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Organoiodine(V) Reagents in Organic Synthesis

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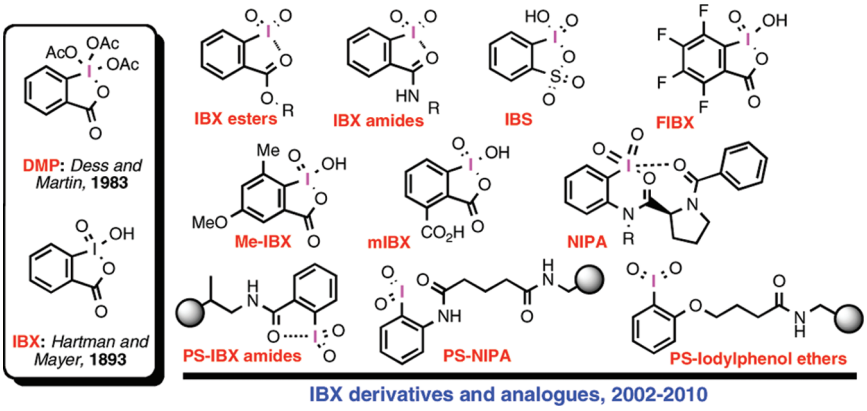

Organohypervalent iodine reagents have attracted significant recent interest as versatile and environmentally benign oxidants with numerous applications in organic synthesis. This Perspective summarizes synthetic applications of hypervalent iodine(V) reagents: 2-iodoxybenzoic acid (IBX), Dess−Martin periodinane (DMP), pseudocyclic iodylarenes, and their recyclable polymer-supported analogues. Recent advances in the development of new catalytic systems based on the generation of hypervalent iodine species in situ are also overviewed.

Introduction

Organohypervalent iodine reagents have attracted significant recent interest as versatile and environmentally benign oxidants with many applications in organic synthesis. Numerous reviews and book chapters summarizing various aspects of hypervalent iodine chemistry have been published just in the last 10 years.[1] Since the beginning of 21st century, the International Conference on Hypervalent Iodine Chemistry is regularly convened in Europe,[2] the Society of Iodine Science (SIS) holds annual meetings in Japan, and the American Chemical Society presents the National Award for Creative Research and Applications of Iodine Chemistry sponsored by SQM S.A. biennially in odd-numbered years. The most impressive recent achievements in the field of organoiodine chemistry include the development of numerous new hypervalent iodine reagents and the discovery of catalytic applications of organoiodine compounds.[1]

Within the broad field of hypervalent iodine chemistry, organoiodine(V) reagents occupy a special place. The interest in these compounds originated in 1983, when D. B. Dess and J. C. Martin published a short communication in *The Journal of Organic Chemistry* describing a simple two-step preparation of organoiodine(V) compound **3** via the bromate oxidation of 2-iodobenzoic acid **1** to 2-iodoxybenzoic acid (IBX, **2**) followed by conversion of IBX **2** to the triacetate **3** by heating with acetic anhydride (Scheme 1).[3] The authors have also found that the triacetate **3**, which they referred to as periodinane, is useful for the facile and efficient oxidation of primary alcohols to aldehydes and secondary alcohols to ketones. Within a few years after publication of this paper, compound **3** has received a widespread application in organic synthesis under the name of Dess−Martin periodinane (DMP), and the original communication[3] has become one of the most cited papers ever published in *J. Org. Chem.* (about 1900 citations according to the ISI Web of Science citation index data on December 2010).

Both IBX **2** and DMP **3** are now extensively employed in organic synthesis as mild and highly selective reagents for the oxidation of alcohols to carbonyl compounds as well as for a variety of other synthetically useful oxidative transformations.

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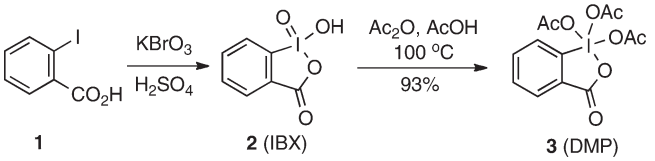


However, despite their importance, IBX and DMP are not perfect reagents and have some serious drawbacks. IBX is potentially explosive, and it is insoluble in common organic solvents due to the strong intermolecular secondary bonding creating a three-dimensional polymeric structure, while DMP is highly sensitive to moisture. In addition, IBX and DMP are not perfect with respect to the principles of Green Chemistry since they are normally used as the nonrecyclable, stoichiometric reagents in nonrecyclable organic solvents, which have potentially damaging environmental effects. A desire to improve IBX and DMP has been the driving force of recent research in the area of organoiodine(V) chemistry. It is the purpose of this Perspective to overview synthetic applications of IBX **2** and DMP **3** and to discuss advances in the development of safe and efficient new organoiodine(V) reagents including the recyclable, polymer-supported reagents. Recent progress in the development of catalytic systems based on the generation of hypervalent iodine species in situ is also overviewed.

2-Iodoxybenzoic Acid (IBX) and Its Analogues

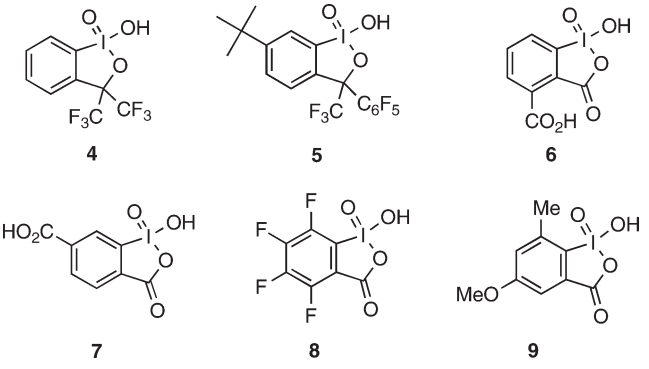
The most important representative of pentavalent iodine compounds, IBX **2**, was first prepared in 1893 by Hartman and Mayer.[4] The structure of IBX as cyclic benziodoxole oxide (1-hydroxy-1-oxo-1*H*-1λ^5-benzo[*d*][1,2]iodoxol-3-one according to the IUPAC nomenclature) has been established by X-ray structural analysis.[5] According to the original procedure, IBX is prepared by the oxidation of 2-iodobenzoic acid with potassium bromate in aqueous solution of sulfuric acid.[3,4] The samples of IBX prepared by this procedure were reported to be explosive under heating or impact, possibly due to the presence of bromate impurities.[6] In 1999 Santagostino and co-workers published a convenient and safe procedure for the preparation of IBX **2** by the oxidation of 2-iodobenzoic acid **1** using Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) in water at 70 °C.[7] This convenient protocol has become the most commonly used method for large scale preparation of IBX.

IBX in the solid state has a complex polymeric structure due to strong intermolecular secondary I···O contacts and hydrogen bonding. Stevenson and co-workers published a detailed X-ray diffraction study of IBX samples, which revealed the presence of the powder and the macrocrystalline forms of IBX.[5a] It was reported that the powder form of IBX is more reactive in the reaction with acetic anhydride than the macrocrystalline form and thus is more useful as the Dess–Martin periodinane precursor. Treatment of the macrocrystalline IBX with aqueous sodium hydroxide and then with HCl can be used to convert it to the more reactive powder form.[5a]

IBX is a potentially dangerous compound, and even the bromate-free samples of IBX are not safe. Santagostino and co-workers reported that as a rule pure IBX explodes at 233 °C.[7] The explosibility tests of analytically pure IBX samples (over 99% purity) confirmed the earlier observations by Plumb and Harper[6a] that IBX is explosive under impact or heating above 200 °C.

Quideau and co-workers have introduced a nonexplosive formulation of IBX (SIBX), consisting of IBX, benzoic acid, and isophthalic acid.[8] The synthetic utility of SIBX has been demonstrated on the reactions of hydroxylative phenol dearomatization,[8a–c] oxidation of sulfides into sulfoxides,[8d] oxidative demethylation of phenolic methyl aryl ethers,[8a] and other useful oxidative transformations.[8a,e]

Due to the polymeric structure, IBX is insoluble in most organic solvents except DMSO. Several research groups have tried to overcome this limitation by performing oxidation at elevated temperatures in other solvents,[9] using an ionic liquid as a reaction medium,[10] and functionalizing IBX aromatic core.[11–15] Numerous analogues of IBX based on a similar benziodoxole heterocyclic system[11] have been reported in the literature. In particular, Martin and co-workers have first introduced bis(trifluoromethyl)benziodoxole oxides **4** and **5**, which are stable and nonexplosive oxidizing reagents soluble in a wide range of organic solvents.[12] Vinod and co-workers have developed the water-soluble analogs of IBX, *m*-iodoxyphthalic acid (mIBX) **6**,[13a] and a similar derivative of terephthalic acid **7**,[13b] which can oxidize benzylic and allylic alcohols to carbonyl compounds in aqueous solutions. Wirth and co-workers have reported the preparation of the tetrafluoro IBX derivative (FIBX, **8**), which is more soluble in organic solvents and has higher reactivity than its nonfluorinated analogue.[14] Moorthy and co-workers have prepared *o*-methyl-substituted IBX (Me-IBX, **9**), which is the first modified analogue of IBX that oxidizes alcohols in common organic solvents at room temperature due to the hypervalent twisting-promoted rate enhancement.[15]



Our own efforts to improve IBX have led to the development of a thia analogue of IBX, 2-iodoxybenzenesulfonic acid **12**.[16] This compound can be prepared by two different pathways: hydrolysis of the methyl ester of 2-iodylbenzenesulfonic acid **10** or direct oxidation of 2-iodobenzenesulfonic acid **11** using Oxone in aqueous solution (Scheme 2). Thia-IBX **12** is a powerful oxidizing reagent, which, however, has low thermal stability. It readily decomposes in solution at room temperature with the formation of the related iodine(III) heterocycle, 2-iodosylbenzenesulfonic acid in the cyclic tautomeric form, as confirmed by single-crystal X-ray diffraction.[16] In a recent study, Ishihara and co-workers have demonstrated that thia-IBX **12** is the most powerful catalyst in the iodine(V)-catalyzed oxidation of alcohols using Oxone as a terminal oxidant.[17]

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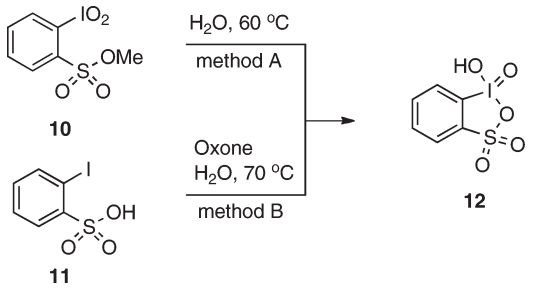

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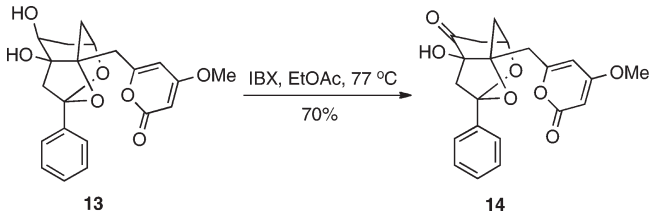

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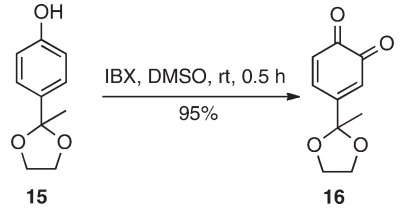

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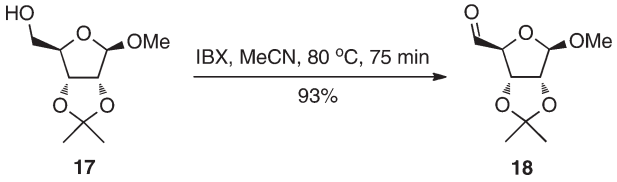


Synthetic Applications of IBX

Applications of IBX in organic synthesis have recently been summarized in a comprehensive review of Pati and coauthors.[1t] IBX is a particularly useful oxidant for the selective oxidation of alcohols to carbonyl compounds, even in complex molecules in the presence of other functional groups. Primary alcohols are oxidized by IBX in DMSO to the corresponding aldehydes at room temperature without overoxidation to the acids. The chiral primary alcohols are oxidized without epimerization, and various functional groups like thioethers, amines, carboxylic acids, esters, carboxamides, and both conjugated and isolated double bonds are compatible with IBX.[1t,18] Selective oxidation of alcohols using IBX has been utilized in numerous syntheses, such as: the total synthesis of (+)-wailupemycin B,[19a] the total synthesis of (−)-decarbamoyloxysaxitoxin,[19b] the total synthesis of abyssomicin C and atrop-abyssomicin C,[19c] the stereoselective synthesis of pachastrissamine (jaspine B),[19d] the syntheses of (±)-pterocarpans and isoflavones,[19e] the total synthesis of (±)-nitidanin,[19f] the total synthesis of lagunamycin,[19g] the synthesis of (−)-agelastatin,[19h] the syntheses of heliannuols B and D,[19i] the total syntheses of (−)-subincanadines A and B,[19j] the synthesis of marine sponge metabolite spiculoic acid A,[19k] the synthesis of optically pure highly functionalized tetrahydroisoquinolines,[19l] and the preparation of Fmoc-protected amino aldehydes from the corresponding alcohols.[19m]

Frigerio and Santagostino reported in 1994 that IBX, in contrast to DMP and iodoxybenzene derivatives, smoothly oxidizes 1,2-diols to α-ketols or α-diketones without cleaving the glycol C−C bond.[18a] More recently, Moorthy and coworkers have investigated the reactions of IBX with various vicinal diols and found that the oxidative cleavage of the C−C bond, as well as the oxidation to α-ketols or α-diketones, can occur in these reactions.[20] In DMSO solutions, IBX oxidatively cleaves strained and sterically hindered *syn* 1,2-diols, while the nonhindered secondary glycols are oxidized to α-ketols or α-diketones. The use of trifluoroacetic acid as a solvent leads to efficient oxidative fragmentation of 1,2-diols of all types.[20] The oxidation of 1,2-diols using IBX in DMSO has been utilized for the synthesis of α-ketols[19a,21] or α-diketones.[22] For example, in a key step of the total synthesis of the streptomyces maritimus metabolite wailupemycin B, IBX oxidation of the diol precursor **13** led to desired hydroxyketone **14** without any cleavage of the glycol C−C bond (Scheme 3).[19a]

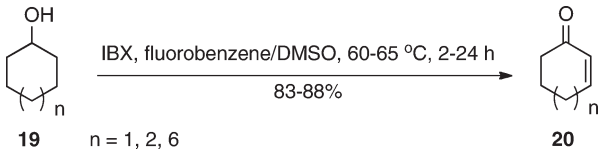
IBX in DMF has been shown to be an excellent reagent for the oxidation of various phenols to *o*-quinones.[23] This procedure was used for the oxidation of phenol **15** to quinone **16** (Scheme 4), a key intermediate in the total synthesis of a novel cyclooxygenase inhibitor (±)-aiphanol.[23b] Pettus and co-workers have utilized a similar protocol in the synthesis of (±)-brazilin, a tinctorial compound found in the alcoholic extracts of trees collectively referred to as Brazil wood.[23c]

The IBX-mediated oxygenative dearomatization of phenols leading to cyclohexa-2,4- or -2,5-dienone systems is a particularly useful synthetic transformation.[24a] Recent examples include the use of IBX in key oxidation steps in the total synthesis of the resveratrol-derived polyphenol natural products (−)-hopeanol and (−)-hopeahainol A,[24b] the synthesis of carnosic acid and carnosol,[27] and the total synthesis of the bissesquiterpene (+)-aquaticol.[8b]

Synthetic applications of IBX are significantly restricted by its insolubility at room temperature in most organic solvents with the exception of DMSO. However, it has been shown that IBX can be used as an effective oxidant in other than DMSO solvents at elevated temperatures.[9] More and Finney have found that primary and secondary alcohols can be oxidized into the corresponding aldehydes or ketones in excellent yields by heating a mixture of the alcohol and IBX to 55−80 °C in common organic solvents, such as chloroform, acetone, acetonitrile, ethyl acetate, and benzene.[9a] The reaction byproduct (predominantly 2-iodosylbenzoic acid) can be removed by filtration and reoxidized to give about 50% of recovered IBX. This method was used for preparation of the ribosyl aldehyde **18** from the corresponding alcohol **17** (Scheme 5), a key intermediate in the stereoselective synthesis of core structure of the polyoxin and nikkomycin antibiotics.[9b]

Practical value of IBX as a reagent has been extended to a variety of other synthetically useful oxidative transformations. Nicolaou and co-workers reported a one-pot procedure for the oxidation of alcohols, ketones, and aldehydes to the corresponding α,β-unsaturated species using IBX under

SCHEME 6



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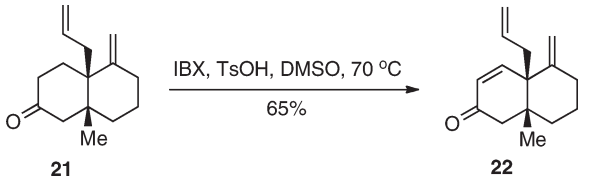

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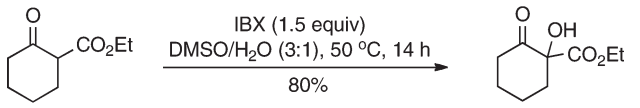


mild conditions. For example, cycloalkanols **19** react with 2 equiv of IBX in a 2:1 mixture of either fluorobenzene or toluene and DMSO at gentle heating to afford the corresponding α,β-unsaturated ketones **20** in good yields (Scheme 6).[25a] A similar oxidative dehydrogenation of a cyclohexanone derivative **21** to the respective enone **22** (Scheme 7) has recently been utilized in the total synthesis of (−)-anominine.[25b]

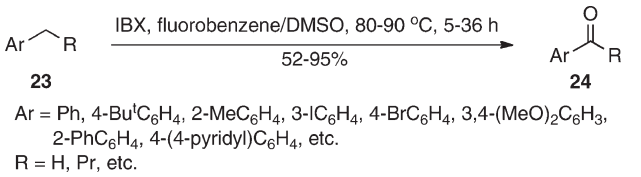
Kirsch and co-workers have further investigated the reactions of IBX with carbonyl compounds and found that depending on a functional group in the α-position of a carbonyl compound the reaction may lead either to the oxidative dehydrogenation (cf. Schemes 6 and 7) or to α-oxygenation.[25c−e] In particular, β-keto esters and some other suitably substituted carbonyl compounds can be selectively α-hydroxylated by treatment with IBX in aqueous DMSO at 50 °C; a representative example of the α-hydroxylation reaction is shown in Scheme 8.[25c]

IBX is an efficient and selective reagent for the oxidation of alkyl-substituted aromatic compounds **23** at the benzylic position to the corresponding carbonyl derivatives **24** (Scheme 9). This reaction is quite general and can tolerate a variety of substituents within the aromatic ring. Overoxidation to the corresponding carboxylic acids is not observed even in the presence of electron-rich substituents.[26a]

Similar to the oxidation of alcohols, secondary amines **25** can be oxidized with IBX in DMSO to yield the corresponding imines **26** in good to excellent yields (Scheme 10).[26b]

A variety of heterocycles **28** can be synthesized by the treatment of unsaturated aryl amides, carbamates, thiocarbamates, and ureas **27** with IBX (Scheme 11).[26c,d] The mechanism of this reaction has been investigated in detail.[26e] On the basis of solvent effects and D-labeling studies, it was proposed that the IBX-mediated cyclization of anilides in THF involves an initial single electron transfer (SET) to a THF−IBX complex followed by deprotonation, radical cyclization, and concluding termination by hydrogen abstraction from THF.[26e] A similar IBX-mediated cyclization was applied in the synthetic protocol for the stereoselective preparation of amino sugars.[26f]

SCHEME 9



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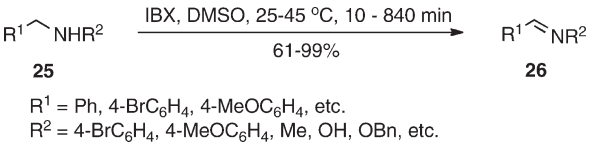

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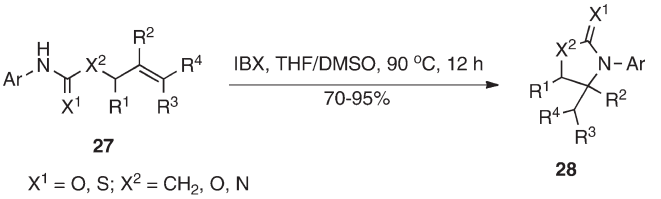

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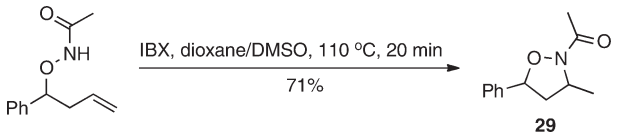

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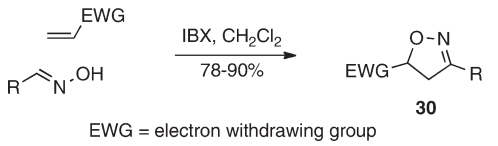


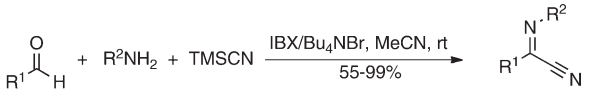
Studer and Janza reported a method for the generation of alkoxyamidyl radicals starting from the corresponding acylated alkoxyamines using IBX as a SET oxidant.[27] For example, the stereoselective 5-*exo* cyclization of the respective N-heteroatom-centered radical led to the formation of isoxazolidine **29** (Scheme 12).[27]

IBX has also been used for the preparation of the 3,5-disubstituted isoxazolines **30**. SET oxidation of substituted aldoximes with IBX in dichloromethane produces the respective nitrile oxide which then undergoes 1,3-dipolar addition with a suitable alkene component (Scheme 13).[28]

Zhu, Masson, and co-workers have reported a one-pot, three-component synthesis of α-iminonitriles **31** by IBX/tetrabutylammonium bromide-mediated oxidative Strecker reaction (Scheme 14).[29a] This methodology was applied to a two-step synthesis of indolizidine via a microwave-assisted intramolecular cycloaddition of α-iminonitrile.

The IBX-mediated oxidative Ugi-type multicomponent reaction of tetrahydroisoquinoline with isocyanides and

SCHEME 14



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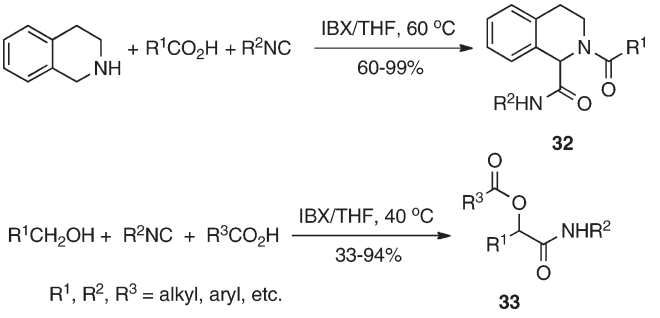

carboxylic acids affords the N and Cl functionalized tetrahydroisoquinolines **32** in good to excellent yields.[29b] Likewise, the three-component Passerini reaction of an alcohol, carboxylic acid, and an isonitrile in the presence of IBX affords the corresponding α-acyloxy carboxamides **33** in generally high yields (Scheme 15).[29c]

Additional representative examples of synthetic applications of IBX include the following oxidative transformations: the aromatization of tetrahydro-β-carbolines under mild conditions applied in a total synthesis of the marine indole alkaloid eudistomin U,[30a] the oxidation of glycosides to the respective 6-carbaldehydes used as precursors in the synthesis of amino-bridged oligosaccharides,[30b] the oxidation of amidoximes to carboxamides or nitriles with IBX or IBX/tetraethylammonium bromide,[30c] the aromatic hydroxylations of flavonoids,[30d] the hydroxylation of resveratrol diacyl derivatives,[30e] the synthesis of DOPA and DOPA peptides by oxidation of tyrosine residue,[30f] the oxidative preparation of γ-hydroxy-α-nitroolefins from α,β-epoxyketoximes,[30g] the aromatization of 1,4-dihydropyridines using IBX in water/acetone in the presence of β-cyclodextrin,[30h] the iodohydroxylation of alkenes and iodination of aromatics using IBX/I_2 in aqueous acetone,[30i] the conversion of alkenes and alkynes into α-iodo ketones using IBX/I_2 in water,[30j] the oxidation of primary amines to nitriles,[30k,l] the oxidative cleavage of acetals using IBX/tetraethylammonium bromide in water,[30m] the one-pot synthesis of trifluoromethyl-containing pyrazoles via sequential Yb(PFO)$_3$-catalyzed three-component reaction and IBX-mediated oxidation,[30n] the oxidative thiocyanation of indoles, pyrrole and arylamines,[30o] the oxidative functionalization of Baylis−Hillman adducts,[30p−r] the construction of multisubstituted 2-acyl furans by the IBX-mediated cascade oxidation/cyclization of *cis*-2-en-4-yn-1-ols,[30s] the one-pot synthesis of substituted salicylnitriles via oxidation of the corresponding imines with IBX,[30t] the conversion of indoles into isatins using indium(III) chloride/IBX,[30u] the synthesis of iminoquinones from anilines,[30v] and the oxidative transformation of primary carboxamides to one-carbon dehomologated nitriles.[30w]

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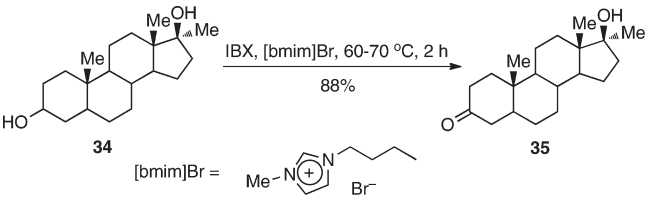

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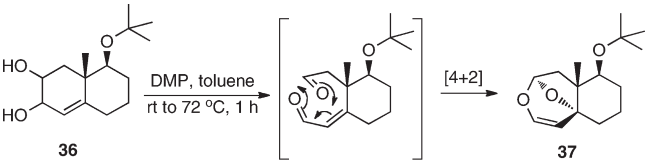


In recent years, ionic liquids have gained recognition as possible environmentally benign alternatives to the more volatile organic solvents. Several research groups have studied ionic liquids as recyclable polar reaction media for IBX-promoted oxidations.[10] Alcohols undergo smooth oxidation with IBX in [bmim]BF_4 and [bmim]PF_6 (bmim = 1-butyl-3-methylimidazolium) ionic liquids at room temperature under mild conditions to afford the corresponding carbonyl compounds in excellent yields with high selectivity.[10a] Similar results were obtained for the oxidation of alcohols with IBX using ionic liquid.[10b,c] IBX-promoted oxidations are faster in ionic liquids when compared to conventional solvents such as DMSO, DMF, ethyl acetate, and water. The recovered ionic liquids can be recycled in subsequent reactions with consistent activity.

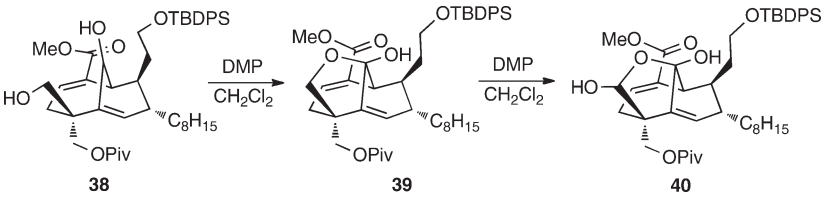
IBX immobilized in the ionic liquid [bmim]Br was found to be an efficient and eco-friendly reagent for the oxidation of 17α-methylandrostan-3β,17β-diol **34** to mestanolone **35** in good yield (Scheme 16).[10d] The product is easily separated from reaction mixture by extraction with diethyl ether.

Dess−Martin Periodinane (DMP)

In modern organic synthesis Dess−Martin periodinane has emerged as the reagent of choice for oxidation of primary and secondary alcohols to the respective carbonyl compounds. DMP is commercially available or can be conveniently prepared by the reaction of IBX with acetic anhydride in the presence of *p*-toluenesulfonic acid.[31]

Due to the mild reaction conditions (room temperature, absence of acidic or basic additives) and high chemoselectivity, DMP is especially suitable for the oxidation of alcohols containing sensitive functional groups, such as unsaturated moieties, amino groups, silyl ethers, phosphine oxides, sulfides, selenides, etc. In case of substrates sensitive to epimerization, DMP affords products of oxidation with virtually no loss of enantiomeric excess. Thus, the oxidation of N-protected β-amino alcohols with DMP afforded the respective aldehydes with 99% ee and excellent yields, while Swern oxidation gives unsatisfactory results (50−68% ee).[32a] The DMP oxidation is accelerated by the addition of water to the reaction mixture immediately before or during the reaction.[32b] The DMP oxidation of 1,2-diols generally cleaves the glycol C−C bond as illustrated by the synthesis of tricyclic enol ether **37**

SCHEME 18



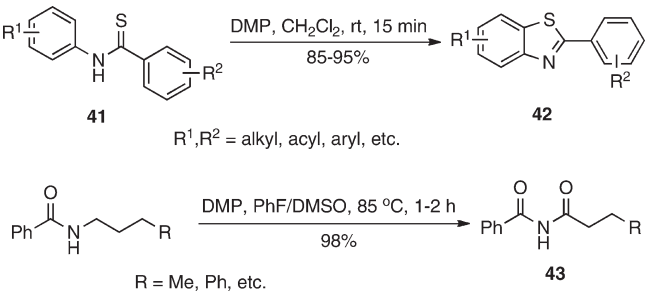
from diol **36** via tandem 1,2-diol cleavage−intramolecular cycloaddition (Scheme 17).[33]

Because of the unique oxidizing properties and convenience of use, DMP is widely employed in the synthesis of biologically important natural products. The most recent, representative examples include the use of DMP in key oxidation steps of the following synthetic works: the synthesis of glycosaminoglycan oligosaccharides, which are potential inhibitors of the enzyme heparanase,[34a] the first catalytic asymmetric total synthesis of *ent*-hyperforin,[34b] the total synthesis of (−)-spirotryprostatin B,[34c] an enantioselective total synthesis of (+)-peloruside A,[34d] an enantioselective synthesis of the antifungal natural product (+)-ambruticin S,[34e] the synthesis of the pentacyclic core of ecteinascidin 743,[34f] the synthesis of the marine natural product iriomoteolide-1a,[34g,h] the synthesis of the tetracyclic core of tetrapetalone A,[34i] the synthesis of a potent antitumor therapeutic 7-Epi (+)-FR900482,[34j] the formal total synthesis of (±)-platensimycin,[34k] the total synthesis of (−)-pseudolaric acid B,[34l] the synthesis of azadirachtin,[34m] the asymmetric synthesis of salvinorin A,[34n] the synthesis of the C31−C67 fragment of amphidinol 3,[34o] and an efficient synthetic approach to the hypoestoxide and verticillane family of natural products.[34p]

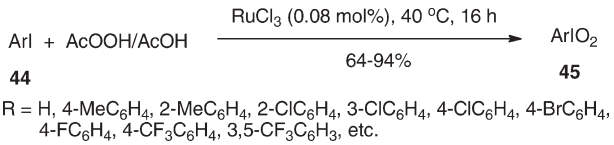
The unique oxidizing properties of DMP can be illustrated by its application in the total synthesis of the CP-molecules, lead structures for cardiovascular and anticancer drugs, published by Nicolaou and co-workers.[35] In this synthetic investigation, a hindered secondary alcohol **38** was oxidized with DMP to the stable diol **40** through intermediate hemiketal **39** (Scheme 18).

The practical value of DMP as a reagent was recently extended to a variety of other synthetically useful oxidative transformations, such as: the dehydration of primary alcohols under extraordinarily mild conditions,[36a] the synthesis of various polycyclic heterocycles via the oxidative cascade cyclization of anilides with pendant double bonds,[36b] the one-pot oxidative allylation of Morita−Baylis−Hillman adducts with allyltrimethylsilane promoted by DMP/$BF_3 \cdot OEt_2$,[36c] the synthesis of 2-amino-1,4-benzoquinone-4-phenylimides from anilines via DMP oxidation,[36d] the α-tosyloxylation of ketones using DMP and *p*-toluenesulfonic acid,[36e] the synthesis of 2-substituted benzothiazoles **42** via oxidative cyclization of thioformanilides **41**,[36f] and the synthesis of imides (e.g., **43**), *N*-acyl vinylogous carbamates and ureas, and nitriles by the oxidation of amides and amines with DMP (Scheme 19).[36g]

SCHEME 19



SCHEME 20



Noncyclic and Pseudocyclic Iodylarenes

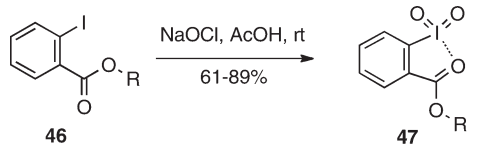
Iodylarenes, $ArIO_2$, which are also known as iodoxy compounds, are commonly prepared by direct oxidation of iodoarenes with strong oxidants or by disproportionation of iodosylarenes. It is assumed that the initial oxidation of ArI usually leads to iodosylarenes, ArIO, which then slowly disproportionate to ArI and $ArIO_2$ upon gentle heating or even at room temperature.[37] The most common oxidizing reagents that are used for the preparation of iodylarenes from iodoarenes include sodium hypochlorite, sodium periodate, dimethyldioxirane, and Oxone. Dry iodylarenes are potentially hazardous compounds, which may explode upon impact, scratching with a spatula, or heating and therefore should be handled with appropriate precautions.

Recently, we have reported a new facile methodolology for the preparation of noncyclic iodylarenes **45** from iodoarenes **44** using peracetic acid as an oxidant in the presence of catalytic amounts of ruthenium trichloride.[38] This procedure allows the preparation of several previously unknown iodylarenes **45** bearing strongly electron-withdrawing CF_3 groups in the aromatic ring (Scheme 20).[38b]

Iodylbenzene, $PhIO_2$, has a polymeric structure, which makes it insoluble in the majority of organic solvents, with the exception of DMSO. X-ray crystal structural investigations of $PhIO_2$ revealed infinite polymeric chains with strong I···O secondary intermolecular interactions.[39] Iodylbenzene and other noncyclic iodylarenes in general have found only very limited practical application due to their low solubility, low stability, and explosive properties.

Aryliodyl derivatives bearing an appropriate substituent in the *ortho* position to the iodine are characterized by the presence of a pseudocyclic structural moiety due to a strong intramolecular secondary bonding between the hypervalent iodine center and the oxygen atom in the *ortho* substituent. Compared to the noncyclic aryliodyl derivatives, pseudocyclic iodine(V) compounds have much better solubility, which is explained by a partial disruption of their polymeric nature

SCHEME 21

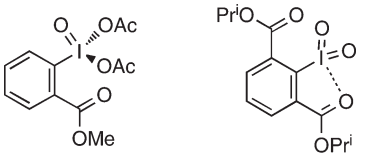


R = Me, Et, Pr^i, (-)-menthyl, (+)-menthyl, (±)-menthyl, [(1*S*)-endo]-(–)-bornyl, 2-adamantyl, 1-adamantyl, Bu^t

due to the redirection of secondary bonding.[37a−c] The first pseudocyclic iodylarene of this type, 1-(*tert*-butylsulfonyl)-2-iodylbenzene, was reported by Protasiewicz and co-workers in 2000.[37a] Single-crystal X-ray structural analysis of this iodylarene showed a relatively short intramolecular distance of 2.693 Å between one of the sulfone oxygen atoms and the hypervalent iodine center.

We have prepared previously unknown esters of 2-iodoxybenzoic acid (IBX-esters, **47**) by the hypochlorite oxidation of readily available esters of 2-iodobenzoic acid **46** (Scheme 21).[40] This procedure can be used for the preparation of products **47** derived from various types of alcohols, such as primary, secondary, and tertiary alcohols, adamantanols, optically active menthols and borneol. X−Ray data on products **47** revealed a pseudobenziodoxole structure in which the intramolecular I···O secondary bonds partially replace the intermolecular I···O secondary bonds disrupting the polymeric structure characteristic of $PhIO_2$[39] and other previously reported iodylarenes. This structural feature substantially increases the solubility of IBX-esters in comparison to other iodine(V) reagents and affects their oxidizing reactivity. IBX-esters can oxidize alcohols to the respective aldehydes or ketones in the presence of trifluoroacetic acid or boron trifluoride etherate.[40] Isopropyl 2-iodoxybenzoate **47** (R = Pr^i) is a particularly useful reagent for the clean and selective oxidation of organic sulfides to sulfoxides.[41a] This reaction proceeds without overoxidation to sulfones and is compatible with the presence of the hydroxy group, double bond, phenol ether, benzylic carbon, and various substituted phenyl rings in the molecule of organic sulfide. We have also found that IBX-esters **47** can serve as stable and efficient sources of oxygen in the metalloporphyrin-catalyzed oxidations of hydrocarbons, and reactivity of isopropyl 2-iodoxybenzoate as an oxygenating reagent is similar to the reactivity of commonly used iodosylbenzene, which is a thermally unstable and potentially explosive compound.[41b,c] Duschek and Kirsch have recently reported that isopropyl 2-iodoxybenzoate in the presence of trifluoroacetic anhydride can be used for α-hydroxylation of β-keto esters (cf. Scheme 8) at room temperature in THF.[25c]

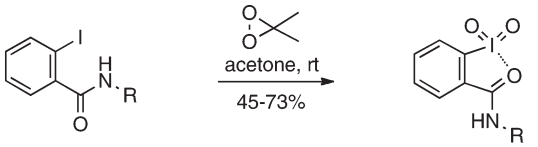
Methyl 2-iodoxybenzoate **47** (R = Me) can be further converted to the diacetate **48** or a similar bis(trifluoroacetate) derivative by treatment with acetic anhydride or trifluoroacetic anhydride, respectively. Single-crystal X-ray diffraction analysis of methyl 2-[(diacetoxy)iodosyl]benzoate **48** revealed a pseudobenziodoxole structure with three relatively weak intramolecular I···O interactions. The dimethyl and diisopropyl esters of 2-iodoxyisophthalic acid were prepared by oxidation of the respective iodoarenes with dimethyldioxirane. Single crystal X-ray diffraction analysis of diisopropyl 2-iodoxyisophthalate **49** showed intramolecular I···O interaction with the carbonyl oxygen of only one of the two carboxylic groups, while NMR spectra in solution indicated equivalency of both ester groups.[40b]



48 **49**

Amides of 2-iodoxybenzoic acid (IBX-amides, **51**) were prepared by the dimethyldioxirane oxidation of the appropriate derivatives of 2-iodobenzoic acid **50** (Scheme 22) in the form of stable, microcrystalline solids moderately soluble in dichloromethane and chloroform.[42] This procedure (Scheme 22) can be used for the preparation of products **51** derived from various types of amino compounds, such as esters of α-amino acids, esters of β-amino acids, and (*R*)-1-phenylethylamine. Single-crystal X-ray analysis of the phenylalanine derivative **51** [R = (*S*)-CH(CH$_2$Ph)CO$_2$Me] revealed a close intramolecular contact of 2.571 Å between the hypervalent iodine center with the oxygen atom of the amido group within each molecule enforcing a planar geometry of the resulting five-membered ring, a geometry that is analogous to that observed for IBX and other benziodoxoles.[42]

SCHEME 22



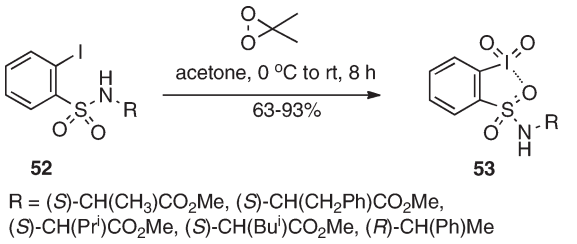
R = (*S*)-CH(CH$_3$)CO$_2$Me, (*R*)-CH(CH$_3$)CO$_2$Me, (*S*)-CH(CH$_2$Ph)CO$_2$Me, (*S*)-CH(Bu^i)CO$_2$Me, CH$_2$CH$_2$CO$_2$H, CH(CH$_3$)CH$_2$CO$_2$H, (*R*)-CH(Ph)Me

2-Iodoxybenzamides **51** are useful oxidizing reagents toward alcohols with a reactivity pattern similar to that of IBX. A wide range of primary and secondary alcohols can be oxidized by these reagents to the respective carbonyl compounds in excellent yields under mild conditions in chloroform.[42,43] Oxidative kinetic resolution of racemic *sec*-phenethyl alcohol using reagents **51** has shown very low enantioselectivity (1−6% ee).[43]

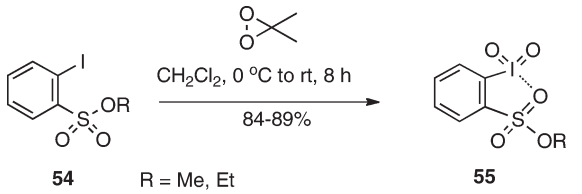
Amides of 2-iodoxybenzenesulfonic acid **53** were prepared by the dioxirane oxidation of the corresponding 2-iodobenzenesulfamides **52** and isolated as stable, microcrystalline products (Scheme 23).[44a] Single-crystal X-ray structures of 2-iodylbenzenesulfonamides reveal a combination of intra- and intermolecular I···O interactions leading to a unique heptacoordinated iodine(V) center in the alanine derivative **53** [R = (*S*)-CH(CH$_3$)CO$_2$Me].[44b] Likewise, esters of 2-iodoxybenzenesulfonic acid **55** were prepared by the dioxirane oxidation in dichloromethane of the respective monovalent iodine derivatives **54** (Scheme 24). These new pseudocyclic hypervalent iodine reagents can selectively oxidize benzyl alcohols to aldehydes, secondary amines to imines, and sulfides to sulfoxides.[44c]

The soluble and stable IBX analogues having pseudobenziodoxazine structure, *N*-(2-iodylphenyl)acylamides (NIPA) **57**, were prepared in good yields by the oxidation of 2-iodoaniline derivatives **56** with dimethyldioxirane under mild

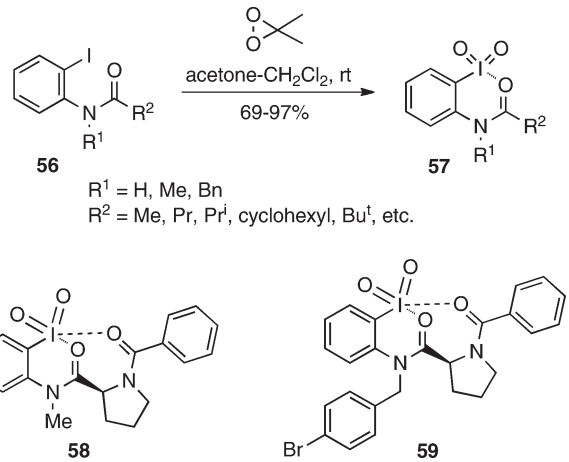
SCHEME 23



SCHEME 24



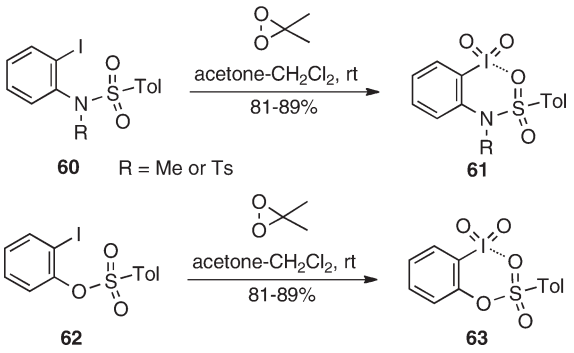
SCHEME 25



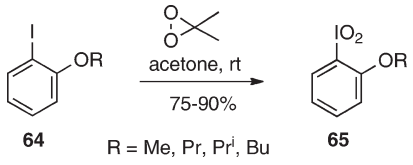
conditions (Scheme 25).[45a] X-ray data on compounds **57** revealed a unique pseudobenziodoxazine structure with a short intramolecular secondary I···O bonding (2.647 Å). NIPA reagents **57** can selectively oxidize either alcohols or sulfides, with the reactivity depending largely on the substitution pattern on the amide group adjacent to the iodyl moiety.[45a] The synthesis of chiral NIPA reagents **58** and **59** has been carried out on the basis of inexpensive and readily available (*S*)-proline.[45b] The evaluation of these compounds as enantioselective oxidizing reagents toward a racemic alcohol, *meso*-diol, and a sulfide was performed and moderate enantioselectivities of 29−41% were achieved. These results indicate that the NIPA scaffold is a promising structure for further elaboration of chiral iodine(V) oxidants.[45b]

Similarly to the NIPA derivatives, the tosyl derivatives of 2-iodylaniline **61** and 2-iodylphenol **63** were prepared by the dimethyldioxirane oxidation of the corresponding 2-iodophenyltosylamides **60** or 2-iodophenyl tosylate **62** (Scheme 26) and isolated as stable, microcrystalline products.[46] Single-crystal X-ray diffraction analysis of tosylamide **61** (R = Me) revealed pseudocyclic structure formed by intramolecular I···O interactions between the hypervalent iodine center and the sulfonyl oxygens in the tosyl group. Tosylamide **61**

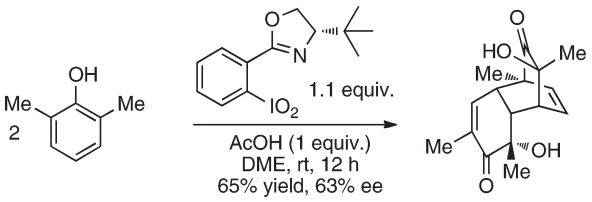
SCHEME 26



SCHEME 27



SCHEME 28



(R = Me) has an excellent solubility in organic solvents and is a potentially useful hypervalent iodine oxidant.

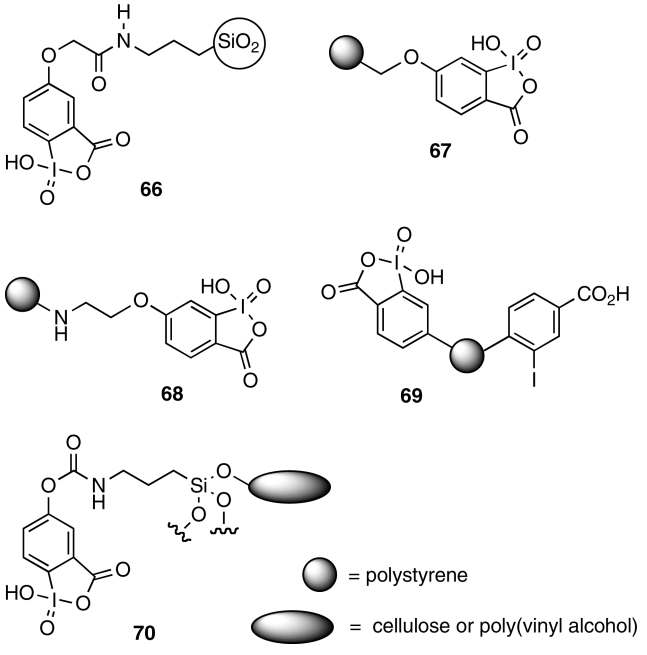
A similar oxidation of 2-iodophenol ethers **64** afforded 2-iodylphenol ethers **65** (Scheme 27), which were isolated as the soluble, stable compounds.[46b] Structures of 1-iodyl-2-isopropoxybenzene and 1-iodyl-2-butoxybenzene were established by single-crystal X-ray diffraction analysis. 2-Iodylphenol ethers **65** can selectively oxidize sulfides to sulfoxides and alcohols to the respective aldehydes or ketones.[46b]

Birman and Boppisetti have recently reported the preparation of several chiral 2-(*o*-iodoxyphenyl)-oxazolines.[47] These compounds have been found to transform *o*-alkylphenols into *o*-quinol Diels−Alder dimers with significant levels of asymmetric induction (Scheme 28).

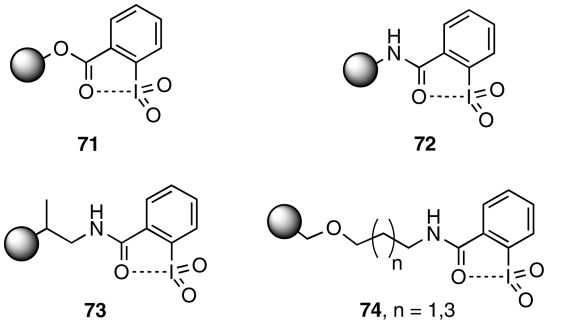
Polymer-Supported Recyclable Iodine(V) Oxidants

Despite their useful reactivity and environmentally benign nature, the hypervalent iodine(V) reagents discussed in previous sections are not perfect with respect to the principles of Green Chemistry. According to one of the basic principles of Green Chemistry, catalytic or recyclable reagents are superior to stoichiometric reagents.[48] Reactions of monomeric hypervalent iodine reagents with organic substrates lead to the respective iodoarenes as byproducts, which in general are not recoverable from a reaction mixture. Polymer-supported modifications of hypervalent iodine reagents retain the useful reactivity of their monomeric analogues with the added advantage of being readily recyclable and reusable.

The preparation and oxidative reactivity of several polymer-supported analogues of IBX have been reported.[49] Giannis and Mülbaier have developed the aminopropylsilica gel based reagent **66**, which can oxidize various primary and secondary alcohols to the respective carbonyl compounds in excellent yields at room temperature in THF under heterogeneous conditions and can be regenerated by oxidation with Oxone without any loss of activity.[49a] Rademann and co-workers prepared the polystyrene-based polymeric analogue of IBX **67**, which was characterized by IR spectroscopy, elemental analysis, and MAS NMR spectroscopy.[49b] Reagent **67** oxidizes various primary, secondary, benzylic, allylic, terpene alcohols, and the carbamate-protected amino alcohols to afford the respective aldehydes or ketones in excellent yields, and it can be recycled by repeated oxidation after extensive washings. Lei and co-workers have developed a polymer-supported IBX derivative **68**, which has the advantages of a simplified preparation method and a high oxidation activity of 1.5 mmol/g.[49c] A conceptually different approach was used by Sutherland and co-workers for the preparation of the polystyrene-based reagent **69**; in this procedure, the iodobenzoic acid moiety was introduced directly to the resin backbone by the iodination/oxidation sequence.[49d] Hatton and co-workers reported the preparation of functional organic–inorganic colloids **70** modified by IBX.[49e]



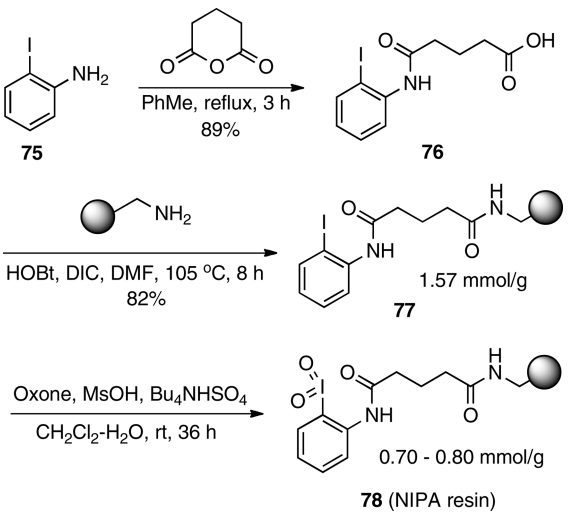
The presence of a functional group in the *ortho*-position of pseudocyclic iodylarenes **47**, **51**, and **57** provides a convenient opportunity of linking a hypervalent iodine(V) reagent to the polymeric backbone. Based on our preparation of IBX-esters **47** and IBX-amides **51**, Lee and co-workers have synthesized the polymer-supported analogues **71**–**73** starting from commercially available hydroxy or amino polystyrene.[50a,b] Resins **71**–**73** were prepared with loadings of 0.65–1.08 mmol/g and were evaluated with a series of alcohol substrates. Polymer-supported IBX-amide **73** exhibited particularly efficient oxidative activities toward a series of alcohols under mild reaction conditions.[50a,b] IBX-amide resin **73** is also an efficient oxidant for oxidative bromination of activated aromatic compounds using tetraethylammonium bromide.[50c] Linclau and co-workers reported an improved synthesis of a solid-supported IBX-amide resins **74** using inexpensive and commercially available 2-iodobenzoyl chloride and Merrifield resin.[50d] Oxidation of various alcohols to the corresponding carbonyl compounds can be accomplished using 1.2 equivalents of resin **74**. Recycling of the resin was also possible with minimal loss of activity after two reoxidations.[50d]



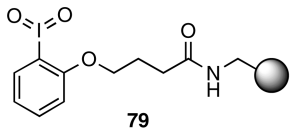
We have prepared a polymer-supported version of *N*-(2-iodylphenyl)acylamides (NIPA, **57**) in three simple steps.[51] Commercially available 2-iodoaniline **75** was reacted with glutaric anhydride to give the acid **76**, which was subsequently coupled to aminomethylpolystyrene with 1-hydroxy-1*H*-benzotriazole/diisopropylcarbodiimide (HOBt/DIC) to give the resin **77**. Oxidation of resin **77** to NIPA resin **78** was performed in a CH_2Cl_2–H_2O biphasic system using Oxone, Bu_4NHSO_4, and methanesulfonic acid (Scheme 29). NIPA resin **78** was shown to effect smooth and efficient oxidation of a broad variety of alcohols to the respective carbonyl compounds.[51] The polymeric material, resulting from the reduction of NIPA resin, can be collected and reoxidized according to the procedure described above (Scheme 29). A moderate decline in oxidative activity is observed after multiple recovery steps.

Polymer-supported analogues of 2-iodylphenol ethers **65** have also been reported.[52] Resins **79** and **80** were prepared starting from commercially available 2-iodophenol and aminomethylated polystyrene or Merrifield resin using 4-hydroxybutanoic acid and 1,4-butanediol, respectively, as linkers.

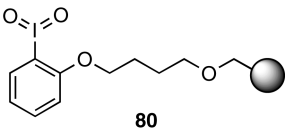
SCHEME 29



These polymer-supported reagents effect clean and efficient conversion of a wide range of alcohols, including heteroatomic and unsaturated structures, to the corresponding carbonyl compounds. Recycling of the resins is possible with minimal loss of activity after several reoxidations.[52]



79 loading up to 0.86 mmol/g

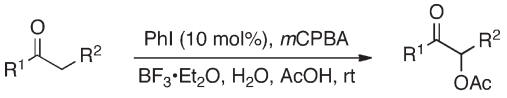


80 loading up to 0.81 mmol/g

Catalytic Application of Hypervalent Iodine Reagents

The discovery of catalytic reactions based on hypervalent iodine species is one of the most impressive recent achievements in the field of organoiodine chemistry, which has been overviewed in several feature articles by Wirth,[53] Ochiai,[1n] Kita,[1m] Ishihara,[1q] and Lupton.[1r] Numerous examples of reactions based on the iodine(I)/iodine(III) or iodine(I)/iodine(V) catalytic cycles have been reported in the last five to six years. In 2005, Ochiai and coauthors reported the first PhI-catalyzed reaction, a catalytic variant of α-acetoxylation of ketones based on the in situ generation of (diacetoxyiodo)-benzene from iodobenzene using *m*-chloroperbenzoic acid (*m*CPBA) as a terminal oxidant (Scheme 30).[54]

SCHEME 30

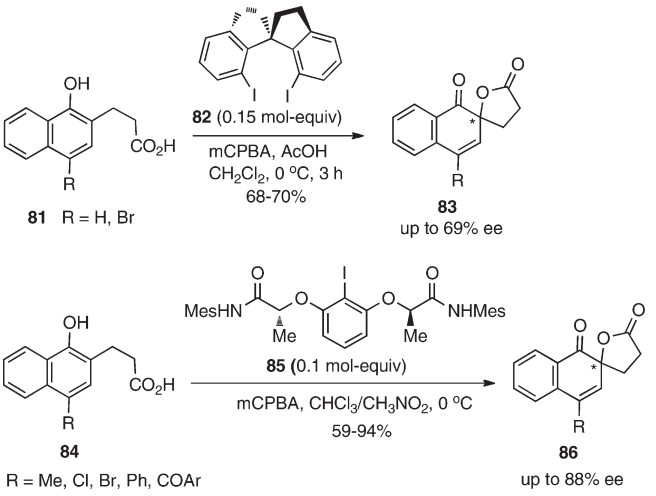


Since 2005, several other reactions based on the generation of iodine(III) species have been reported. Most impressive recent examples include the enantioselective catalytic oxidative spirocyclization reactions of phenolic substrates using chiral organic iodides as the catalysts.[55] In particular, the chiral catalyst **82** with a rigid spirobiindane backbone was reported to enantioselectively dearomatize naphtholic substrates **81** in a highly selective manner giving optically active products **83** with up to 69% ee (Scheme 31).[55a] Ishihara and co-workers designed a conformationally flexible C_2-symmetric iodoarene catalyst **85** for a similar enantioselective oxidative spirolactonization.[55b,c] Hydroxynaphthalenyl propanoic acid derivatives **84** underwent dearomatization and spirocyclization in the presence of catalyst **85** to afford the corresponding spirolactones **86** in yields up to 94% with enantioselectivity up to 88% (Scheme 31).

Most recently, Ishihara and co-workers reported the chiral quaternary ammonium iodide catalyst **88** for highly enantioselective oxidative cycloetherification of substrates **87** using hydrogen peroxide as the stoichiometric oxidant (Scheme 32).[55d]

A catalytic version of the intermolecular oxidative coupling of phenolic ethers using [bis(trifluoroacetoxy)iodo]benzene (0.125 equiv) as a catalyst and *m*CPBA as the stoichiometric oxidant has also been reported.[56] Kita and co-workers have developed a H_2O_2/acid anhydride system for the iodoarene-catalyzed intramolecular C−C cyclization of phenolic derivatives; a representative example of this catalytic cyclization is shown in Scheme 33.[56b]

SCHEME 31



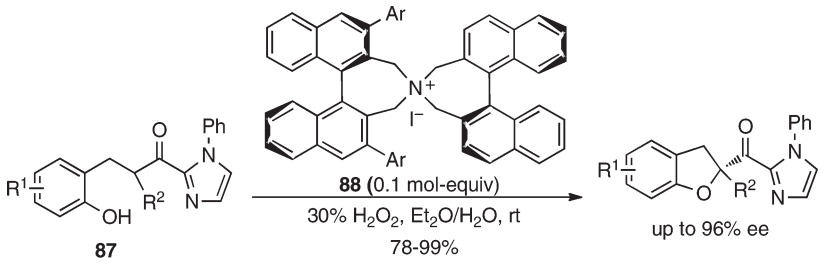
We have found that hypervalent iodine species have a pronounced catalytic effect on the metalloporphyrin-mediated oxygenations of aromatic hydrocarbons.[57] In particular, the oxidation of anthracene **89** to anthraquinone **91** with Oxone readily occurs at room temperature in aqueous acetonitrile in the presence of 5−20 mol % of iodobenzene and 5 mol % of a water-soluble iron(III)−porphyrin complex **90** (Scheme 34). 2-*tert*-Butylanthracene and phenanthrene also can be oxygenated under similar conditions in the presence of 50 mol % of iodobenzene. The oxidation of styrene in the presence of 20 mol % of iodobenzene leads to a mixture of products of epoxidation and cleavage of the double bond. Partially hydrogenated aromatic hydrocarbons (e.g., 9,10-dihydroanthracene, 1,2,3,4-tetrahydronaphthalene, and 2,3-dihydro-1*H*-indene) afford under these conditions products of oxidation at the benzylic position in moderate yields.[57]

The proposed mechanism for these catalytic oxidations (Scheme 33) includes two catalytic redox cycles: (1) initial oxidation of iodobenzene with Oxone producing hydroxy(phenyl)iodonium ion and hydrated iodosylbenzene and (2) the oxidation of iron(III)−porphyrin to the oxoiron(IV)−porphyrin cation−radical complex by the intermediate iodine(III) species. The oxoiron(IV)−porphyrin cation−radical complex acts as the actual oxygenating agent toward aromatic hydrocarbons.[57]

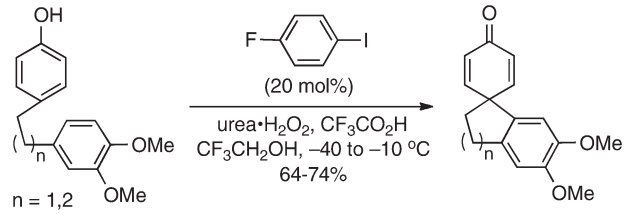
First examples of catalytic application of the iodine(V) species in the oxidation of alcohols using Oxone as a stoichiometric oxidant were independently reported by the groups of Vinod[58a] in 2005 and Giannis[58b] in 2006. The iodine(V)-based catalytic cycles employing Oxone as a -stoichiometric oxidant have been used for the oxidation of alcohols (Scheme 35)[17,58] and the oxidation of benzylic C−H bonds.[59] For example, Ishihara and coauthors have developed an optimized procedure for the catalytic oxidation of alcohols using 2-iodylbenzenesulfonic acid as an extremely active catalyst and Oxone as terminal oxidant.[17] However, the synthetic value of the iodine(V) based catalytic cycle is limited by the reoxidation step of iodine(I) or iodine(III) to the iodine(V) species, which proceeds relatively slowly even at temperatures above 70 °C.[17,58,59]

On the basis of our studies of $RuCl_3$-catalyzed disproportionation of iodine(III) species to iodobenzene and iodylbenzene,[38]

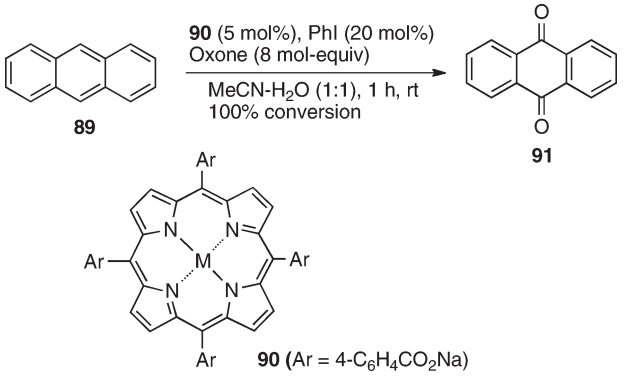
SCHEME 32



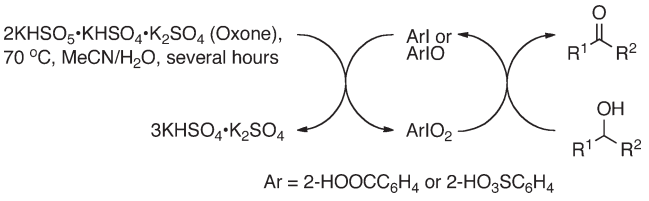
SCHEME 33



SCHEME 34



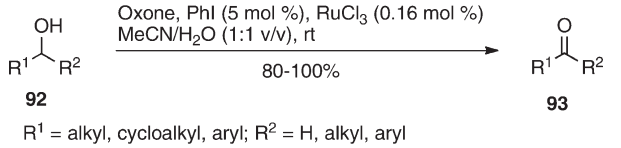
SCHEME 35



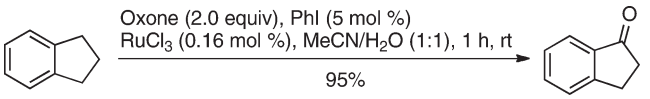
we have developed an extremely mild and efficient tandem catalytic system for the oxidation of alcohols and hydrocarbons via a Ru(III)-catalyzed reoxidation of ArIO to $ArIO_2$ using Oxone as a stoichiometric oxidant.[60] In particular, various alcohols **92** are smoothly oxidized in the presence of catalytic PhI and $RuCl_3$ in aqueous acetonitrile to afford the respective oxidation products **93** in excellent isolated yields at room temperature (Scheme 36).[60]

Likewise, various alkylbenzenes are selectively oxidized under these mild catalytic conditions to respective aromatic ketones in high yield; a representative example is shown in Scheme 37.[60] Compared to the high-temperature IBX/Oxone procedure,[59] our protocol is much more selective and

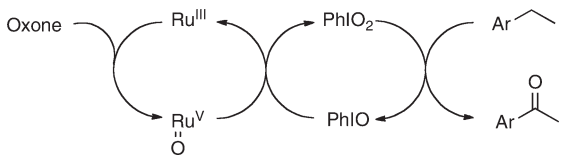
SCHEME 36



SCHEME 37



SCHEME 38



generally does not afford products of C−C bond cleavage and carboxylic acids.

A plausible, simplified mechanism for these catalytic oxidations includes two catalytic redox cycles (Scheme 38).[60] The reaction starts with the initial oxidation of PhI to PhIO and then to $PhIO_2$ by the Oxone/Ru(III,V) system. The generated in situ, highly active monomeric $PhIO_2$ species are responsible for actual oxidation of organic substrates by known mechanisms.

Conclusion and Outlook

The field of hypervalent iodine(V) chemistry has tremendously grown since 1983, when D. B. Dess and J. C. Martin published a groundbreaking communication describing the preparation and reactions of periodinane **3**.[3] The survey of current literature on organoiodine(V) chemistry demonstrates an active current interest in synthetic applications of the traditional benziodoxole based oxidants, IBX and DMP. At the same time, numerous new organoiodine(V) reagents have recently been developed, and it is anticipated that these safe and efficient derivatives and analogues of IBX will find widespread synthetic application in the future. The discovery of recyclable reagents and catalytic systems based on the iodine redox chemistry has initiated a major surge of research activity and added a new dimension to the field of hypervalent iodine chemistry. Taking into account the importance of

environmental aspects, it can be expected that the current trend toward synthetic application of recyclable reagents and catalytic systems based on hypervalent iodine chemistry will continue in the future. We hope and anticipate that recent studies described in this Perspective will provide a stimulus for further advances in the field of hypervalent organoiodine chemistry.

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