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ARTICLE

Hypervalent Iodine Catalysis for Selective Oxidation of Baylis–Hillman adducts *via* In Situ Generation of o-Iodoxybenzoic Acid (IBX) from 2-Iodosobenzoic acid (IBA) in Presence of Oxone

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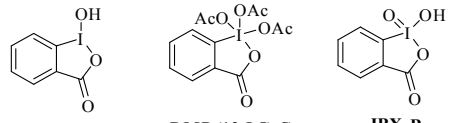
An efficient, environmentally benign, eco-friendly protocol for selective oxidation of primary and secondary Baylis–Hillman alcohols to the corresponding carbonyl compounds has been developed. We have demonstrated the catalytic use of o-iodoxybenzoic acid (IBX) generated in situ from 2-Iodosobenzoic acid (IBA) in presence of oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) as a co-oxidant. This efficient method notably enables better to high yields without the use of any toxic heavy metals and direct use of tricky IBX. Furthermore, the synthesized catalyst could be recovered conveniently using a reductive work-up.

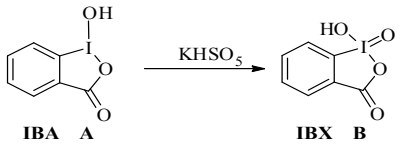
Introduction

Selective oxidation of primary and secondary alcohols to aldehydes, ketones are important fundamental transformations in synthetic organic chemistry. To date, many excellent catalytic methods have been developed for oxidations of alcohols.[1] However there is a strong impetus to develop efficient, greener methods with greater selectivity without the use of transition metals. Such methods are highly desirable, and very important for both chemical and pharmaceutical industry.[2]

During the past decade hypervalent iodine compounds have attracted a significant interest as mild, selective, easily available and environmentally benign reagents with high oxidizing capabilities in synthetic organic chemistry.[3] The most important representatives of this class of compounds are 2-iodosylbenzoic acid (IBA), iodoxybenzoic acid (IBX) and Dess-Martin periodinane (DMP) which have found wide applications as oxidizing reagents in the synthesis of biologically important complex organic molecules.[4] Recently 2-Iodoxybenzenesulfonic Acid was proved to be an extremely active catalyst for the selective oxidations in the presence of catalytic iodine(V)/Oxone oxidation system.[5] In particular, hypervalent iodine heterocycles derived from benziodoxoles with pentavalent iodine are Dess–Martin periodinane (DMP, **C**)[6] and 1-hydroxy-1, 2-benziodoxol-3-(1H)-one-1-oxide (IBX, **B**)[7] have emerged as the reagents of choice for selective oxidative transformations. Despite the polymeric structure of IBX, its low solubility and potentially explosive nature restrict the practical application of IBX.[8]



In order to solve this problem catalytic systems with in situ generation of iodine (V) species from the corresponding iodine reagents have also been developed to minimize the hazardness of highly reactive iodine (V) species during the reaction.[9] We have thus planned in situ formation of active I (V) state of IBX from catalytic amounts of iodosobenzoic acid (IBA) (Scheme 1), by employing oxone as a co-oxidant. The application of oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) has increased rapidly as it offers several advantages, such as stability, nontoxic, simple handling, controllable addition etc.[10]



Scheme 1. Insitu generation of iodoxybenzoic acid (IBX)

The Morita–Baylis–Hillman (MBH) reaction is an organocatalyzed chemical transformation used for the preparation of natural products, heterocycles and drugs.[11] MBH adducts are highly functionalized small molecules with high synthetic versatility.[12] Recently our group has reported the successful synthesis of new epalrestat analogues from Morita–Baylis–Hillman adducts, especially for those derived from aromatic aldehydes with nitrile functionality.[13] It is worth noting that the oxidation reaction can be troublesome for MBH adducts derived from acrylic esters to form aldehydes, since they are prone to extensive oxidative degradation.

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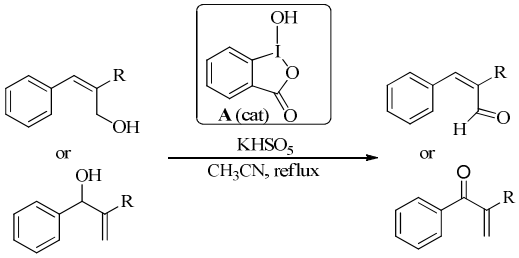
The biological and chemical relevance of these adducts justify the development of alternative methods for their oxidations as they have conjugated, highly reactive functionalisations. The synthesis of this potential 1,1-dicarbonyl-substituted alkene **3** has been reported from the corresponding saturated 1-phenylsulfinyl derivatives, either by oxidation of β-hydroxy-α-phenylsulfenyl carbonyl compounds or direct acylation of α-phenylsulfenyl enolate anions with acid chloride in the literature.[14] Herein we employ MBH derived alcohols as synthetic equivalents for selective production of 1,1-dicarbonyl-substituted alkenes making this approach a valuable alternative for their synthesis.

In recent years IBX has been used for oxidative transformations involving MBH adducts.[15] In all the cases they have employed IBX 1.5-3.0 equivalents for oxidation of Morita–Baylis–Hillman adducts.[16] However, there have been no reports on the catalytic use of IBA for in situ generation of IBX for oxidation of MBH adducts. Thus, we sought to develop highly efficient benziodoxole derived iodine(III)-analogs as catalysts for the oxidation of alcohols with oxone allowing high selectivity under mild conditions.



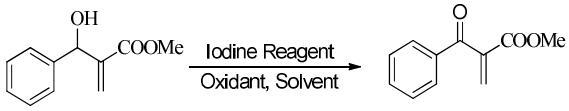
Scheme 2. Oxidation of MBH derived alcohols to carbonyl compounds using a catalytic amount of IBA.

In continuation to our interest to develop metal free oxidative protocols with hypervalent iodine reagents,[17] we envisaged that in situ generated IBX could function as efficient system for selective formation of carbonyls from MBH derived alcohols. Till date very few reports are available in literature for isolating the MBH derived aldehydes with ester functionality.[18] We have successfully circumvented the over oxidation issues associated with the oxidation of MBH adducts and their derived alcohols, as they have conjugated system with competiting groups. By employing this in situ iodine (V) strategy as a key step for the oxidations of variety of MBH adducts with excellent yields and high selectivity. A wide variety of Morita-Baylis–Hillman adducts and their derived alcohols could be selectively oxidized directly leading to carbonyl compounds in simple manner (Scheme 2).

Results and Discussion

Our initial attempts were directed towards identifying suitable hypervalent iodine based catalytic system for selective oxidation of MBH derived alcohols. Methyl 2-benzoylacrylate was selected as a model substrate to identify the suitable catalytic system (Table 1).

Table 1: Screening of Hypervalent iodine induced oxidation reactions[a]



Entry	Reagent (equiv)	Oxidant (equiv)	Solvent	Yield (%)[b]
1	2-IBAcid (2)	none	CH_3CN	NR
2	PIDA (2)	none	CH_3CN	20
3	IBP (2)	none	CH_3CN	NR
4	2-IBAcid (1)	Oxone (2)	CH_3CN	NR
5	PIDA (1)	Oxone (1)	CH_3CN	40
6	IBA (1)	none	DMSO	trace
7	IBA (1)	TBHP (2)	CH_3CN	NR
8	IBA (0.5)	Oxygen	CH_3CN	trace
9	IBA (0.6)	Oxone (1)	CH_3CN	95
10	IBA (0.5)	Oxone (1)	CH_3CN	95
11	IBA (0.2)	Oxone (1)	CH_3CN	94
12	IBA (0.2)	Oxone (1)	EtOAc	60
13	IBA (0.2)	Oxone (1)	DMSO	50
14	IBA (0.2)	Oxone (1)	Toluene[c]	90
15	IBA (0.2)	Oxone (1)	DCM[d]	50
16	IBA (0.2)	Oxone (1)	THF[e]	30
17	-	Oxone (1)	CH_3CN	NR
18	-	TBHP (1)	CH_3CN	NR

[a] All reactions were carried out at 1mmol scale at 80 °C for 6h in 2mL of solvent. [b] Isolated Yield. [c]Temperature at 100 °C for 24h, [d]40 °C, [e]60 °C.

Reactions were carried with 2-iodo benzoic acid (2IBAcid), Phenyl iodine(III) diacetate (PIDA), 1-(*tert*-Butylperoxy)-1,2-benziodoxol-3(1H)-one (IBP) by employing 2 equiv without using any external oxidant (entries 1 to 3). Although PIDA gave 20% yield (entry 2), 2IBAcid and IBP could not furnish the desired product (entries 1 and 3). In pursuit we have chosen oxone as an environmentally safe co-oxidant for a catalytic hypervalent iodine oxidation with 2IBAcid and PIDA as they are commercially available. The 2IBAcid was found to be ineffective even in presence of co-oxidant (entry 4), however PIDA gave the corresponding oxidized product in 40% yield (entry 5). Then we have synthesized IBA from 2-iodo benzoic acid and

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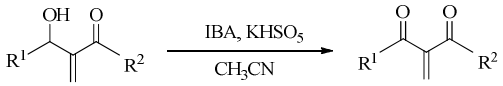
DMSO as a solvent system, only trace amount of oxidized product was observed (entry 6). Then TBHP, oxygen and oxone were employed as oxidants with IBA system (entries 7 to 9). To our surprise the corresponding carbonyl compound was formed in 95% yield with in-situ generated IBX oxidation (entry 9). The molar ratios of IBA and oxone required to achieve quantitative conversion of primary alcohols was closely monitored. Among them 0.6, 0.5 and 0.2 equiv gave 95%, 95% and 94% yields respectively. Remarkable solvent effects were observed with catalytic hypervalent iodine oxidation system (entries 12-16). However the reaction was sluggish with other solvents and the yield of **3a** was only 60% with EtOAC, and 50% with DCM and DMSO. It gave only 30 % with THF and 90 % yield with toluene only after 24h. The reaction did not proceed with oxone and TBHP in the absence of IBA (entry 17 and 18). Thus with only 0.2 equiv of **B** and 1 equiv of oxone, the reaction was finished within 4 h to give the desired product **3a** in 94% yield in CH_3CN system (entry 11).

Table 2: Oxidation of MBH adduct with IBA/Oxone[a]



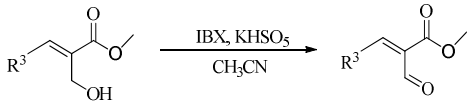
2a-2s **3a-3s**

Entry	MBH (**2**)	Keto Product (**3**)	Time [h]	Yield (%)[b]
1	**2a**, R^1 = Phenyl; R^2 = OMe	**3a**, R^1 = Phenyl; R^2 = OMe	4	94
2	**2b**, R^1 = 3-OMe Phenyl; R^2 = OMe	**3b**, R^1 = 3-OMe Phenyl; R^2 = OMe	4	92
3	**2c**, R^1 = 4F- Phenyl; R^2 = OMe	**3c**, R^1 = 4F- Phenyl; R^2 = OMe	4	88
4	**2d**, R^1 = 4-OMe Phenyl; R^2 = OMe	**3d**, R^1 = 4-OMe Phenyl; R^2 = OMe	4	94
5	**2e**, R^1 = 4Cl- Phenyl; R^2 = OMe	**3e**, R^1 = 4Cl- Phenyl; R^2 = OMe	6	89
6	**2f**, R^1 = 4Me- Phenyl; R^2 = OMe	**3f**, R^1 = 4Me- Phenyl; R^2 = OMe	4	95
7	**2g**, R^1 = 3Br- Phenyl; R^2 = OMe	**3g**, R^1 = 3Br- Phenyl; R^2 = OMe	4	84
8	**2h**, R^1 = 3Me- Phenyl; R^2 = OMe	**3h**, R^1 = 3Me- Phenyl; R^2 = OMe	4	91
9	**2i**, R^1 = 3Cl- Phenyl; R^2 = OMe	**3i**, R^1 = 3Cl- Phenyl; R^2 = OMe	6	89
10	**2j**, R^1 = Phenyl; R^2 = OEt	**3j**, R^1 = 3Br- Phenyl; R^2 = OEt	4	95
11	**2k**, R^1 = 3Br- Phenyl; R^2 = OEt	**3k**, R^1 = 3Br- Phenyl; R^2 = OEt	8	85
12	**2l**, R^1 = 4Cl- Phenyl; R^2 = OEt	**3l**, R^1 = 4Cl- Phenyl; R^2 = OEt	6	92
13	**2m**,R^1 = 4Me- Phenyl; R^2 = OEt	**3m**, R^1 = 4Me- Phenyl; R^2 = OEt	4	96
14	**2n**, R^1 = 3Me- Phenyl; R^2 = OEt	**3n**, R^1 = 3Me- Phenyl; R^2 = OEt	4	94
15	**2o**, R^1 = 3-OMe- Phenyl; R^2 = OEt	**3o**, R^1 = 3-OMe- Phenyl; R^2 = OEt	4	92

[a] All reactions were carried out at 1mmol scale, IBA (0.2 equiv), Oxone (1 equiv) in 2mL of CH_3CN, reflux. [b]Isolated Yield.

To explore the generality of the *in situ* generated **B** catalyzed oxidation of alcohols with oxone, various structurally diverse secondary alcohols were examined as substrates under optimized conditions. First, MBH adducts were prepared from acrylates and were tested for IBA oxidations. All the MBH adducts (**2a-2s)** gave corresponding keto derivatives (**3a-3s)** with good to excellent yields Table 2. The reactions with different electron-donating and electron-withdrawing substituents on the phenyl ring of BH adducts were tolerated leading to the high yields of oxidized products. There is not much change in the yields for *para* and *meta* substituted MBH alcohol derivatives. The unsubstituted phenyl ring with methyl (**3a**) and ethyl (**3j**) ester functionality proceeded to give the desired products in good to excellent yields 94% and 95% respectively. The bromo substitution at *meta* position containing products delivered in low yields (**3g** and **3k**) 84%, 85% when compared to *chloro* substituted *meta* isomer (**3i)** with 89%. The *meta* (CH_3, OMe) substituted MBH adducts with ethyl ester functionality gave (**3n**) 94%, (**3o**) 92%, whereas with methyl acrylate derived BH alcohols resulted in (**3h**) 91%, (**3b**) 92% yields of the desired products. However electron-donating group substituted MBH adducts (OMe, CH_3) gave better yields, (**3d)** 94%, (**3f**) 95% and (**3m**) 96% than electron withdrawing substituents. In case of *para* fluoro substituted the desired product was achieved in (**3c**) 88%, and chloro substituted with (**3e**) 89%, (**3l**) 92% yields respectively.

Table 3: Oxidation of MBH allylic Alcohol with IBA/Oxone[a]



4a–4h **5a-5h**

Entry	MBH (**4**)	Keto Product (**5**)	Time (h)	Yield (%)[b]
1	**4a**, R^3 = Phenyl	**5a**, R^3= Phenyl	4	98
2	**4b**, R^3 = 2-Me Phenyl	**5b**, R^3= 2-Me Phenyl	4	90
3	**4c**, R^3= 3-Me Phenyl	**5c**, R^3 = 3-Me Phenyl	5	92
4	**4d**, R^3= 4-Me Phenyl	**5d**, R^3 = 4-Me Phenyl	4	95
5	**4e**, R^3 = 3-OMe Phenyl	**5e**, R^3 = 3-OMe Phenyl	4	93
6	**4f**, R^3= 4F- Phenyl	**5f**, R^3 = 4F- Phenyl	8	85

[a] All reactions were carried out at 1mmol scale, IBA (0.2 equiv), Oxone (1 equiv) in 2mL of CH_3CN, reflux. [b]Isolated Yield.

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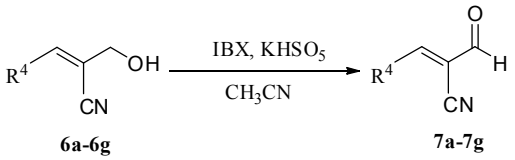
Table 4: Oxidation of MBH allylic Alcohol with IBA/Oxone:



6a-6g **7a-7g**

Entry	MBH	Keto Product	Time (h)	Yield (%)[b]
1	**6a**, R^4 = Phenyl	**7a**, R^4 = Phenyl	4	95
2	**6b**, R^4= 4-Me Phenyl	**7b**, R^4 = 4-Me Phenyl	4	96
3	**6c**, R^4 = 4-Et Phenyl	**7c**, R^4 = 4-Et Phenyl	4	95
4	**6d**, R^4 = 4-OMe Phenyl	**7d**, R^4 = 4-OMe Phenyl	4	95
5	**6e**, R^4= 3-OMe Phenyl	**7e**, R^4 = 3-OMe Phenyl	5	92
6	**6f**, R^4 = 2-OMe Phenyl	**7f**, R^4 = 3-OMe Phenyl	5	91
7	**6g**, R^4 = 4-Br Phenyl	**7g**, R^4 = 2-OMe Phenyl	6	88

[a] All reactions were carried out at 1mmol scale, IBX (0.2 equiv), oxone (1 equiv) in 2mL of CH_3CN, reflux. [b]Isolated Yield.

In addition, we also tested the reaction with more challenging MBH derived allylic alcohols with ester functionality for selective oxidation to aldehydes, and the results are represented in Table 3. To extend this methodology we have synthesised (2*E*)-3-phenyl-2-hydroxymethylprop-2-enoate (**4a**) directly from methyl 3-phenyl-3-hydroxy-2-methylenepropanoate (**2a**) under reported reaction conditions.[19] It is interesting to note that BH derived allylic alcohols (**4a**) proceeded reaction well with 100% conversion, selectively (**5a**) with 98% yield of the aldehyde as desired product. It is noteworthy to observe only aldehyde as oxidised product for primary allylic alcohols (Table 3) when compared to reported oxidation of primary alcohols to corresponding carboxylic acids.[9a] Notably *para*, *meta*, *ortho* substituted Me gave (**5d**) 95%, (**5c**) 92%, (**5b**) 90% and *meta* substituted OMe resulted in (**5e**) 85%, yield of the corresponding aldehydes. In case of fluoro substitution at phenyl the product (**5f**) was formed with 85% yield (Table 3, entries 1 to 6).

Further, we extended scope of the reaction with various BH alcohols with ester functionality for selective oxidation to aldehydes under the optimized reaction conditions (Table 4, entry 1 to 7). Then we have carried out the synthesis of [*E*]-α cyano cinnamyl alcohols from Baylis-Hillman adducts,[20] and their subsequent oxidation to aldehydes. All cyano cinnamyl alcohols (**6a-6g**) were oxidized selectively with major [*E*]- α-cyanocinnamic aldehydes (**7a-7g**) in excellent yields.

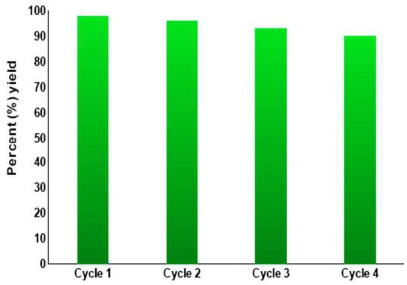
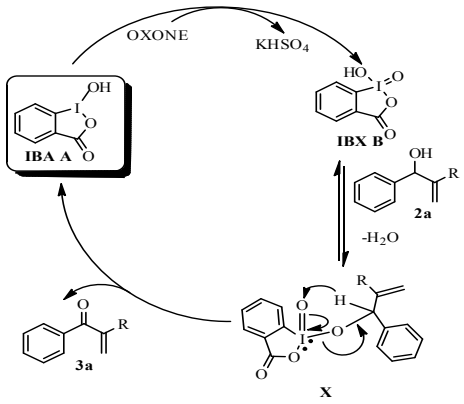


Fig 1: Reusability of IBA **A**

In order to show the scale-up potential of this efficient selective transformation, we have conducted a gram-scale synthesis of **3a** and **5a** using respective MBH adduct (40 mmol), IBA (8 equiv), Oxone (40 equiv) in 80 mL of CH_3CN for about 6h under reflux conditions. This gave excellent yield of the desired products, demonstrating the industrial viability for selective synthesis of MBH oxidized products.

We have proposed a possible reaction pathway for oxidation of alcohols with IBX **B** is represented in Scheme 3.[5a,21] The catalytic cycle of **B**, which was prepared in situ from **A**, could be accomplished by regenerating **A** through the oxidation of **3a** with oxone. It was experimentally confirmed that IBX is the true active species with oxidation state of "I(V)" which is essential in the catalytic cycle of IBA-catalyzed oxidation with oxone.[5a] Initially IBA gets oxidized by oxone to generate IBX, which will activate the Baylis Hillman alcohol **2a** with elimination of water molecule and generate the intermediate **X**.[5a] This will undergo elimination of alpha hydrogen and further rearrange to form the oxidized product **3a** with regeneration of the IBA **A** as demonstrated in **X** of Scheme 3. At the end of reaction the reduced form of IBX **B** is easily separated by simple filtration and can be regenerated by oxidation with oxone[9] and can be reused for four cycles without any appreciable loss in its activity as shown in Figure 1.



Scheme 3: Plausible Reaction Mechanism

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Conclusion

In summary, we report a facile oxidation system for one-step conversion of the Baylis-Hillman adducts to potential synthons *i.e.,* secondary alcohols to ketones and primary alcohols to aldehydes in the presence of IBA. Several significant features of this protocol are the catalytic use of 2-iodosobenzoic acid (IBA) **A** that tolerates the presence of a wide range of substituents on substrates under mild conditions with high selectivity. We anticipate that the simplicity, catalytic nature of this system, regeneration by simple filtration, with no byproducts, high selectivity meet the desirable goals of eco-friendly chemical transformations.

ExperimentalSection

General Procedure for IBA A-Catalyzed Oxidation: An oven-dried flask was charged with stir bar, BH derived alcohol **2(a-o),** (1.0 mmol), IBA **A** (0.2 equiv), Oxone (1 equiv) in dry acetonitrile (2.0 mL) under reflux conditions. Then the reaction mixture was stirred until complete conversion takes place as indicated by TLC analysis. The crude reaction was cooled to room temperature, the 2-iodosylbenzoic acid (IBA) was filtered off and the solvent was removed under vacuum. The filtrate was concentrated in vacuo and was purified by silica gel column chromatography to afford the desired products **3(a–o**). The IBA was reoxidized using oxone and can be reused for consecutive cycles.

Acknowledgements

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Graphical Abstract:

An efficient, eco-friendly protocol for selective oxidation of primary and secondary Baylis–Hillman alcohols to the corresponding carbonyl compounds in high yields has been developed with 2-Iodosobenzoic acid (IBA).