undergoes intramolecular cyclization to afford aziridinium ion **46**. Finally, an additional methanol molecule captures the ring-opened intermediate **47** to afford the final product **48** (Scheme 19).

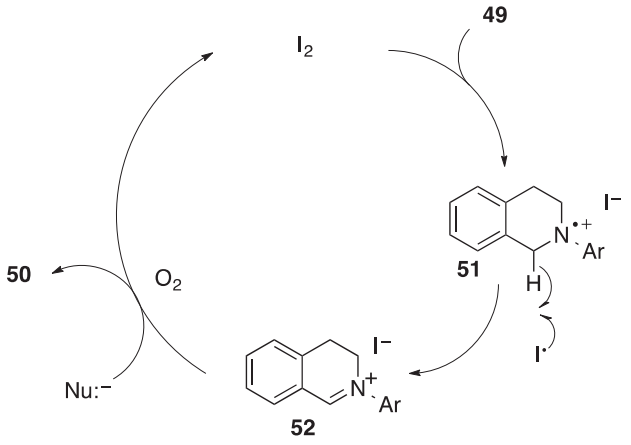
Prabhu and co-workers developed a versatile iodine-based aerobic catalytic system (I_2 and O_2) for the C—H functionalization of tetrahydroisoquinolines **49** with a nucleophile (Nu:) (Scheme 20) [33]. This cross-dehydrogenative coupling reaction is performed under mild conditions and gives generally high yields of products with a large number of nucleophiles. The proposed reaction mechanism includes the generation of iminium iodide **52** by the reaction of tetrahydroisoquinoline **49** with molecular I_2 through a radical-cation intermediate **51**, followed by the reaction of iminium iodide **52** with the nucleophile and O_2 furnishing the coupled product **50** and regenerating I_2 (Scheme 20) [33].

3. Catalytic cycles based on iodine(III) species

Catalytic reactions of this type involve the reoxidation of iodoarene to aryliodine(III) species *in situ* using such oxidants



Nu: = coumarin, nitroalkane, phosphite, TMSCN, phenol, indole, ketone, active methylene compounds, imide, amide, etc.

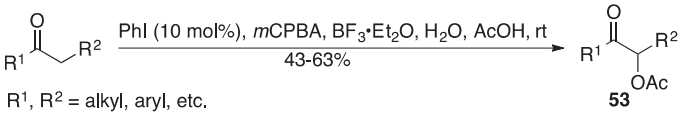


Scheme 20. Iodine-based aerobic catalytic system for the C—H functionalization of tetrahydroisoquinolines.

as hydrogen peroxide, peroxycarboxylic acids, sodium perborate, or Oxone under mild conditions. The choice of an oxidant in these reactions is critically important; the oxidant should not react with the substrate, and the substrate should only be oxidized by the hypervalent iodine species. The oxidant has to be carefully selected to achieve the re-oxidation of iodoarene under homogeneous and mild reaction conditions. The nature of iodoarene is also important. Iodobenzene is commonly used as the catalyst; however, numerous other iodoarenes are also active in these reactions. Particularly important are the enantioselective reactions catalyzed by chiral iodoarenes [34,35].

3.1. Oxidative α-functionalization of carbonyl compounds

The first iodobenzene-catalyzed reaction, a catalytic variant of α-acetoxylation of ketones based on the *in situ* re-generation of (diacetoxyiodo)benzene from iodobenzene using *m*-chloroperoxybenzoic acid (*m*CPBA) as oxidant, was reported by Ochiai and co-workers in 2005 [36]. The oxidation of a ketone with *m*CPBA in acetic acid in the presence of a catalytic amount of iodobenzene, BF_3•OEt_2 and water at room temperature under argon affords the respective α-acetoxyketone **53** in a moderate yield (Scheme 21). 4-Iodotoluene and 4-chloroiodobenzene can also serve as catalysts in the α-acetoxylation of ketones under these reaction conditions; however, the use of iodobenzene results in the highest yields [36]. The use of at least 10 mol% iodobenzene in this reaction is necessary; when smaller amounts are used, the reaction slows, and Baeyer–Villiger oxidation products resulting from a direct reaction of *m*CPBA and the ketone are observed [36].



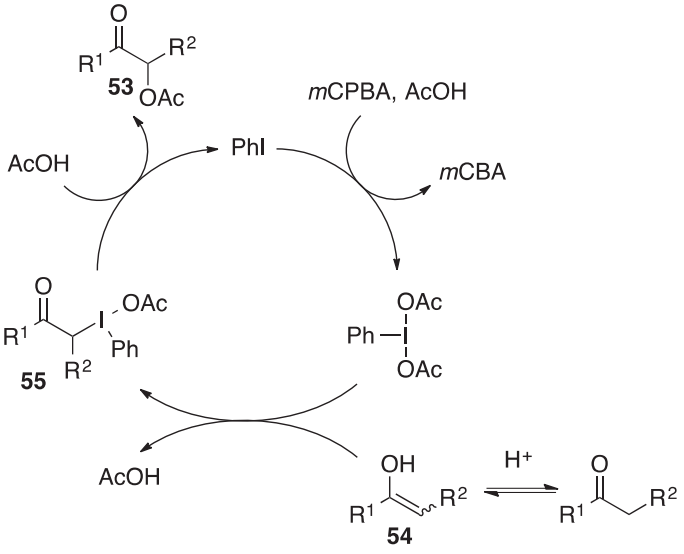
Scheme 21. Catalytic of α-acetoxylation of ketones.

The mechanism of this oxidation is shown in Scheme 22. Boron trifluoride etherate accelerates the initial oxidation of iodobenzene to (diacyloxyiodo)benzene by *m*CPBA in the presence of acetic acid. Ligand exchange of $PhI(OAc)_2$ with enol **54** derived from a ketone produces an alkyliodonium intermediate **55**, which upon S_N2 displacement by acetic acid affords an α-acetoxyketone **53** with liberation of iodobenzene [36].

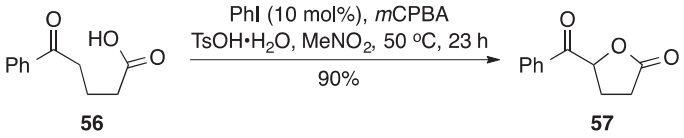
A study of the catalytic α-acetoxylation reaction of acetophenone by electrospray ionization tandem mass spectrometry (ESI–MS/MS) has confirmed the mechanism shown in Scheme 22. Specifically, the iodine(III) species were detected when iodobenzene and *m*CPBA in acetic acid were mixed, which indicated the facile oxidation of catalytic PhI by *m*CPBA. The protonated alkyliodonium intermediate **55** (R^1 = Ph, R^2 = H) was observed at m/z 383 from the reaction solution, and this ion gave the protonated α-acetoxylation product **53** at m/z 179 in MS/MS by an intramolecular reductive elimination of PhI [37].

Based on the Ochiai's procedure for α-acetoxylation of ketones, Ishihara and co-workers have developed hypervalent iodine-catalyzed oxylactonization of ketocarboxylic acids to ketolactones [38]. The reaction is performed by the treatment of a ketocarboxylic acid with iodobenzene (10 mol%), *p*-toluenesulfonic acid monohydrate (20 mol%), and *m*CPBA as a stoichiometric oxidant in nitromethane solution; a representative example of the cyclization of ketocarboxylic acid **56** to ketolactone **57** is shown in Scheme 23.

A similar catalytic procedure for α-oxytosylation of ketones using *m*CPBA as stoichiometric oxidant and iodoarenes as



Scheme 22. Mechanism of catalytic of α-acetoxylation of ketones.



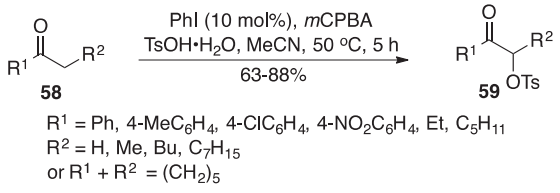
Scheme 23. Hypervalent iodine-catalyzed cyclization of ketocarboxylic acid.

catalysts in the presence of *p*-toluenesulfonic acid has been developed. Various α-tosyloxyketones **59** can be efficiently prepared in high yields from the reaction of ketones **58** with *m*CPBA and *p*-toluenesulfonic acid in the presence of iodobenzene as a catalyst at moderate warming (Scheme 24) [39]. The mechanism of this reaction includes initial oxidation of PhI by *m*CPBA in the presence of *p*-toluenesulfonic acid to generate [hydroxy(tosyloxy)iodo]benzene *in situ*, which then reacts with the enol form of ketone to give α-tosyloxyketone.

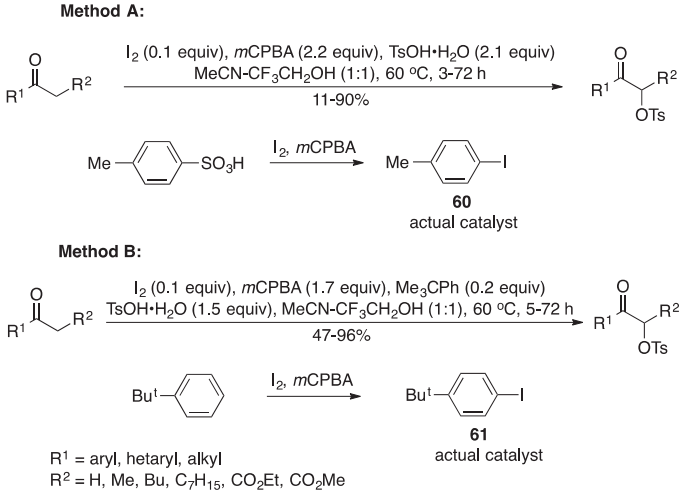
Further modification of this reaction (Scheme 24) involves the use of polystyrene-supported iodobenzene as a recyclable catalyst, which can be recovered by simple filtration of the reaction mixture and reused [40]. Alcohols can be used instead of ketones in this reaction; in this case an excess of *m*CPBA (2.1 equiv) is employed in the presence of KBr (0.1 equiv) and PhI or poly(4-iodostyrene) as the catalysts [40]. Recyclable ionic-liquid supported iodoarenes have also been used as catalysts in the reaction of α-tosyloxylation of ketones with *m*CPBA and *p*-toluenesulfonic acid [41].

Tanaka and Togo have utilized Oxone ($2KHSO_5•KHSO_4•K_2SO_4$) as the stochiometric oxidant in the iodoarene-mediated α-tosyloxylation of ketones [42]. Various alkyl aryl ketones, dialkyl ketones, and cycloheptanone can be converted into the corresponding α-tosyloxyketones in good yields by the reaction with Oxone and *p*-toluenesulfonic acid in the presence of *p*-iodotoluene in acetonitrile. In these reactions, *p*-iodotoluene, 4-MeC_6H_4I, is the pre-catalyst, and 4-$MeC_6H_4I(OH)OTs$ is formed *in situ* as the reactive species for the α-tosyloxylation of ketones. However, catalytic efficiency of this reaction is low, because *p*-iodotoluene is partially oxidized by Oxone to the iodine(V) species, which are not active in the α-tosyloxylation of ketones [42].

Togo and co-workers have found that alkyl aryl ketones and dialkyl ketones could be converted into the corresponding α-tosyloxyketones in generally low yields by treatment with *m*CPBA and *p*-toluenesulfonic acid in the presence of catalytic molecular iodine in a mixture of acetonitrile and 2,2,2-trifluoroethanol (Method A, Scheme 25) [43]. A similar conversion of ketones into the corresponding α-tosyloxyketones could be carried out by the reaction with *m*CPBA and $TsOH•H_2O$



Scheme 24. Hypervalent iodine-catalyzed α-tosyloxylation of ketones.

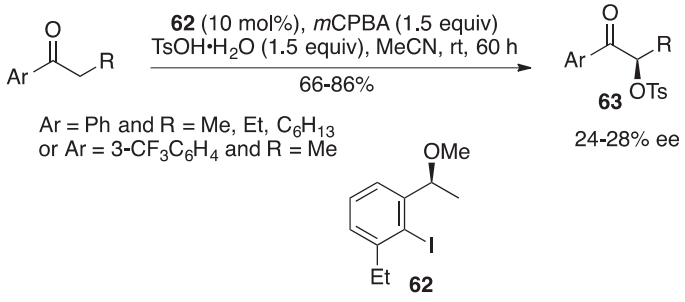


Scheme 25. Catalytic α-tosyloxylation of ketones.

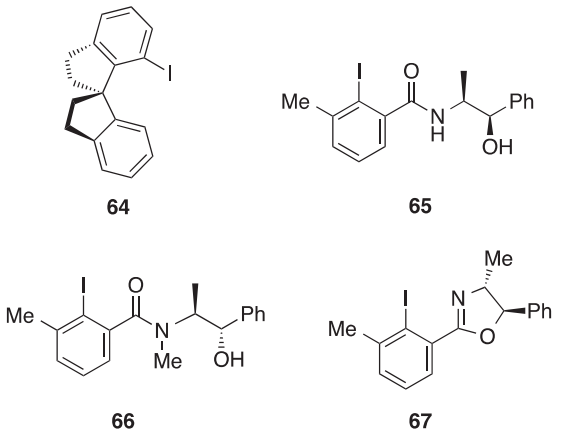
in the presence of catalytic amounts of iodine and *tert*-butylbenzene (Method B). In both reactions, *p*-iodotoluene **60** (Method A) or 4-*tert*-butyl-1-iodobenzene **61** (Method B) are initially formed followed by conversion to the corresponding [hydroxy(tosyloxy)iodo]arenes, ArI(OH)OTs by the reaction with *m*CPBA and $TsOH•H_2O$. [Hydroxy(tosyloxy)iodo]arenes are the actual reagents for the α-tosyloxylation of ketones in this catalytic cycle. Oxone can also be used as the oxidant for α-tosyloxylation of ketones in the presence of catalytic I_2 (0.7 equiv) [44].

Wirth and co-workers have reported an enantioselective α-oxytosylation of ketones; in this case the enantiopure chiral iodoarene **62** is used as a catalyst in a reaction leading to the enantioenriched α-tosyloxyketones **63** (Scheme 26) [45]. The authors have tested numerous chiral iodoarenes as catalysts, but the enantioselectivity of this reaction was low [45–47].

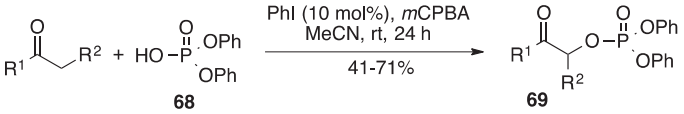
Chi Zhang and co-workers have achieved better levels of enantioselectivity by using spirobiindane-based chiral iodoarenes as the catalysts. In particular, the use of chiral catalyst **64** (Scheme 27) allowed to obtain α-tosyloxylated ketones in up to 58% enantiomeric excess [48]. Moran and Rodriguez have prepared several chiral aryl iodides (*e.g.*, structures **65** and **66**) and tested them as catalysts in the enantioselective α-oxytosylation of propiophenone and in the oxidative cyclization of 5-oxo-5-phenylpentanoic acid to 5-benzoyldihydrofuran-2(3*H*)-one [49]. The highest



Scheme 26. Enantioselective catalytic α-oxytosylation of ketones.



Scheme 27. Chiral aryl iodides used as catalysts in the enantioselective α-oxytosylation of ketones.



R^1 = Ph, 4-MeC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 4-$NO_2C_6H_4$, 3-$NO_2C_6H_4$, Me, Et
R^2 = H, Me

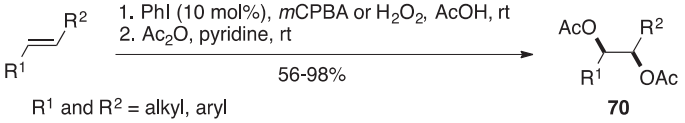
Scheme 28. Hypervalent iodine-catalyzed α-phosphoryloxylation of ketones.

enantioselectivities obtained were 18% for the α-oxytosylation using catalyst **65** and 51% ee for the oxidative cyclization using catalyst **66**. Legault and co-workers have developed a family of iodooxazoline catalysts (*e.g.*, structure **67**) for the iodine(III)-mediated α-tosyloxylation of ketone derivatives [50]. The use of catalyst **67** (10 mol%) in dichloromethane solution gives the best levels of enantioselectivity (up to 54% ee). The observed enhancement in catalytic activity was explained by the introduction of steric hindrance *ortho* to the iodine atom of the catalyst (*e.g.*, methyl group in catalyst **67**) [51]. Enantioselective tosyloxylation of carbonyl compounds is a potentially important methodology for pharmaceutical research.

Similarly to the α-oxytosylation, an effective catalytic method for the α-phosphoryloxylation of ketones has been developed [52]. The treatment of ketones with phosphates **68** in the presence of iodobenzene as the catalyst and *m*CPBA as the oxidant in acetonitrile at room temperature affords respective keto phosphates **69** in moderate to good yields (Scheme 28) [52].

3.2. Oxidative functionalization of alkenes and alkynes

Several examples of hypervalent iodine-catalyzed reactions of alkenes and alkynes have been reported. A method for the organocatalytic *syn* diacetoxylation of alkenes has been developed using aryl iodides as efficient catalysts and hydrogen peroxide or *m*CPBA as terminal oxidants (Scheme 29) [53]. Various substrates, including electron-rich as well as electron-deficient alkenes, are smoothly transformed by this procedure to the respective diacetoxylation products **70** in good to excellent yields with high diastereoselectivity (up to >19:1 dr).

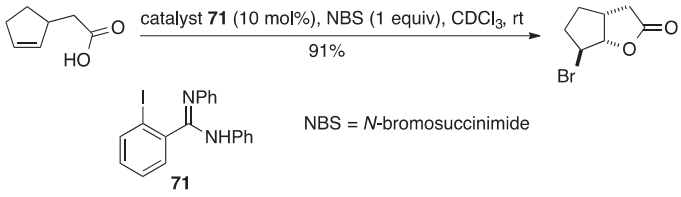


Scheme 29. Organocatalytic *syn* diacetoxylation of alkenes.

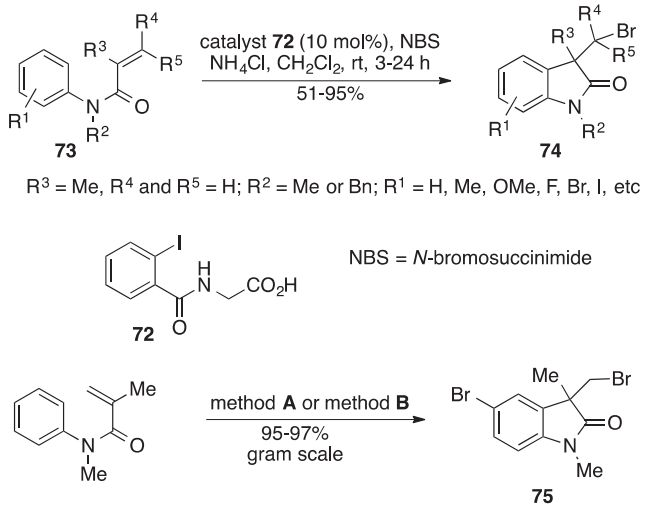
Iodobenzene of 4-iodotoluene have been used as the catalysts in this reaction.

Braddock and co-workers have demonstrated that suitably *ortho*-substituted iodobenzenes act as organocatalysts for the transfer of electrophilic bromine from *N*-bromosuccinimide to alkenes via the intermediacy of bromoiodinanes [54]. Particularly active catalyst is the *ortho*-substituted iodoarene **71**, as illustrated by a bromolactonization reaction shown in Scheme 30. An alternative procedure for the bromolactonization of alkenoic acids employs iodobenzene as a catalyst, sodium bromide as the source of bromine, and Oxone as the terminal oxidant in trifluoroethanol at room temperature [55].

Based on the hypervalent iodine-catalyzed bromocarbocyclization of appropriate alkenoic precursors **73**, Gulder and co-workers have developed an efficient synthetic approach to 3,3-disubstituted oxoindoles **74** (Scheme 31) [56]. These cyclizations are catalyzed by 2-iodobenzamide **72** at room temperature using NBS as the source of electrophilic bromine. Alternatively, KBr can be used as the source of bromine in the



Scheme 30. Catalytic bromolactonization of alkenoic acids.



A: catalyst **72** (10 mol%), NBS (2.4 equiv), NH_4Cl (10 mol%), CH_2Cl_2, rt, 12 h
B: catalyst **72** (10 mol%), KBr (2.4 equiv), Oxone (2.4 equiv), CH_2Cl_2, rt, 12 h

Scheme 31. Catalytic synthesis of 3,3-disubstituted oxoindoles.

presence of Oxone as a terminal oxidant. Synthetic utility of this cyclization has been demonstrated by preparation of product **75**, which is the key intermediate in the formal synthesis of the acetylcholinesterase inhibitor physostigmine [56].

A catalytic procedure for the (diacetoxyiodo)benzene-mediated oxidative iodolactonization of pentenoic, pentynoic, and hexynoic acids in the presence of tetrabutylammonium iodide has been reported [57]. In this procedure, (diacetoxyiodo)benzene is generated *in situ* using a catalytic amount of iodobenzene with sodium perborate monohydrate as the stoichiometric oxidant. A variety of unsaturated acids including δ-pentenoic acids **76**, δ-pentynoic acids **78** and δ-hexynoic acid afforded the respective lactones (*e.g.*, **77** and **79**) using this organocatalytic methodology (Scheme 32) [57].

An efficient catalytic method for sulfonyloxylactonization of alkenoic acids using (diacetoxyiodo)benzene as a catalyst in combination with *m*-chloroperoxybenzoic acid as an oxidant in the presence of a sulfonic acid has been reported [58]. The cyclization of alkenoic acids **80** is performed in dichloromethane at room temperature giving tosyloxylactones **81** in good yields (Scheme 33).

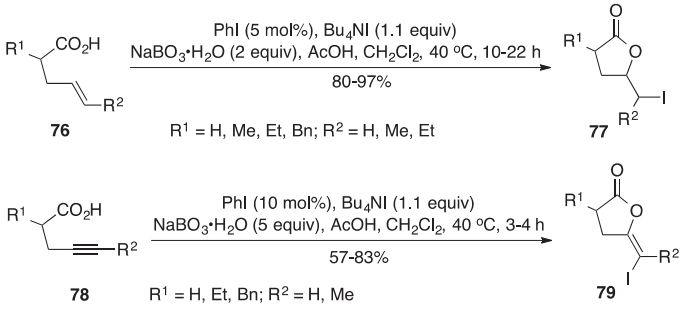
A similar catalytic phosphoryloxylactonization of pentenoic acids has been developed. The cyclization of 4-pentenoic acids **82** with phosphates using iodobenzene as a catalyst in combination with *m*CPBA as the terminal oxidant in trifluoroethanol at room temperature affords phosphoryloxylactones **83** in good yields (Scheme 34) [59].

Iodobenzene has been shown to catalyze the 5-*exo*-*dig* cyclization of δ-alkynyl β-ketoesters **84** under oxidative conditions that generate hypervalent iodine species *in situ* (Scheme 35) [25]. The cyclopentane products **85** contain adjacent quaternary and tertiary stereocenters, which are formed with excellent diastereoselectivity (up to over 20:1 dr).

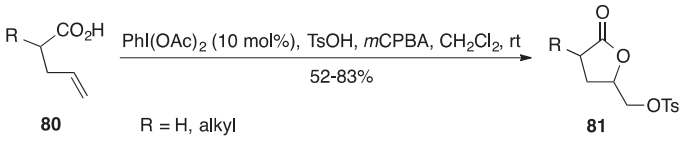
Ochiai and co-workers have developed an efficient iodoarene-catalyzed oxidative cleavage of alkenes and alkynes using *m*CPBA as a terminal oxidant [60]. Various cyclic and acyclic alkenes as well as aliphatic and aromatic alkynes are smoothly cleaved to carboxylic acids under these organocatalytic conditions (Scheme 36) [60].

A convenient procedure for the aminobromination of electron-deficient olefins using *N*-bromosuccinimide/tosylamide (Scheme 37) or Bromamine-T promoted by (diacetoxyiodo)benzene has been reported [61,62]. This efficient metal-free protocol affords the vicinal bromamines **86** with excellent stereoselectivities. A similar (diacetoxyiodo)benzene-catalyzed aminochlorination can be performed by using Chloramine-T as nitrogen and chlorine source [63].

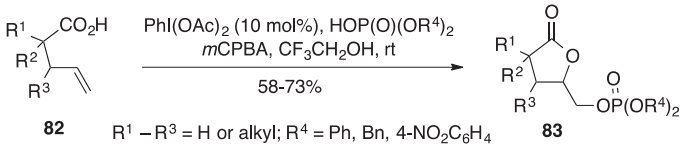
Wirth and co-workers have published in 2007 a detailed study of the aziridination of alkenes with the $PhI(OAc)_2$/N-substituted hydrazine system (Scheme 38) and, in particular, reported tentative evidence that this reaction proceeds through the formation of an aminoiodane that reacts directly with the alkene [64]. Furthermore, the authors of this publication have analyzed the requirements to make this reaction catalytic in iodoarene. This reaction requires an oxidant that will oxidize iodoarenes but that does not oxidize alkenes, and it is possible that no such oxidant actually exists [64]. Despite this prediction, the catalytic variant of a similar aziridination reaction has been developed later employing iodide–hypoiodite catalytic cycle [22].



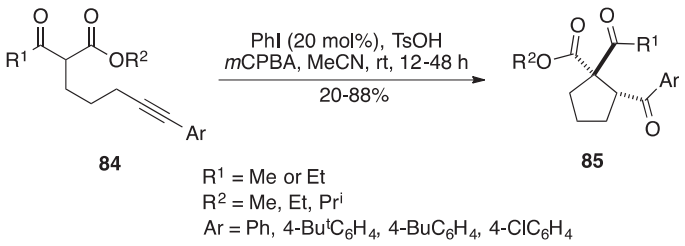
Scheme 32. Hypervalent iodine-catalyzed oxidative iodolactonization reactions.



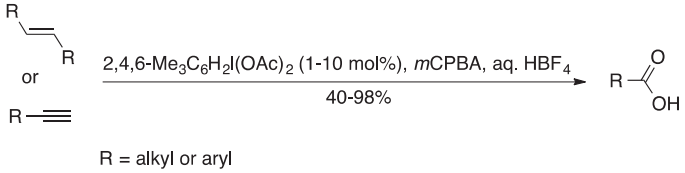
Scheme 33. Catalytic sulfonyloxylactonization of alkenoic acids.



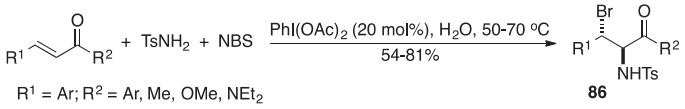
Scheme 34. Catalytic phosphoryloxylactonization of pentenoic acids.



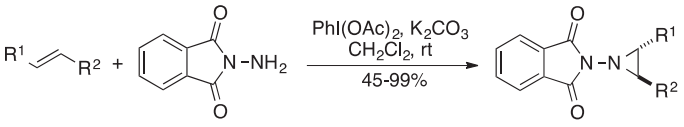
Scheme 35. Catalytic cyclization of δ-alkynyl β-ketoesters.



Scheme 36. Iodoarene-catalyzed oxidative cleavage of alkenes and alkynes.



Scheme 37. Catalytic aminobromination of electron-deficient olefins.



Scheme 38. Aziridination of alkenes with the $PhI(OAc)_2$/N-substituted hydrazine system.

3.3. Oxidative bromination of aromatic compounds

Oxidative bromination of arenes can be achieved by using a source of bromide anion and an appropriate iodine(III) oxidant, possibly via intermediate formation of electrophilic bromoiodanes. An efficient and regioselective monobromination of electron-rich aromatic compounds has been developed, in which iodobenzene is used as the catalyst in combination with *m*CPBA as the terminal oxidant. The bromination of arenes **87** with lithium bromide readily proceeds in THF at room temperature affording regioselective monobrominated products **88** in good yields (Scheme 39) [65].

The proposed catalytic cycle for this reaction includes the initial formation of [hydroxyl(tosyloxy)iodo]benzene **89** by oxidation of iodobenzene in the presence of toluenesulfonic acid followed by its conversion to the bromoiodane **90** via ligand exchange, and then the bromination of arene gives aryl bromide (Scheme 40). The reduced by-product, iodobenzene, is again reoxidized into hypervalent iodine reagent by the oxidation with *m*CPBA [65].

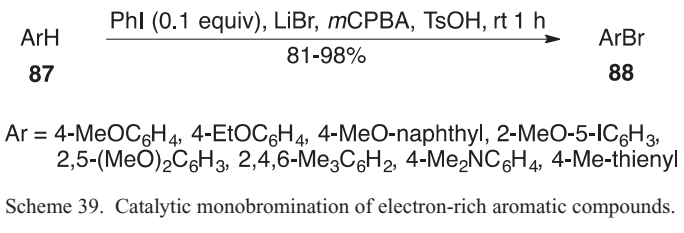
3.4. Oxidative amination of aromatic compounds

Aromatic C—H bond can be aminated in intermolecular or intramolecular mode using amides as the nitrogen source, catalytic iodoarene, and an appropriate oxidant, such as peroxycarboxylic acid. Antonchick and co-workers have developed an atom-efficient and environmentally friendly direct oxidative intermolecular procedure for amination and hydrazination of nonfunctionalized arenes [66]. A wide range of arenes **91**, including simple benzene, can be aminated using *N*-methoxybenzamide **92** as amination reagent in the presence of peracetic and trifluoroacetic acids giving products **94** as illustrated by Scheme 41. Even electron-poor arenes like chlorobenzene and fluorobenzene can be selectively functionalized in the *para*-position using this mild method. The reactions of electron-rich arenes afford products of amination in the highest yield. Out of several catalysts tested, 2,2′-diiodo-4,4′,6,6′-tetramethylbiphenyl **93** has shown the highest catalytic activity in this reaction.

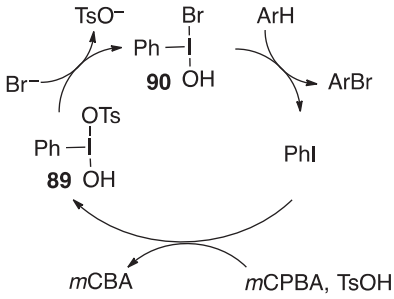
This procedure has been extended to organocatalytic hydrazination of arenes to products **96** using *N*-(1,3-dioxoisoindolin-2-yl)acetamide **95** as the nitrogen source (Scheme 42) [66]. This new approach to acetanilides may find practical use in the synthesis of isocyanates from substituted benzenes.

The mechanism of this reaction involves initial oxidation of aryl iodide **93** by peracetic acid to the active hypervalent iodine species **97**, followed by the ligand substitution at iodine(III) by nitrogen sources **92** or **95** generating hypervalent iodine species **98**, which undergo oxidative fragmentation to form nitrenium ions **99**. Reaction of an arene with the electron-deficient nitrenium ion **99** affords final products of amination and the reduced intermediate **100**, which is reoxidized to the species **97** (Scheme 43) [66].

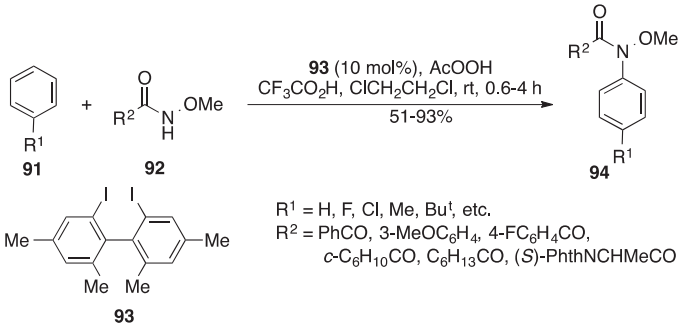
Several examples of hypervalent iodine-catalyzed cyclizations leading to intramolecular C—N bond formation have been reported. Antonchick and co-workers have developed an efficient catalytic method for the preparation of carbazoles through oxidative C—N bond formation [67]. The best yields of products were obtained in hexafluoro-2-propanol as a solvent using 2,2′-diiodo-4,4′,6,6′-tetramethylbiphenyl **93** as a catalyst and peracetic acid as the oxidant, as illustrated by a reaction shown in Scheme 44.



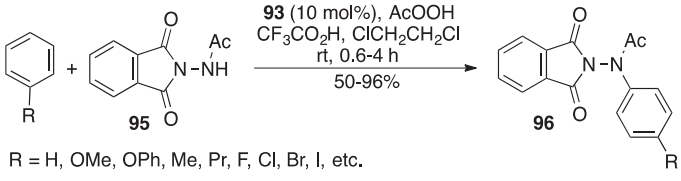
Scheme 39. Catalytic monobromination of electron-rich aromatic compounds.



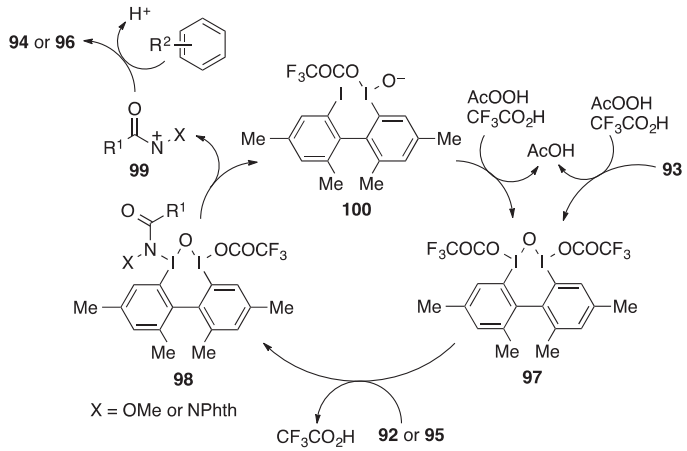
Scheme 40. Catalytic cycle for oxidative bromination of aromatic compounds.



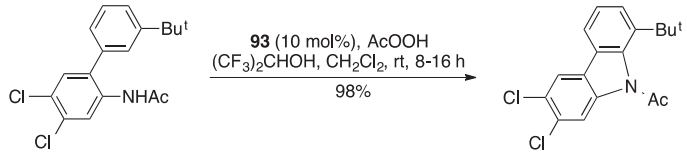
Scheme 41. Catalytic amination of aromatic compounds.



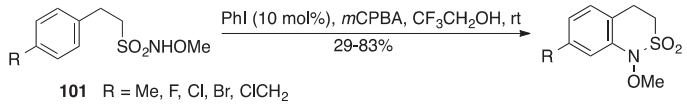
Scheme 42. Organocatalytic hydrazination of arenes.



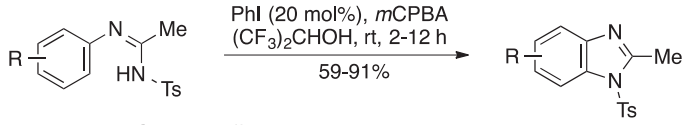
Scheme 43. Mechanism of oxidative amination of aromatic compounds.



Scheme 44. Hypervalent iodine-catalyzed cyclizations leading to intramolecular C—N bond formation.



Scheme 45. Hypervalent iodine-catalyzed cyclization of 2-aryl-N-methoxyethanesulfonamides.



Scheme 46. Hypervalent iodine-catalyzed cyclization of *N*-aryl-*N*′-tosylamidines.

Togo and Moroda have reported a (diacetoxyiodo)benzene-catalyzed cyclization of 2-aryl-*N*-methoxyethanesulfonamides **101** using iodobenzene as a catalyst and *m*-CPBA as the stoichiometric oxidant (Scheme 45) [68]. A similar catalytic cyclization has also been performed using Oxone in acetonitrile [69].

In a similar fashion, the oxidative C—H amination of *N*″-aryl-*N*′-tosyl/*N*′-methylsulfonylamidines and *N,N*′-bis(aryl)amidines has been accomplished using iodobenzene as a catalyst to give 1,2-disubstituted benzimidazoles in the presence of *m*CPBA as a terminal oxidant at room temperature (Scheme 46) [70]. This is a general reaction affording benzimidazoles in moderate to high yields.

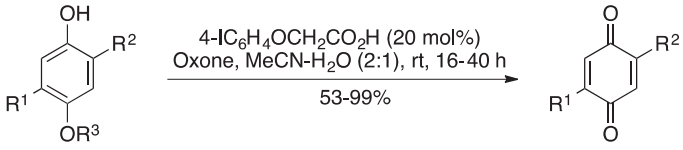
3.5. Oxidation of phenolic substrates to quinones and quinols

Oxidation of phenols or *o*- and *p*-hydroquinones with stoichiometric [bis(acyloxy)iodo]arenes to the corresponding benzoquinones is one of the most typical synthetic applications of hypervalent iodine reagents. The catalytic version of this reaction was first reported by Yakura and Konishi in 2007 [71]. In this work, the reaction of *p*-alkoxyphenols **102** in the presence of catalytic amounts of 4-iodophenoxyacetic acid with Oxone as the terminal oxidant in aqueous acetonitrile at room temperature affords *p*-quinones **103** in high yields (Scheme 47) [71]. 4-Iodophenoxyacetic acid is a readily available, water-soluble aromatic iodide that has a particularly high catalytic activity in this reaction.

Yakura and Konishi proposed a catalytic cycle based on the iodine(V) species was proposed for this reaction (Scheme 47) [71]; however, the more recent studies have demonstrated that the oxidation of iodoarenes with Oxone at room temperature generates active iodine(III) species, and heating to about 70 °C or the presence of ruthenium catalyst is required to oxidize ArI to $ArIO_2$ [72].

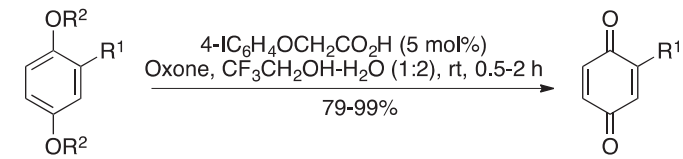
Several modifications of the procedure shown in Scheme 47 have been reported [73–75]. The reaction of *p*-dialkoxybenzenes **104** with a catalytic amount of 4-iodophenoxyacetic acid in the presence of Oxone as the oxidant in aqueous trifluoroethanol affords the corresponding *p*-quinones **105** in excellent yields (Scheme 48) [73,75]. The same solvent system, 2,2,2-trifluoroethanol-water (1:2), has been also used in the efficient oxidation of *p*-alkoxyphenols to *p*-quinones [74].

The catalytic oxidation of *p*-substituted phenols bearing an alkyl or aryl group in the *para* position gives the corresponding *p*-quinols. In particular, the reaction of *p*-substituted phenols **106** with a catalytic amount of 4-iodophenoxyacetic acid and Oxone as the oxidant affords *p*-quinols **107** in generally high yields (Scheme 49) [75,76].



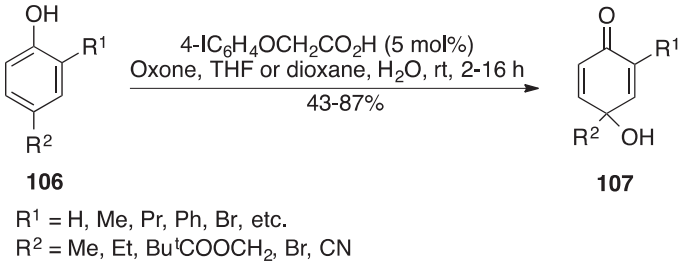
R^1 = H or $MeCH_2CH_2CMe_2$
R^2 = H, Bu^t, $MeCH_2CH_2CMe_2$, $Bu^tPh_2SiOCH_2$, N_3CH_2, phthalimide
R^3 = Me or Et

Scheme 47. Catalytic oxidation of *p*-alkoxyphenols to *p*-quinones.



R^1 = H, Me, Bu^t, $CH_2CH_2CO_2Me$, etc.
R^2 = Me, Et, Bu^tMe_2Si

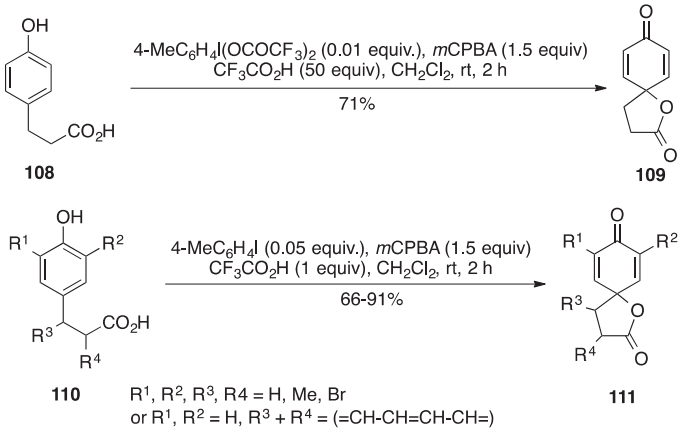
Scheme 48. Catalytic oxidation of *p*-dialkoxybenzenes.



Scheme 49. Catalytic oxidation of *p*-substituted phenols bearing an alkyl or aryl group in the *para* position.

3.6. Oxidative spirocyclization of aromatic substrates

The oxidative dearomatization of phenolic substrates resulting in intramolecular cyclization with the formation of spirocyclic products represents one of the most powerful synthetic tools in modern organic synthesis. Kita and co-workers have reported the first example of catalytic oxidative spirocyclization reaction based on the *in situ* regeneration of a [bis(trifluoroacetoxy)iodo]arene from iodoarene with *m*CPBA as a terminal oxidant [77]. In a specific example, the oxidation of the phenolic substrate **108** with *m*CPBA in dichloromethane in the presence of a catalytic amount of *p*-[bis(trifluoroacetoxy)iodo]toluene (1 mol%) and trifluoroacetic acid at room temperature affords the respective spirolactone **109** in good yield (Scheme 50). A variety of other [bis(trifluoroacetoxy)iodo]arenes [*e.g.*, $PhI(OCOCF_3)_2$, $4\text{-}MeOC_6H_4I(OCOCF_3)_2$ and $2,4\text{-}F_2C_6H_3I(OCOCF_3)_2$] and different acidic additives (acetic acid, $BF_3{\bullet}OEt_2$, TMSOTf, molecular sieves) have been tested as catalysts in this reaction; however, the $4\text{-}MeC_6H_4I(OCOCF_3)_2$/trifluoroacetic acid system generally provides the best catalytic efficiency. Under optimized conditions, various phenolic substrates **110** have been oxidized to spirolactones **111** in the presence of catalytic amounts of *p*-iodotoluene (Scheme 50) [77]. A modification of this catalytic procedure involves the use of peracetic acid as the oxidant in fluoroalcohol solvents [78].



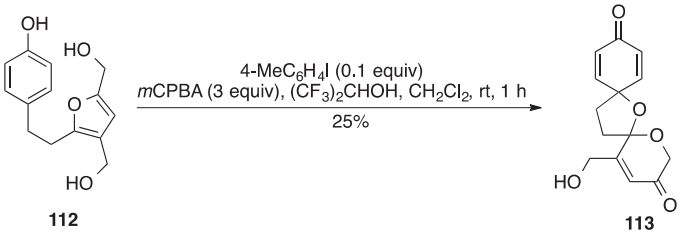
Scheme 50. Catalytic oxidative spirocyclization reactions.

In a more recent work, the Kita's catalytic spirocyclization has been tested in the synthesis of bioactive polyspirocyclohexa-2,5-dienones, as shown in Scheme 51 [79]. The target product **113** was isolated in a low yield, probably due to the competitive oxidation of substrate **112** directly by *m*CPBA to give unwanted side products.

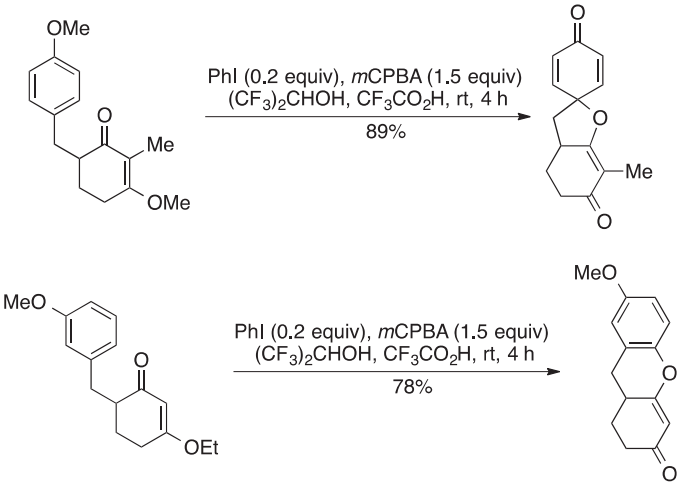
Ngatimin et al. have developed a procedure for the iodobenzene-catalyzed synthesis of spirofurans and benzopyrans by oxidative cyclization of vinylogous esters [80]. Vinylogous esters bearing *para* or *meta* methoxy benzyl groups undergo oxidative cyclization with 5–20 mol% iodobenzene and *m*CPBA to give spirofuran or benzopyran containing heterocycles as illustrated by two specific examples shown in Scheme 52. These cyclizations allow rapid synthesis of skeletally complex products in good to excellent yields [80].

A similar procedure allows catalytic oxidation of the amide derivatives of phenolic substrates **114** to the respective N-fused spirolactams **115** using *p*-iodotoluene as the catalyst and *m*CPBA as the terminal oxidant (Scheme 53) [81].

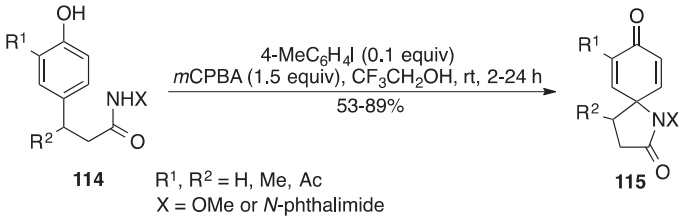
The catalytic spirocyclization procedure has been further improved by using 2,2′-diiodo-4,4′,6,6′-tetramethylbiphenyl **93** as the catalyst instead of *p*-iodotoluene. Diiodide **93** has demonstrated a high catalytic activity in this reaction in the presence of peracetic acid as the terminal oxidant, as illustrated by Scheme 54 [82]. It has been proposed that the *in situ* generated μ-oxo-bridged hypervalent iodine(III) species are the actual active species in this catalytic cycle [82].



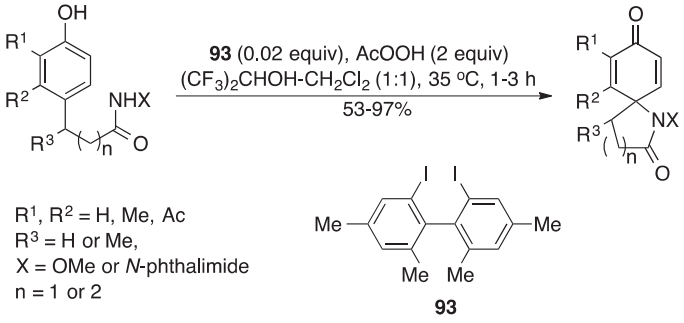
Scheme 51. Synthesis of bioactive polyspirocyclohexa-2,5-dienones via catalytic spirocyclization.



Scheme 52. Iodobenzene-catalyzed synthesis of spirofurans and benzopyrans.

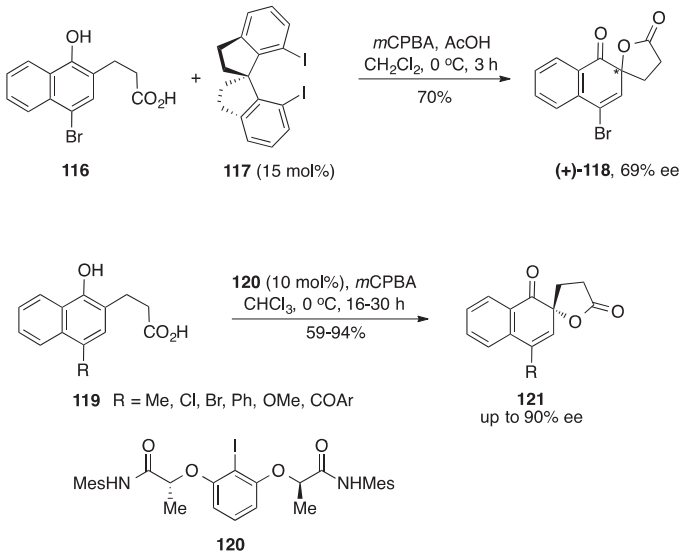


Scheme 53. Catalytic oxidation of the amide derivatives of phenolic substrates.



Scheme 54. Catalytic oxidative spirocyclization reactions using 2,2′-diiodo-4,4′,6,6′-tetramethylbiphenyl as catalyst.

The catalytic spirocyclization of phenolic substrates can be performed as an enantioselective reaction using chiral, non-racemic organic iodides as the catalysts [83–85]. In particular, the chiral iodoarene **117** with a rigid spirobiindane backbone has been found to catalyze enantioselectively the dearomatization of naphtholic substrates **116** in a highly selective manner giving optically active products **118** with up to 69% ee (Scheme 55) [83]. Ishihara and co-workers have designed a conformationally flexible C_2-symmetric iodoarene catalyst **120** for a similar enantioselective oxidative spirolactonization [84,86,87]. For example, hydroxynaphthalenyl propanoic acid derivatives **119** undergo dearomatization in the presence of catalyst **120** to give the corresponding spirolactones **121** in yields up to 94% with enantioselectivity up to 90% (Scheme 55) [84].



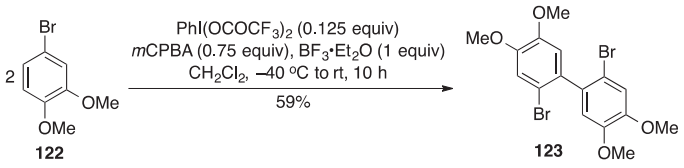
Scheme 55. Enantioselective catalytic oxidative spirocyclization reactions using chiral iodoarene as catalyst.

3.7. Carbon–carbon bond forming reactions

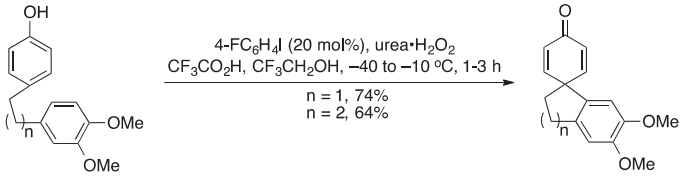
In the 2005 seminal work, Kita and co-workers reported the first example of an intermolecular C—C bond formation reaction catalyzed by an iodoarene [77]. Specifically, the oxidative coupling of phenolic ether **122** using [bis(trifluoroacetoxy)iodo]benzene as a catalyst and *m*CPBA as a terminal oxidant afforded product **123** in moderate yield (Scheme 56). More recently, this C—C coupling reaction was extended to a selective coupling of *N*-methanesulfonyl anilides with aromatic hydrocarbons [88].

Kita and co-workers have developed an H_2O_2/acid anhydride system for the iodoarene-catalyzed intramolecular C—C cyclization of phenolic derivatives; an example of this catalytic cyclization is shown in Scheme 57 [89].

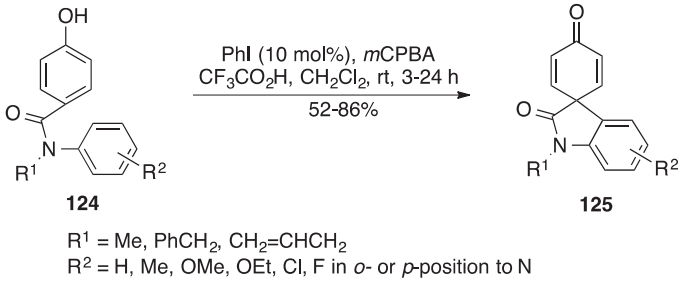
In a similar fashion, the intramolecular oxidative coupling of substituted 4-hydroxyphenyl-*N*-phenylbenzamides **124** has been performed by using iodobenzene as a catalyst and *m*-chloroperoxybenzoic acid or urea•H_2O_2 as the oxidant (Scheme 58). This reaction provides an efficient synthetic approach to spirooxindoles **125** [90].



Scheme 56. Catalytic intermolecular C—C bond formation reaction.



Scheme 57. Iodoarene-catalyzed intramolecular C—C cyclization of phenolic derivatives.



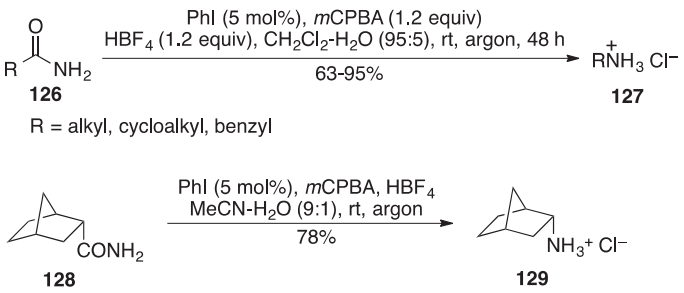
Scheme 58. Catalytic intramolecular oxidative coupling of substituted 4-hydroxyphenyl-*N*-phenylbenzamides.

3.8. Hofmann rearrangement of carboxamides

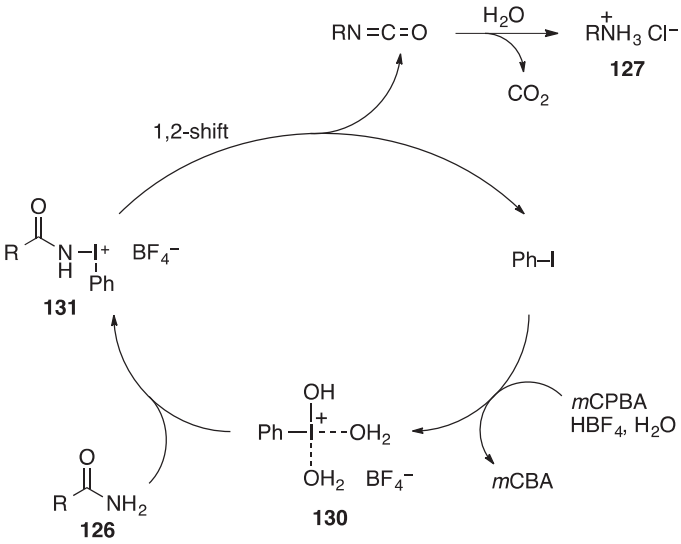
Hypervalent iodine reagents have been employed in numerous synthetic works as oxidants for the Hofmann-type rearrangements, including the preparation of pharmaceutical products in industrial scale [91]. Synthetic procedures for Hofmann rearrangement using stoichiometric organohypervalent iodine species generated *in situ* from iodoarenes and appropriate oxidants have also been reported [92,93]. In particular, alkylcarboxamides can be converted to the respective amines by Hofmann rearrangement using hypervalent iodine species generated *in situ* from stoichiometric amounts of iodobenzene and Oxone in aqueous acetonitrile [92]. Likewise, the Hofmann-type rearrangement of aromatic and aliphatic imides using a hypervalent iodine(III) reagent generated *in situ* from stoichiometric PhI, *m*CPBA, and TsOH•H_2O has also been reported [93].

The first truly catalytic version of Hofmann rearrangement using aryliodides as catalysts and *m*CPBA as terminal oxidant was reported by Ochiai and co-workers in 2012 [94]. Catalytic efficiency of several substituted iodobenzenes and aliphatic alkyl iodides in Hofmann rearrangement of benzylic carboxamides has been tested to demonstrate that iodobenzene is the best catalyst. Introduction of electron-donating (4-methyl, 3,5-dimethyl and 2,4,6-trimethyl) or electron-withdrawing groups (4-Cl and 4-CF_3) into iodobenzene decreased the yield of products. Aliphatic iodides such as methyl, trifluoroethyl, and 1-adamantyl iodides showed no catalytic efficiency. Under optimized reaction conditions, various linear, branched, and cyclic aliphatic carboxamides **126** afford alkylammonium chlorides **127** in high yields (Scheme 59). These catalytic conditions are compatible with the presence of various functionalities such as halogens (F, Cl, Br), sulfonamides, amines and methoxy and nitro groups. Bicyclic amide **128** affords *endo*-ammonium chloride **129** stereoselectively in a good yield, which suggests retention of stereochemistry of the migrating groups in the catalytic rearrangement of carboxamides, same as observed in the classical Hofmann rearrangement. This procedure for the preparation of various amines from commercially available amides represents a potentially useful resource efficient technology for organic synthesis.

The catalytic cycle for this reaction probably involves *in situ* generation of a tetracoordinated square planar bis(aqua)(hydroxy)phenyliodine(III) complex **130** as an active oxidant formed from iodobenzene by the reaction with *m*CPBA in the presence of aqueous HBF_4 (Scheme 60). Complex **130**



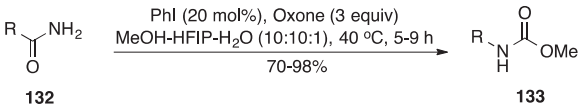
Scheme 59. Catalytic version of Hofmann rearrangement using aryliodides as catalysts.



Scheme 60. Catalytic cycle for hypervalent iodine-catalyzed Hofmann rearrangement.

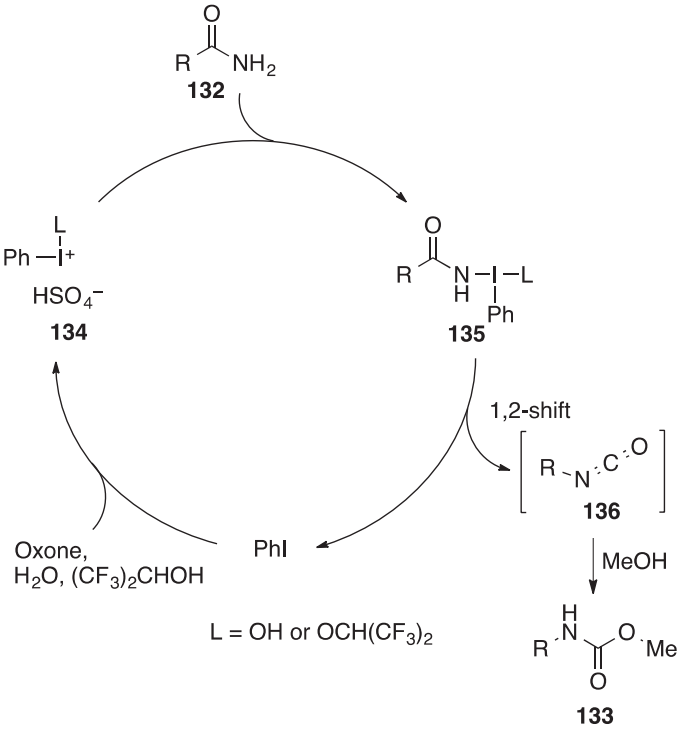
promotes the Hofmann rearrangement of carboxamides **126**, probably via intermediate formation of *N*-(phenyliodanyl)carboxamides **131** [94].

Our group has reported the hypervalent iodine-catalyzed Hofmann rearrangement of carboxamides to carbamates using Oxone as the oxidant [95]. This reaction involves hypervalent iodine species generated *in situ* from catalytic amounts of PhI and Oxone in the presence of hexafluoroisopropanol (HFIP) in aqueous methanol solutions. Under these conditions, Hofmann rearrangement of various carboxamides **132** affords corresponding carbamates **133** in high yields (Scheme 61). The addition of small amount of water is required to dissolve Oxone in the reaction mixture, and the presence of HFIP in the mixture dramatically improves the yield of carbamates **133**. Iodobenzene is the most active pre-catalyst in this reaction; the use of other iodine containing pre-catalysts (2,4,6-$Me_3C_6H_2I$, 4-MeC_6H_4I, 4-$CF_3C_6H_4I$, 3-$HO_2CC_6H_4I$, Bu_4NI) instead of PhI gives poor results. In general, the reactions of benzylcarboxamides with either electron-donating or electron-withdrawing substituents give corresponding carbamates **133** in good yields. Various aliphatic amides, including primary, secondly, tertiary and cyclic alkylcarboxamides, also smoothly react under these conditions. Compared to the previous reported method of Hofmann rearrangement with the *in situ*-generated stoichiometric hypervalent iodine species [92], the catalytic method affords carbamates **133** in comparable yields.



R = $PhCH_2$, 4-$MeC_6H_4CH_2$, 4-$FC_6H_4CH_2$, 4-$ClC_6H_4CH_2$, 3-$ClC_6H_4CH_2$, 2-$ClC_6H_4CH_2$, 4-$BrC_6H_4CH_2$, 4-$CF_3C_6H_4CH_2$, Ph(Et)CH, C_5H_{11}, $PhCH_2CH_2$, C_6H_{13}, $BuMe_2C$, cyclopentyl, cyclohexyl, 1-adamantyl, etc.

Scheme 61. Hypervalent iodine-catalyzed Hofmann rearrangement of carboxamides to carbamates.

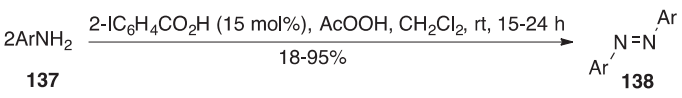


Scheme 62. Mechanism of PhI-catalyzed Hofmann rearrangement of carboxamides to carbamates.

The catalytic cycle for this reaction involves the reactive species **134** generated from PhI and Oxone in aqueous HFIP, which further react with carboxamide **132** to give the hypervalent amidoiodane **135** via ligand exchange (Scheme 62). Amidoiodane **135** then undergoes the reductive elimination of iodobenzene and the 1,2-shift at the electron-deficient nitrenium nitrogen atom to give isocyanate **136**. Subsequently, the addition of methanol to isocyanate **136** gives the final carbamate **133**. The regenerated PhI continues catalytic cycle. The presence of HFIP may help to generate more electron-deficient active species **134** and **135** via ligand exchange with hydroxy(phenyl)iodonium ion or hypervalent aminoiodine, which help to accelerate further steps of the catalytic cycle, such as ligand exchange and 1,2-shift.

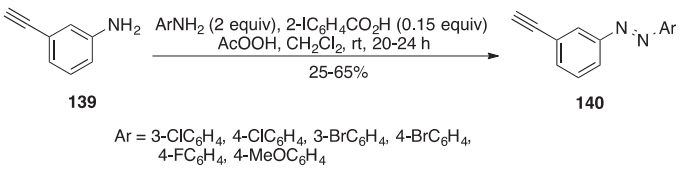
3.9. Oxidation of anilines

Anilines can be oxidized to azobenzenes under hypervalent iodine catalysis using peracetic acid as the oxidant (Scheme 63) [96]. 2-Iodobenzoic acid has the best catalytic effect compared to other aryl iodides (PhI, 4-$MeOC_6H_4I$, 4-$NO_2C_6H_4I$, 3-$IC_6H_4CO_2H$, 4-$IC_6H_4CO_2H$). This metal-free oxidation system demonstrates wide substituent tolerance, and the

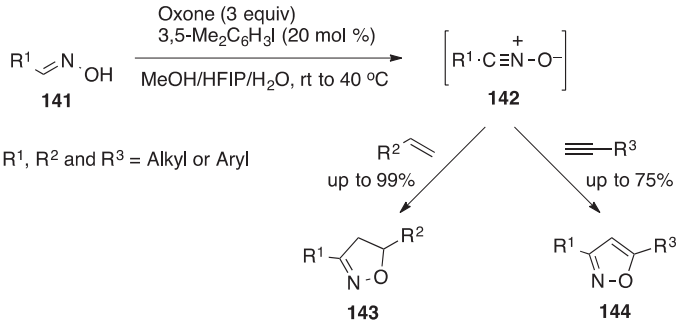


Ar = H, 2-ClC_6H_4, 3-ClC_6H_4, 4-ClC_6H_4, 2-BrC_6H_4, 3-BrC_6H_4, 4-BrC_6H_4, 4-FC_6H_4, 4-MeC_6H_4, 3,5-$Me_2C_6H_4$, 4-$MeOC_6H_4$, 4-$NH_2C_6H_4$, 2-$HO_2CC_6H_4$, 4-(4'-NH_2-3'-MeC_6H_3)-2-MeC_6H_3, 3-HC≡CC_6H_4

Scheme 63. Catalytic oxidation of anilines to azobenzenes.



Scheme 64. Catalytic preparation of non-symmetrical azo compounds.



Scheme 65. Hypervalent iodine catalyzed oxidation of aldoximes to nitrile oxides and their cycloaddition with with alkenes and alkynes.

corresponding products are formed in generally good yields. The large-scale preparation of azo compounds also could be carried out successfully by this method. Azobenzenes are key compounds in the dye industry, so this catalytic technology is important from the industrial viewpoint.

The asymmetrical azo compounds **140** have also been prepared under these conditions in moderate yields by coupling 3-ethynylaniline **139** with excessive amounts of a less reactive aniline (Scheme 64) [96].

3.10. Generation of nitrile oxides from oximes

Hypervalent iodine catalyzed oxidation of aldoximes **141** using oxone as a terminal oxidant generates nitrile oxides **142**, which react with alkenes and alkynes to give the corresponding isoxazolines **143** and isoxazoles **144** in moderate to good yields (Scheme 65) [97]. This reaction involves active hypervalent iodine species formed *in situ* from catalytic iodoarene and oxone in the presence of hexafluoroisopropanol in aqueous methanol solution.

4. Catalytic cycles based on iodine(V) species

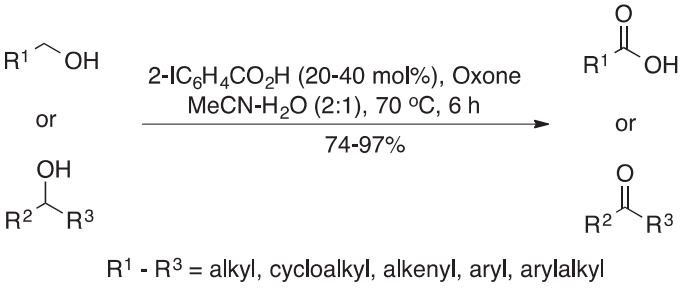
Hypervalent iodine(V) reagents, such as 2-iodoxybenzoic acid (IBX) and Dess–Martin periodinane (DMP), have found widespread synthetic application as stoichiometric oxidants for the facile and selective oxidation of alcohols to respective carbonyl compounds and also for some other important oxidative transformations. Catalytic application of iodine(V) species in oxidation of alcohols has previously been reviewed by Uyanik and Ishihara [98,99]. First examples of a catalytic application of the iodine(V) species such as IBX in the oxidation of alcohols using Oxone as the oxidant were independently reported by the groups of Vinod [100] in 2005 and Giannis [101] in 2006. In particular, Vinod's group employed 20–40 mol% of 2-iodobenzoic acid in a water–acetonitrile biphasic solvent

system; under these conditions primary and secondary alcohols were oxidized to carboxylic acids and ketones, respectively (Scheme 66) [100].

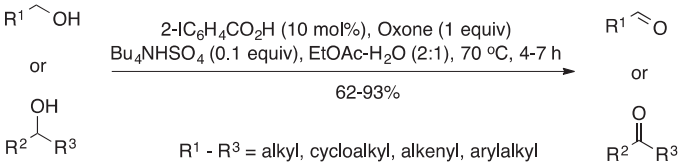
In a similar catalytic oxidation, Giannis' group utilized a water–ethyl acetate biphasic solvent system in the presence of 10 mol% of 2-iodobenzoic acid and tetrabutylammonium hydrogen sulfate as a phase-transfer catalyst. In this system, primary benzylic alcohols were oxidized to the corresponding aldehydes, which, in contrast to Vinod's procedure, did not undergo further oxidation (Scheme 67) [101].

Page and co-workers have demonstrated that primary and secondary alcohols can be oxidized to the respective aldehydes and ketones under reflux conditions in acetonitrile or dichloroethane in the presence of catalytic amount of 2-iodobenzoic acid and using tetraphenylphosphonium monoperoxysulfate, $Ph_4P^+HSO_5^-$, as the oxidant (Scheme 68) [102]. Tetraphenylphosphonium monoperoxysulfate is prepared from Oxone by treatment with tetraphenylphosphonium chloride. This catalytic system is useful for the oxidation of primary alcohols to the corresponding aldehydes without further oxidation to the carboxylic acids.

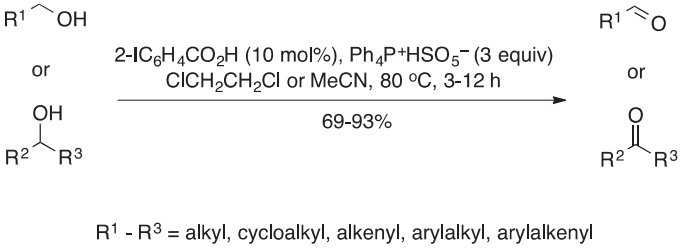
All these catalytic oxidations (Schemes 66–68) utilize catalytic cycle involving IBX **146** as the reactive species generated *in situ* from 2-iodosylbenzoic acid (IBA, **145**) and monoperoxysulfate salts as terminal oxidants (Scheme 69)



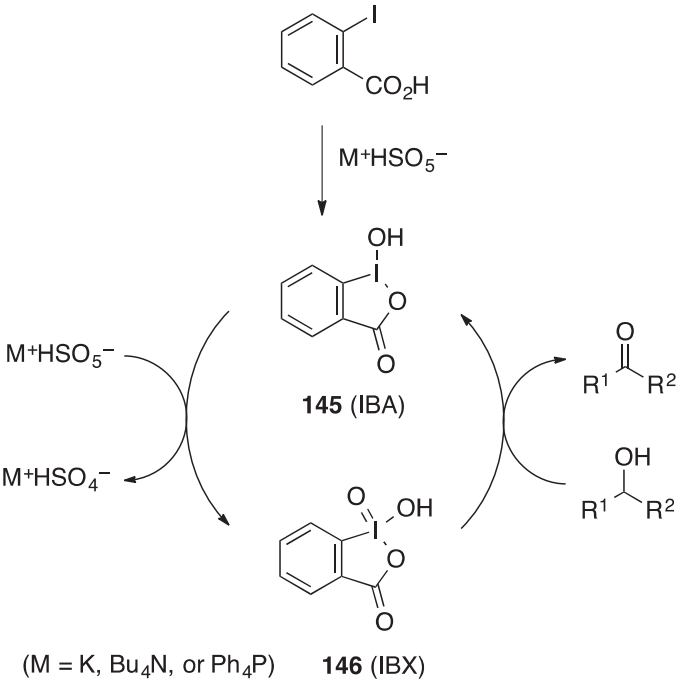
Scheme 66. Catalytic oxidation of primary and secondary alcohols.



Scheme 67. Catalytic oxidation of primary and secondary alcohols in biphasic solvent system.



Scheme 68. Catalytic oxidation of primary and secondary alcohols using tetraphenylphosphonium monoperoxysulfate as oxidant.

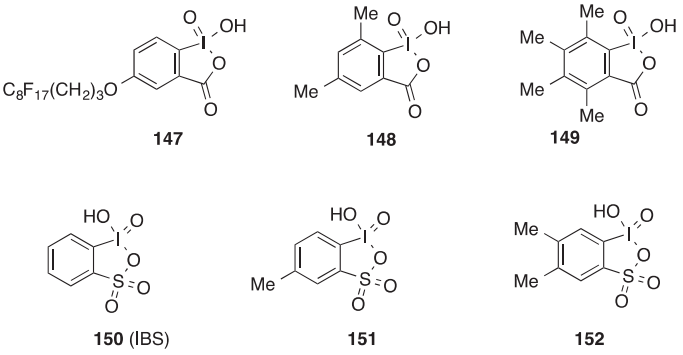


Scheme 69. Mechanism of catalytic oxidation of alcohols.

[99]. The synthetic value of this iodine(V)-based catalytic cycle is limited by the reoxidation step of IBA to IBX, which proceeds relatively slowly even at temperatures above 70 °C.

Several modified catalysts for the iodine(V)-mediated oxidation of alcohols have been developed based on the IBX derivatives and analogs (Scheme 70). In particular, the "fluorous IBX" **147** efficiently works as a catalyst for oxidation of various alcohols to the corresponding carbonyl compounds in good to high yields [103]. Fluorous IBX **147** can be regenerated from "fluorous IBA", which is readily recovered from the reaction mixture by simple filtration. The recovered reagent **147**, without further purification, retains its catalytic activity for at least five cycles.

The "twisted" dimethyl-IBX **148** and tetramethyl-IBX **149** have especially high catalytic activity and are capable to catalyze the oxidations of alcohols and sulfides with Oxone at room temperature in common organic solvents [104]. The *ortho*-methyl



Scheme 70. Modified catalysts for the iodine(V)-mediated oxidation of alcohols.

groups in reagents **148** and **149** lower the activation energy corresponding to the rate-determining hypervalent twisting, and also the steric relay between successive methyl groups twists the structure, which manifests in significant solubility in common organic solvents.

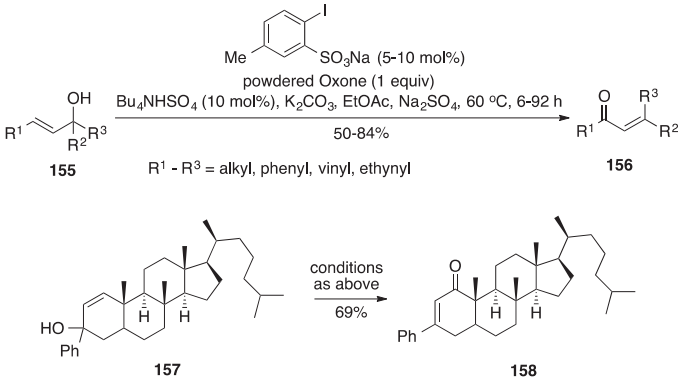
Ishihara and co-workers have found that 2-iodylbenzenesulfonic acid (IBS **150**) [105] is an extremely active catalyst in the oxidations of alcohols with Oxone as the terminal oxidant [106]. Methyl substituted IBS derivatives **151** and **156** have even slightly higher catalytic activity. Catalysts **150**–**152** can be conveniently generated *in situ* by using sodium or potassium salts of the respective 2-iodylbenzenesulfonic acids and Oxone in such solvents as acetonitrile, ethyl acetate, or nitromethane. The catalytic oxidation of alcohols using IBS and Oxone is illustrated by Scheme 71. Primary alcohols are oxidized to aldehydes, when smaller quantity of Oxone (0.6–0.8 equiv) is used, or to carboxylic acids in the presence of excessive Oxone (1.2 equiv) [106]. This reaction (Scheme 71) has been used for a selective larger scale oxidation of 4-bromobenzyl alcohol (6 g) to the corresponding aldehyde or carboxylic acid in excellent yields by controlling the amount of Oxone added in the presence of 1 mol% of the precatalyst, potassium 2-iodo-5-methylbenzenesulfonate [99].

Konno and co-workers investigated in detail the oxidation of various fluoroalkyl-substituted alcohols in the presence of a catalytic amount of sodium 2-iodobenzenesulfonate and Oxone in acetonitrile or nitromethane [107]. The efficiency of this oxidation was also evaluated by comparison to other oxidations, such as the Dess–Martin, pyridinium dichromate, and Swern oxidations. It was demonstrated that the hypervalent iodine(V)-catalyzed oxidation could be applied for almost all types of fluorinated alcohols, and it was comparable to Dess–Martin oxidation, while pyridinium dichromate and Swern oxidations could not be employed for allylic and propargylic alcohols as well as the alcohols having an aliphatic side chain. Moreover, the hypervalent iodine-catalyzed oxidation could be applied for a larger scale reaction as demonstrated for the oxidation of fluoroalcohol **153** to the respective ketone **154** (Scheme 72) [107].

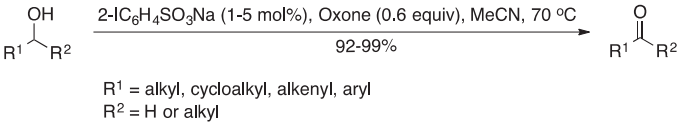
Ishihara and co-workers have developed an oxidative rearrangement of tertiary allylic alcohols **155** to enones **156** with Oxone promoted by catalytic quantities of sodium 2-iodobenzenesulfonate (Scheme 73) [108]. Under these conditions, 5-methyl-IBS **95** is generated *in situ* and serves as the actual catalyst for the oxidation. Cyclic and acyclic substrates afford the corresponding enones in moderate to high yields. Notably, sterically demanding steroidal alcohol **157** has been converted into enone **158** in high yield [108].

During the course of research on the oxidation of cycloalkanols, Ishihara and co-workers have also found that the selective oxidation of 4-*tert*-butylcyclohexanol **159** to 4-*tert*-butyl-2-cyclohexenone **160** can be achieved in excellent yield in the presence of a catalytic amount of sodium 2-iodobenzenesulfonate and 2 equivalents of Oxone (Scheme 74) [106]. Using this procedure, five- and six-membered cycloalkanols can be transformed into the corresponding enones **161**–**165** in good yields [106].

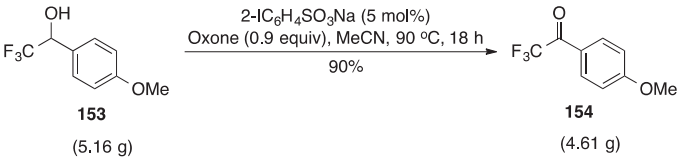
Vinod and co-workers have first developed a selective procedure for oxidation of benzylic C—H bonds to the corresponding carbonyl functionalities using a catalytic amount of 2-iodobenzoic acid and Oxone as a stoichiometric oxidant in aqueous acetonitrile under reflux conditions (Scheme 75) [109]. The authors hypothesized that the active hypervalent iodine oxidant generated *in situ* might not be IBX, but a soluble derivative of IBX **166**, incorporating a peroxysulfate ligand. This intermediate is believed to oxidize a benzylic C—H bond via a single electron transfer (SET) mechanism [109].



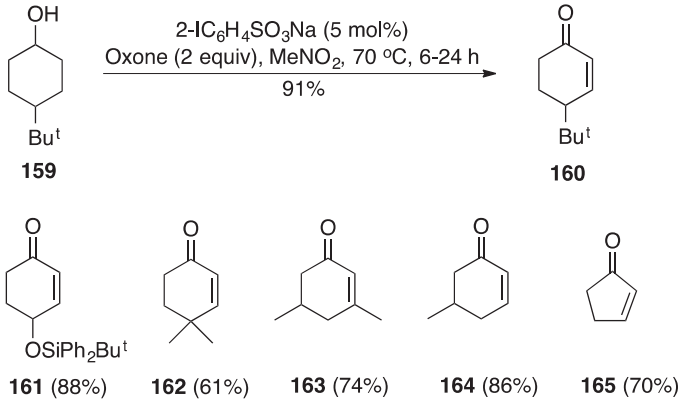
Scheme 73. Catalytic oxidative rearrangement of tertiary allylic alcohols to enones.



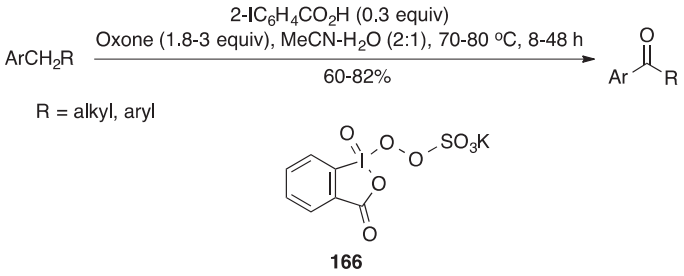
Scheme 71. 2-Iodylbenzenesulfonic acid as an extremely active catalyst in the oxidations of alcohols with Oxone.



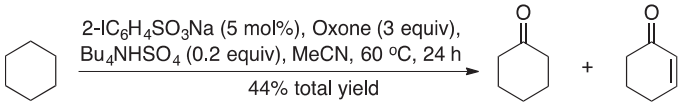
Scheme 72. Larger scale oxidation of a fluoroalcohol.



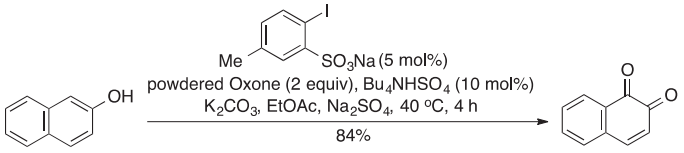
Scheme 74. Catalytic oxidation of cycloalkanols to enones.



Scheme 75. Catalytic oxidation of benzylic C—H bonds to carbonyl group.



Scheme 76. Catalytic oxidation of cyclohexane.



Scheme 77. Iodine(V)-catalyzed regioselective oxidation of phenols to *o*-quinones.

Zhang and co-workers have further improved the procedure for catalytic oxidation of benzylic C—H bonds using IBS as a catalyst, which is generated *in situ* by the oxidation of sodium 2-iodobenzenesulfonate (5 mol%) by Oxone in the presence of a phase-transfer catalyst, tetrabutylammonium hydrogen sulfate, in anhydrous acetonitrile at 60 °C [110]. Various alkylbenzenes, including methyl- and ethylarenes, substituted alkylbenzenes containing acetoxy or cyclic acetal functionalities, and a cyclic benzyl ether could be efficiently oxidized. The same catalytic system can also be applied to the oxidation of alkanes as illustrated by Scheme 76 [110]. This catalytic procedure may serve as an alternative method for the existing industrial technology of preparation of cyclohexanone.

Ishihara and co-workers have reported the first example of hypervalent iodine(V)-catalyzed regioselective oxidation of phenols to *o*-quinones [111]. Various phenols could be oxidized to the corresponding *o*-quinones in good to excellent yields using catalytic amounts of sodium 2-iodo-5-methylbenzenesulfonate and stoichiometric amounts of Oxone as a co-oxidant under mild conditions; a representative example is shown in Scheme 77 [111].

5. Conclusions

This review demonstrates an active current interest in catalytic applications of iodine compounds. Compounds of iodine possess similar to transition metals reactivity, but have the advantage of environmental sustainability and efficient utilization of natural resources. Iodine is an environmentally friendly and a relatively inexpensive element, which is currently underutilized in industrial applications. We hope that this review will attract attention of industrial researchers to the benefits of using catalytic iodine in chemical technology as an environmentally sustainable alternative to transition metals.

Acknowledgment

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