Deoximation of Oximes with 2-Iodylbenzoic Acid in Water in the Presence of β-Cyclodextrin[1]

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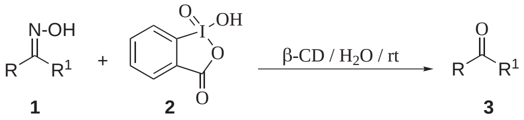
Abstract: Oximes of various aldehydes and ketones can be converted to the corresponding carbonyl compounds at room temperature in impressive yields with 2-iodylbenzoic acid in water in the presence of β-cyclodextrin.

Key words: oximes, 2-iodylbenzoic acid, β-cyclodextrin, water

There is a growing interest for generating carbonyl compounds from oximes since these can be prepared from noncarbonyl precursors as well as used for the protection and purification of carbonyl compounds.[2] In view of the importance of deoximation, several methods have been developed for the cleavage of oximes, such as acid-catalyzed hydrolysis,[3] oxidative,[4] reductive,[5] clay-supported ferric nitrite,[6] trimethylsilyl chlorochromate,[7] titanium silicalite-1,[8] zirconium sulfophenyl phosphonate,[9] *N*-haloamides,[10] manganese triacetate,[11] microwave assisted,[12] pyridinium chlorochromate,[13] pyridinium chlorochromate/H_2O_2,[5c] 2-iodylbenzoic acid/DMSO–THF,[14] trimethylammonium chlorochromate,[15] chromium trioxide/chlorotrimethylsilane,[16] photochemical deprotection,[17] etc. Though different approaches have been reported with various limitations such as hazardous reagents and solvents, higher temperatures, longer reaction times, lower yields, etc.[18] no attempt has yet been made to involve supramolecular catalysis, with water as solvent, which would be environmentally benign. In our efforts to develop biomimetic approaches through supramolecular catalysis involving cyclodextrins,[19] we explored the deoximation of oximes using a mild and environmentally friendly oxidizing agent, catalyzed by cyclodextrins with water as solvent. Cyclodextrins are cyclic oligosaccharides, which exert a microenvironmental effect. They catalyze reactions by supramolecular catalysis through noncovalent bonding as for example seen in enzymes.

Amongst various oxidizing agents 2-iodylbenzoic acid (**2**), a hypervalent iodine reagent, attracted our attention due to its low toxicity, and high selectivity.[20] We report herein the first examples of the deoximation of various oximes **1** to carbonyl compounds **3** under supramolecular catalysis with β-cyclodextrin (β-CD = cycloheptaamylose) using 2-iodylbenzoic acid (**2**) in water (Scheme 1).



Scheme 1

The reactions were carried out by dissolving β-cyclodextrin in water followed by the addition of oxime **1** and 2-iodylbenzoic acid (**2**) at room temperature. The deoximation yields obtained were impressive ranging up to 96%. The yields from oximes with an aromatic moiety were comparatively better than that from the saturated ones. This methodology is also compatible with functionalities such as halo, nitro, hydroxy, methoxy, methylenedioxy, isopropoxy, and conjugated double bonds (Table 1). β-Cyclodextrin was used as a catalyst since it is easily accessible and inexpensive among various cyclodextrins. β-CD was used only in catalytic amounts. These deoximation reactions do not take place in the absence of β-cyclodextrin.

The role of CD appears to be to activate not only the oxime but may also be forming a CD·**2** complex through hydrogen bonding, which then oxidizes the oxime to the corresponding carbonyl compound. In these reactions, reduced 2-iodylbenzoic acid, i.e. 2-iodosobenzoic acid has been recycled by oxidation to 2-iodylbenzoic acid.[21] The β-cyclodextrin has also been recovered and reused.

In conclusion, this methodology, involving β-cyclodextrin in water with 2-iodylbenzoic acid as an oxidizing agent, is the first of its kind to be developed for the deoximation of oximes and has several advantages over the existing methodologies.

Deoximation of Oximes; General Procedure

To a solution of β-cyclodextrin (113.5 mg, 0.1 mmol) in distilled H_2O (15 mL) at r.t. was added the appropriate oxime (1 mmol) dissolved in acetone (2 mL), followed by the addition of 2-iodylbenzoic acid (280 mg, 1 mmol). The reaction mixture was stirred at r.t. for 12 h. The product was extracted with EtOAc (3 × 15 mL), the combined organic phases were dried (Na_2SO_4) and concentrated under vacuum. The crude product thus obtained was purified by column chromatography on silica gel (60–120 mesh) using EtOAc–hexane (9:1) and identified by IR spectra and by comparison with authentic samples and known compounds.[22]

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Table 1 Deoximation with 2-Iodylbenzoic Acid in Water in the Presence of β-CD at Room Temperature

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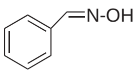
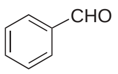
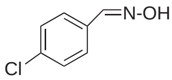
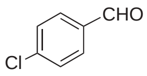
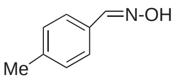
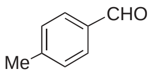
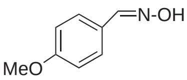
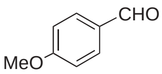
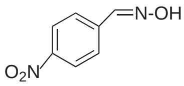
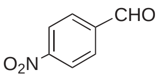
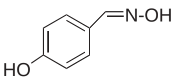
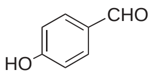
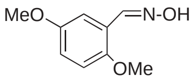
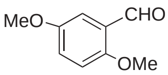
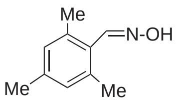
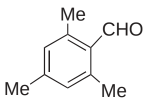
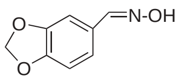
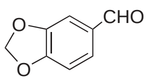
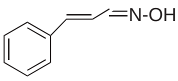
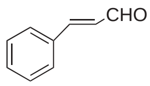
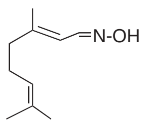
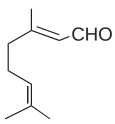
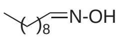
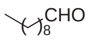
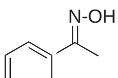
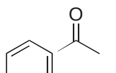
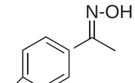
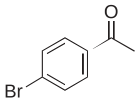
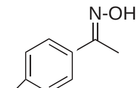
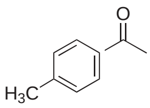
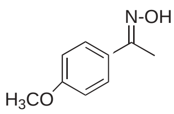
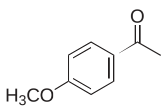
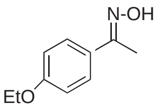
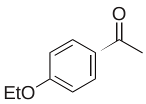
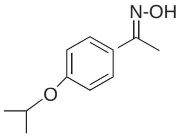
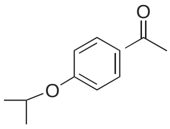
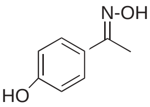
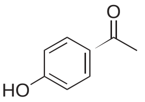
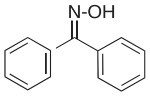
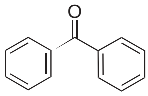
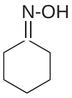
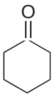
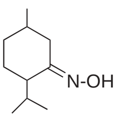
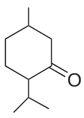
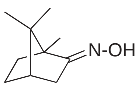
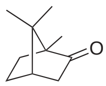
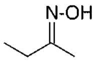
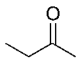
1			92
2			96
3			94
4			96
5			89
6			90
7			91
8			90
9			95
10			88
11			85
12			85
13			95
14			96
15			94
16			92
17			92
18			94
19			90
20			94
21			84
22			82
23			88
24			82

[a] All Products were identified by IR, NMR, and mass spectroscopy.

[b] Yields of products isolated after column chromatography.

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