

Notes

Efficient, Catalytic and Oxidative Deoxygenation of Aldoximes and Ketoximes by Ferric Nitrate and Catalytic Amounts of Bromide Ion

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Received October 17, 2008

Key Words : Deoxygenation, Ferric nitrate [Fe(NO₃)₃·9H₂O], KBr, NaBr, Oximes

Finding molecules which are able to catalyze the reaction between others is an important contribution of molecular chemists to increase the efficiency of chemical reactions whereby our daily life based on consumption of chemicals is shifted closer to an ecologically and economically tolerable equilibrium with our environment.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 Development of efficient and new catalytic systems for various organic transformations is an active research area with the aim to develop milder reaction conditions.⁴

Carbonyl compounds occupy a central position in organic syntheses.⁵ Oximes are easily prepared and highly stable compounds. They are extensively used for protection, characterization and purification of carbonyl compounds.⁶ Since oximes can be prepared from non-carbonyl compounds, the regeneration of carbonyl compounds from oximes provides an alternative method for the preparation of aldehyde and ketones.⁷⁻⁹ Despite of protecting role of oximes, also they are valuable intermediates in the preparation of nitriles¹⁰ and amides.¹¹

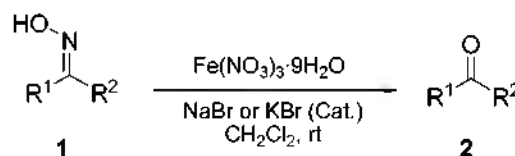
Although a number of methods¹²⁻²³ for deoxygenation reaction have emerged in the recent years there is still a scope for newer reagents, because the existing oxidative methods suffer from some disadvantages like long reaction time, difficulties in isolation of products, and formation of over-oxidation products leading to low yields.

As part of our continuous effort devoted to catalytic reactions,²⁴⁻²⁸ we have been engaged in the development of a new catalytic media based on in situ generation of Br⁺ for the selective regeneration of carbonyl compounds from aldoximes and ketoximes.

In this article, we report a novel heterogeneous catalytic protocol for the effective regeneration of carbonyl compounds from oximes using ferric nitrate in the presence of catalytic amounts of NaBr and/or KBr.

Various aldoximes and ketoximes **1** were deoxygenated with combination of Fe(NO₃)₃·9H₂O **I** and catalytic amounts of NaBr **II** or KBr **III** (Scheme 1) in dichloromethane at room

temperature. The reaction proceeds efficiently in good yields, and the results are summarized in Table 1.

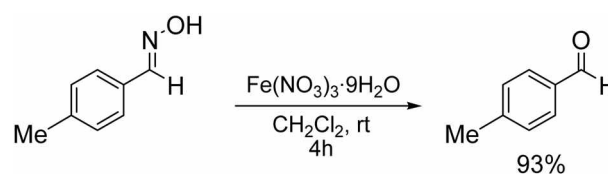


Scheme 1

Notably, the reagent and catalysts are entirely insoluble in reaction solvent. Consequently deoxygenation reaction was carried out under completely heterogeneous conditions. We believe that the catalytic part of this heterogeneous system is bromonium cation (Br^+), which could be generated *via* treatment of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and bromide anion (Br^-). This result is in close agreement with our previously reported works.^{24,25,29}

Meanwhile, to approve the catalytic role of KBr or NaBr, *para*-methylbenzaldehyde oxime (**1m**), as a typical example, was subjected to deoxygenation reaction without potassium or sodium bromide. Surprisingly, it was observed that the reaction time increased to 4 hours (Table 1, entry 27 & Scheme 2). Consequently 0.05% mol of sodium or potassium bromide, as a very cheap catalyst, could be increased the reaction rate around four times.

In conclusion, we have proposed a new catalytic protocol for selective oxidative regeneration of carbonyl compounds



Scheme 2

from aldoximes and ketoximes using catalytic *in situ* generated Br^+ . This methodology is efficient, simple, chemoselective, and high yielding.

Experimental

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

Deoxygenation of acetophenone oxime 1b to acetophenone 2b using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and KBr. A mixture of acetophenone oxime **1b** (0.135 g, 1 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.485, 1.2 mmol) and KBr (0.006 g, 0.05 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 30 minute (the reaction progress was monitored by TLC). After reaction completion, reaction mixture was filtered off and the residue was washed with CH_2Cl_2 (4×5 mL). Then CH_2Cl_2 was removed by water-bath (40–50 °C) and simple distillation. Consequently acetophenone **2b** was obtained in 97% yield (0.119 g).

Acknowledgments. Financial support for this work by the research facilities of Ilam University, Ilam, Iran is gratefully acknowledged.

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Table 1. Regeneration of carbonyl compounds from oximes using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ I in the presence of catalytic amounts of NaBr II or KBr III in CH_2Cl_2 at room temperature

Entry	Substrate	Product	Substrate/Reagent/Catalysts (mmol)			Time (Min)	Yield (%) ^a
			I	II	III		
1	1a	2a	1.2	0.05	–	35	96
2	1a	2a	1.2	–	0.05	40	98
3	1b	2b	1.2	0.05	–	35	99
4	1b	2b	1.2	–	0.05	30	97
5	1c	2c	1.2	0.05	–	30	98
6	1c	2c	1.2	–	0.05	35	88
7	1d	2d	1.2	0.05	–	30	99
8	1d	2d	1.2	–	0.05	45	99
9	1e	2e	1.2	0.05	–	20	100
10	1e	2e	1.2	–	0.05	40	99
11	1f	2f	1.2	0.05	–	30	88
12	1f	2f	1.2	–	0.05	30	94
13	1g	2g	2	0.05	–	5.75 h	93
14	1g	2g	2	–	0.05	5.5 h	82
15	1h	2h	4	0.05	–	6.75 h	62
16	1h	2h	4	–	0.05	6.75 h	84
17	1i	2i	2	0.05	–	35	98
18	1i	2i	2	–	0.05	50	94
19	1j	2j	2	0.05	–	35	99
20	1j	2j	2	–	0.05	25	91
21	1k	2k	2	0.05	–	45	92
22	1k	2k	2	–	0.05	75	81
23	1l	2l	2	0.05	–	20	86
24	1l	2l	2	–	0.05	75	85
25	1m	2m	2	0.05	–	90	97
26	1m	2m	2	–	0.05	95	98
27	1m	2m	2	–	–	4 h	93 ^b
28	1n	2n	2	0.05	–	130	99
29	1n	2n	2	–	0.05	125	76

^aIsolated yields. ^bWithout catalyst.

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