

A mild and selective method for the conversion of oximes into ketones and aldehydes by the use of *N*-bromophthalimide

Ardeshir Khazaei*, Abbas Amini Manesh and Amin Rostami

Department of Chemistry, Faculty of Sciences, Bu-Ali Sina University, Hamadan, Iran

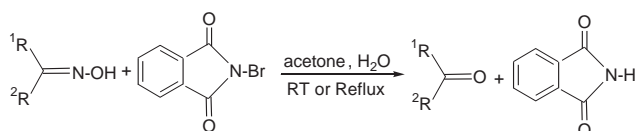
N-Bromophthalimide has been found to be an efficient and selective reagent for the mild oxidative cleavage of oximes to yield their corresponding carbonyl compounds in good to excellent yields.

Keywords: aldehydes, ketones, *N*-bromophthalimide, oximes

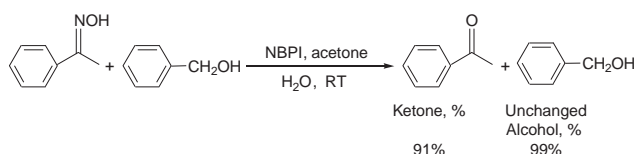
Oximes are easily obtained from carbonyl compounds, and have great potential as intermediates in organic synthesis.^{1,2} So there has been considerable interest in the development of mild methods for the regeneration of carbonyl compounds from stable and readily prepared oximes and tosylhydrazones³ due to the fact that such derivatives offer efficient protection for aldehydes and ketones in organic synthesis.² Moreover, since oximes can be prepared from non-carbonyl compounds⁴ the formation of carbonyl compounds from oximes provides an alternative method for the preparation of aldehydes and ketones. Most of the known methods of generating carbonyl compounds from their nitrogen derivatives require strongly acidic,⁵ oxidative,⁶ or reductive conditions. Recently, pyridinium dichromate-*t*-butyl hydroperoxide,⁸ iodobenzene diacetate,⁹ the titanium silicalite-1-H₂O₂ combination¹⁰ and 70% TBHP¹¹ have been reported to cleave the C=N bond of oximes and tosylhydrazones. However, many of the conventional procedures for regeneration of the carbonyl function from such nitrogen derivatives have several limitations: some of the reagents are hazardous, very toxic, expensive or not readily available, or they need to be freshly prepared and the reactions require drastic work-up conditions.¹² Therefore, it is desirable that a method which involves relatively mild reaction conditions should be available, leading to high recoveries of a wide range of aldehydes and ketones. We now report an efficient and general method for the effective and selective cleavage of oximes with *N*-bromophthalimide (NBPI) under neutral and mild conditions, Scheme 1.

The results of the conversions of various oximes into their corresponding carbonyl compounds are presented in Table 1.

Dissolution of oximes in acetone with addition of a small amount of water and subsequent reaction with NBPI under



Scheme 1



Scheme 2 Selective deoxygenation in the presence of benzyl alcohol.

stirring at room temperature or reflux gave the corresponding carbonyl compounds in good yields. Even the sterically hindered ketone oxime (entry 13) was successfully oxidatively cleaved to the corresponding ketone in good yield. The aldoximes were converted into the corresponding aldehydes and no any acid was formed due to overoxidation of the regenerated aldehyde (entries 3,4,7,10). This procedure is also useful for the chemoselective oxidative deoxygenation of oximes in the presence of alcohols or for oximes that contain –OH functional group (entry 12). Thus, when equimolar mixtures of acetophenone oxime and benzyl alcohol in acetone and water were allowed to react with NBPI at room temperature, the ketone oxime underwent chemoselectively oxidative deoxygenation giving (91%) acetophenone, whereas the benzyl alcohol was recovered unchanged, Scheme 2.

Table 1 Deoxygenation with NBPI at room temperature

Entry	Substrate	Product	Time/h	Yield/% ^{a,b}
1	Cyclohexanone oxime	Cyclohexanone	1.5	93
2	Acetophenone oxime	Acetophenone	1.5	92
3	Benzaldehyde oxime	Benzaldehyde	1.5	92
4	4-Chlorobenzaldehyde oxime	4-Chlorobenzaldehyde	1.5	91
5	Benzophenone oxime	Benzophenone	1.5	91
6	4-Methylacetophenone oxime	4-Methyl acetophenone	1.5	90
7	Isobutyraldehyde oxime	Isobutyraldehyde	2	90 ^d
8	Isobutyl methyl ketone oxime	Isobutyl methyl ketone	2	90
9	Diisopropyl ketone oxime	Diisopropyl ketone	2	90
10	2-Chlorobenzaldehyde oxime	2-Chlorobenzaldehyde	2.5	89 ^c
11	Ethyl methyl ketone oxime	Ethyl methyl ketone	2	88
12	Benzoin oxime	Benzoin	2.5	88 ^c
13	Camphor oxime	Camphor	4	85 ^c
14	Cyclopentanone oxime	Cyclopentanone	2	

^aProducts were characterised by their physical constants, comparison with authentic samples and melting points of 2,4-dinitrophenyl hydrazone derivatives and by their IR and NMR spectra.¹³

^bIsolated yields.

^cUnder reflux conditions.

^dCH₂Cl₂/H₂O was used as reaction solvent.

* Correspondence. E-mail: a_khazaei@basu.ac.ir

Also in this reaction, as shown in Scheme 1, *N*-bromophthalimide was converted into the phthalimide, which could be isolated, brominated and reused as a deoximating reagent.

In conclusion, the described procedure has remarkable advantages such as simple reaction conditions, simplicity of work-up, absence of overoxidation and the oxidative reagent (NBPI) can be regenerated many times.

Experimental

General procedure A mixture of the oxime (3 mmol) and NBPI (3.5 mmol), in acetone (10 ml) and water (1 ml) was stirred at the temperature giving in Table 1 for the specified time. After the reaction was completed (TLC), the solvent was removed under reduced pressure, and diethyl ether (20 ml) was added to the mixture. It was stirred for 10 minutes, and then the phthalimide was removed by filtration and the product was purified by column chromatography (hexane/ diethyl ether).

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References:

- 1 S. Patai, *The Chemistry of the Carbon-Nitrogen Double Bond*, John Wiley and Sons, Inc., London, 1970.
- 2 T.W. Green and P.G.M. Wuts, *Protective Groups in Organic Synthesis*, 2nd edn., John Wiley and Sons, Inc., Toronto, 1991, pp. 175-223.
- 3 Y.H. Kim, J.C. Jung and K.S. Kim, *Chem. Ind. Lond.*, 1992, 31.
- 4 G.W. Kabalka, R.D. Pace and P.P. Wadgaonkar, *Synth. Commun.* 1990, **20**, 2453.
- 5 R.E. Donaldson, J.C. Saddler, S. Byrn, A.T. Mckenzie and P.L. Fuch, *J. Org. Chem.*, 1983, **48**, 2167.
- 6 B. Tamami and N. Goudarzian, *Eur. Polym. J.*, 1992, **28**, 1035.
- 7 D.P. Curran, J.F. Brill and D.M. Rakiewicz, *J. Org. Chem.*, 1984, **49**, 1654.
- 8 N. Chidambaram, K. Satyanarayan and S. Chandrasekaran, *Synth. Commun.*, 1989, **19**, 1727.
- 9 R.M. Moriarty, O. Prakash and P.R. Vavilikolanu, *Synth. Commun.* 1986, **16**, 1247.
- 10 R. Joseph, A. Sudalai and T. Ravindranthan, *J. Chem. Soc. Chem. Commun.*, 1993, **15**, 1553.
- 11 N.B. Barhate, A.S. Gajare, R.D. Wakharkar and A. Sudalai, *Tetrahedron Lett.*, 1997, **38**, 653-656.
- 12 B.P. Bandgar, S.I. Shaikh and S. Iyyer, *Synth. Commun.*, 1996, **26**, 1163.
- 13 J.G. Grasselli and W.M. Ritchey, *Atlas of Spectral Data and Physical Constants for Organic Compounds*, 2nd edn. Cleveland, Ohio, CRC Press Inc., 1975.