Hypervalent iodine(V) reagents in organic synthesis

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Abstract
This review summarizes the synthetic applications of hypervalent iodine(V) reagents: iodylbenzene, IBX (2-iodoxybenzoic acid), DMP (Dess-Martin periodinane) and pseudocyclic IBX analogs. Application of these reagents allows mild and highly selective oxidative transformations in a facile and environmentally friendly manner.

Keywords: Hypervalent iodine, oxidation, iodylbenzene, IBX, DMP

Contents

1. Introduction

In the past decade, the organic chemistry of hypervalent iodine compounds has experienced an immense development. This growing interest in iodine compounds is due to the mild and highly chemoselective oxidizing properties of polyvalent organic iodine reagents, combined with their benign environmental character and commercial availability. A variety of new chemical

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transformations effected by hypervalent iodine reagents have recently been developed by many synthetic chemists. These protocols include catalytic imidations with iodonium imides, hypervalent iodine mediated oxidative coupling of phenols and related compounds, applications of iodine(III) compounds as useful carbene and nitrene precursors and the broad synthetic applications of hypervalent iodine heterocycles derived from benziodoxoles and benziodazoles. Many reviews, some comprehensive, but most dealing with specific aspects of hypervalent organoiodine chemistry, have been published just in the last 5-6 years.[1-34] Most notable are the monograph by Varvoglis on the application of hypervalent iodine compounds in organic synthesis[1] and the volume of Topics in Current Chemistry on hypervalent iodine chemistry.[2]

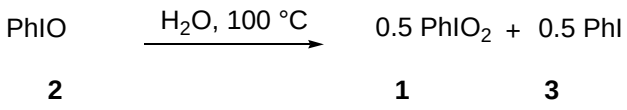
Despite being less developed in comparison with trivalent iodine reagents, the chemistry of iodine(V) compounds (λ^5-iodanes) has also attracted substantial attention in recent years. This widespread practical interest to λ^5-iodanes is mainly due to Dess-Martin periodinane (DMP) and, especially, to 2-iodoxybenzoic acid (IBX), both of which are mild and useful oxidizers for alcohols and amines, for conversions of carbonyl compounds to the respective α,β-unsaturated derivatives and for effecting a number of other unique and useful synthetic transformations. Various IBX analogs, having better solubility profile and/or being recyclable, have emerged recently. Several aspects of λ^5-iodanes have been highlighted in chemical literature.[25-26, 32-34] However, the chemistry of iodine(V) reagents have never been systematically reviewed. The purpose of the present review is to summarize the recent literature data on synthetically useful hypervalent iodine(V) reagents; literature coverage is through the first half of 2005.

2. Iodylbenzene and other noncyclic reagents

The noncyclic iodyl (also known as iodoxy) compounds, RIO_2, in general have found only very limited practical application due to their low stability. While the aryl derivatives, $ArIO_2$, can form relatively stable compounds, iodylalkanes are extremely unstable and can exist only at very low temperatures. Thus, Clark and coworkers reported the matrix isolation and FTIR spectra of the unstable iodyl derivatives, RIO_2, generated by the co-deposition and photolysis of ozone with iodoethane, 2-iodopropane, pentafluoroiodoethane, 1,1,1-trifluoroiodoethane, 1,1,2,2-tetrafluoroiodoethane, 1,1,1,2-tetrafluoroiodoethane, or iodine cyanide in an argon matrix at 14-16 K.[35-37]

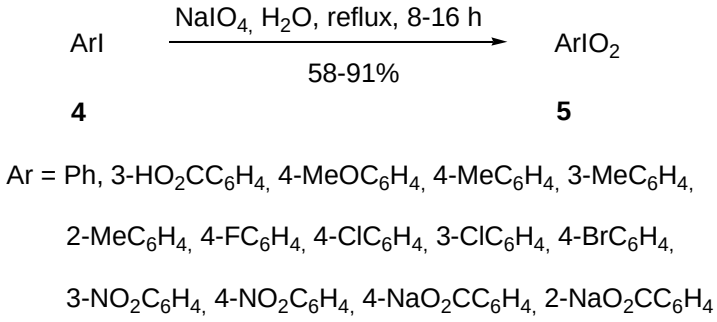
Several noncyclic $ArIO_2$ have been reported in the literature. These compounds possess a polymeric structure, which makes them insoluble in the majority of organic solvents, with the exception of DMSO. Structural investigations revealed infinite polymeric chains with strong I···O secondary intermolecular interactions.[38-39] Also noncyclic iodylarenes are explosive under excessive heating (> 200 ^oC) or mechanical impact. Despite their low solubility and explosive character, iodylarenes have found some practical application as oxidizing reagents. Among various $ArIO_2$, iodylbenzene $PhIO_2$ is the most popular reagent.[40]

The first preparation of iodylbenzene, $PhIO_2$ (**1**), dates back to more then 100 years ago. Specifically, Willgerodt observed that the disproportionation of iodosylbenzene **2** under steam distillation afforded iodylbenzene **1** and iodobenzene **3** (Scheme 1).[41]



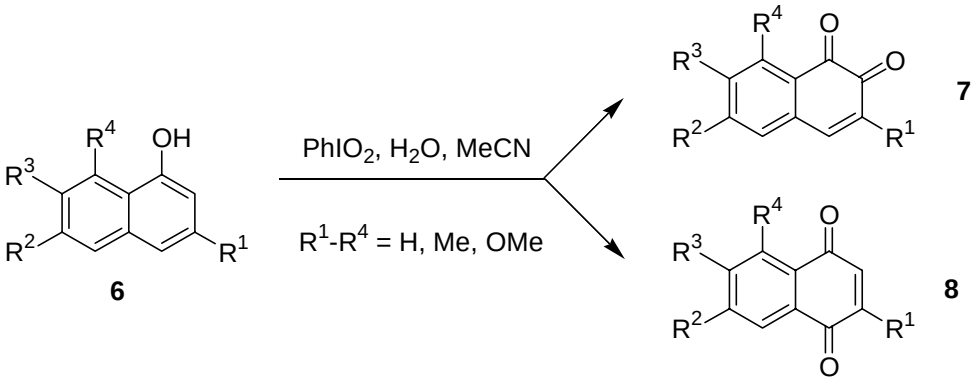
Scheme 1

Several methods for the selective preparation of iodylarenes from iodoarenes have been reported. These methods include the oxidation of iodoarenes with inorganic oxidants such as Caro's acid, potassium bromate and sodium hypochlorite.[42] Recently Skulski and coworkers developed a new procedure for the preparation of various iodylarenes from the corresponding iodoarenes **4** using sodium periodate as the oxidant (Scheme 2).[40]



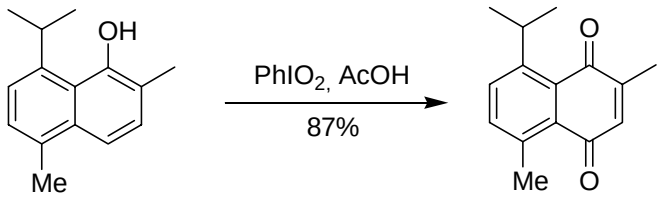
Scheme 2

Iodylbenzene in an aqueous acetonitrile or acetic acid media oxidizes activated aromatic rings, yielding quinones or quinine imines. Rao *et al.* reported a number of transformations, including conversion of substituted 1-naphthols **6** into corresponding 1,2 and 1,4 naphthoquinones **7** and **8** (Scheme 3).[43]



Scheme 3

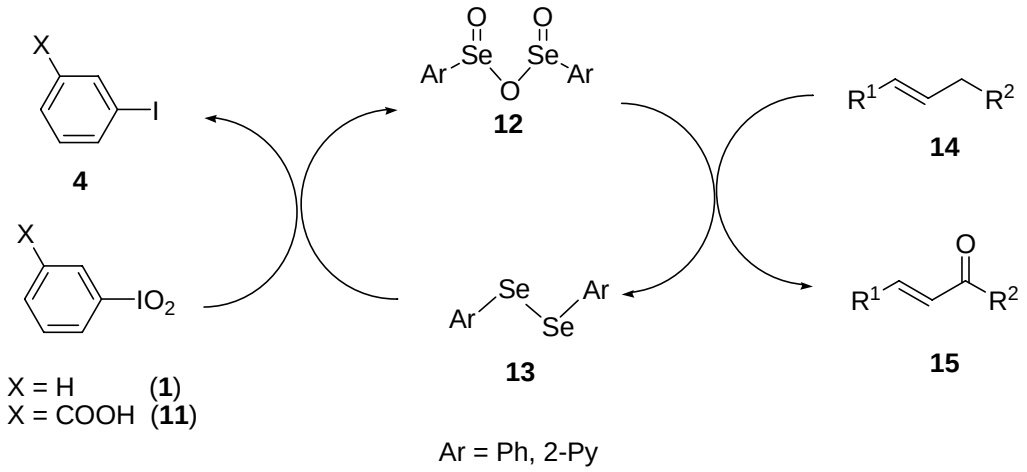
This protocol was utilized in the synthesis of cadalenquinone **10**, a naturally occurring sesquiterpene, starting from naphthol **9** (Scheme 4).[44]



9 **10**

Scheme 4

Several catalytic oxidative systems which employ iodylbenzene as a stoichiometric co-oxidant have been developed. Barton and coauthors reported an efficient allylic oxidation protocol with 2-pyridineseleninic anhydride **12** (Ar = 2-Py) as the principal oxidant, generated *in situ* by oxidation of the corresponding diselenide **13** with iodylbenzene **1** or 3-iodylbenzoic acid **11** (Scheme 5).[45]

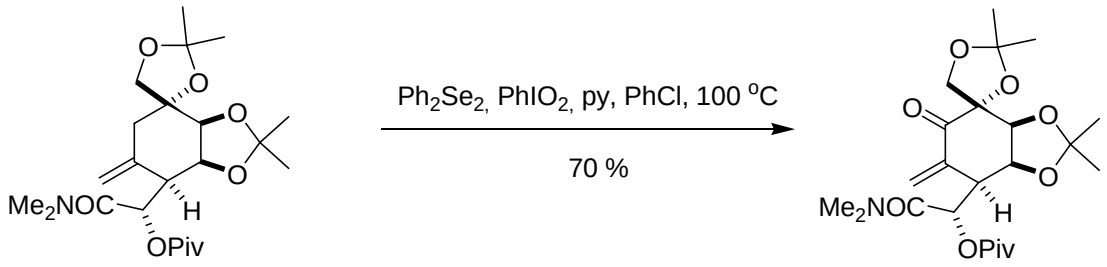


Scheme 5

This reaction proceeds in chlorobenzene at 100 ºC within 2.5-3 hours. Most likely the initial oxidation leads to the formation of allylic alcohols, which undergo further oxidation into α,β-unsaturated ketones **15**. In contrast with the classic allylic oxidation technique employing selenium dioxide, only a catalytic amount of the corresponding diselenide is required. In order to simplify the reaction workup, iodylbenzene **1** can be replaced with 3-iodylbenzoic acid **11**. In the latter case an excess of pyridine has to be added into the reaction mixture to neutralize acid **11**.

This convenient oxidation protocol was recently used in a number of syntheses of complex organic molecules. In the stereoselective synthesis of (-)-tetrodotoxin by Du Bois and coworkers,

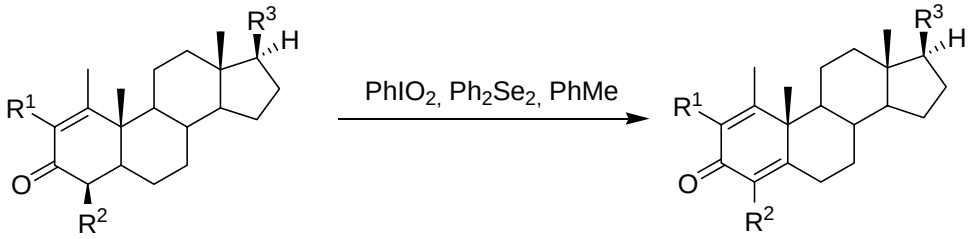
the protected pentaol **16** was oxidized with $PhIO_2/Py_2Se_2$ to afford the unsaturated carbonyl compound **17** in a good yield (Scheme 6).[46]



16 **17**

Scheme 6

Kuenzer *et al*. reported a dehydrogenation protocol in the regioselective synthesis of ring A of polymethylated steroids. Intermediates **18** were converted into the corresponding 1,4-dienes **19**, which are the key precursors to the target steroids (Scheme 7).[47]

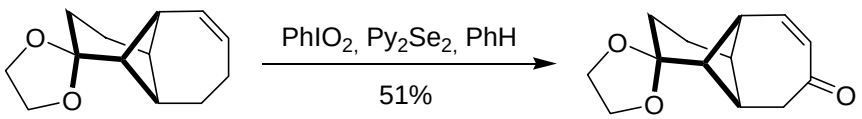


18 **19**

R^1 = H, R^2 = Me, R^3 = OTBDMS; R^1 = Me, R^2 = H, Me, R^3 = OAc

Scheme 7

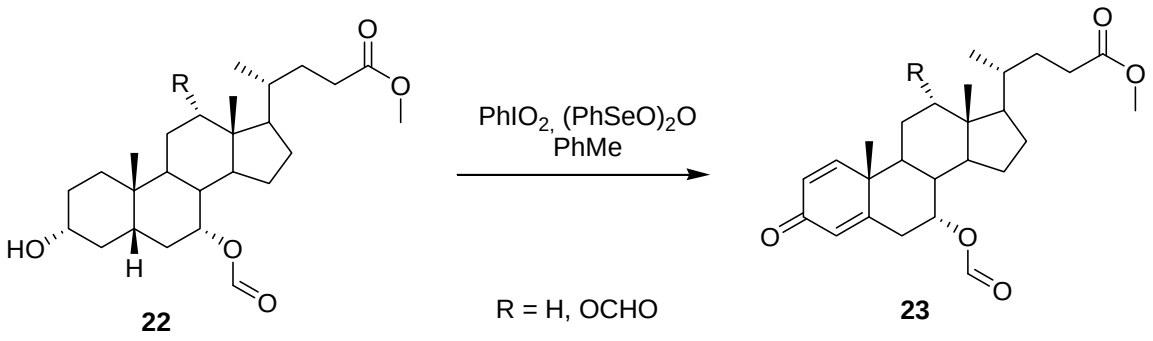
The original procedure, employing 2-pyridyldiselenide was used in the synthesis of tricyclo[5.4.0.$0^{2,8}$]undeca-3,5,9-triene, an interesting spiro compound with two mutually perpendicular π-systems.[48] In the course of this synthesis, the protected ketone **20** was oxidized to give the unsaturated ketone **21** in 51% yield (Scheme 8).



20 **21**

Scheme 8

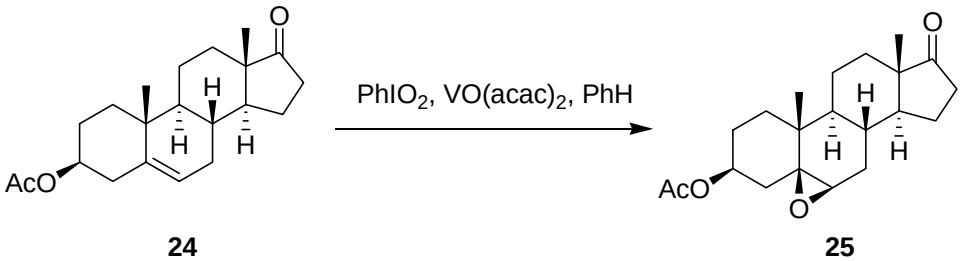
A new method for the preparation of allochenodeoxycholic and allocholic acids from the corresponding cholic acids was reported by Iida *et al*. The key step in the synthesis is the oxidation-dehydrogenation of 3α-hydroxy-5β-bile acid formyl esters **22** to give oxodienes **23** (Scheme 9).[49]



22 **23**

Scheme 9

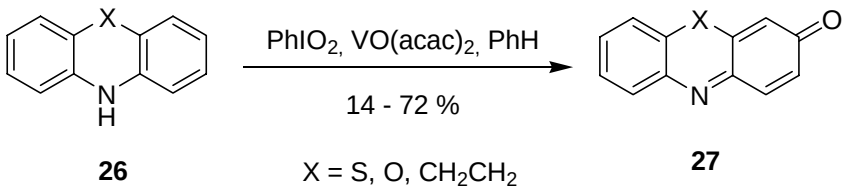
A series of oxidative transformations with iodylbenzene **1** as the co-oxidant of vanadyl bis(acetylacetonate) have been reported by Barret e*t al.*[50-52] In the presence of $VO(acac)_2$, iodylbenzene oxidizes Δ5-steroids into epoxides; a radical mechanism was suggested for this reaction. Epoxidation of cholest-5-ene-3-one occurred with high α-selectivity, while the remaining substrates gave mainly β-epoxides. Oxidation of *trans*-dehydroepiandrosterone acetate **24** afforded epoxide **25** (Scheme 10).[50]



24 **25**

Scheme 10

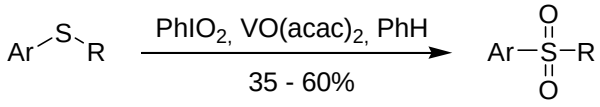
The above mentioned research group introduced a new route to quinine imines. The oxidation of the tricyclic scaffold **26** gives quinine imines **27** in 14-72% yield (Scheme 11).[51]



26 **27**

Scheme 11

Aryl sulfides **28** could be also converted by the abovementioned reagent $PhIO_2/VO(acac)_2$ into sulfoxides, sulfones and S-dealkylated products. Repeated treatment affords sulfones **29** in 35% to 60% yield (Scheme 12).[52]

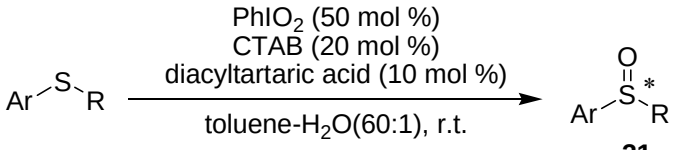


28 **29**

Ar = Ph, 4-FC_6H_4,
R= Me, $MeO(CO)CH_2$, $Ph(CO)CH_2$, CH_2CN, $PhCH_2$

Scheme 12

Kita and coworkers developed a new catalytic asymmetric oxidation using iodoxybenzene in a cationic reversed micellar system in the presence of chiral tartaric acid derivatives. Under these conditions, sulfides **30** are oxidized to sulfoxides **31** in high chemical yield with moderate to good enantioselectivity (Scheme 13).[53]



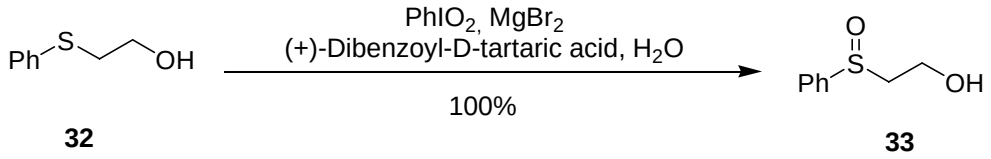
30 **31**

Ar = 4-MeC_6H_4, 4-$NO_2C_6H_4$, 3-$NO_2C_6H_4$, 4-CNC_6H_4,
4-BrC_6H_4, 4-$MeOC_6H_4$, 2-naphthyl,
R = Me, Et

Scheme 13

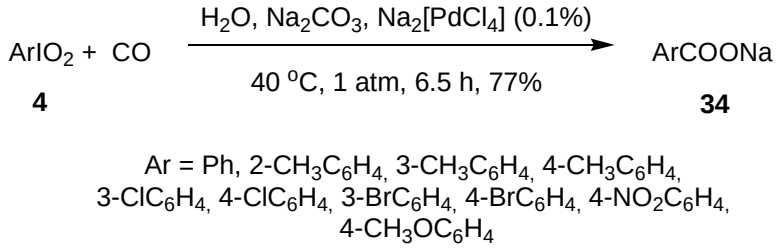
A purely water-based oxidation technique developed by Kita two years later employs magnesium bromide as a catalyst instead of cetyltrimethylammonium bromide (CTAB). An asymmetric oxidizing reagent was formed by mixing (+)-dibenzoyl-D-tartaric acid, $MgBr_2$, and

$PhIO_2$ in water for five minutes at room temperature. Treatment of 4-MeC_6H_4SMe with this oxidizing reagent at 0 °C for 24 hours gave (R)-4-$MeC_6H_4S(O)Me$ in quantitative yield and 59% enantiomeric excess. Oxidation of 2-(phenylthio) ethanol **32** left the primary hydroxyl unaffected (Scheme 14).[54]



Scheme 14

Iodylarenes **4** react with CO in water in the presence of sodium tetrachloropalladate (II) and sodium hydrocarbonate at ambient temperature giving the corresponding carboxylic acid salts **34**. A particularly attractive feature of this reaction is that, unlike most iodoarenes, $ArIO_2$ can be carbonylated in aqueous medium avoiding the use of organic solvents (Scheme 15).[55]

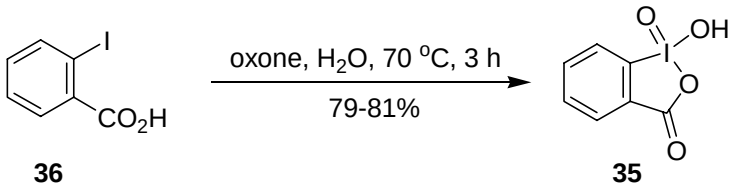


Scheme 15

3. Five-membered iodine(V) heterocycles: benzoiodoxole oxides

The most important representative of pentavalent iodine heterocycles, 2-iodoxybenzoic acid (IBX, **35**), was first prepared in 1893 by Hartman and Mayer.[56] IBX has the structure of the cyclic benziodoxole oxide (1-hydroxy-1-oxo-1*H*-1λ^5-benzo[*d*][1,2]iodoxol-3-one according to the IUPAC nomenclature), as determined by X-ray structural analysis.[57, 58] Most commonly IBX is prepared by the oxidation of 2-iodobenzoic acid with potassium bromate in aqueous solution of sulfuric acid.[59] IBX was reported to be explosive under excessive heating or impact, and Dess and Martin attributed the explosive properties of some samples to the presence of bromate impurities.[60] An alternative preparation of IBX involves oxidation of 2-iodobenzoic acid **36** with excess peracetic acid or aqueous sodium hypochlorite.[61] A convenient procedure for the preparation of IBX **35** which involves oxidation of 2-iodobenzoic acid **36** with Oxone (Scheme

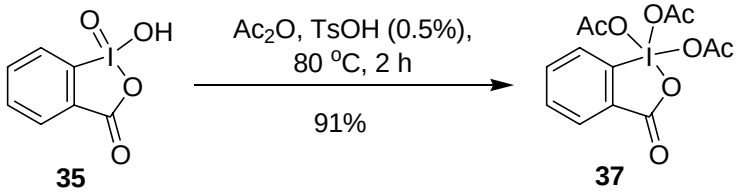
16) was reported by Santagostino and coworkers.[62] This protocol substantially reduced the amount of explosive impurities in the prepared IBX samples.



36 **35**

Scheme 16

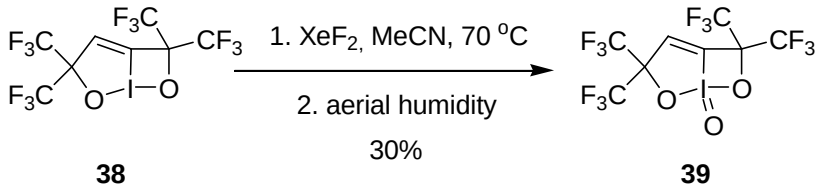
Until the 1990s IBX was rarely used in organic synthesis, apparently because of its insolubility in most organic solvents. In 1983 Dess and Martin transformed IBX to the soluble triacetoxybenziodoxole **37** by heating IBX with acetic anhydride to 100 °C.[63] In the following years, the triacetate **37** has emerged as the reagent of choice for the oxidation of alcohols to the respective carbonyl compounds,[64] and now it is commonly referred to as Dess-Martin periodinane (DMP). An improved procedure for the preparation of DMP **37** consists in the reaction of IBX with acetic anhydride in the presence of *p*-toluenesulfonic acid (TsOH) (Scheme 17).[65]



35 **37**

Scheme 17

Recently, Kawashima *et al.* reported on the preparation and oxidative properties of aliphatic iodoxole oxide **39**, which is the first example of this class of iodine(V) compounds.[66] The tetracoordinate 1,2-iodoxetane **39** was prepared by the fluorination of a tricoordinate 1,2-iodoxetane **38** with xenon difluoride followed by hydrolysis (Scheme 18). Compound **39** oxidized alcohols and a sulfide to the corresponding aldehydes and ketones and a sulfoxide, respectively, in good yields under mild conditions.



38 **39**

Scheme 18

Since the seminal works of Dess and Martin,[63,64] a variety of benziodoxole oxide derivatives including solid-supported reagents have been disclosed as mild and selective oxidizing reagents.

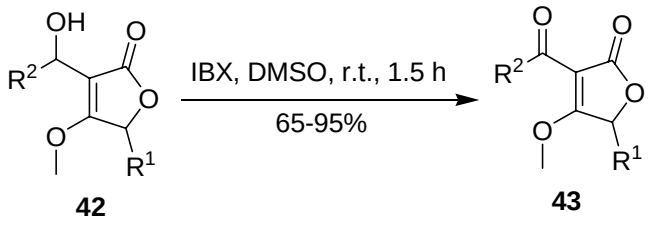
3.1 IBX and analogous reagents

In 1994 Frigerio and Santagostino reported that IBX, the DMP precursor, could also be used in the oxidation of alcohols in dimethyl sulfoxide (DMSO).[67] Thereafter, IBX and its analogs have attracted increasing interest as mild and selective oxidizing reagents. Solutions of IBX in DMSO are useful for the selective oxidation of alcohols to carbonyl compounds even in the presence of other functional groups.[67-80] Specifically, the allylic alcohols **40** are selectively oxidized by IBX to ketones **41** in high yield (Scheme 19).[67]

40 **41**

Scheme 19

The oxidation of alcohols **42** with IBX selectively affords 5-monosubstituted 3-acyl-4-*O*-methyl tetronates **43** (Scheme 20), which are structurally similar to the tetrodecamycin antibiotics.[68]

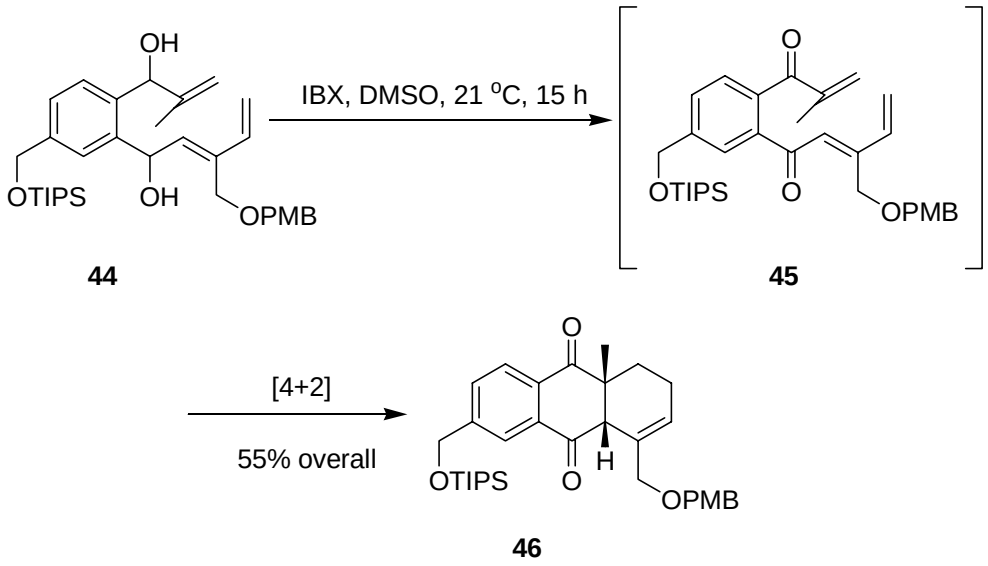


42 **43**

R^1 = H, Me; R^2 = *i*-Bu, *t*-Bu, Pr, Ph, $(CH_2)_2CH_2OTBDMS$

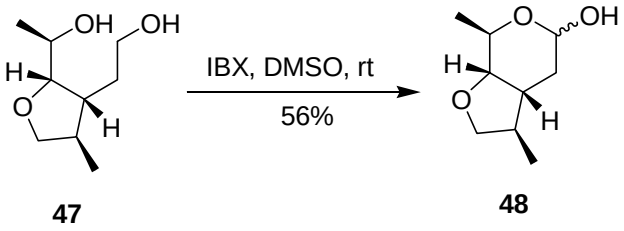
Scheme 20

The IBX oxidation of diol **44** was applied in the synthesis of the functionalized hexahydroanthracene dione **46** (Scheme 21), a model for the D ring of taxoids.[69]



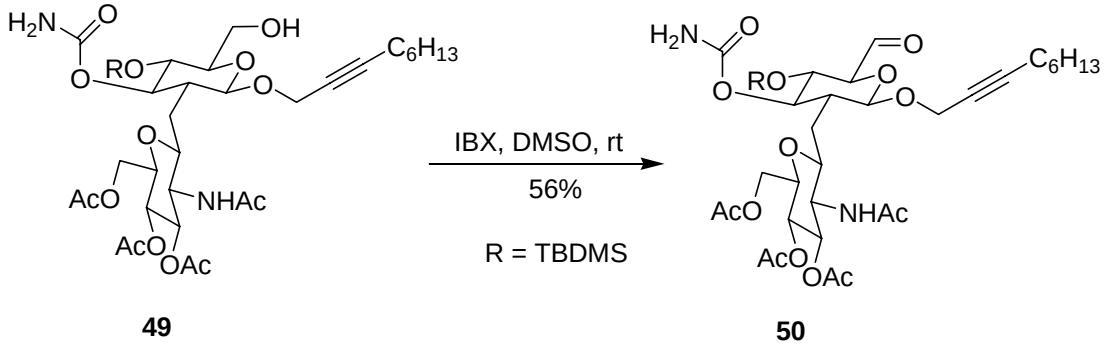
Scheme 21

Likewise, the total synthesis of the antifungal agent GM222712 was accomplished by a selective oxidation of diol **47** to hemiacetal **48** (Scheme 22).[70]



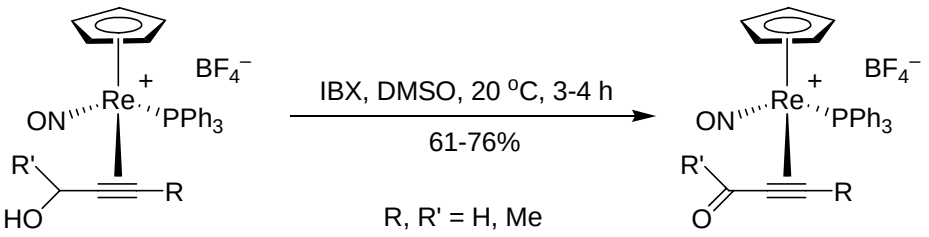
Scheme 22

The IBX oxidation of carbohydrate **49** was utilized in the synthetic studies of moenomycin A disaccharide analogs (Scheme 23).[71]



Scheme 23

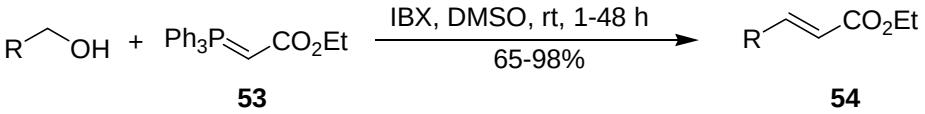
The chiral rhenium complexes of allylic and propargylic alcohols **51** are selectively oxidized by IBX to the unsaturated carbonyl compounds **52** in good yields (Scheme 24).[72]



51 **52**

Scheme 24

A one pot oxidation of benzylic, allylic, and propargylic alcohols, as well as diols, with IBX in the presence of the stabilized Wittig ylide **53** affords α,β-unsaturated esters **54** in generally good yields (Scheme 25).[73] This is a useful one-pot procedure because the intermediate aldehydes are often unstable and difficult to isolate.



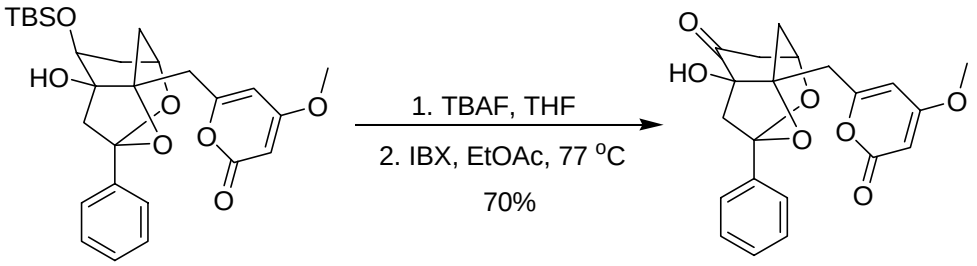
53 **54**

R = Ph, PhCH=CH, $Me_2C=CHCH_2CH_2(Me)C=CH$, HC≡C, $C_5H_{11}C≡C$, etc.

Scheme 25

The oxidation of alcohols with IBX in DMSO was also used in the development of a new silyl ether linker for solid-phase organic synthesis,[74] in the kinetic study of organic reactions on polystyrene grafted microtubes[75] and in the total synthesis of a cyclic depsipeptide somamide A.[76]

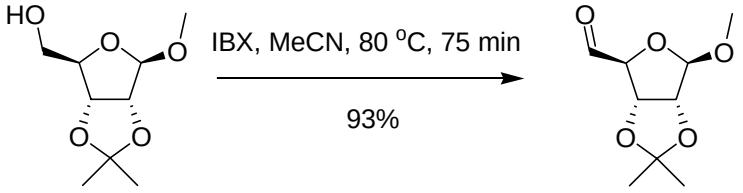
IBX is especially useful for the oxidation of 1,2-diols. In contrast to DMP, which generally cleaves the glycol C–C bond, IBX in DMSO oxidizes 1,2-diols to α-ketols[77,78] or α-diketones.[66,79] In the key step of the total synthesis of *Streptomyces maritimus* metabolite - wailupemycin B **56**, the IBX oxidation led to the desired hydroxyketone moiety without any cleavage of the glycol C-C bond (Scheme 26).[80]



55 **56**

Scheme 26

The synthetic usefulness of IBX in general is significantly restricted by its low solubility in most organic solvents with the exception of DMSO. However, in several recent reports[81-83] it has been shown that IBX can be used as effective oxidant in other than DMSO solvents. More and Finney have found that primary and secondary alcohols can be oxidized into the corresponding aldehydes or ketones in excellent yields (90-100%) by heating a mixture of alcohol and IBX in common organic solvents.[81] All reaction by-products can be completely removed by filtration. This method was recently used for the efficient preparation of the ribosyl aldehyde **58** (Scheme 27), the key intermediate in the stereoselective synthesis of the core structure of the polyoxin and nikkomycin antibiotics.[82]

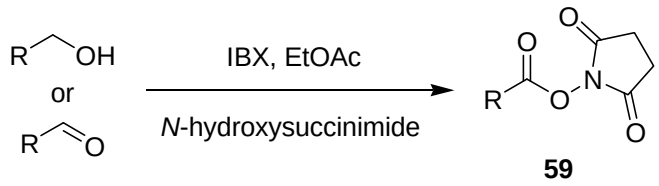


57 **58**

Scheme 27

Chen and co-workers reported a mild, efficient, and environmentally benign protocol for the oxidation of alcohols with IBX in the ionic liquid 1-butyl-3-methylimidazolium chloride and water.[83] Upon stirring a solution of the alcohol and IBX in 1-butyl-3-methyl-imidazolium chloride followed by removal of water at room temperature and subsequent extraction with ether or ethyl acetate and removal of the solvent gives excellent yields (88-99%) of the corresponding carbonyl compounds. No overoxidation to acids was observed in the case of aldehyde products, and various functionalities such as methoxy and nitro groups, double bonds, and a furan ring can be tolerated. The oxidation of glycols under these conditions, depending of the amount of IBX used, affords α-ketols or α-diketones.

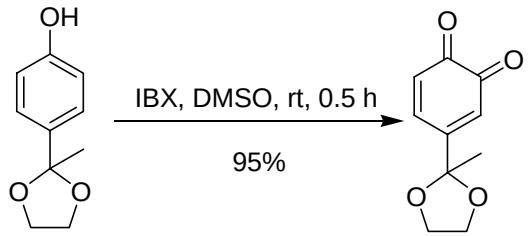
An interesting IBX-mediated oxidation of primary alcohols (or aldehydes) to *N*-hydroxysuccinimide esters **59** was developed by Giannis and coworkers.[84] The generality of this procedure was demonstrated on a variety of aliphatic, allylic, and benzylic alcohols (Scheme 28).



59

Scheme 28

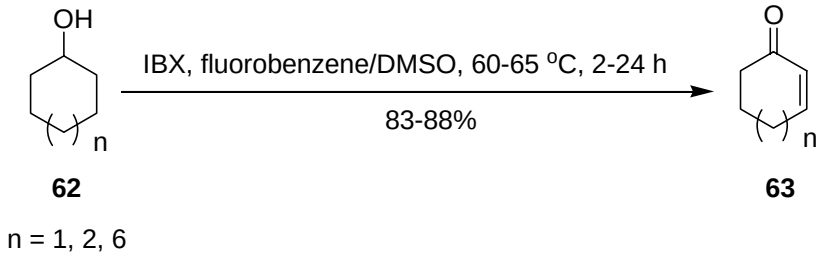
IBX in DMF has been shown to be an excellent reagent for the oxidation of various phenols to *o*-quinones.[85] This procedure was recently used for the oxidation of phenol **60** to quinone **61** (Scheme 29), the key intermediate in total synthesis of a novel cyclooxygenase inhibitor (±)-aiphanol.[86a] The same protocol was recently utilized in the synthesis of (±)-brazilin, a tinctorial compound found in the alcoholic extracts of trees collectively referred to as Brazil wood, by Pettus *et al.*[86b]



60 **61**

Scheme 29

The practical value of IBX as a reagent was recently extended to a variety of other synthetically useful oxidative transformations.[87-94] In a series of papers, Nicolaou and coworkers have demonstrated the utility of IBX for the one-step synthesis of α, β-unsaturated carbonyl systems from saturated alcohols and carbonyl compounds,[87,88] for the selective oxidation of the benzylic carbon,[89] for the oxidative cyclization of anilides and related compounds,[90,91] and for the synthesis of amino sugars and libraries thereof.[92] Specifically, alcohols, ketones, and aldehydes are oxidized to the corresponding α,β -unsaturated species in one pot using IBX under mild conditions.[87] For example, cycloalkanols **62** react with two equivalents 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 **63** in good yields (Scheme 30).

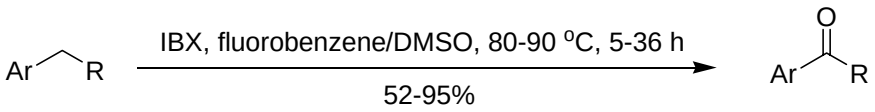


62 **63**

n = 1, 2, 6

Scheme 30

IBX is an efficient and a selective reagent for the oxidation of benzylic positions (Scheme 31).[89a] 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.

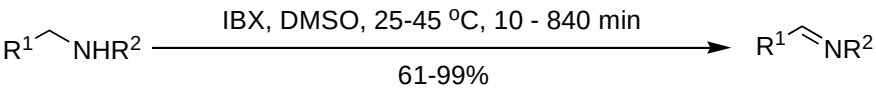


64 **65**

Ar = Ph, 4-*t*-BuC_6H_4, 2-MeC_6H_4, 3-IC_6H_4, 4-BrC_6H_4, 3,4-$(MeO)_2C_6H_3$, 2-PhC_6H_4, 4-(4-pyridyl)C_6H_4, etc.
R = H, C_3H_7, etc.

Scheme 31

Similar to the oxidation of alcohols, secondary amines can be oxidized with IBX in DMSO to yield the corresponding imines **66** in good to excellent yields (Scheme 32).[89b]



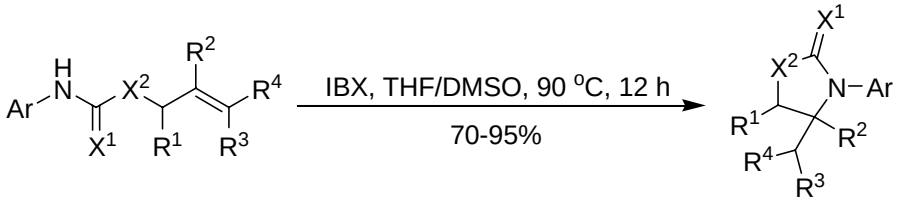
66

R^1 = Ph, 4-BrC_6H_4, 4-MeOC_6H_4, etc.
R^2 = 4-BrC_6H_4, 4-MeOC_6H_4, CH_3, OH, OBn, etc.

Scheme 32

A variety of new heterocycles **67** can be synthesized by the treatment of unsaturated aryl amides, carbamates, thiocarbamates, and ureas with IBX (Scheme 33).[90] The mechanism of this reaction has been investigated in detail.[91a] 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.



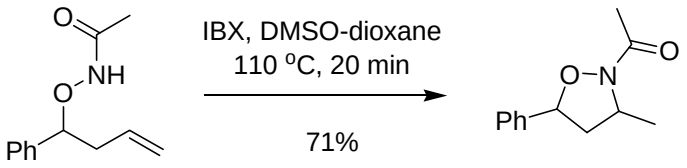
67

X^1 = O, S; X^2 = CH_2, O, N
Ar = Ph, 3-EtC_6H_4, 3-BrC_6H_4, 3-FC_6H_4, 4-EtC_6H_4, etc.
R^1 - R^4 = H, alkyl, cycloalkyl, etc.

Scheme 33

A similar IBX-mediated cyclization was applied in the synthetic protocol for the stereoselective preparation of amino sugars.[91b]

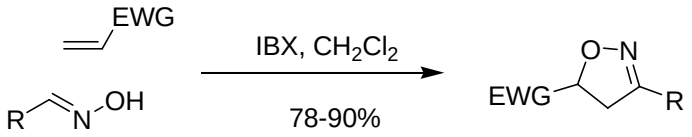
Recently, Studer and coworkers reported a method for the generation of alkoxyamidyl radicals starting from the corresponding acylated alkoxyamines using IBX as a single electron transfer (SET) oxidant. Stereoselective 5-*exo* and 6-*exo* reactions with these *N*-heteroatom-centered radicals lead to isoxazolidines and [1,2]oxazinanes (Scheme 34).[92a]



68 **69**

Scheme 34

IBX has also been used for the preparation of the 3,5-disubstituted isoxazolines **70**. SET oxidation of substituted aldoximes with IBX in CH_2Cl_2 produces the respective nitrile oxide which is then undergoes 1,3-dipolar addition with an alkene component (Scheme 35).[92b]

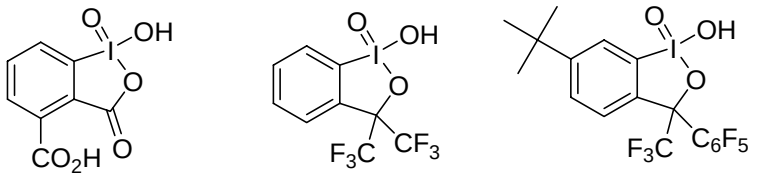


70

EWG = electron withdrawing group

Scheme 35

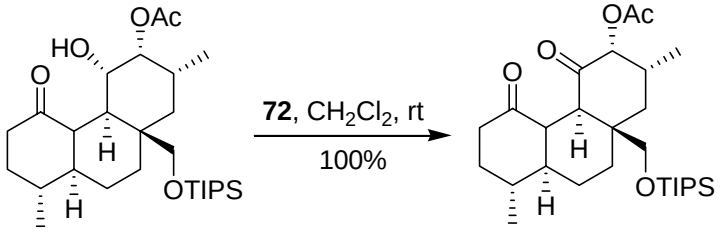
Several analogs of IBX have been reported in the literature.[93-96] Thottumkara and Vinod have reported the preparation of the water-soluble analog of IBX, *m*-iodoxyphthalic acid (mIBX) **71**, which oxidizes benzylic and allylic alcohols to carbonyl compounds in water.[93] Two bis(trifluoromethyl)benziodoxole oxides **72**[60] and **73**[94], which are prepared from the corresponding iodoalcohols, are stable, non-explosive and soluble in a wide range of organic solvents (Scheme 36).



71 **72** **73**

Scheme 36

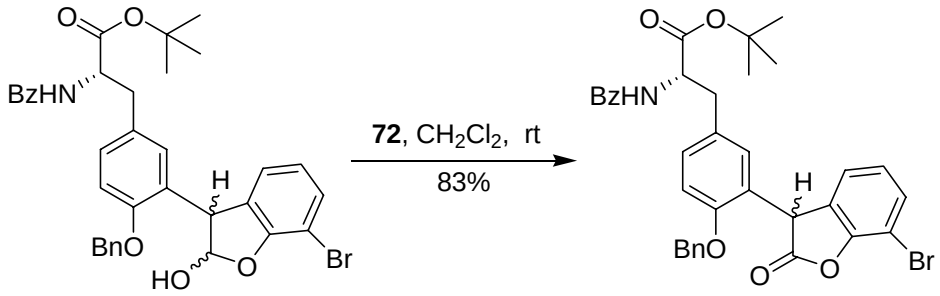
Grieco and coworkers have applied reagent **72** in the total syntheses of des-D-chaparrinone, bruceoside C and (-)-glaucarubolone.[95a,b,c] Specifically, the oxidation of the alcohol **74** with reagent **72** under mild conditions quantitatively afforded ketone **75**, an important intermediate in the synthesis of des-D-chaparrinone (Scheme 37).[95a]



74 **75**

Scheme 37

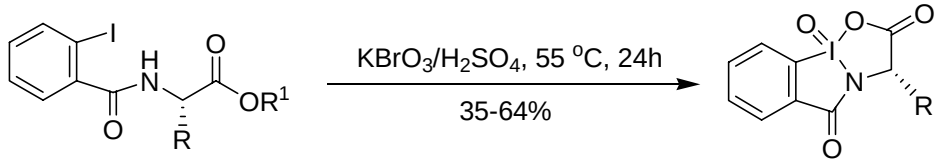
Moody and coworkers used reagent **72** under similar conditions in the synthesis of benzofuranone derivative **77**, a potential precursor for the synthesis of the cytotoxic marine alkaloid diazonamide A (Scheme 38).[96]



76 **77**

Scheme 38

New benziodazole oxides **79** were prepared by oxidation of the readily available 2-iodobenzamides **78** with potassium bromate (Scheme 39).[97]



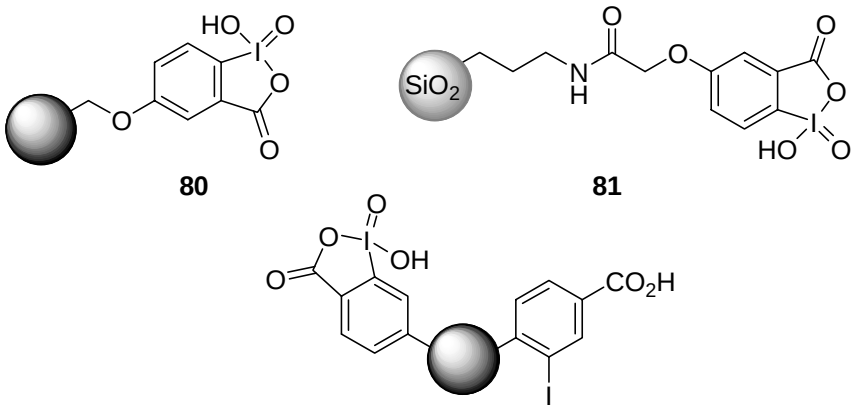
78 R = CH_3, *i*-Pr, *i*-Bu; R^1 = H or CH_3 **79**

Scheme 39

Benziodazole oxides **79** can be regarded as selective, chiral oxidizing reagents for organic synthesis. Preliminary results indicate that reagents **79** can selectively oxidize primary alcohols to aldehydes in chloroform at 50 ^{o}C. Under similar conditions, reagents **79** oxidize organic sulfides to sulfoxides in almost quantitative yield. Oxidation of non-symmetric sulfides affords chiral sulfoxides with moderate enantioselectivity (11-16% ee).[97]

Various groups have reported on the immobilization of IBX onto solid or soluble polymeric supports.[98-101] These supported IBX reagents are non-explosive and can be used in common organic solvents like THF or dichloromethane. Three research groups have used 4-hydroxy-2-iodobenzoic acid as derivative, suitable for attaching onto a variety of resins. Rademann and coworkers employed Merrifield resin as a solid support to give a derivative **80** with a loading of 0.8 mmol g^{-1} (Scheme 40).[98] Janda *et al.* used a similar ether linkage to attach 4-hydroxy-2-iodobenzoic to a set of soluble and insoluble polymer supports.[99] In the other

synthesis by Giannis and coworkers aminopropyl-silica gel was employed as a solid matrix affording a supported reagent **81** (Scheme 40).[100] In the latter case, Oxone in aqueous medium was used for resin activation. A conceptually different approach was used by Sutherland *et al.*[101] Thus, during the preparation of the oxidizing polymer **82**, iodobenzoic acid moiety was introduced directly to the resin backbone by iodination/oxidation sequence (Scheme 40). Reagents **80-82** oxidize various primary, secondary, benzylic, allylic, terpene alcohols, and the carbamate-protected aminoalcohols to afford the respective aldehydes or ketones in excellent yields and purities. Polymers **80-82** can be recycled by repeated oxidation after extensive washings.



Scheme 40

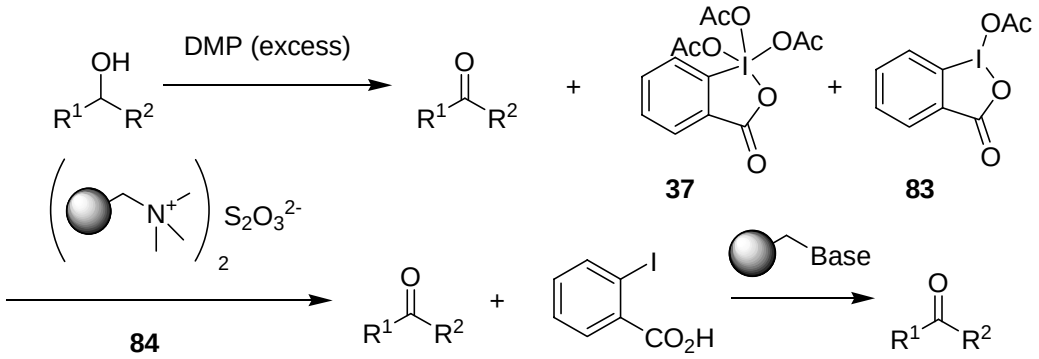
3.2 Dess-Martin Periodinane

In recent years, the acetate derivative of IBX, **37**, which is commonly known as Dess-Martin periodinane [DMP; 1,1,1-tris(acetyloxy)-1,1-dihydro-1,2-benziodoxol-3-(1*H*)-one] has emerged as a reagent of choice for the oxidation of primary and secondary alcohols to aldehydes and ketones, respectively. In addition, DMP is currently commercially available from Sigma-Aldrich[102] and other chemical companies. The synthetic applications of DMP were highlighted in two overviews.[103,104]

The mild reaction conditions (room temperature, absence of acidic or basic additives), high chemoselectivity, and preparative convenience have made this reagent especially suitable for the oxidation of substrates containing sensitive functional groups (*e.g.* unsaturated moieties, amino groups, silyl ethers, phosphine oxides, sulfides, selenides). In case of epimerization sensitive substrates, DMP allows clean oxidation with virtually no loss of enantiomeric excess. Thus, oxidation of *N*-protected β-amino alcohols with DMP afforded the respective aldehydes with 99% ee and excellent chemical yields, while Swern oxidation gave unsatisfactory results (50-

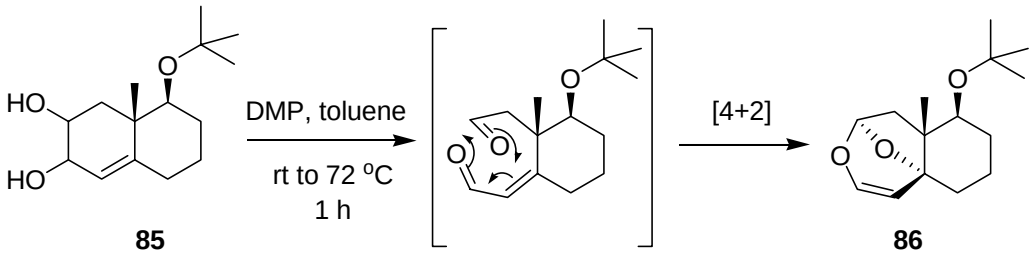
68% ee).[105] DMP oxidation is accelerated by the addition of water to the reaction mixture immediately before or during the reaction.[106]

Parlow and coworkers developed an efficient and convenient method for entrapping excess DMP and acetoxybenziodoxole byproduct **83** from the solution phase using a thiosulfate resin **84**. All the hypervalent iodine species are reduced to 2-iodobenzoic acid, which is then sequestered by the basic resin leaving the pure carbonyl product in solution (Scheme 41).[107]



Scheme 41

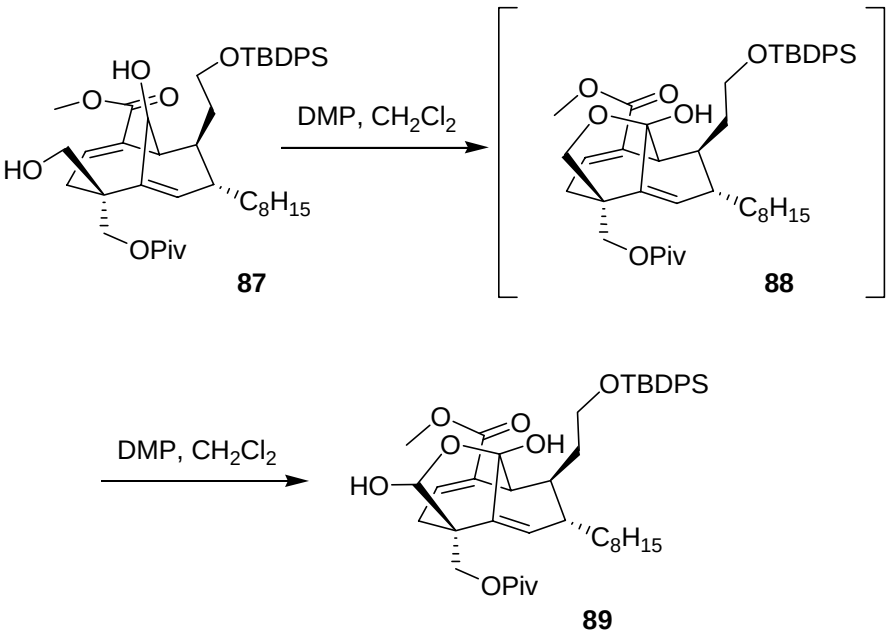
It is worth mentioning that during oxidation of 1,2-diols DMP generally cleaves the glycol C-C bond. When IBX is employed, exclusive formation of 1,2-diketones or 2-hydroxyketones is observed, and no C-C bond cleavage occurs. Different product distribution from 1,2-diols in case of DMP and IBX was rationalized in terms of the different intermediate periodinane adducts DMP and IBX can form.[108] This characteristic difference in DMP reactivity was utilized during the synthesis of tricyclic enol ether **86** by tandem 1,2-diol cleavage-intramolecular cycloaddition (Scheme 42).[109]



Scheme 42

Unique oxidizing properties and convenience of use advance DMP to be widely employed in the synthesis of biologically important natural products. Recently DMP was used in the key oxidation steps in the total syntheses of cyclotheonamide B,[110] (±)-deoxypreussomerin A,[111]

racemic brevioxime,[112] erythromycin B,[113] (+)-discodermolide,[114] (+)-cephalostatin 7,[115] (+)-cephalostatin 12,[115] (+)-ritterazine K,[115] 3-*O*-galloyl-(2*R*,3*R*)-epicatechin-4β,8-[3-*O*-galloyl-(2*R*,3*R*)-epicatechin],[116] fredericamycin A,[117] indolizidine alkaloids (-)-205A, (-)-207A, and (-)-235B,[118] 1,19-aza-1,19-desoxy-avermectin B_{1a},[119] angucytcline antibiotics,[120] tricyclic β-lactam antibiotics,[121] and the platelet aggregation-inhibiting γ-lactam PI-091.[122] The unique oxidizing properties of DMP can be best illustrated by its application in the total synthesis of the CP-molecules, lead structures for cardiovascular and anticancer drugs, published by Nicolaou and coworkers.[123-126] In this synthetic investigation, hindered secondary alcohol **87** was oxidized with DMP to stable diol **89** through intermediate hemiketal **88** (Scheme 43).

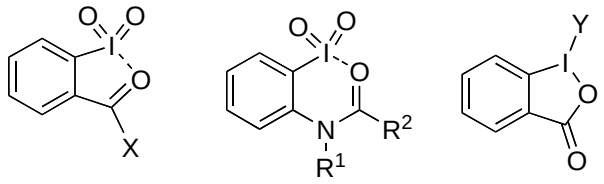


Scheme 43

4. Pseudocyclic Iodine(V) Reagents

Noncovalent, attractive interactions between iodine and oxygen atoms are extremely important forces that can influence molecular, solution, and solid state properties. Being often termed secondary bonds[127], such interactions can be successfully utilized in the design of new hypervalent iodine(V) reagents. 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. When iodine(V) atom and the *ortho*-sustituent's oxygen atom are located in 1,5-position, the planar, five-membered pseudo-benziodoxole structural moiety **90** arises. On the other hand, 1,6-arrangement of iodine and oxygen atoms

results in a non-planar six-membered ring of pseudo-benziodoxazines **91**. Generally, the distance between the iodine and oxygen atoms amounts to 2.6 - 2.7 Å in pseudo-benziodoxoles **90** and pseudo-benziodoxazines **91**,[128-134] which is comparable with the I-O bond length in benziodoxoles **92** from 2.2 Å to 2.5 Å (Scheme 44).



90 **91** **92**

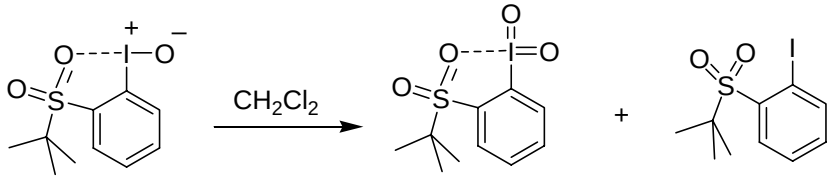
X = OR, NHR, etc.; R^1, R^2 = H, alkyl, aryl; Y = OH, N_3, Ph, etc.

Scheme 44

Compared to the non-cyclic aryliodyl derivatives, pseudocyclic iodine(V) compounds have much better solubility, which is explained by a partial disruption of their polymeric nature due to the redirection of secondary bonding.[128-134] In recent years, pseudo-benziodoxoles and pseudo-benziodoxazines have found increasing practical application in organic synthesis as efficient oxidizing reagents.

4.1 Pseudo-benziodoxoles

Protasiewicz *et al.* reported the preparation of a soluble iodylbenzene derivative **95** which was obtained by disproportionation of iodosylarene **93** (Scheme 45).[128]



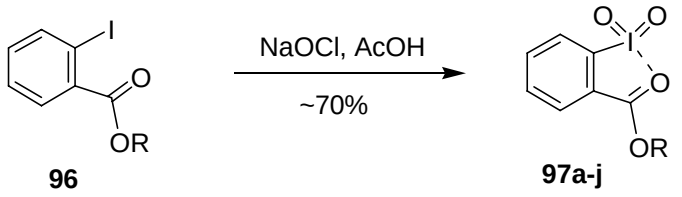
93 **95** **94**

Scheme 45

The X-ray structure of product **95** shows a pseudo octahedral geometry with the I–O bond lengths in the iodyl group of 1.796 and 1.822 Å and an intramolecular distance of 2.693 Å between one of the sulfone oxygen atoms and the hypervalent iodine center.[128] Authors stated that if strong internal dipoles (such as sulfonyl or carbonyl groups) are introduced into the *ortho*

position to the IO_2 group, they are capable of introducing *intramolecular* I···O secondary bonds, replacing the *intermolecular* ones. This secondary bond redirection leads to structures which are less polymeric and more soluble in the conventional organic solvents, such as dichloromethane and benzene.

Esters of 2-iodoxybenzoic acid (IBX–esters) **97**, a new class of pentavalent iodine compounds with a pseudo-benziodoxole structure, can be conveniently prepared by hypochlorite oxidation of iodobenzoate esters **96** in the form of stable, white, microcrystalline solids (Scheme 46).[131,134] This facile procedure allows for the preparation of reagents **97** derived from a wide variety of precursors, including primary, secondary, and tertiary alcohols, adamantanols, as well as optically active menthols and borneol. All products **97** have moderate to good solubility in common organic solvents, such as chloroform, dichloromethane, and acetonitrile.



96 **97a-j**

a: R = Me; **b:** R = Et; **c:** R **=** *i*-Pr; **d:** R **=** *tert*-Bu;
e: R = (–)-menthyl; **f:** R = (+)-menthyl; **g:** R = (±)-menthyl;
h: R = [(1*S*)-*endo*]-(–)-bornyl; **i:** R = 2-adamantyl; **j:** R = 1-adamantyl

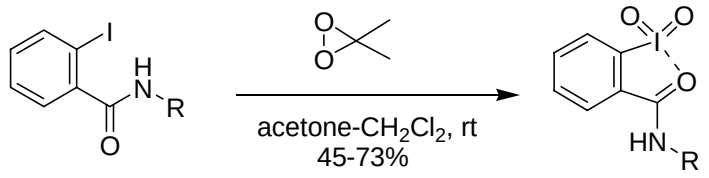
Scheme 46

Structures of compounds **97a**, **c, d** were established by single crystal X–ray analysis. In particular, the structure of **97c** shows a unit cell consisting of two crystallographically independent molecules. Strong secondary I•••O bonding interactions between neighboring molecules affords dimeric pairs, which are then linked together by a combination of strong and weak interactions, forming a polymeric motif. Within each molecule, an intramolecular close contact of 2.697 Å between the iodine(V) center and the oxygen atom of the ester group affords the pseudo-benziodoxole ring.[131,134]

A range of alcohols can be oxidized by reagents **97** to the respective carbonyl compounds under mild conditions. For example, oxidation of benzyl alcohol in the presence of KBr in chloroform at 50 ^{o}C cleanly gives benzaldehyde as the only product detected by ^{1}H NMR spectroscopy. A variety of secondary alcohols, such as cyclohexanol and cycloheptanol, are converted to the corresponding ketones in 95-98% yields.[131,134]

The novel 2–iodoxybenzamides (IBX-amides) **99**, prepared by our group, are stable and soluble compounds with unique and synthetically valuable oxidizing properties.[132] These compounds are synthesized by the dioxirane oxidation of the readily available 2–iodobenzamides **98** (Scheme 47). This procedure allows for the preparation of products **99** derived from numerous types of amino compounds, such as esters of natural α–amino acids **99a, c–d**, an

unnatural amino acid **99b**, β–amino acids **99e,f**, and (*R*)–1–phenylethylamine **99g**. X–Ray data on **99c** reveals a pseudo-benziodoxole structure in which the intramolecular I•••O secondary bonds (2.594 Å) partially replace the intermolecular I•••O secondary bonds responsible for the polymeric structure of $PhIO_2$ and other previously reported iodylarenes. This structural characteristic substantially increases solubility and stability of these compounds in comparison to other I(V) reagents.



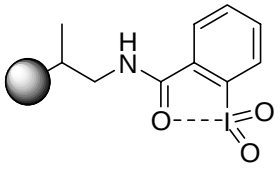
98 **99a-g**

a: R = (*S*)-CH(CH$_3$)CO$_2$CH$_3$; **b**: R = (*R*)-CH(CH$_3$)CO$_2$CH$_3$;
c: R = (*S*)-CH(CH$_2$Ph)CO$_2$CH$_3$; **d**: R = (*S*)-CH(*i*-Bu)CO$_2$CH$_3$;
e: R = CH$_2$CH$_2$CO$_2$H; **f**: R = CH(CH$_3$)CH$_2$CO$_2$H; **g**: R = (*R*)-CH(Ph)CH$_3$

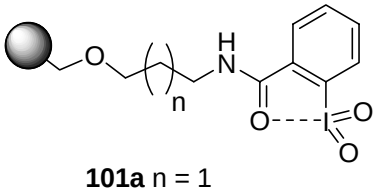
Scheme 47

2–Iodoxybenzamides **99** are useful oxidizing reagents towards alcohols with a reactivity pattern similar to IBX. A wide range of alcohols can be oxidized by these reagents to the respective carbonyl compounds under mild conditions in chloroform.[134,135] For example, benzyl alcohol cleanly gives benzaldehyde as the only product detected by ^{1}H NMR spectroscopy. A variety of secondary alcohols are effectively converted to the corresponding ketones in good yields using any of the reagents **99a**–**c**. Oxidative kinetic resolution of racemic *sec*–phenethyl alcohol using reagents **99** has also been investigated. In particular, the reaction of **99c** showed a very modest 9% ee. In contrast to DMP, reaction of reagent **99b** with *cis*–hexanediol effects oxidative cleavage to give hexanedial in 30% yield. It should be emphasized that iodylbenzene, $PhIO_2$, as well as other non–cyclic iodylarenes, do not react with alcohols in the absence of acidic catalysis. In agreement with their structural features, the oxidizing reactivity of 2–iodoxybenzamides **99** is closer to the benziodoxole–based pentavalent iodine reagents, in contrast to the non–cyclic iodylarenes.

Lee and coworkers have synthesized an IBX-amide resin **100** based on BTCore EM OH resin (Scheme 48).[136,137] A loading of 0.98 mmol g^{-1} was achieved and 2 equiv of resin were necessary for the total conversion of an alcohol to the corresponding carbonyl compound. Linclau *et al.* reported an improved synthesis of a solid-supported IBX amide resins **101a, b** using inexpensive and commercially available 2-iodobenzoic acid chloride and Merrifield resin (Scheme 48).[138] Oxidation of a range of alcohols to the corresponding carbonyl compounds can be accomplished using 1.2 equiv of the resins **101a, b**. Recycling of the resin was also possible with minimal loss of activity after two reoxidations.



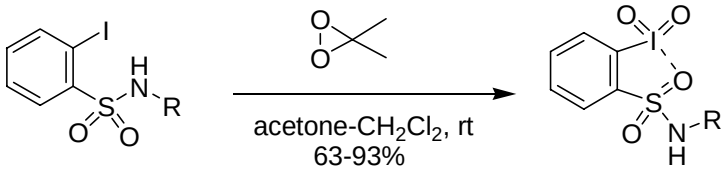
100



101a n = 1
101b n = 3

Scheme 48

Amides of 2-iodoxybenzenesulfonic acid **103a-e** were recently prepared by the dioxirane oxidation of the corresponding 2-iodobenzenesulfamides and isolated as stable, microcrystalline products (Scheme 49).[139] These newest representatives of the pseudocyclic hypervalent iodine compounds can selectively oxidize benzyl alcohols to aldehydes.

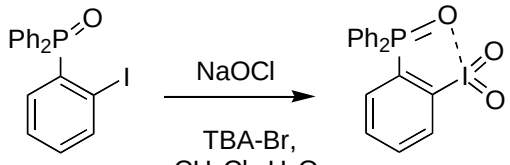


102 **103a-e**

a: R = (*S*)-CH(CH$_3$)CO$_2$CH$_3$; **b**: R = (*S*)-CH(CH$_2$Ph)CO$_2$CH$_3$;
c: R = (*S*)-CH(*i*-Pr)CO$_2$CH$_3$; **d**: R = (*S*)-CH(*i*-Bu)CO$_2$CH$_3$;
e: R = (*R*)-CH(Ph)CH$_3$

Scheme 49

Recently, Protasiewicz *et al.* reported the synthesis and reactivity of a new IBX analogue (2-iodylphenyl)diphenyl-phosphine oxide **105** (Scheme 50).[140] Analysis by single crystal X-ray diffraction showed a significant intramolecular I•••O interaction (2.612 Å) forming a pseudo-benziodoxole structure.



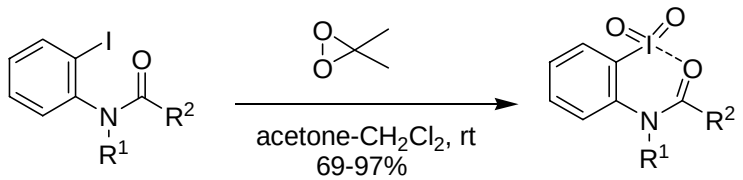
104 **105**

Scheme 50

Compound **105** can oxidize triphenylphosphine and methyl *p*-tolyl sulfide to the corresponding phosphine oxide and sulfoxide.

4.2 Pseudo-benziodoxazines

Very recently, we have described the design, preparation, structure and oxidative properties of novel *N*-(2-iodyl-phenyl)-acylamides **91** (Scheme 51).[133] X-ray data on compounds **91** revealed a unique pseudo benziodoxazine structure with intramolecular secondary I•••O (2.647 Å) bonding, which is the first reported example of six-membered pseudo-cyclic scaffold for iodine(V). Preliminary experiments indicate the reagents **91** can oxidize alcohols and sulfides, the reactivity very largely depending on the substitution pattern on amide group adjacent to iodyl moiety. A mechanistic rationale accounting for the **91** reactivity pattern was recently proposed.[133]

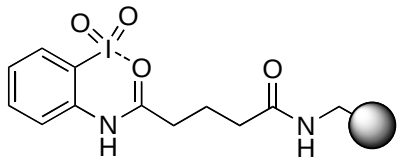


106 **91**

R^1 = H, Me, Bn
R^2 = Me, *n*-Pr, *i*-Pr, Cy, *t*-Bu

Scheme 51

In the context of these findings, the polymer-supported *N*-(2-iodyl-phenyl)-acylamide reagent (NIPA resin) **107** has been recently synthesized (Scheme 52).[141]



107

Scheme 52

The synthesis employs commercially available aminomethylated polystyrene, includes three simple steps, and affords the resin with good loading of 0.70 – 0.80 mmol g^{-1}. The prepared resin **107** effects fast and efficient oxidation of a wide range of alcohols, including heteroatomic and unsaturated structures.

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Viktor V. Zhdankin was born in 1956 in Sverdlovsk, Russia. His M.S. (1978), Ph.D. (1981), and Dr.Chem.Sci. (1986) degrees were earned at Moscow State University in the research laboratories of Professor N. S. Zefirov. In 1987 he was appointed as Senior Research Fellow - Head of Research Group at the Department of Chemistry, Moscow State University, in Russia. He moved to the University of Utah in 1990, where he worked for three years as Instructor of organic chemistry and Research Associate with Professor P. J. Stang. In 1993 he joined the faculty of the University of Minnesota Duluth where he is currently a Professor of Chemistry. He has published more than 160 research papers as well as seventeen reviews and book chapters. His main research interests are in the fields of synthetic and mechanistic organic chemistry of hypervalent main-group elements (iodine, xenon, selenium, sulfur, and phosphorus), organofluorine chemistry, and chemistry of acetylenes.

Uladzimir Ladziata was born in 1981 in Pinsk, Belarus. In 2003 he graduated from Belarusian State University (Minsk) with MS degree in Medicinal Chemistry. In 2004 he joined the research group of Professor Viktor V. Zhdankin at the University of Minnesota Duluth. Research interests include rational drug design and synthesis of biologically active compounds. His current research is focused on the development of new hypervalent iodine reagents as useful synthetic tools for organic and medicinal chemistry.