

Hypervalent iodine (V) catalyzed reactions

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Received mm-dd-yyyy

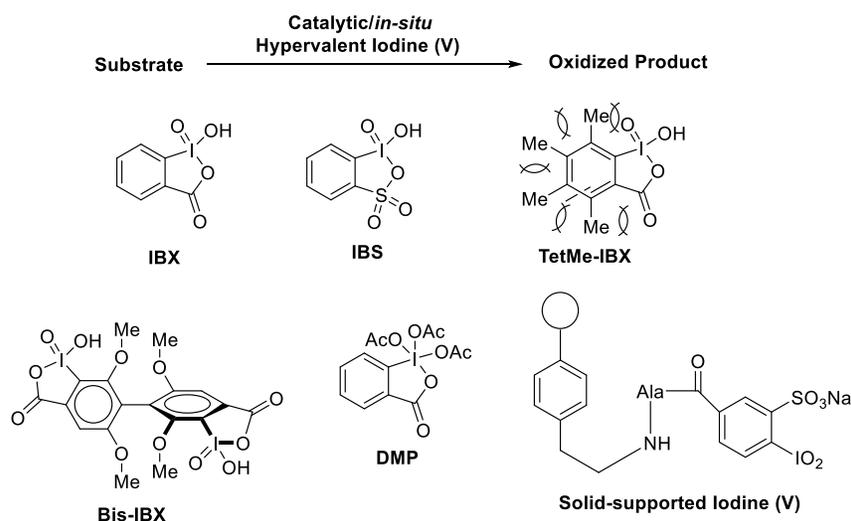
Accepted mm-dd-yyyy

Published on line mm-dd-yyyy

Dates to be inserted by editorial office

Abstract

The chemistry of hypervalent iodine compounds has been widely recognized in the synthetic community. The utilization of hypervalent iodine compounds as stoichiometric reagents as well as catalysts has tremendously been studied in recent decades. Hypervalent iodine (V)-catalyzed reactions are proven to be versatile catalytic systems to access various oxidative transformations. In this review, the versatility of hypervalent iodine (V)-catalyzed reactions have been discussed in detail. This review highlights the oxidation of various substrates using catalytic amounts of *o*-iodoxybenzoic acid (IBX), modified IBX derivatives, *o*-iodoxybenzenesulfonic acid (IBS), recyclable iodine (V), and non-cyclic/pseudocyclic iodine (V) compounds.



Keywords: Hypervalent compounds, iodine (V), catalysis, oxidation

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1. Introduction

Hypervalent iodine compounds have been extensively studied in organic synthetic chemistry over the last decades. It is well-documented in the literature that these compounds have similar reactivity patterns as that of transition metal-organic complexes, however, their excellent oxidizing ability, low cost, mild reaction conditions, low toxicity over heavy-metal reagents, and easy handling make them superior alternatives to heavy-metal reagents.¹⁻⁹ Hypervalent iodine reagents can be effectively utilized for various transformations such as for oxidation of alcohols,^{10,11} sulfides,¹² arylations,^{13,14} C-H functionalization,¹⁵⁻¹⁷ and oxidative coupling reactions¹⁸ among others. The practical interest of these reagents is increasing day by day due to their widespread applicability as powerful oxidizing agents. However, catalytic reactions using hypervalent iodine compounds were not explored until the beginning of the 21st century. Groundbreaking reports on the catalytic use of hypervalent iodine (III) species were independently published by Kita¹⁹ and Ochiai²⁰ groups in 2005. The groups reported the catalytic utilization of these compounds in presence of stoichiometric amounts of co-oxidant, *m*-chloroperbenzoic acid (*m*-CPBA). These catalytic oxidative transformations include the selective *in-situ* generation of hypervalent iodine (III) species. In this series, Vinod²¹ and Giannis²² reported the first examples of the catalytic application of hypervalent iodine (V) species for the oxidation of alcohols using aryl iodide and

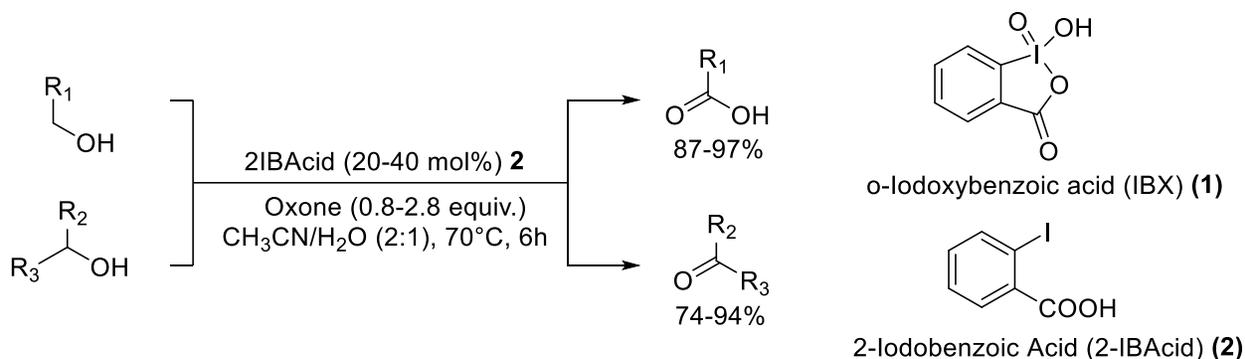
Oxone[®] (2KHSO₅.KHSO₄.K₂SO₄) as the terminal oxidant. These preliminary reports became the basis of the discovery of numerous other catalytic reactions involving hypervalent iodine (III) and hypervalent iodine (V) species. Many articles on different aspects of hypervalent iodine (V) reagents/catalysts have been published previously which include their preparations and diverse applications.^{6,23-27} We herein elaborate on the hypervalent iodine (V)-mediated catalytic reactions. This review is divided into five sections based on the type of hypervalent iodine catalysts.

2. Hypervalent Iodine (V)-Catalyzed Reactions

2.1. *o*-Iodoxybenzoic acid (IBX)- catalyzed reactions

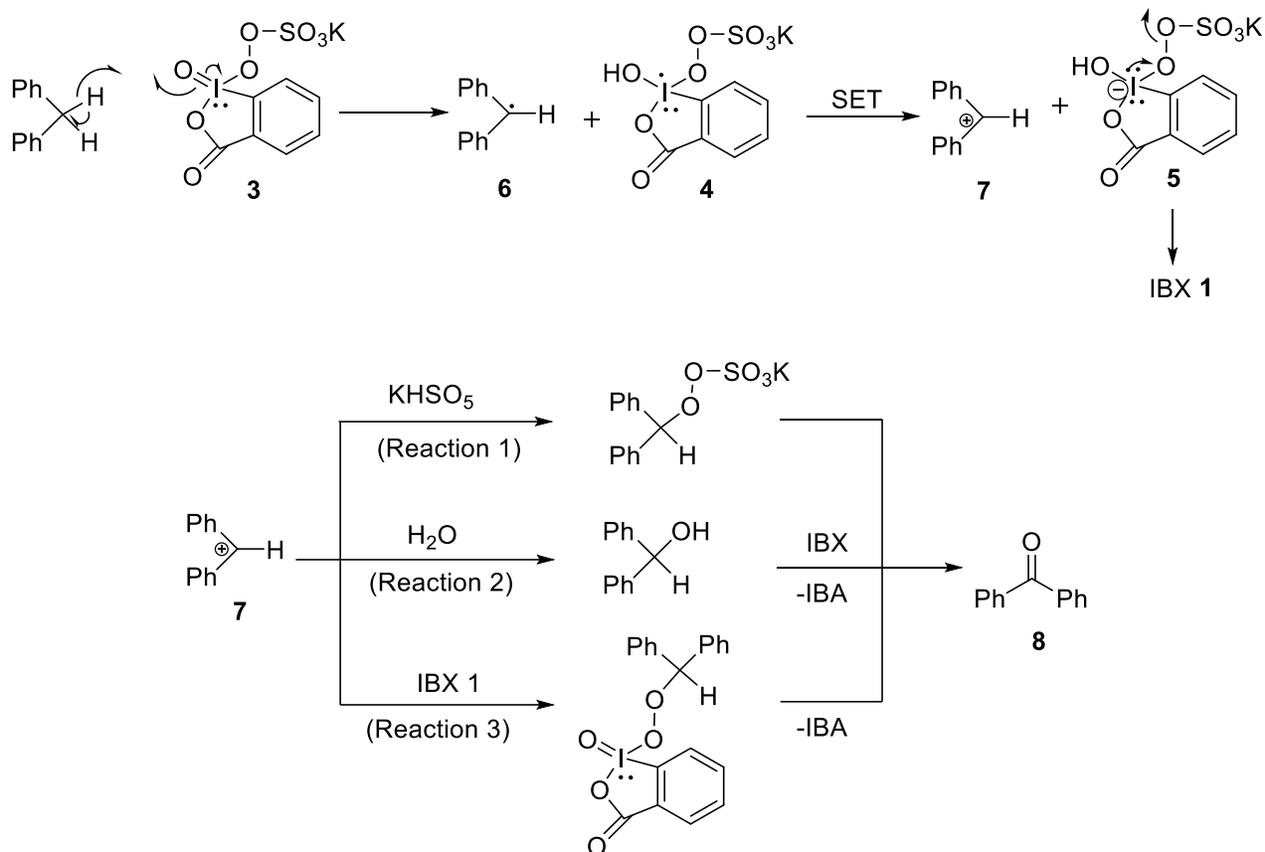
o-Iodoxybenzoic acid (IBX) **1** has a widespread applicability as an oxidant in a number of organic transformations. It is used as a selective reagent for numerous transformations, like oxidation of allylic and benzylic alcohols^{11,28-30}, amines³¹⁻³⁴, and dehydrogenation of carbonyls³⁵, etc. IBX (**1**) was firstly used for selective oxidation of alcohols by Frigerio and Santagostino in 1994.³⁶ However, the usefulness of IBX (**1**) was limited due to its insolubility in almost all solvents except DMSO.

2.1.1. Oxidation of alcohols. Vinod and co-workers generated IBX (**1**) *in-situ* by oxidizing 2-iodobenzoic acid (2IBAcid, **2**) using eco-friendly oxone as co-oxidant. Oxidation of primary and secondary alcohols using catalytic 2IBAcid (20-40 mol%) (**2**) and oxone as co-oxidant in water-acetonitrile biphasic solvent system afforded the corresponding carboxylic acids and ketones, respectively (Scheme 1).²¹ In another report by Vinod and co-workers, selective oxidation of benzylic C-H using catalytic 2IBAcid (**2**) and oxone as co-oxidant was elaborated leading to the formation of corresponding carbonyl functionalities.³⁷ A single electron transfer (SET) mechanism was proposed by the group as depicted in Scheme 2.



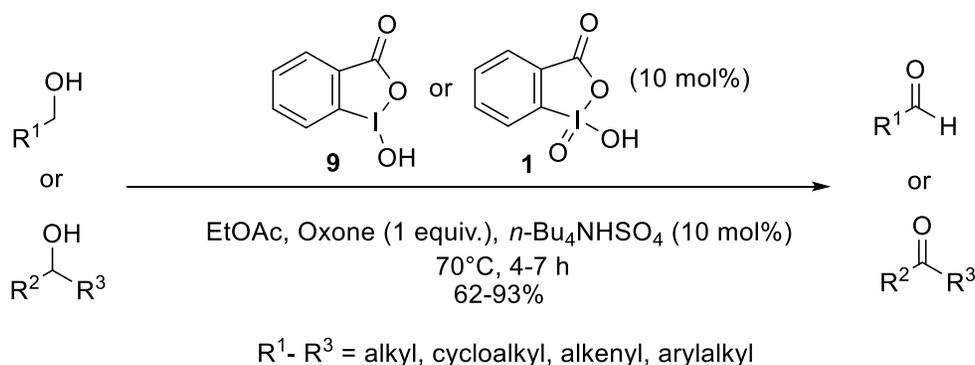
Scheme 1. Oxidation of alcohols via *in-situ* generated IBX **1**.

Salient features of the proposed mechanism involve initiation via a benzylic H-atom abstraction by the I=O bond, similar to the first step in C–H oxidation by reagents that possess a metal=O bond, followed by a single-electron transfer (SET) from the resonance stabilized benzylic radical **6** to the odd electron iodine center in **4** that produces the crucial diphenyl carbocation **7** and the peroxy-IBX anion **5**. The collapse of peroxy-IBX anion **5** regenerates IBX (**1**) which can re-enter the catalytic cycle through further activation by KHSO₅. Finally, three plausible routes (Reaction 1-3) for the transformation of **7** to **8** are shown in Scheme 2.

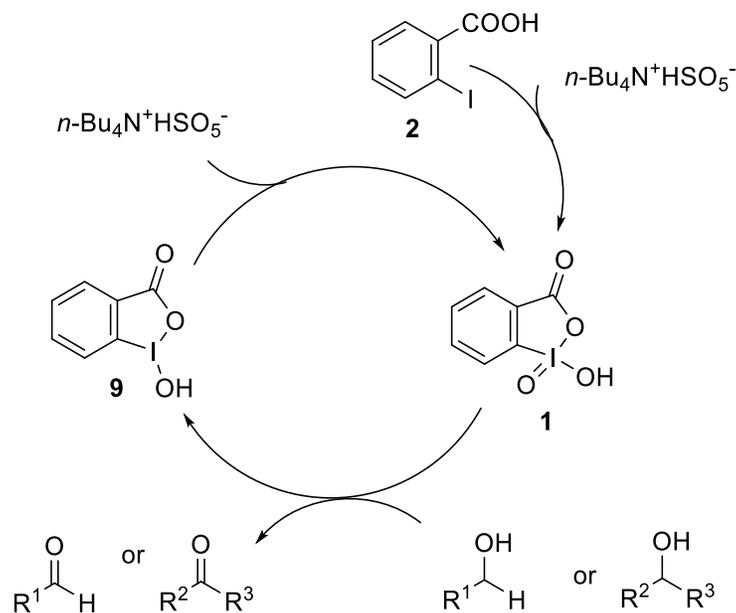


Scheme 2. Proposed free radical mechanism of oxidation of diphenylmethane.

In a similar report, Giannis and Schulze utilized 10 mol% of 2-iodobenzoic acid (2IBAcid, **2**) (or 10 mol% of IBX (**1**)) in ethyl acetate-water biphasic solvent system, in which benzylic alcohols were transformed to their corresponding aldehydes while secondary alcohols were converted to ketones (Scheme 3).²² However, primary aliphatic alcohols afforded corresponding carboxylic acids. Moreover, in case of allylic and homoallylic alcohols, reaction with IBX (**1**) gave a complex reaction mixture. The proposed mechanism for the catalytic cycle for the oxidation of alcohols is depicted in Scheme 4. Tetra-*n*-butylammonium oxone oxidizes the 2-iodobenzoic acid (**2**) to IBX (**1**) which oxidizes the alcohols and, resulted in to reduced IBX **9**. This reduced IBX **9** gets converted back to IBX (**1**) using *tetra-n*-butylammonium oxone.

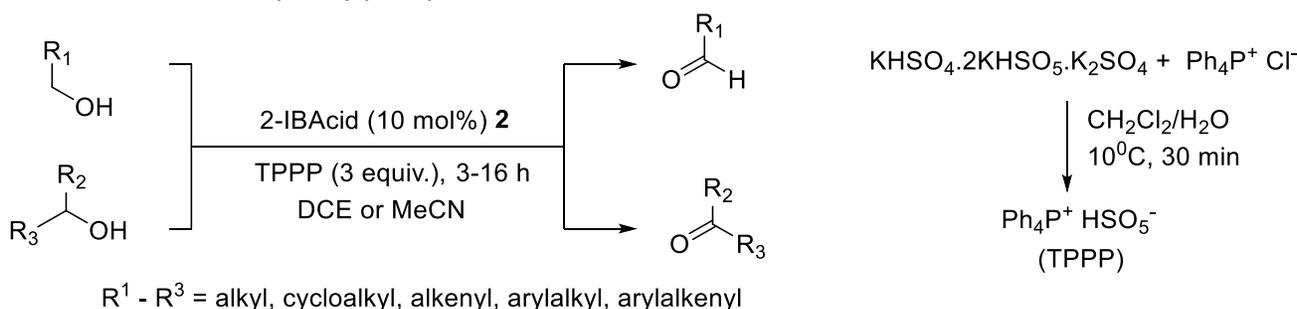


Scheme 3. IBX **1**-catalyzed oxidation of alcohols.



Scheme 4. Catalytic oxidation of alcohols using IBX **1**.

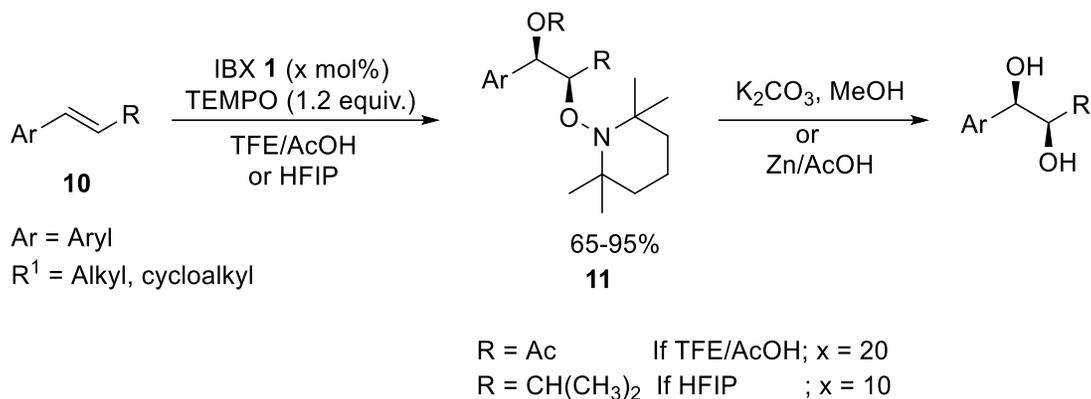
Page and coworkers developed an efficient catalytic system for the oxidation of primary and secondary alcohols by using catalytic amount of 2-iodobenzoic acid (2-IBAcid) **2** in presence of oxidant, tetraphenylphosphonium monoperoxysulfate (TPPP) in acetonitrile or dichloroethane (DCE) or 4-methylpentan-2-one (Scheme 5).³⁸ However, the reaction did not proceed in some of the substrates in case of 4-methylpentan-2-one. One of the salient features of the developed protocol is the oxidation of primary alcohols into corresponding aldehydes avoiding the formation of over-oxidized carboxylic acids. Oxidation of alcohols with TPPP in the absence of 2-iodobenzoic acid afforded the corresponding carbonyl product, however, the reaction time was roughly double. Further, the oxidant, TPPP can be easily prepared by simple counterion exchange between oxone® and tetraphenylphosphonium chloride.



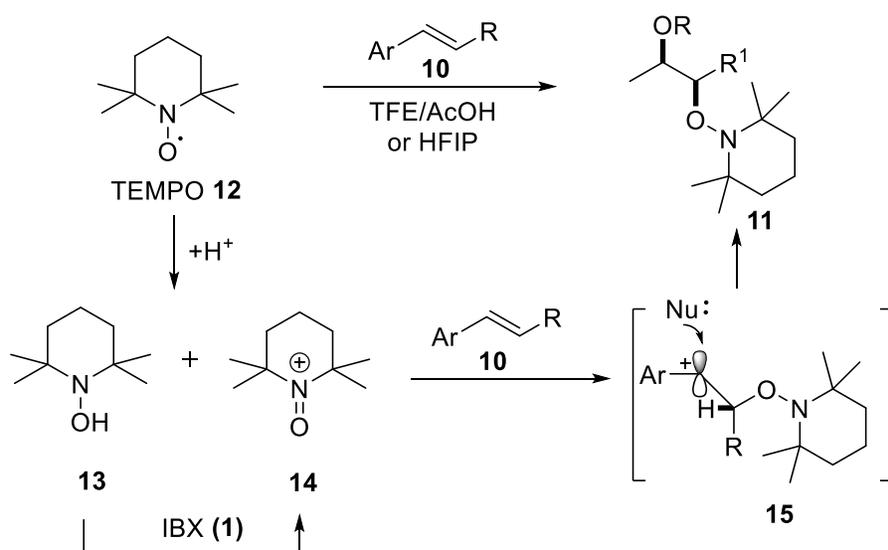
Scheme 5. Oxidation of alcohols using catalyst 2-iodobenzoic acid (**2**).

2.1.2. Oxidation of alkenes. Donohoe and coworkers reported IBX (**1**) catalysed stereoselective, metal-free *syn*-dihydroxylation of electron-rich alkenes using TEMPO in fluorinated solvents i.e. hexafluoroisopropanol (HFIP) or trifluoroethanol (TFE). Alkenes on treatment with IBX/TEMPO afforded orthogonally protected *syn* 1,2-diols **10** up to 95% yield with high stereocontrol that can be deprotected using K₂CO₃/MeOH or Zn/AcOH (Scheme 6).³⁹ The proposed mechanism involves disproportionation of TEMPO **12** in acidic medium that resulted into the generation of hydroxylamine **13** and oxoammonium cation **14**. Reaction of the electron-rich olefin **10** with oxoammonium cation (**12**) may form benzylic cation intermediate **15**, which can then be trapped by external nucleophile. The *syn*-stereochemistry of the product may be attributed to the cation trapping in which the

external nucleophile approaches antiperiplanar to R group, that minimizes the allylic strain and gives net *syn* dihydroxylation **11** (Scheme 7).



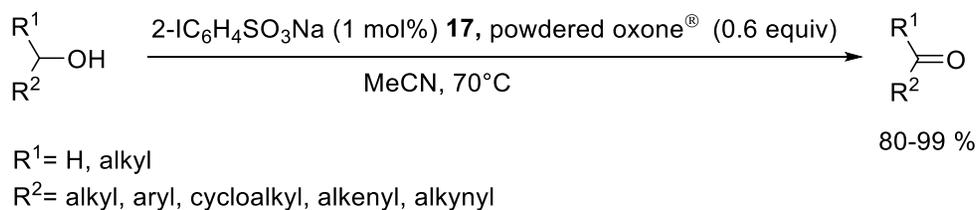
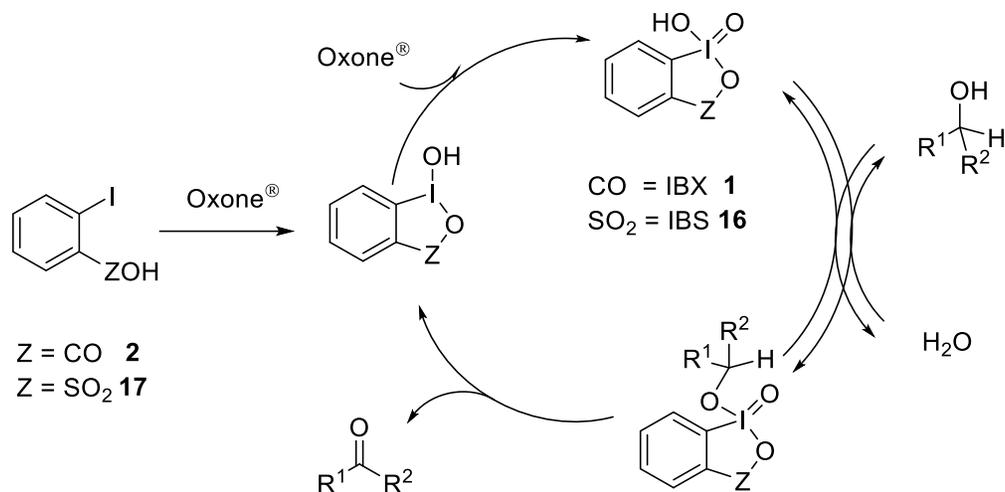
Scheme 6. Stereoselective *syn*-dioxygenation of electron-rich alkene using catalyst IBX (**1**).



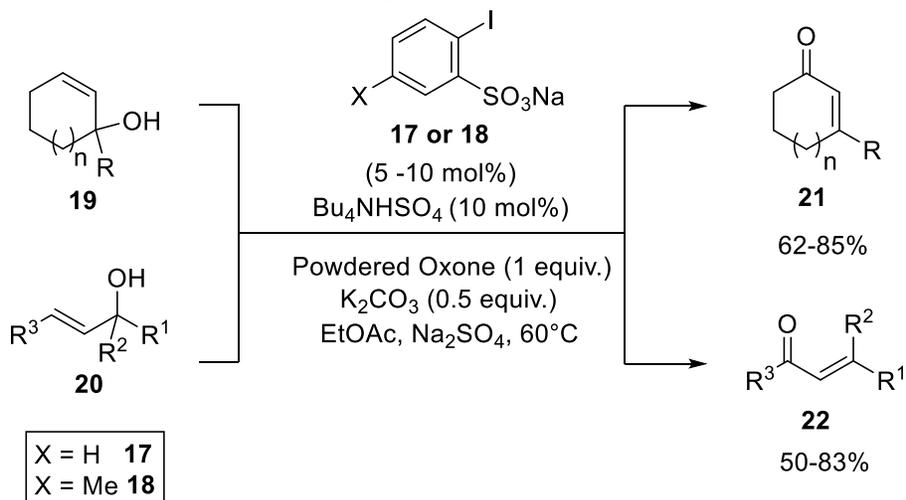
Scheme 7. Proposed mechanism for dioxygenation of electron-rich alkenes **10**.

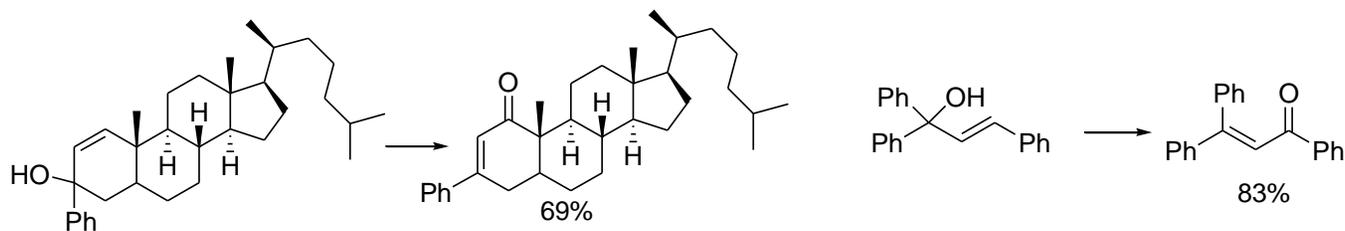
2.2. *o*-Iodoxybenzenesulfonic acid (IBS)- catalyzed reactions

2.2.1. Oxidation of alcohols. Ishihara and coworkers demonstrated the catalytic efficiency of various modified IBX-derivatives and, 2-iodoxybenzenesulfonic acid (IBS, **16**) (Scheme 8).⁴⁰ 2-iodoxybenzenesulfonic acid (IBS, **16**) was prepared by Zhdankin and Tykwinski *et al* from 2-iodobenzenesulfonic acid (**17**) and Oxone in water, however, its oxidative ability was not investigated due to its low stability⁴². Ishihara's group reported that IBS (**16**) is more active catalyst than modified IBX-derivatives for the selective oxidation of alcohols to aldehydes, ketones, carboxylic acids and enones using oxone as terminal oxidant. Moreover, electron-donating group-substituted derivatives, such as, 5-Me-IBS, 5-OMe-IBS and, 4,5-Me₂-IBS showed superior catalytic properties towards alcohol oxidation. *In-situ* generation of IBX (**1**) or IBS (**16**) and catalytic cycle of alcohol oxidation is shown in Scheme 9. The developed protocol was extended towards the large scale oxidation of 4-bromobenzyl alcohol using 1 mol% of the pre-catalyst, potassium 2-iodo-5-methylbenzenesulfonate (**18**), which gave either the formation of 4-bromobenzaldehyde or 4-bromobenzoic acid depending on the amount of oxone used in the reaction.⁴³

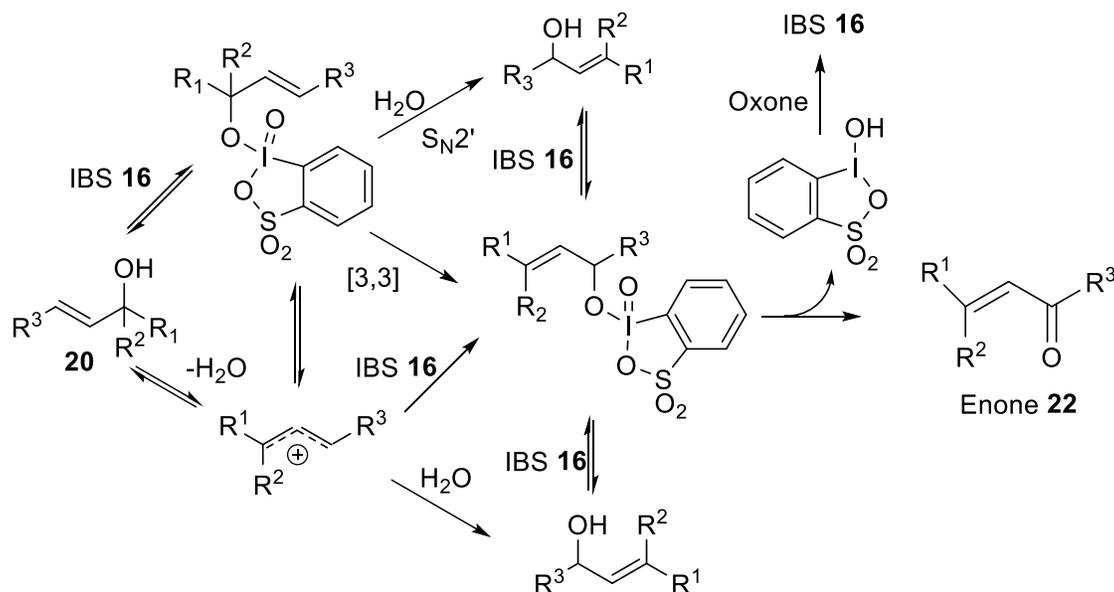
Scheme 8. IBS (**16**)-catalyzed selective oxidation of alcohols.Scheme 9. Catalytic cycle of oxidation of alcohols with IBS (**16**).

Further, Ishihara group reported the oxidative rearrangement of cyclic and acyclic tertiary allylic alcohols, **19** and **20**, to their corresponding enones **21** and **22**, respectively, using pre-catalysts **17** (or **18**) and powdered oxone that generates IBS (**16**) (or 5-MeIBS, **23**) in presence of tetrabutylammonium hydrogensulfate (Bu_4NHSO_4) as phase transfer-catalyst (Scheme 10).⁴⁴ This method is extremely effective as it avoids the use of hazardous and expensive reagents and, afforded desired products in good yield (i.e. up to 85%). 5-Me-IBS **23** gets regenerated faster than IBS thus giving much better catalytic activity. The plausible oxidative rearrangement mechanism of tertiary allylic alcohols **20** to enones **22** is depicted in Scheme 11. Selective substrates are also shown in Scheme 10 with the yield of the rearranged products.



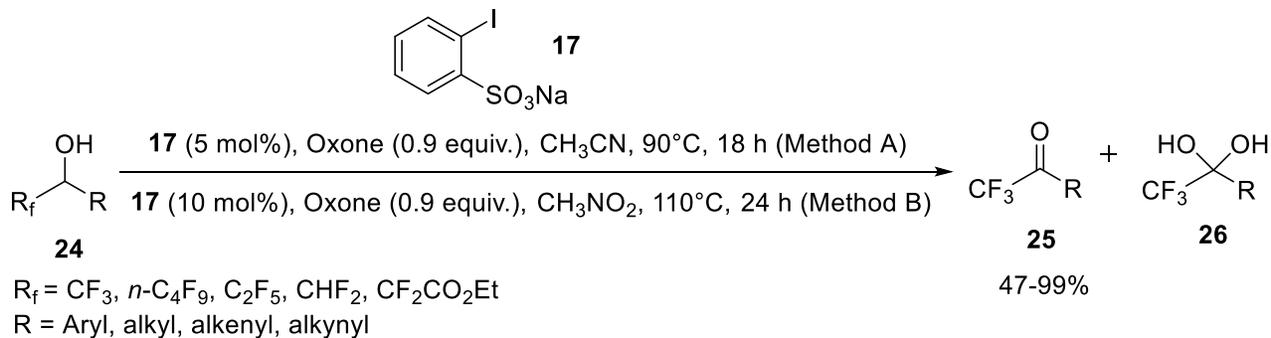


Scheme 10. Oxidative rearrangement of tertiary alcohols **19** and **20** to enones **21** and **22** via *in-situ* generated IBS (**16**) with some examples.



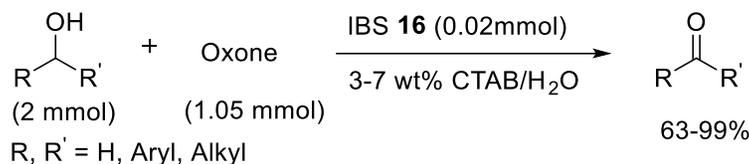
Scheme 11. Proposed mechanism of rearrangement of tertiary alcohols **20** to enones **22**.

Konno and coworkers oxidized various fluoroalkyl-substituted methanol derivatives **24** using catalytic amount of sodium 2-iodobenzenesulfonate (**17**) (5 mol% or 10 mol%) and oxone in acetonitrile or nitromethane as solvent.⁴⁵ Oxidation afforded corresponding ketones **25** in 47-99% yield, however, hydrates **26** were found in some cases in low yields, except for 2,2,2-trifluoro-1-(4-nitrophenyl)ethane-1,1-diol and 2,2,2-trifluoro-1-(4-(trifluoro methyl)phenyl)ethane-1,1-diol, in which hydrates were obtained in 49% and 40 % yields. The catalytic efficiency was compared to other oxidants, such as Dess-Martin reagent, pyridinium dichromate (PDC) and Swern oxidation and, it was observed that this oxidative protocol showed comparable reactivity to Dess-Martin reagents for almost all substrates. Moreover, pyridinium dichromate (PDC) and Swern oxidation could not be used for allylic, propargylic alcohols as well as for alcohols with aliphatic side chain (Scheme 12).



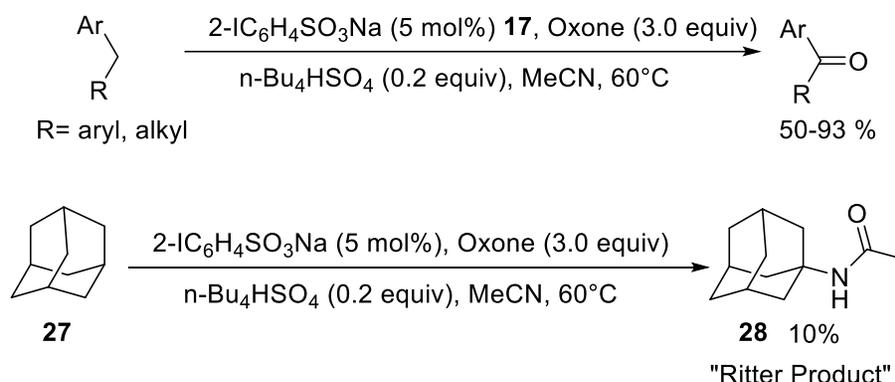
Scheme 12. Oxidation of fluoroalkyl-substituted methanols with sodium 2-iodobenzenesulfonate (**17**).

Micellar catalysis has gained much importance as it uses water as solvent instead of organic solvents. As a commercially available surfactant, cetyltrimethylammonium bromide (CTAB) can form aqueous micelles and has been used in diverse reactions. Wang and coworkers reported the oxidation of primary and secondary alcohols using IBS (**16**) in catalytic amount (0.02 mmol) with oxone in cetyl trimethylammonium bromide (CTAB) in water (Scheme 13).⁴⁶ Secondary benzyl alcohols on oxidation afforded corresponding ketones while primary benzyl alcohols gave corresponding aldehydes in 63-99% yield. However, harsher conditions led to the over-oxidation.



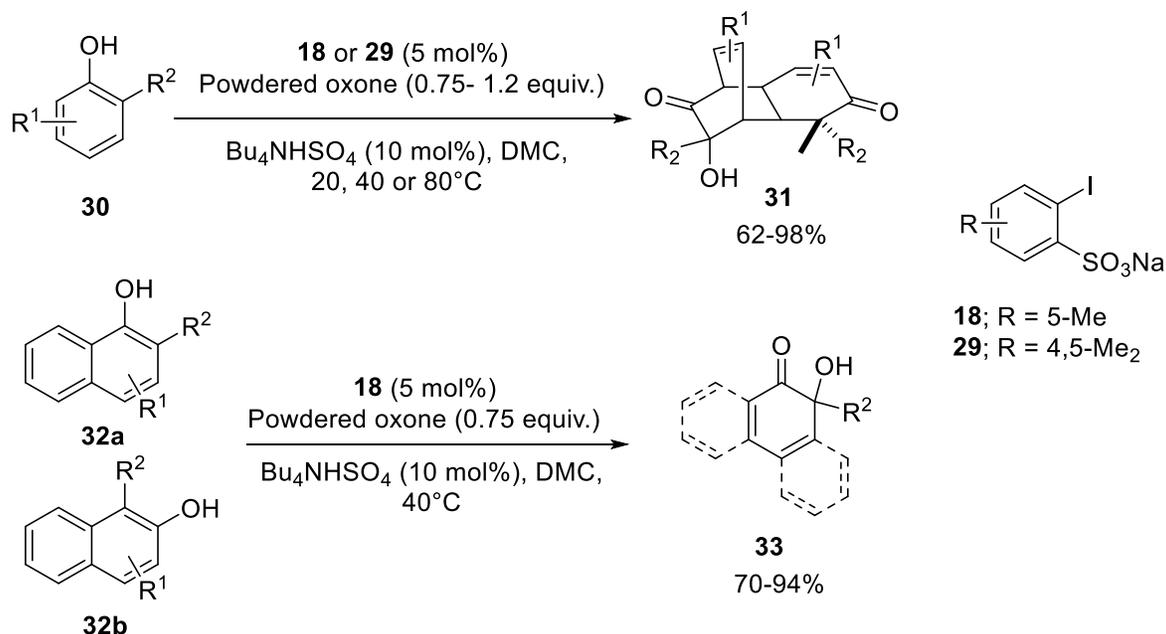
Scheme 13. IBS (**16**)-catalyzed oxidation of alcohols in CTAB micelles.

2.2.2. Oxidation of benzylic and alkane C-H bonds. Zhang and coworkers efficiently utilized the IBS (**16**)-catalyzed oxidation of benzylic and alkane C-H bonds using oxone as terminal oxidant and tetrabutylammonium hydrogensulfate (Bu_4NHSO_4) as phase transfer-catalyst in anhydrous acetonitrile at 60°C (Scheme 14).⁴⁷ Various alkylbenzenes, including toluene and ethylbenzene, several oxygen-containing functionalities substituted alkylbenzenes, cyclic benzylether could be efficiently oxidized in good yields. This catalytic system can also be used to the oxidation of alkanes. Moreover, in order to get insight into the mechanistic pathway, catalytic oxidation of adamantane **27** under N_2 was investigated, which afforded 1-acetamidoadamantane **28**, indicating the intermediacy of carbocation in the adamantane oxidation.



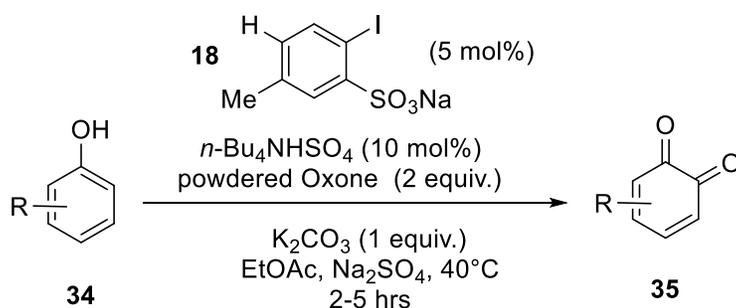
Scheme 14. Oxidation of benzylic and alkane C-H bonds via in-situ generated IBS (**16**).

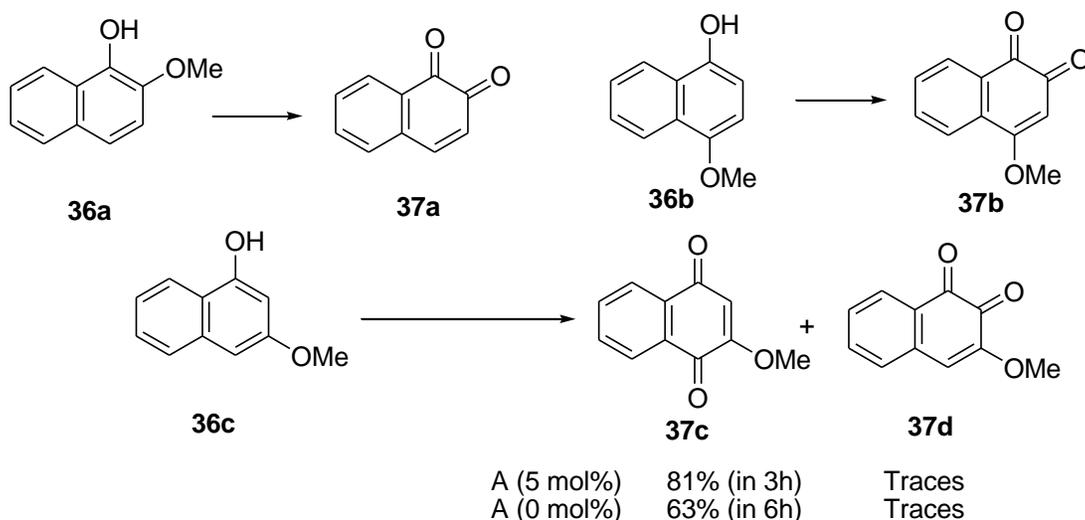
2.2.3. Oxidation of phenols. Ishihara and coworkers developed the site-selective hydroxylative dearomatization of 2-substituted phenols, using pre-catalysts, 5-methyl-2-iodobenzenesulfonic acid **18** or 4,5-dimethyl-2-iodobenzenesulfonic acid **29**, with powdered oxone, that led to either 1,2-quinols or [4+2]-cyclodimers.⁴⁸ Oxidation of 2-substituted phenols **30** afforded [4+2]-cyclodimers **31** in 62-98% yield (Scheme 15). Further, site-selective oxidation of substituted 1-naphthols **32a** and 2-naphthols **32b** gave corresponding *o*-naphthoquinols **33** in 70-94% yield. Rate of the reaction and chemoselectivity gets enhanced by using 4,5-dimethyl-2-iodobenzenesulfonic acid (**29**) and buffered oxone. The group also synthesized natural products such as biscarvacrol and lacinilene C methyl ether with similar procedure under mild conditions. Furthermore, 1,2-quinols on [4+2]-cycloaddition cascade reaction could be transformed into various structural motifs.



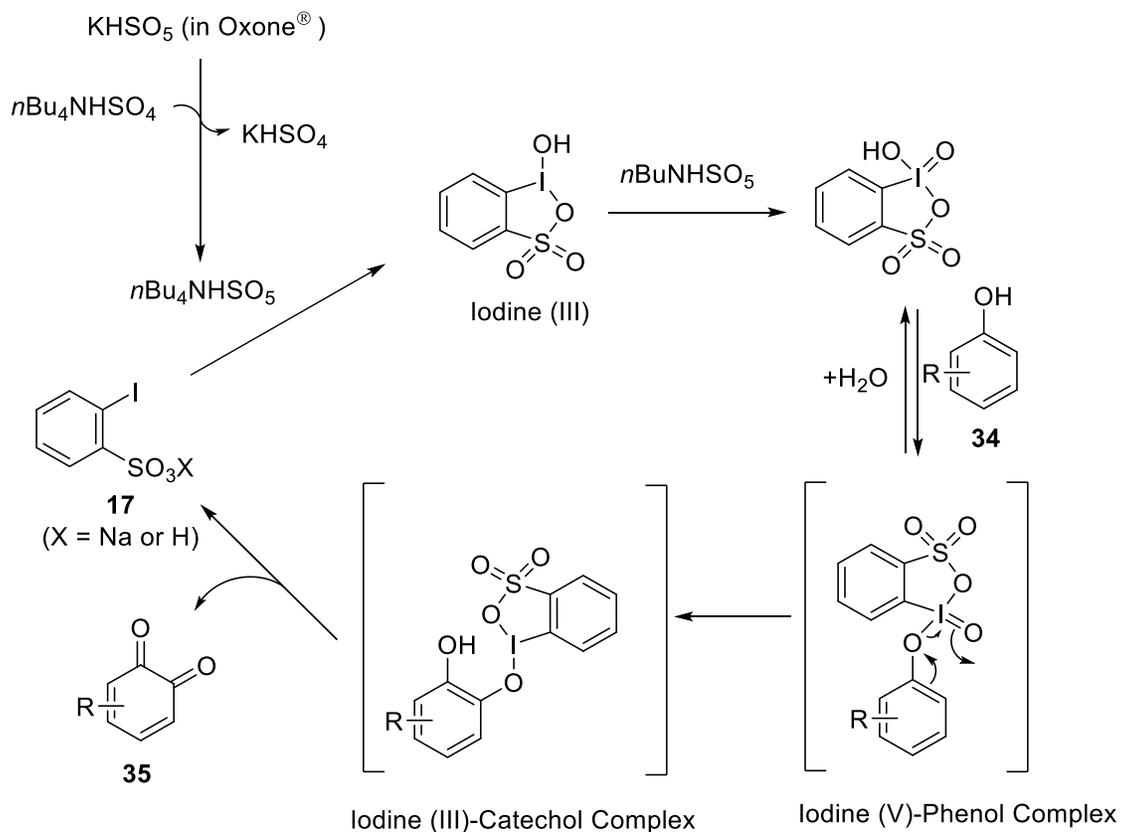
Scheme 15. Site-selective oxidation of 2-substituted phenols and naphthols using pre-catalysts, substituted-2-iodobenzenesulfonic acids **18** and **29**.

Ishihara and co-workers reported the 5-Me-IBS (**23**)-catalyzed regioselective oxidation of phenols, naphthols and phenanthrols using stoichiometric amounts of oxone as co-oxidant (Scheme 16).⁴⁹ Compounds **34** were oxidized by catalytic amount of pre-catalyst **18**, with oxone in the presence of K_2CO_3 and phase catalyst *n*- Bu_4NHSO_4 into their corresponding *o*-quinones **35** in 2-5 hours up to 84% yield. Interestingly, 2-methoxy-1-naphthol **36a** and 4-methoxy-1-naphthol **36b** afforded corresponding *o*-quinone derivatives **37a** or **37b**, while, 3-methoxy-1-naphthol **36c** on oxidation gave corresponding 1,4-quinone **37c** in 81% yield and, only trace amounts of 1,2-quinone **37d** was obtained. The mechanism of IBS-catalyzed oxidation of various phenols to corresponding *o*-quinones is shown in Scheme 17.





Scheme 16. 5-Me-IBS **23**-catalysed oxidation of phenols, naphthols and phenanthrols.

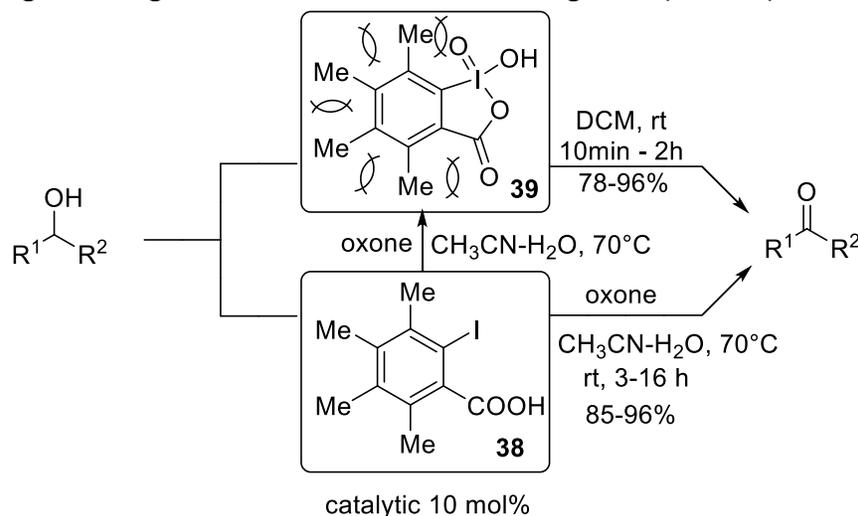


Scheme 17. Mechanism of IBS-catalyzed oxidation of phenols **34** into *o*-quinones **35**.

2.3. Substituted/modified IBX-catalyzed reactions.

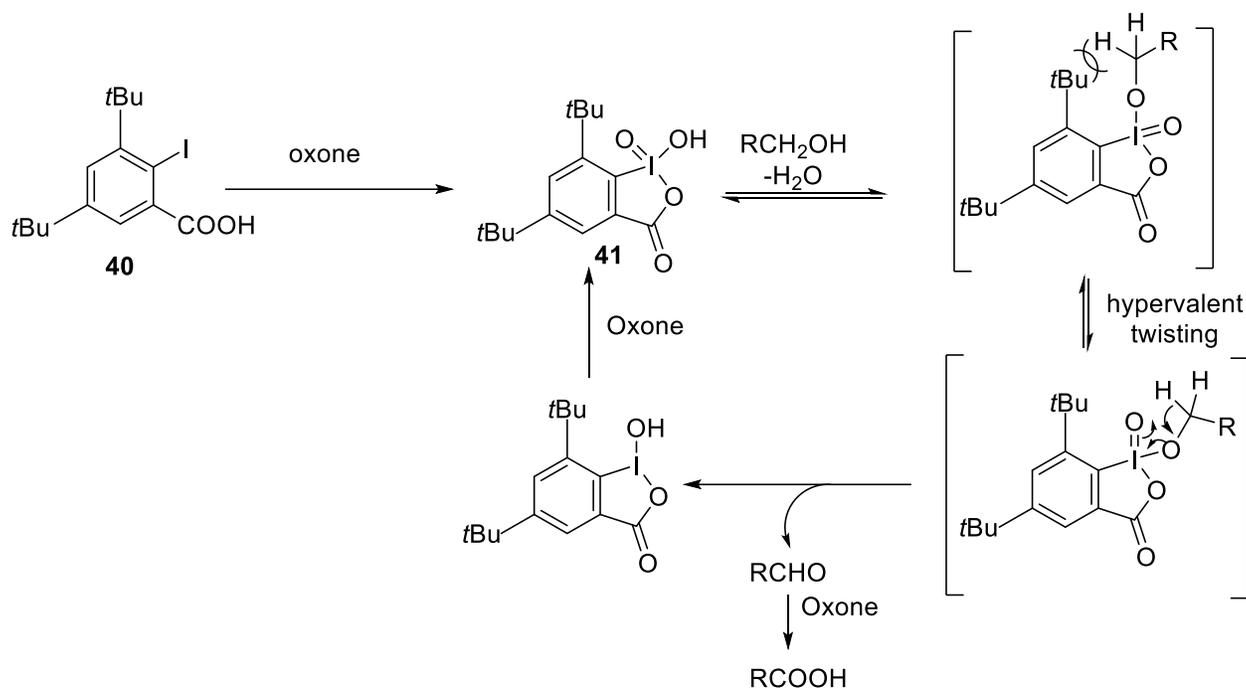
2.3.1. Oxidation of alcohols. Moorthy and co-workers developed 3,5-dimethyl-2-iodobenzoic acid and, 2-iodo-3,4,5,6-tetramethyl-2-iodobenzoic acid **38** as precatalysts, for the *in-situ* generation of IBX-derivatives **39** using oxone as terminal oxidant. Tetramethyl-iodo acid **38**, the precursor for Tet-Me IBX **39** works very nicely in presence of oxone in MeCN : H₂O (1 :1) for the oxidation of variety of alcohols at room temperature (Scheme 18).⁵⁰ The DFT calculations revealed that the methyl groups present in the iodine (V) reagent, Tet-Me IBX **39**

lowers the activation energy corresponding to the hypervalent twisting. It is pertinent to mention that Su and Goddard III earlier demonstrated the effect of hypervalent twist on the enhancement of IBX reactivity.⁵¹ Further, the steric relay between successive methyl groups twists the structure, which enhances its solubility in organic solvents. Primary and secondary alcohols are converted to carboxylic acids and ketones, respectively in MeCN : H₂O solvent system, while primary alcohols selectively afforded aldehydes in case of nitromethane as solvent. In 2016, the same research group published another report for the synthesis of lactones through domino oxidation of diols through *in-situ* generation of TetME-IBX **39** using DIDA (5 mol%) and oxone.⁵²

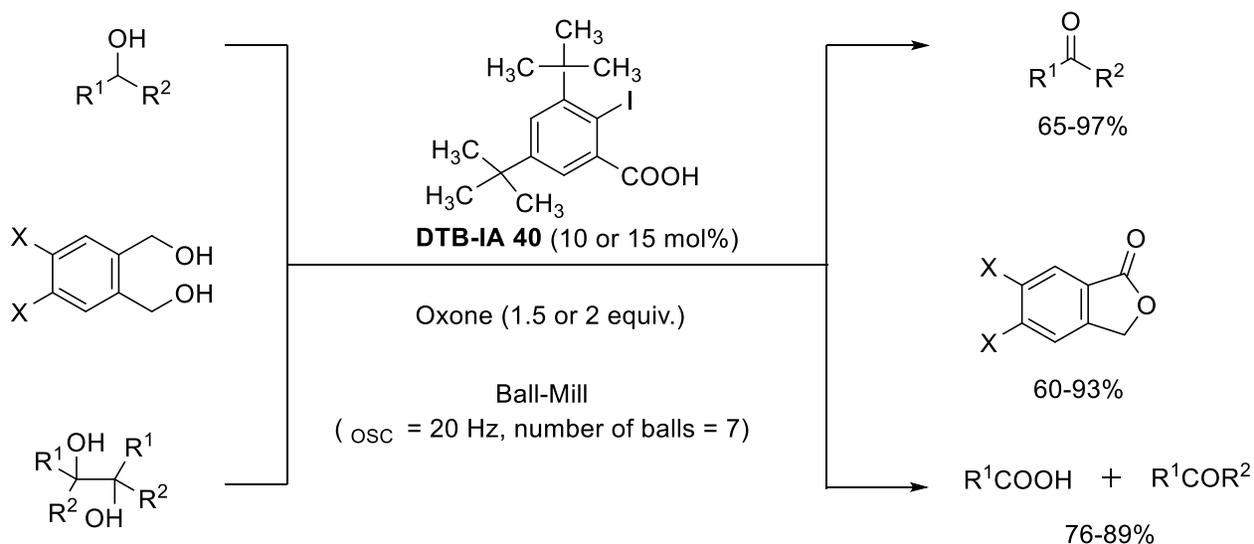


Scheme 18. 3,4,5,6-Tetramethyl-2-iodobenzoic acid **38**-catalysed oxidation of alcohols.

Moorthy and co-workers demonstrated the catalytic oxidations using pre-catalyst, 3,5-di-tert-butyl-2-iodobenzoic acid (DTB-IA) **40** and oxone as terminal oxidant in solid state under mechanochemical ball-milling conditions (Scheme 20).⁵³ Oxidation of alcohols, vicinal diols and non-vicinal diols using *in-situ* generated, iodine (V) reagent, 3,5-di-tert-butyl-2-iodoxybenzoic acid (DTB-IBX) **41** from the sterically crowded catalyst DTB-IA (**40**) gave corresponding carbonyl compounds, oxidatively cleaved products and lactones respectively. Primary aliphatic alcohols under similar conditions afforded corresponding carboxylic acid, while benzylic alcohols afforded carboxylic acid as well as aldehydes. The mechanism of catalytic oxidation in solid state is also presented, in which exchange of alcohols is rapid process while hypervalent twist of alkoxyperiodinane is the rate-determining step (Scheme 19).



Scheme 19. Mechanism of oxidation of alcohols using pre catalyst **40**.



Scheme 20. Oxidation of alcohols by *in-situ* generated 3,5-di-tert-butyl-2-iodoxybenzoic acid (DTB-IBX) **41**.

In another report, Moorthy and co-workers designed and synthesized the twisted 3,3'-diiodo-2,2',6,6'-tetramethoxybiphenyl-4,4'-dicarboxylic acid (**DIDA**) **42**, another modified IBX-precatalyst for the *in-situ* generation of Bis-IBX **39** (Figure 1).⁵⁴ Bis-IBX **43**, containing perpendicular aromatic planes, presumably undergoes insufficient aggregation that results in good solubility and enhanced reactivity. Bis-IBX **43** oxidizes the primary alcohols to either corresponding carboxylic acid or aldehydes depending upon the solvent system used. The developed oxidative protocol is associated with good chemoselectivity as the aliphatic alcohols remain untouched and the selective oxidation of benzylic alcohols can occur selectively. A selective example is given in Scheme 21. Furthermore, oxidation of 1,4- and 1,6-diols using DIDA in presence of co-oxidant, oxone led to the formation of corresponding lactones.

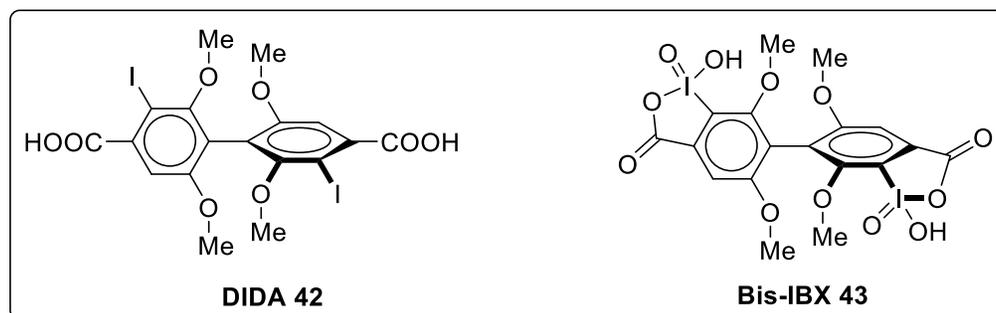
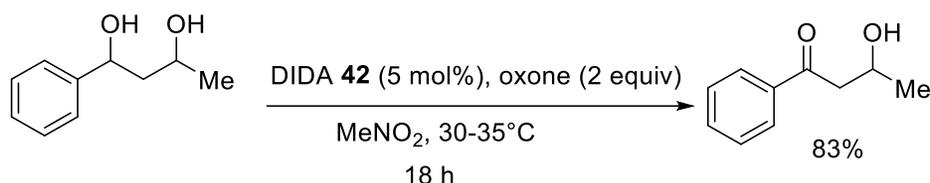
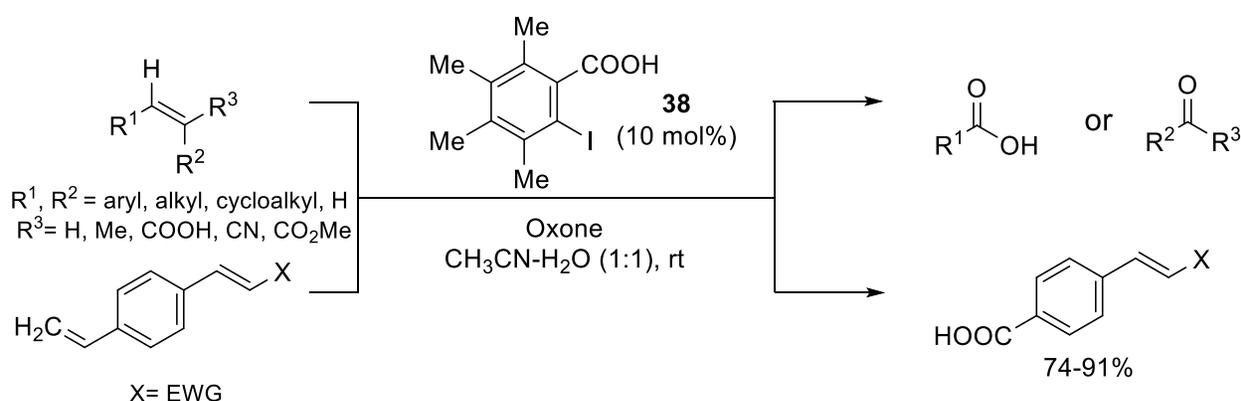


Figure 1.

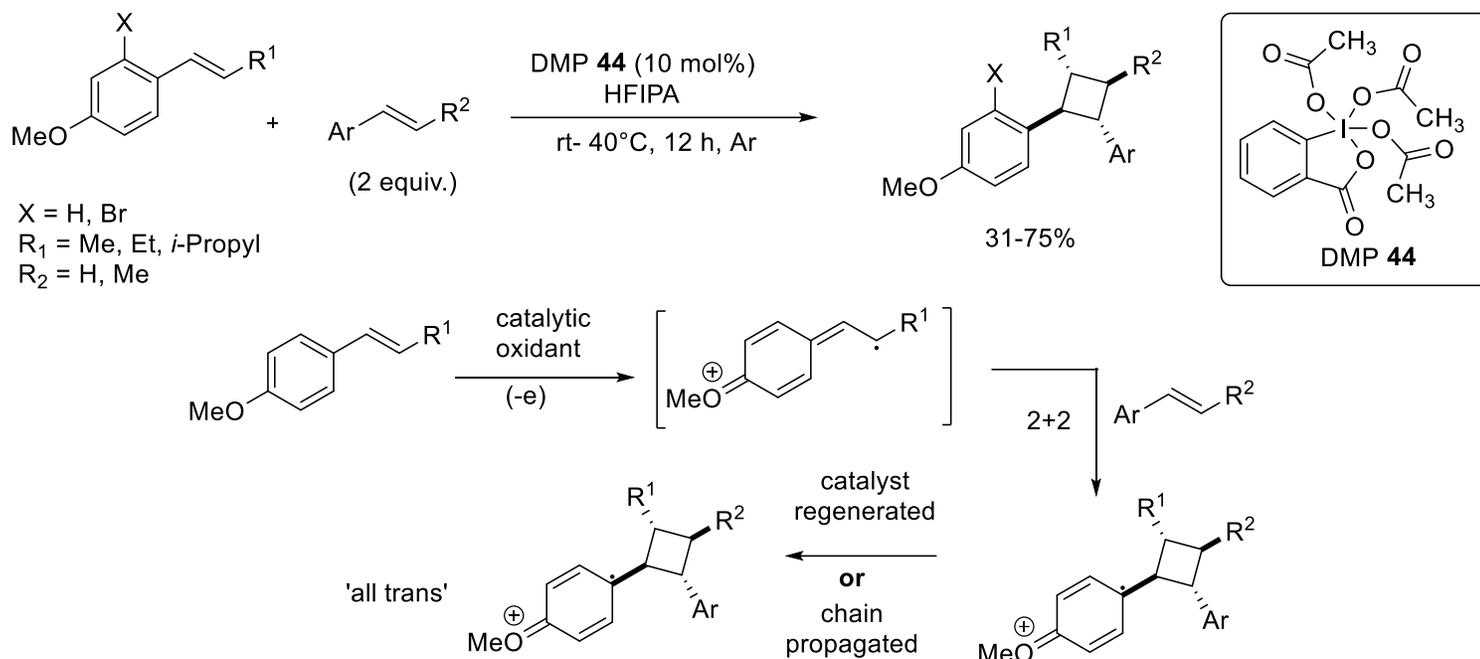


Scheme 21. DIDA 42-catalysed oxidation of alcohols.

2.3.2. Oxidative cleavage of alkenes. Moorthy and coworkers further explored the catalytic efficiency of the pre-catalyst, 3,4,5,6,-tetramethyl-2-iodobenzoic acid (TetMe-IA, **38**) towards the oxidative cleavage of olefins at room temperature.⁵⁵ TetMe-IA **38** catalyzed oxidation of olefins using oxone as co-oxidant afforded corresponding ketones/carboxylic acids. The oxidation starts with dihydroxylation of double bond with oxone, followed by oxidative cleavage by *in-situ* generated 3,4,5,6-tetramethyl-2-iodoxybenzoic acid (TetMe-IBX, **39**), which resulted into the formation of corresponding aldehydes or ketones. In case of aldehydes, further oxidation by oxone gave corresponding carboxylic acids as final product. It is worthwhile to mention that for substrates bearing both electron-rich and electron-deficient double bonds, oxidation takes place in chemoselective manner (Scheme 22).

Scheme 22. Oxidative cleavage of olefins using 3,4,5,6,-tetramethyl-2-iodobenzoic acid (TetMe-IA) **38**.

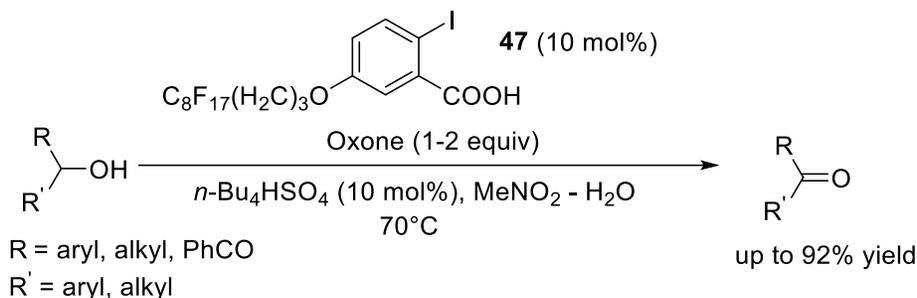
2.3.3. Dimerization of alkenes. Donohoe group also reported the dimerization/heterodimerization of electron-rich alkenes to access cyclobutanes (symmetrical/unsymmetrical) using catalytic amounts of Dess-Martin periodinane (DMP) **44** in fluorinated solvent, HFIPA (Scheme 23).⁵⁶ The protocol was highly diastereoselective, giving all trans, by a head to head coupling process. Moreover, the group explored the synthetic utility of this developed protocol for the synthesis of natural product, Nigramide R in 24% yield.



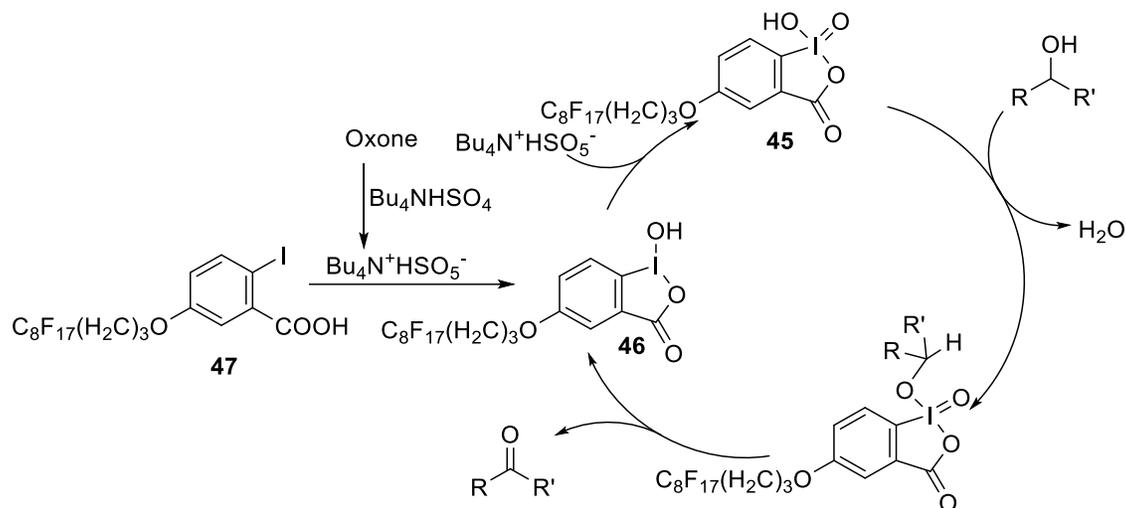
Scheme 23. Dimerization/heterodimerization of electron-rich alkenes into cyclobutanes by catalyst DMP 44.

2.4. Recyclable hypervalent iodine (V) reagents-catalyzed reactions

2.4.1. Oxidation of alcohols. With the objectives to recover and reuse IBA 9 in IBX 1-mediated/catalyzed reactions, Miura and coworkers developed hypervalent iodine catalyst with a fluoros tag, fluoros IBX 45 (Scheme 24).⁵⁷ Oxidation of secondary alcohols using reusable fluoros IBX 45 in the presence of co-oxidant oxone and Bu₄NHSO₄ afforded corresponding ketones in 70-88%. Primary alcohols under similar reaction conditions afforded corresponding carboxylic acids in MeNO₂-H₂O, while in nitromethane as a solvent, afforded corresponding aldehydes. Fluorous hypervalent iodine (V) can be regenerated from fluoros IBA 46, which can be easily recovered by simple filtration. The recovered reagent 46, works very well for at least five catalytic cycles. The mechanism highlighting the generation of fluoros-IBX 45 and its use for the oxidation of alcohols is depicted in Scheme 25.

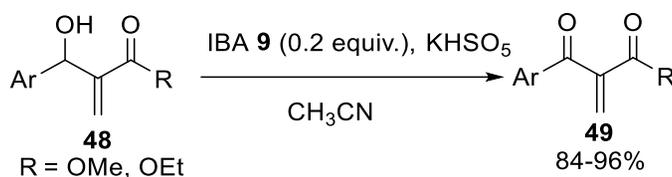


Scheme 24. Oxidation of alcohols using pre catalyst 47.



Scheme 25. Proposed mechanism of catalytic oxidation of alcohols using fluororous IBX **45**.

Selective oxidation of primary and secondary Morita Baylis-Hillman (MBH) alcohols **48** to their corresponding carbonyl compounds **49** was successfully developed by Rao and coworkers.⁵⁸ Catalytic IBA **9** in presence of 1.0 equiv of oxone was utilized for the oxidation of MBH alcohols to their corresponding carbonyl compounds in 84-96% yield (Scheme 26). Furthermore, the developed protocol was extended towards oxidation of MBH alcohols having an ester functionality. The alcoholic group was oxidized to corresponding aldehyde product in these MBH alcohols. Similar controlled oxidation was reported in case of MBH alcohols bearing cyano group. Catalyst **9** could be regenerated by filtration followed by oxidation with oxone and can be reused up to 4 times without any significant loss in activity.



Scheme 26. Selective oxidation of MBH alcohols using catalyst IBA (**9**).

In 2019, Kirsch and Ballaschk synthesized solid-supported hypervalent iodine (V) catalysts (**50**, **51**) derived from IBX and IBS derivatives for the oxidation of secondary alcohols (Figure 2).⁵⁹ Treatment of secondary alcohols with hypervalent iodine (V) (5 mol%) and oxone as co-oxidant resulted in the formation of ketones upto 98% yield. IBS-derived catalyst **51** showed superior reactivity over **50** and requires less reaction time as compared to **50**. Catalyst **50** and **51** can be separated by simple filtration and reuse for multiple times (Scheme 27).

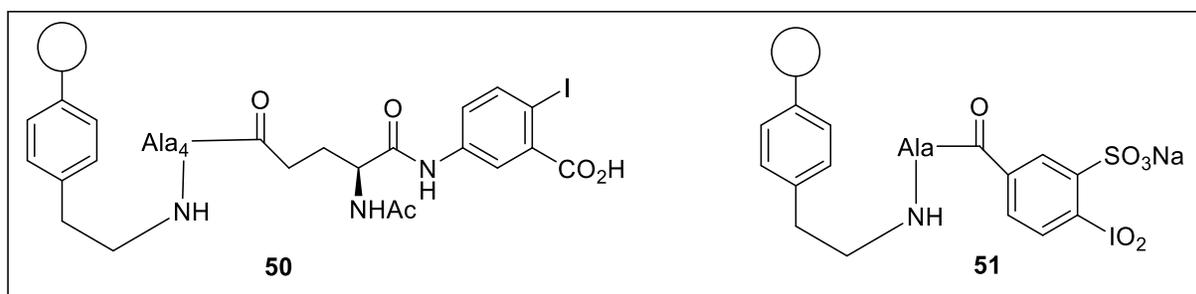
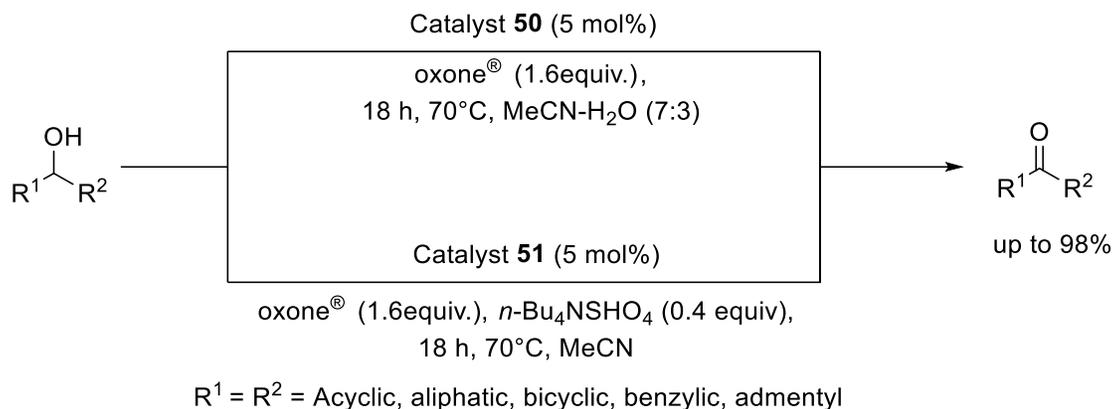
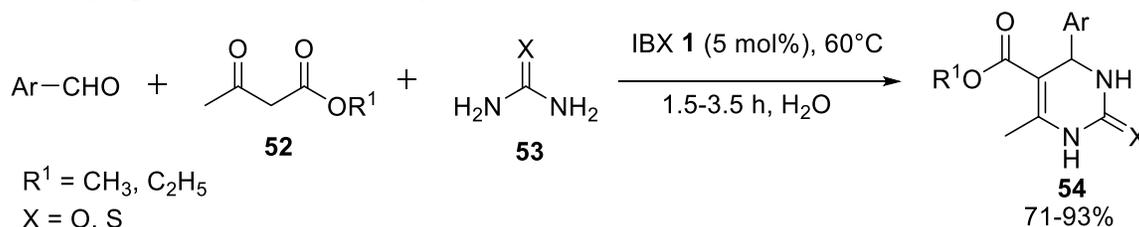


Figure 2 : Solid-supported oxidation catalysts derived from IBX (**1**) and IBS (**16**).



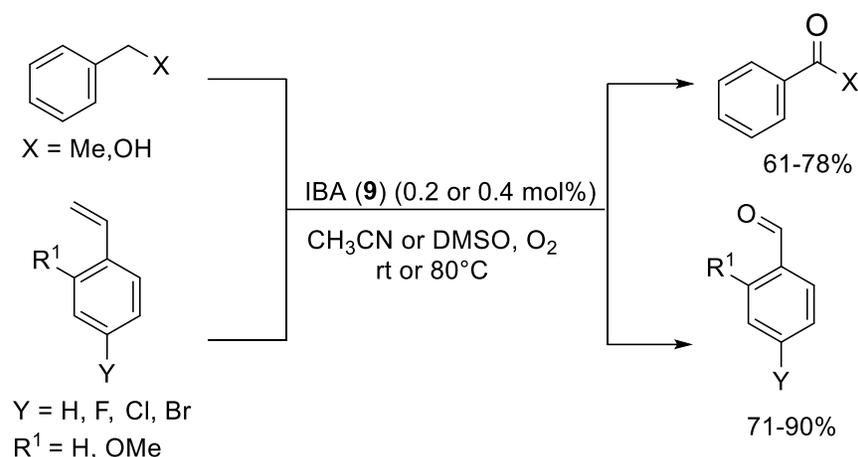
Scheme 27. Solid-supported hypervalent iodine-catalysed oxidation of secondary alcohols.

2.4.2. Synthesis of heterocycles. Chaskar and coworkers performed the multicomponent one-pot Biginelli reaction between aldehydes, β -ketoesters **52** and urea/thiourea **53** using catalytic IBX **1** (5 mol%) in aqueous media to synthesize dihydropyrimidinones (DHPMs) **54** in 71-93% yield (Scheme 28).⁶⁰ It was revealed that IBX **1** activates the carbonyl group of ketones and aldehydes which accelerates the iminium formation followed by nucleophilic addition of enolised β -keto ester. One of the salient features of this developed protocol is that after the completion reaction, about 60% of catalyst can be easily recovered by filtration and reused for few reaction cycles without any significant loss of activity.



Scheme 28. Synthesis of dihydropyrimidinones using catalyst IBX (**1**).

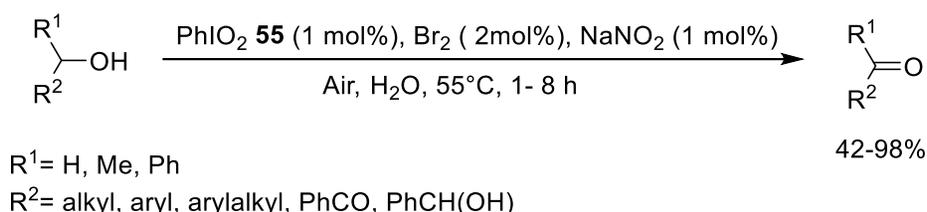
2.4.3. Oxidation of benzylic and aromatic C-H. In another report, Rao group reported the selective oxidation of active methylenes, indoles and styrene C-H bonds in to their corresponding carbonyl compounds by using catalytic IBA **9** in DMSO (Scheme 29).⁶¹ Oxygen/DMSO act as oxidants for activation of organocatalytic C-H bond under mild and metal-free conditions. After each cycle, IBA (**9**) can be simply filtered out and reused up to four cycles without any loss of activity.



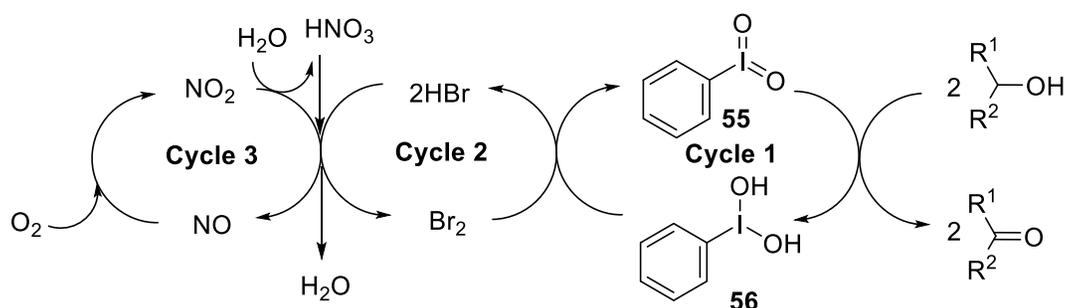
Scheme 29. IBA (**9**)-catalyzed oxidation of benzylic and aromatic C-H.

2.5. Non-Cyclic and pseudocyclic hypervalent iodine (V)- catalyzed reactions.

2.5.1. Oxidation of alcohols and alkanes. Liu and co-workers developed an efficient tandem catalytic aerobic oxidation of alcohols in water using catalytic amounts of iodoxybenzene **55**, bromine, and sodium nitrite (Scheme 30).⁶² Benzylic alcohols on oxidation gave corresponding benzaldehydes without over-oxidation while primary alcohols produced the corresponding aldehydes albeit in low yield. Moreover, aromatic and aliphatic secondary alcohols afforded the corresponding ketones while benzoin and meso-hydrobenzoin gave the C-C bond cleavage products. The proposed mechanism of this oxidative transformation includes three redox cycles. The first redox cycle involves the oxidation of alcohol to the corresponding carbonyl product by PhIO_2 **55**, which is reduced to (dihydroxy)iodobenzene ($\text{PhI}(\text{OH})_2$) **56**. This cycle is followed by cycle 2 which involves the reoxidation of $\text{PhI}(\text{OH})_2$ **56** to iodoxybenzene **55** with Br_2 , which is reduced to HBr . Finally, in the third cycle, the oxidation of NO with O_2 produces NO_2 , which converts HBr back to Br_2 (Scheme 31). Notably, Ishihara's group suggested that the actual oxidant, in this case, is Br_2 rather than PhIO_2 **55**.⁶³

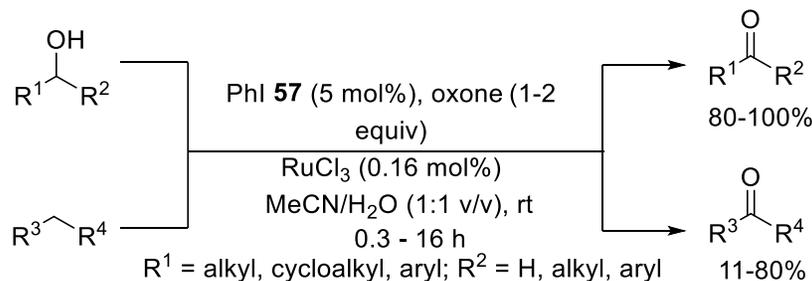


Scheme 30. Iodoxybenzene **55**-catalysed oxidation of alcohols.

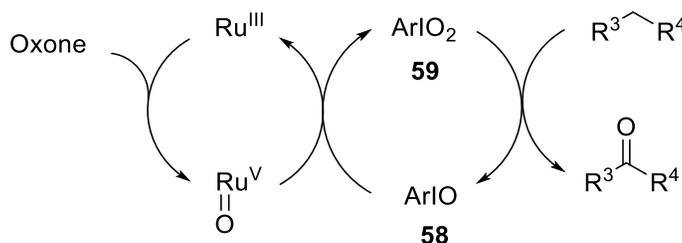


Scheme 31. Tandem catalytic cycle for the oxidation of alcohols.

Yusubov and Zhdankin *et al* developed a mild and efficient ArI/RuCl₃ tandem catalytic system for the oxidation of alcohols and hydrocarbons by using oxone as stoichiometric oxidant (Scheme 32).^{64, 65} A plausible mechanism for this catalytic oxidation includes two catalytic redox cycles. The reaction begins with the initial oxidation of ArI **57** to ArIO **58** and then to ArIO₂ **59** by the Oxone/Ru(III,V) system. The *in-situ* generated monomeric ArIO₂ **59** is responsible for the oxidation of organic substrates and, oxoruthenium complexes are responsible for the oxidation of ArIO to ArIO₂ as shown in Scheme 33.

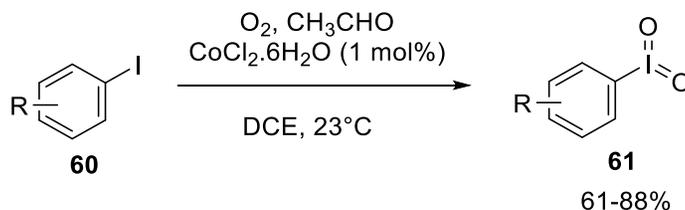


Scheme 32. Oxidation of alcohols and alkanes using PhI **57** as catalyst.

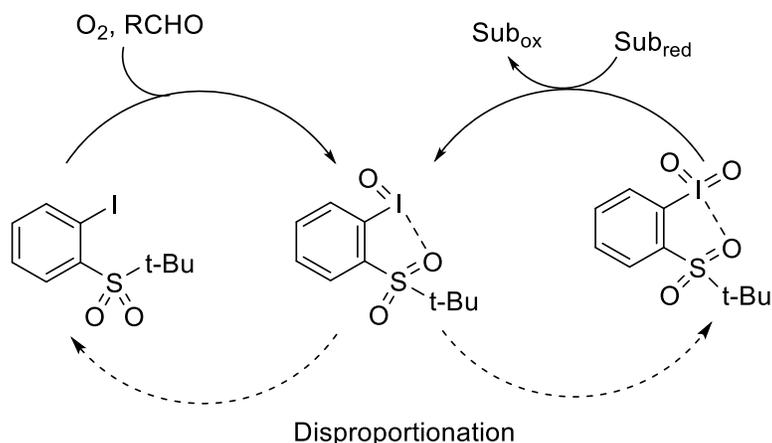


Scheme 33. ArI/RuCl₃ tandem catalytic cycle for the oxidation of alcohols.

In 2018, Powers and coworkers developed synthesis of I(V) reagents by coupling the aerobic oxidation of I(I) **60** to I(III) with facile disproportionation of initially formed iodine (III) reagents to I(V) reagents **61**. Aryl iodides on treatment with catalytic CoCl₂·H₂O (1 mol%) using dioxygen (O₂) as oxidant in 1,2-dichloroethane afforded I(V) reagents with upto 88% (Scheme 34).⁶⁶ Ar-I catalyzed oxidation of secondary alcohols in presence of O₂ using initiator CoCl₂·6H₂O gave corresponding ketones. Primary alcohols and 1,2-diols afforded corresponding acids under similar reaction conditions while 1,4-diols yielded corresponding lactones. The proposed catalytic cycle for the aerobic oxidation of aryl iodides is also depicted below in Scheme 35.

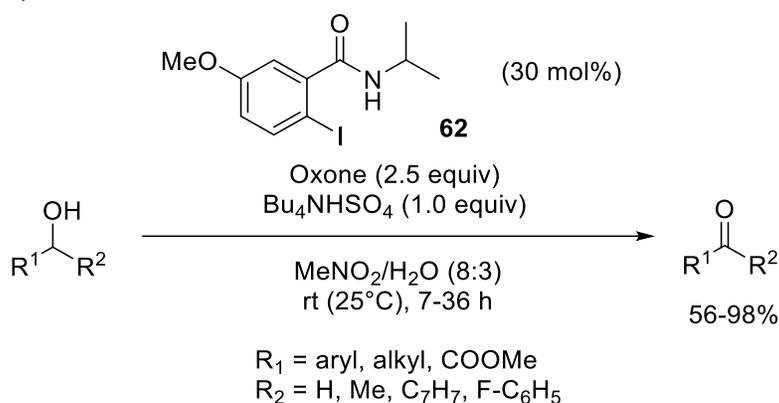


Scheme 34. Aerobically synthesis of iodylbenzene reagents.



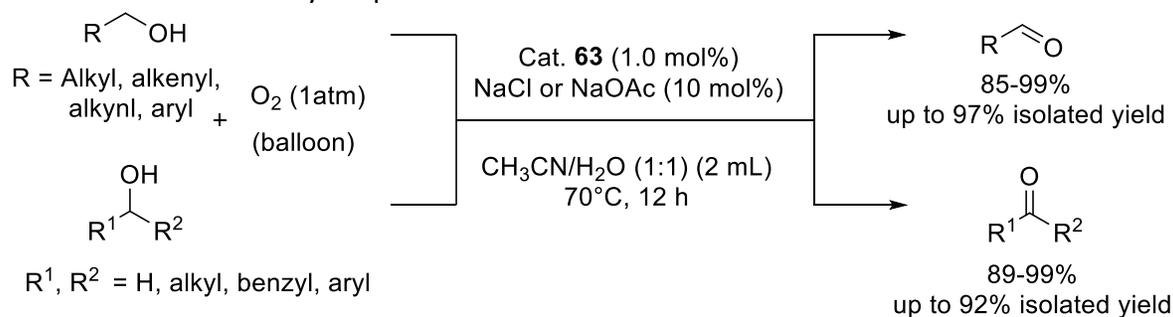
Scheme 35. Proposed catalytic cycle for the aerobic oxidation of aryl iodides.

Yakura and coworkers synthesized and screened various 2-iodobenzamides as catalysts using oxone as co-oxidant towards the oxidation of benzhydrols to corresponding benzophenones.⁶⁷ The catalyst **62**, bearing 5-OMe group in the benzene ring was found to be most reactive amongst others. The high reactivity of this catalyst was attributed to the rapid generation of iodine (V) reagent. Various benzylic and aliphatic alcohols were subjected to oxidation using catalytic amount of **62** using 2.5 equiv of oxone in a mixture of nitromethane and water mixture (Scheme 36).



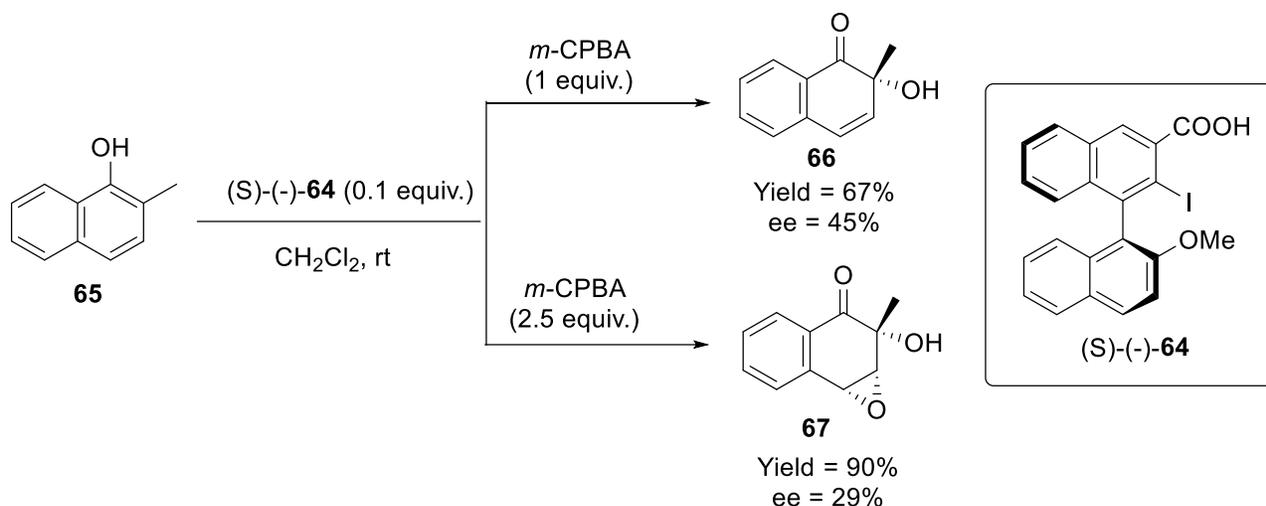
Scheme 36. Oxidation of alcohols using catalyst 2-iodo-N-isopropyl-5-methoxybenzamide **62**.

In 2018, Wei group reported the inorganic-ligand supported iodine catalyst **63**, $(\text{NH}_4)_5[\text{IMo}_6\text{O}_{24}]$ for oxidation of primary and secondary alcohols.⁶⁸ This catalyst **63**, showed high stability and efficiently oxidizes various aromatic as well as aliphatic alcohols with high selectivity (Scheme 37). It avoids the use of toxic and sensitive organic ligands and can be easily recovered. The catalyst could be recycled up to six times without any further purification and can be isolated by simple filtration.



Scheme 37. Aerobic oxidation of alcohols using catalyst inorganic-ligand supported iodine **63**.

2.5.2. Oxidative dearomatization of phenols. In 2009, Quideau *et al* reported the first example of asymmetric hydroxylative phenol dearomatization (HPD) via *in-situ* generation of iodanes from iodoarenes using *m*-CPBA as oxidant.⁶⁹ In a specific example, the asymmetric hydroxylative dearomatization of 2-methylnaphthalen-1-ol **65** using chiral iodoarene (S)-(-)-iodoarene **64** as catalyst accomplished product **66** in 67% yield with ee 45% (Scheme 38). When *m*CPBA was used in excess, the regio- and distereoselective epoxidation of intermediate i.e. **67** was achieved in 90% yield and 29% ee. They monitored the HPD reaction by electrospray ionization mass spectrometric analysis and concluded that the iodine (V) were generated *in-situ* during the reaction.



Scheme 38. Asymmetric hydroxylation phenol dearomatization using chiral iodoarenes **64**.

3. Conclusion

In recent years, the area of hypervalent iodine (V) catalysts has shown tremendous growth. Numerous hypervalent iodine (V) catalysts have been developed, and diverse oxidative transformations have been achieved using these catalytic systems. The discovery of safer and efficient methods for the *in-situ* utilization of iodine (V) has initiated a major surge of research activity and, added a new dimension to the field of organocatalytic systems. Taking into account the environmental aspects and efficient catalytic systems, it is expected that the utilization of these catalytic systems and the development of new hypervalent iodine (V) catalysts will continue in the future. We hope that this review article will provide a stimulus for further investigations in hypervalent iodine (V) chemistry.

Acknowledgement

R.K. is thankful to J C Bose University of Science and Technology, YMCA, Seed Grant R&D/SG/2020-21/166 and DST-Haryana for the research grant, HSCSIT/R&D/163. Moreover, T.D. acknowledges support from JSPS KAKENHI Grant Number 19K05466, JST CREST Grant Number JPMJCR20R1, and the Ritsumeikan Global Innovation Research Organization (R-GIRO) project. K.K. acknowledges support from JSPS KAKENHI Grant

Number 18H02014. Furthermore, V.V.Z. is thankful to the National Science Foundation (CHE-1759798) for support of his research program on hypervalent iodine chemistry.

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Kotaro Kikushima received his PhD in 2010 from Osaka University under the supervision of Prof. Toshikazu Hirao. In 2010, he joined the group of Prof. Brian M. Stoltz at the California Institute of Technology as a postdoctoral research fellow. After working in Nagoya City University (the Nakamura group) and then Okayama University (the Nishina group), he moved to Osaka University working with Prof. Sensuke Ogoshi in 2014. KK is an Assistant Professor in the group of Prof. Toshifumi Dohi at Ritsumeikan University since 2018. His current research interest includes the development of cost-effective synthetic methods for functional organic molecules.



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This manuscript has been corrected by the author, checked and corrected by the scientific editor, and contains all necessary changes.