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# A novel catalytic method for the regeneration of carbonyl compounds from oximes using aluminum nitrate and NaBr as catalyst

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#### Abstract

A wide variety of aldoximes and ketoximes were regenerated to corresponding carbonyl compounds with  $Al(NO_3)_3 \cdot 9H_2O$  in presence of catalytic amounts of NaBr in  $CH_2Cl_2$  at room temperature.

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Recently, development of efficient and new catalytic systems for various organic transformations is an active ongoing research area and the scope for further improvement towards milder reaction conditions [1]. The development of heterogeneous catalysts for fine chemicals synthesis has become a major area of research [2]. Also important aspect of clean technology is the use of environmentally friendly catalysts [3].

Developing mild and efficient methods for the selective cleavage of nitrogen-containing derivatives to afford carbonyl compounds continues to be a significant aspect of organic chemical transformation [4]. Apart from their usefulness as latent protected forms of aldehydes and ketones, oximes occupy a key position in the chemical space that correlates carbonyl compounds with nitroalkanes, amines and carboxamides [5]. Oximes are easily prepared. Also they are highly stable and crystalline compounds, which are used for the isolation, purification and characterization of carbonyl compounds. Since oximes can be prepared from non-carbonyl compounds, the regeneration of carbonyl compounds from oximes provides an alternative method for the preparation of aldehydes and ketones [6–8].

Even though various approaches have been reported for deoximation reaction such as silica chromate [9], aqueous  $H_3PO_4$  [10], tungstate sulfuric acid (TSA)/KMnO\_4 [11], tetra-*n*-alkylammonium bromates [12], *tert*-butyl hypoiodite [13], 2-iodobenzoic acid/ $\beta$ -cyclodextrin/H<sub>2</sub>O [14], tungstate sulfuric acid/NaNO<sub>2</sub> [15], BAcImBF<sub>4</sub>/silica gel [16], H<sub>2</sub>O<sub>2</sub>/montmorillonite-K10 supported CoCl<sub>2</sub> [17], *N*-bromophthalimide [18], and bispyridine-silver(I) dichromate [19], but these methods suffer from some disadvantages like long reaction times, expensive reagent and catalyst, difficulties in isolation of products, and formation of over-oxidation products leading to low yields.

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Recently we have shown that bromonium ion  $(Br^+)$  can effectively apply for the oxidation of different types of organic compounds [20–24]. Therefore we wish to examine  $Br^+$  for the regeneration of carbonyl compounds from oximes. However a mixture of aluminum nitrate in the presence of catalytic amount of NaBr was applied for the *in situ* generation of  $Br^+$ .

In this communication we report a novel catalytic media for the effective regeneration of carbonyl compounds from aldoximes and ketoximes using  $Al(NO_3)_3$ ·9H<sub>2</sub>O in the presence of catalytic amounts of NaBr.

Therefore, various aldoximes and ketoximes 1 were deoximated with combination of  $Al(NO_3)_3 \cdot 9H_2O$  I and catalytic amounts of NaBr II in dichloromethane at room temperature in good to high yields (Scheme 1 and Table 1).

The deoximation reactions were carried out under completely heterogeneous conditions in dichloromethane at room temperature. The reaction procedure is very simple and the products are easily isolated from the reaction media because in this heterogeneous system the reagent and catalyst are insoluble in dichloromethane; therefore products can be easily obtained by simple filtration and evaporation of  $CH_2Cl_2$ .

To approve the catalytic role of NaBr in this catalytic system, *para*-methyl benzaldehyde oxime (1m), as typical example, was subjected to deoximation reaction without sodium bromide. Surprisingly, it was observed that the reaction time increased to 22.5 h (entry 14, Scheme 2).

A possible mechanism of this oxidizing system is shown in Scheme 3.

One of the observed evidence for this mechanism is evolving of NO from the reaction vessel that can be converted to the nitrogen brown-color oxides, which can be observed on the top of the reaction solution.

In conclusion, we have developed a novel, heterogeneous and catalytic protocol for the selective deoximation of aldoximes and ketoximes into corresponding carbonyl compounds *via* combination of aluminum nitrate and catalytic amount of NaBr. Furthermore, this method exhibits substrate versatility, mild reaction conditions, and easy and clean work-up of products.

### 1. Experimental

All ketoximes and aldoximes were prepared by aldehydes and ketones, which were purchased from Fluka, Merck and Aldrich chemical companies.



Scheme 1.

Table 1 Regeneration of carbonyl compounds from oximes using  $Al(NO_3)_3$ ·9H<sub>2</sub>O I in the presence of catalytic amounts of NaBr II in CH<sub>2</sub>Cl<sub>2</sub> at room temperature.

Entry	Substrate	Product	Substrate/reagent/catalyst (mmol)		Time (min)	Yield (%) <sup>a,b</sup>
			I	II		
1	1a	2a	1.2	0.05	55	98
2	1b	2b	1.2	0.05	110	98
3	1c	2c	1.2	0.05	45	89
4	1d	2d	1.2	0.05	160	97
5	1e	2e	1.2	0.05	105	97
6	1f	2f	1.2	0.05	220	91
7	1g	2g	2	0.05	190	79
8	1h	2h	4	0.05	30.5h	58
9	1i	2i	2	0.05	240	83
10	1j	2j	2	0.05	6.75h	96
11	1k	2k	2	0.05	195	89
12	11	21	2	0.05	180	99
13	1m	2m	2	0.05	210	90
14	1m	2m	2	_	22.5h	88 <sup>c</sup>
15	1n	2n	2	0.05	195	94

<sup>a</sup> Isolated yields.

<sup>b</sup> The oxidation products (aldehydes and ketones) were characterized by comparison of their spectral (IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR) and physical data with authentic samples.

<sup>c</sup> Without catalyst.



Scheme 2.



Scheme 3.

### 1.1. Deoximation of cyclohexane oxime 1c to cyclohexanone 2c using $Al(NO_3)_3$ -9H<sub>2</sub>O and NaBr

A mixture of cyclohexane oxime **1c** (0.113 g, 1 mmol),  $Al(NO_3)_3 \cdot 9H_2O$  (0.344, 1.2 mmol) and NaBr (0.005 g, 0.05 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was stirred at room temperature for 45 min (the reaction progress was monitored by TLC). After reaction completion, reaction mixture was filtered and the residue was washed with CH<sub>2</sub>Cl<sub>2</sub> (20 mL). Finally CH<sub>2</sub>Cl<sub>2</sub> was removed and the yield was 0.087 g (89%).

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