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# Regeneration of Carbonyl Compounds by Oxidative Cleavage of Oximes with NBS in the Presence of β-Cyclodextrin in Water

M. Somi Reddy<sup>a</sup>, M. Narender<sup>a</sup> & K. Rama Rao<sup>a</sup> <sup>a</sup> Organic Chemistry Division-I, Indian Institute of Chemical Technology, Hyderabad, 500 007, India Published online: 12 Jan 2011.

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## Regeneration of Carbonyl Compounds by Oxidative Cleavage of Oximes with NBS in the Presence of β-Cyclodextrin in Water

M. Somi Reddy, M. Narender, and K. Rama Rao\*

Organic Chemistry Division-I, Indian Institute of Chemical Technology, Hyderabad, India

#### ABSTRACT

The conversion of different oximes to the corresponding carbonyl compounds was carried out at room temperature in good to high yields with N-bromosuccinimide in water in the presence of  $\beta$ -cyclodextrin.

*Key Words:* Oximes; NBS;  $\beta$ -Cyclodextrin; Biomimetic; Oxidative cleavage; Water.

#### 3875

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<sup>\*</sup>Correspondence: K. Rama Rao, Organic Chemistry Division-I, Indian Institute of Chemical Technology, Hyderabad 500 007, India; Fax: +91-40-27160757; E-mail: drkrrao@yahoo.com.

#### INTRODUCTION

Regeneration of carbonyl compounds from oximes is of great significance in synthetic organic chemistry, since oximes can be prepared both from carbonyl and noncarbonyl precursors.<sup>[1]</sup> They are utilized in the purification and characterization of carbonyl compounds as well as in a variety of organic reactions.<sup>[2]</sup> Therefore, regeneration of carbonyl compounds from stable oximes under mild conditions is an important process. Various methods reported to generate carbonyl compounds from oximes involve hydrolytic<sup>[3]</sup> (acid-catalyzed), reductive,<sup>[4]</sup> oxidative,<sup>[5]</sup> clay supported ferric nitrite,<sup>[6]</sup> microwave assisted,<sup>[7]</sup> N-halo amides,<sup>[8]</sup> manganese triacetate,<sup>[9]</sup> PCC,<sup>[10]</sup> photochemical deprotection,<sup>[11]</sup> etc. However, only a few methods are available under mild conditions and hence, there is continued interest to explore new methodologies, especially using water as a solvent. In our efforts to develop biomimetic approaches through supramolecular catalysis with water as a solvent involving cyclodextrins,<sup>[12]</sup> we have attempted the oxidative cleavage of oximes with NBS in the presence of  $\beta$ -cyclodextrin ( $\beta$ -CD) in water (Sch. 1).

#### **RESULTS AND DISCUSSION**

We report herein a new methodology for the deoximation of various oximes (1) to carbonyl compounds (3) under supramolecular catalysis with  $\beta$ -cyclodextrin using N-bromosuccinimide (2) in water. Cyclodextrins are cyclic oligosaccharides, which exert microenvironmental effect. They catalyze reactions by supramolecular catalysis through noncovalent bonding as seen in enzymes.  $\beta$ -CD was used as a catalyst because it is easily accessible and inexpensive among various cyclodextrins. N-bromosuccinimide has



#### Regeneration of Carbonyl Compounds by Oxidative Cleavage of Oximes 3877

been utilized as an effective deoximating agent under mild conditions to yield carbonyl compounds in excellent yields.

These reactions were carried out by dissolving  $\beta$ -CD in water at room temperature followed by the addition of oxime (1) and N-bromosuccinimide (2). The yields of the products were impressive, ranging from 80% to 90% (Table 1). It is also noteworthy that no over-oxidation to acids was observed. It is also observed that the reaction times were extended in the absence of  $\beta$ -CD. In a specific example, the reaction of 4-methyl benzaldoxime **4** (Table 1), which takes 20 min for completion in the presence of  $\beta$ -CD, was extended up to 40 min in the absence of  $\beta$ -CD.  $\beta$ -Cyclodextrin was used only in catalytic amount (0.1 mmol of CD per 1.0 mmol of the oxime). Products were separated and purified by chromatographic techniques and were also identified by IR, NMR, Mass spectroscopy, and by comparison with the authentic samples.<sup>[13]</sup>

In conclusion, we have presented a simple methodology for the deprotection of a variety of oximes using NBS at room temperature with water as a solvent under supramolecular catalysis.

#### **EXPERIMENTAL SECTION**

#### Materials

All reactions were carried out without any special precautions in an atmosphere of air. Chemicals and solvents were purchased from Fluka and S. D. Fine Chemicals and used as received. <sup>1</sup>H NMR spectra were obtained on a Gemini-200 or 300 MHz spectrometer. IR spectra were recorded on a NICOLET FT-IR spectrometer. Mass spectra were observed on V. G. Auto spectrometer. All oximes were prepared using standard synthetic methods.<sup>[1]</sup>

#### **General Procedure**

To a solution of  $\beta$ -cyclodextrin (113.5 mg, 0.1 mmol) in distilled water (15 mL) at room temperature was added the appropriate oxime (1.0 mmol) dissolved in acetone (2 mL), followed by the addition of N-Bromosuccinimide (2.0 mmol). The reaction mixture was stirred at room temperature for the specified time (Table 1). The product was extracted with ethyl acetate (3 × 15 mL) and washed with brine solution. The combined organic phases

Entry	Substrate	Product <sup>a</sup>	Time (min)	% Yield <sup>b</sup>
1	N-OH	СНО	25	82
2	CI N-OH	СІСНО	30	84
3	Br	Br	25	85
4	Me N-OH	Me	20	80
5	MeO	MeO	20	82
6	MeO N-OH	MeO CHO OMe	20	80
7	MeO H	MeOCHO OH	45	81
8	но Пон	но	45	82
9	N-OH	CHO 6	20	80
10	N-OH	CHO 3	20	80
11	N-OH	o C	35	89
12	N-OH	CI	40	88

*Table 1.* Oxidative cleavage of oximes with NBS in the presence of  $\beta$ -CD in water.

(continued)

Entry	Substrate	Product <sup>a</sup>	Time (min)	% Yield <sup>b</sup>
13	Br N-OH	Br	45	87
14	H <sub>3</sub> C	H <sub>3</sub> C	50	87
15	N-OH H <sub>3</sub> CO	H <sub>3</sub> CO	25	90
16	N-OH	° C	25	90
17	N-OH		25	87
18	N-OH	0 	20	84
19	N-OH		25	90

Table 1. Continued.

<sup>a</sup>All products were identified by IR, NMR, and mass spectroscopy. <sup>b</sup>Yields of products isolated after column chromatography.

were dried  $(Na_2SO_4)$  and concentrated under vacuum. The crude product thus obtained was purified by column chromatography on silicagel (60–120 mesh) using ethyl acetate: n-hexane (1:9).

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