Asian Journal of Chemistry; Vol. 23, No. 2 (2011), 762-764

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

A Convenient Method for Deoximation of Oximes by Using N-Iodosuccinimide Under Microwave Irradiation

ABBAS AMINI MANESH[1,*] and ARDESHIR KHAZAEI[2]

[1]Payam Noor University, Hamedan, Iran
[2]Department of Chemistry, Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran

*Corresponding author: Fax: +98 8112546840; Tel: +98 8112546838; E-mail: a_aminima@yahoo.com

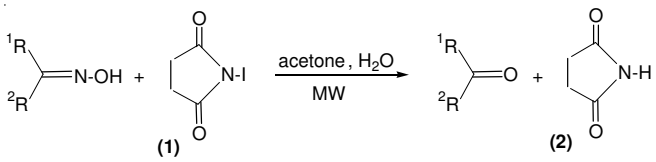
(*Received*: 22 March 2010; *Accepted*: 1 October 2010) AJC-9156

A rapid and selective method for the cleavage of oximes has been achieved by a simple reaction of a ketoxime or an aldoxime with N-iodosuccinimide in acetone under microwave irradiations.

Key Words: Aldoxime, Ketoxime, Microwave, N-Iodosuccinimide, Selective.

INTRODUCTION

Oximes are extensively used as preferred derivatives for purification and characterization of carbonyl compounds[1] and as synthetic intermediates en route to amines[2] and nitriles[3]. Their synthesis from non-carbonyl compounds offers an alternative route to aldehyde and ketones[4]. So regeneration of carbonyl compounds from the corresponding oximes is a very important reaction. Advantages such as cleaner reactions, very short reaction times and ease in work-up have kindled a special interest in microwave chemistry[5]. We extended our work on the use of N-halo reagents, in organic methodology[6], by the use of N-iodosuccinimide. In this letter, we report a good oxidative method for chemoselective deoximation under microwave irradiations using N-iodosuccinimide (**1**), as an effective oxidizing agent, **Scheme-I**.



Scheme-I

EXPERIMENTAL

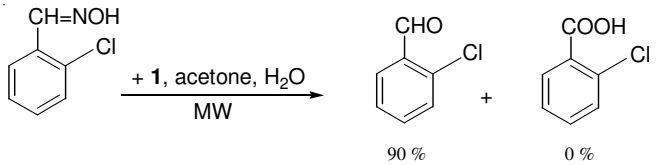
General procedure: A mixture of the oxime (3 mmol) and N-iodosuccinimide (3.5 mmol), in acetone (10 mL) and water (0.1 mL), were introduced in a two necked flask and irradiated in a microwave oven at a power output of 300 W for the appropriate times as indicated in Table-1. After the reaction was completed, the solvent was removed under reduced pressure and 20 mL of diethyl ether or chloroform was added to the mixture and it was stirred for 10 min; then the succinimide (**2**), was removed by filtration and the product was purified by column chromatography (hexane/diethyl ether:4/1).

Products (aldehydes and ketones) were characterized by their physical constants, by comparison with authentic samples and the melting points of 2,4-dinitrophenyl hydrazone derivatives and by their IR and ^{1}H NMR spectra.

RESULTS AND DISCUSSION

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

The aldoximes were converted to the corresponding aldehydes and no acid was formed due to overoxidation of the regenerated aldehyde (entries 3, 5, 8 and 12), **Scheme-II**.



Scheme-II: Selective formation of aldehyde from aldoxime

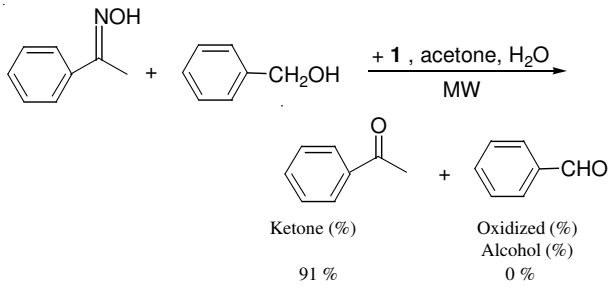
This procedure is also useful for the chemoselective oxidative deoximation of oximes in the presence of alcohols or for oximes that contain -OH functional group (entry 1). Thus, when equimolar mixtures of acetophenone oxime and benzyl alcohol in acetone and water were allowed to react with N-iodosuccinimide under microwave irradiation, the ketoxime underwent chemoselectively oxidative deoximation giving acetophenone (91 %), whereas

TABLE-1
DEOXIMATION WITH N-IODOSUCCINIMIDE (**1**) UNDER MICROWAVE IRRADIATION

Entry	Substrate	Product	Time (min)	Yield (%)[a,b]
1	Benzoin oxime	Benzoin	3.0	89
2	Camphor oxime	Camphor	3.0	87
3	4-Chloro benzaldehyde oxime	4-Chloro benzaldehyde	2.0	92
4	Benzophenone oxime	Benzophenone	2.0	90
5	Cinnamaldehyde oxime	Cinnamaldehyde	2.5	90
6	Acetophenone oxime	Acetophenone	2.0	91
7	Cyclohexanone oxime	Cyclohexanone	2.0	92
8	Benzaldehyde oxime	Benzaldehyde	2.0	93
9	Cyclopentanone oxime	Cyclopentanone	3.0	90
10	4-Methyl acetophenone oxime	4-Methyl acetophenone	2.5	90
11	Diisopropyl ketone oxime	Diisopropyl ketone	3.0	87
12	2-Chloro benzaldehyde oxime	2-Chloro benzaldehyde	2.5	90

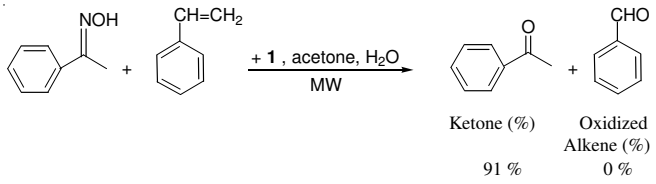
a: Products were characterized by their physical constants, comparison with authentic samples and melting points of 2,4-dinitro phenyl hydrazone derivatives and by their IR and NMR spectra. b: Isolated yields.

the benzyl alcohol does not get oxidized to benzaldehyde, **Scheme-III** (was checked by TLC).



Scheme-III: Chemoselective deoximation in the presence of benzyl alcohol

The unsaturated oxime (entry 5) was cleaved to the corresponding unsaturated aldehyde without affecting the double bond. So we observed the competitive oxidation of oximes in the presence of alkenes. In a control experiment, when equimolar mixtures of acetophenone oxime and styrene in acetone and water were allowed to react with N-iodosuccinimide, under microwave irradiation, the ketone oxime underwent chemoselectively oxidative deoximation giving (91 %) acetophenone, whereas the styrene does not get oxidized to benzaldehyde, **Scheme-IV** (was checked by TLC).



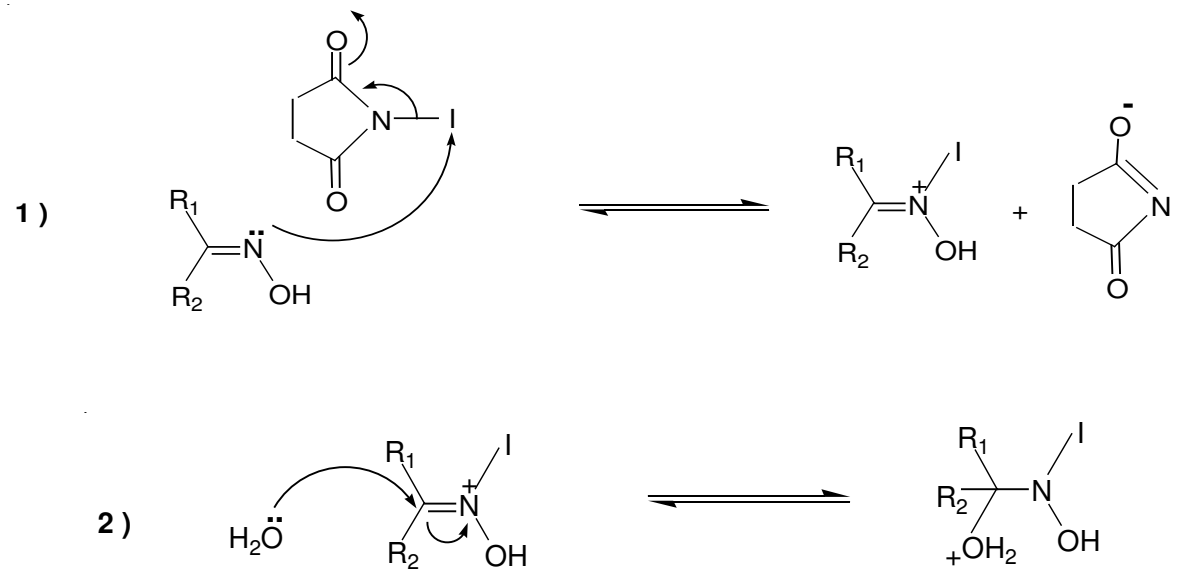
Scheme-IV: Chemoselective deoximation in the presence of styrene

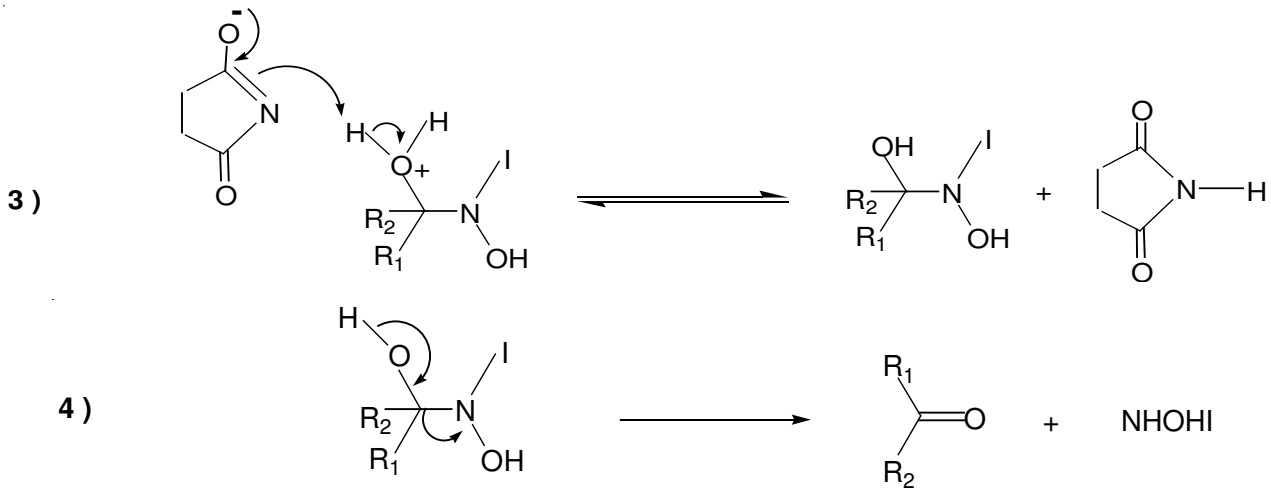
After the reaction was completed, according to **Scheme-I**, N-iodosuccinimide (**1**), was converted to succinimide (**2**), which can be isolated, iodinated and reused many times as deoximating reagent.

Conclusion

In conclusion, the striking features of our method are; (i) very short reaction times, (ii) no formation of over oxidation products due to high chemoselectivity, (iii) mild nature of N-iodosuccinimide, (iv) easy work-up procedure and (v) good yields. The OH and C=C functional groups in the oxime structure does not get oxidized to other functional groups and finally, the deiodinated product (**2**) can be converted to (**1**) and reused several times.

The proposed mechanism for deoximation by title reagent is shown in **Scheme-V**.





Scheme-V

ACKNOWLEDGEMENTS

The authors acknowledged Hamedan Payam Noor University Research Councils, Bu-Ali Sina University Research Councils, Center of Excellence in Development of Chemistry Methods (CEDCM) and National Foundation of Elites (NFE) for support of this work.

REFERENCES

1. T.W. Greene, P.G.M. Wuts, Protective Groups in Organic Synthesis, John Wiley: New York, edn. 3, pp. 355-356 (1999).
2. E.H. Massey, B. Kitchell, L.D. Martin, K. Gerzon and H.W. Murphy, *Tetrahedron Lett*., 157 (1970).
3. R.V. Stevens, F.C.A. Gaeta and D. Lawrence, *J. Am. Chem. Soc*., **105**, 7713 (1983).
4. G.A. Olah, Q. Liao, S.C. Lee and G.K. Surya Perakash, *Synlett*, 427 (1993).
5. G. Majetich and R. Hicks, *Radiat. Phys. Chem*., **45**, 567 (1995).
6. (a) A. Khazaei and R.G. Vaghei, *Tetrahedron Lett*., **43**, 3073 (2002); (b) A. Khazaei, R.G. Vaghei and M. Tajbakhsh, *Tetrahedron Lett*., **42**, 5099 (2001); (c) K. Ardeshir and S. Abbas, *Synth. Commun*., **29**, 4079 (1999); (d) A. Khazaei, K. Bridson and R.G. Pitchard, *Cryst. Str. Commun. C5*., 970 (2001); (e) A. Khazaei, E. Mehdipour, B. Roodpeyma, *Iran. J. Chem. Chem. Eng*., **14**, 77 (1995); (f) A. Khazaei, M.A. Zolfigol and A. Rostami, *Synthesis*, 2959 (2004); (g) A. Khazaei, A.A. Manesh and A. Rostami, *J. Chem. Res*., 391 (2005); (h) A. Khazaei, A.A. Manesh and V.R. Safi, *J. Chin. Chem. Soc*., **52**, 559 (2005); (i) A. Khazaei and A.A. Manesh, *J. Chin. Chem. Soc*., **52**, 1017 (2005); (j) A. Khazaei, A. Rostami and A.A. Manesh, *J. Chin. Chem. Soc*., **53**, 437 (2006).