JOC*Note*

Mild Oxidation of Alcohols with *o*-Iodoxybenzoic Acid (IBX) in Water/Acetone Mixture in the Presence of *β*-Cyclodextrin†

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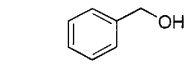
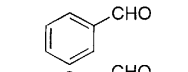
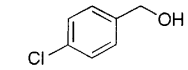
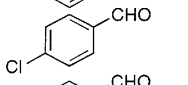
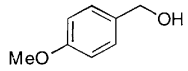
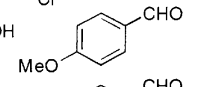
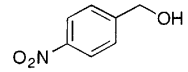
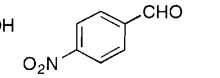
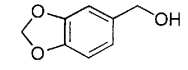
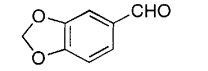
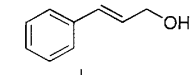
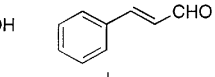
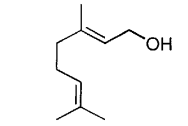
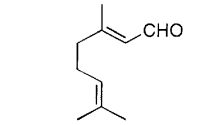
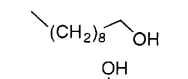
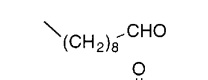
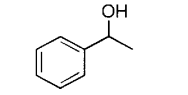
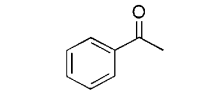
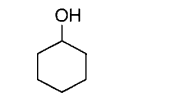
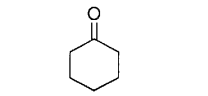
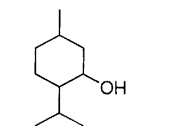
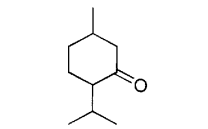
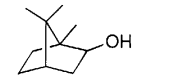
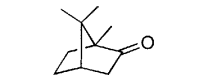
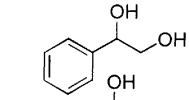
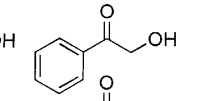
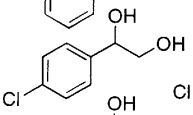
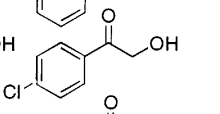
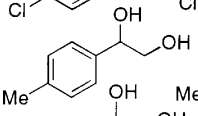
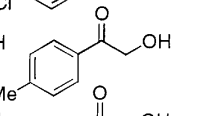
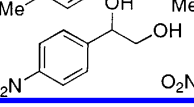
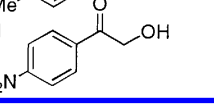
Abstract: A mild and efficient oxidation of alcohols with *o*-iodoxybenzoic acid (IBX) catalyzed by *β*-cyclodextrin in a water/acetone mixture (86:14) has been developed. A series of alcohols were oxidized at room temperature in excellent yields.

The goal in present day organic synthesis is to perform organic reactions in aqueous medium because of the environmentally benign nature of the solvent.[1] The use of aqueous medium as solvent also reduces the harmful effects of organic solvents. This becomes further sophisticated if these reactions can be performed involving supramolecular catalysis. In recent years much attention has been focused on oxidations involving hypervalent iodine reagents.

Hypervalent iodine reagents are well-known for their selective, efficient, mild, and environ friendly properties as oxidizing agents.[2] Although *o*-iodoxybenzoic acid (IBX) and Dess−Martin periodinane (DMP) are two important reagents that are suitable for a wide range of chemical transformations, IBX has become the reagent of choice. IBX smoothly oxidizes primary and secondary alcohols to aldehydes and ketones, respectively, and also 1,2-diols to α-ketols or α-diketones without any oxidative cleavage of the glycol bond.[3] It is stable against moisture and highly efficient. Even though it was discovered some time ago, its significant utilization as a reagent is of recent origin due to its insolubility in most solvents. The limited solubility of IBX has also led to many variations.[4] Of recent, there is also an example of modification of IBX through a series of steps to make it soluble in water.[5] Thus, there is need to develop methodologies to utilize IBX, which is easily accessible, in aqueous medium for commercially viable processes.

TABLE 1. Oxidation of Alcohols with IBX in Presence of *β*-CD in Water/Acetone Mixture (86:14)

Entry	Substrate	Product [a]	Yield(%) [b]
1			96
2			98
3			96
4			90
5			94
6			90
7			90
8			92
9			96
10			88
11			86
12			85
13			94
14			96
15			96
16			85

[a] All products were identified by IR, NMR, and mass spectroscopy. [b] Yields of products isolated after column chromatography.

In our efforts to develop biomimetic approaches for chemical reactions involving cyclodextrins (CD),[6] we report herein an efficient, simple, and practical method for the oxidation of alcohols and diols with IBX catalyzed

† IICT Communication no. 021013.

(1) (a) Grieco, P. A. *Organic Synthesis in Water*; Blackie Academic and Professional: London, 1998. (b)Li, C. J.; Chan, T. H. *Organic Reactions in Aqueous Media*; John Wiley and Sons: New York, 1997; p 159.

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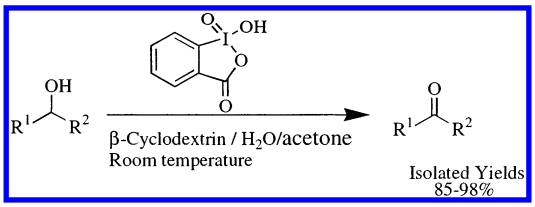
SCHEME 1



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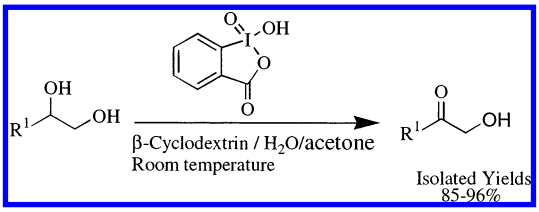

by β-cyclodextrin (β-CD) using a water/acetone mixture (86:14) as the solvent.

Cyclodextrins (CDs), which are cyclic oligosaccharides, exert microenvironmental effects leading to selective reactions. They catalyze reactions by supramolecular catalysis through noncovalent bonding as seen in enzymes.

The reactions were carriedout by dissolving β-Cyclodextrin in water at room temperature followed by the addition of the alcohol. All the alcohols investigated gave impressive yields ranging from 85% to 98% (Table 1). No overoxidation to acids was observed in the case of aldehyde products (entries 1−8, purities as assessed by HPTLC >90%). Arylcarbinols gave comparatively better yields than the aliphatic alcohols. This methodology is also compatible in the presence of other functionalities such as methoxy, methylenedioxy, nitro, hydroxy, and alkene double bonds. This reaction is highly selective for vicinaldiols in oxidizing only the secondary hydroxy group α to the benzene ring (entries 13−16, Table 1). β-Cyclodextrin was used as the catalyst because it is easily accessible and inexpensive among the CDs. β-CD was used only in a catalytic amount (0.1 mmol of CD per mmol of the alcohol). These reactions did not take place in the absence of CD. All of the compounds were characterized by mass, ^{1}H NMR, and IR and by comparison with the known compounds.[4,7]

In these reactions, iodosobenzoic acid (IBA) obtained from the reduction of IBX has been recycled by oxidation to IBX.[8] Cyclodextrin has also been recovered and reused.

In conclusion, we have presented an elegant and simple methodology for the oxidation of a variety of alcohols using IBX at room temperature with a water/acetone mixture (86:14) as solvent under supramolecular catalysis.

Experimental Section

Materials. Alcohols were either purchased commercially or synthesized as reported in the literature.[9]

General Procedure for Oxidation. To a solution of β-cyclodextrin (0.1 mmol) in distilled water (15 mL) was added the alcohol (1 mmol) in acetone (2 mL) followed by IBX (1 mmol) at room temperature. The reaction mixture was stirred at room temperature for 12 h, and then the product was extracted with ethyl acetate (3 × 15 mL). The organic phase was dried over anhydrous sodium sulfate and concentrated under vacuum. The crude product thus obtained was purified by column chromatography on silica gel (60−120 mesh) using ethyl acetate/hexane (1:9) as eluent.

After extraction with ethyl acetate, the reaction mixture was filtered to isolate IBA, and the aqueous phase was lyophilized to obtain the CD.

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Supporting Information Available: Experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

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