Russian Journal of Organic Chemistry, Vol. 39, No. 7, 2003, pp. 1053–1054. From Zhurnal Organicheskoi Khimii, Vol. 39, No. 7, 2003, pp. 1117–1118.
Original English Text Copyright © 2003 by Tajbaksh, Khazaei, Shabani Mahalli, Ghorbani Vaghei.

SHORT COMMUNICATIONS

Deoximation with *N*-Bromosulfonamides*

M. Tajbaksh[1], A. Khazaei[2], M. Shabani Mahalli[1], and R. Ghorbani Vaghei[2]

[1] *Department of Chemistry, College of Sciences, University of Mazandaran, Babolsar, Iran*
Phone: +98 11 252 34 338; Fax: +98 11 252 42 029; e-mail: tajbaksh@umcc.ac.ir

[2] *Department of Chemistry, Bu-Ali Sina University, Hamadan, Iran*

Received December 20, 2001

Ketone and aldehyde oximes are readily crystallizable substances which are widely used for purification and identification of carbonyl compounds. Oximes can be converted into amides via the Beckmann rearrangement [1]. Insofar as oximes may also be prepared from noncarbonyl compounds [2–6], regeneration of carbonyl compounds therefrom is an alternative method of synthesis of aldehydes and ketones. A classical procedure for the recovery of ketones and aldehydes from the corresponding oximes is based on their acid hydrolysis which removes the amine from the equilibrium. However, the scope of application of this reaction is limited, for acid-sensitive aldehydes and ketones cannot be obtained in such a way. Some reagents used for deoximation [7–9] are often hazardous or very toxic, expensive or difficultly accessible, or they should be taken freshly prepared. The reactions with such reagents require drastic conditions, take a long time, and involve laborious treatment of the reaction mixture. Therefore, milder, more selective, nonhazardous, and inexpensive reagents are still required for these transformations.

In the present communication we report on a convenient and efficient procedure for deoximation of ketone and aldehyde oximes to the corresponding carbonyl compounds with the aid of *N*,*N*-dibromobenzenesulfonamide. As follows from the data in Table 1, a number of aldehyde and ketone oximes

Table 1. Deoximation of aldehyde and ketone oximes with *N*,*N*-dibromobenzenesulfonamide

Run no.	Substrate	Product[a]	Reaction time, min	Yield, %
1	Benzophenone oxime	Benzophenone	15	94
2	*p*-Bromoacetophenone oxime	*p*-Bromoacetophenone	10	96
3	*o*-Methoxybenzaldehyde oxime	*o*-Methoxybenzaldehyde	5	97
4	*p*-Phenylacetophenone oxime	*p*-Phenylacetophenone	10	92
5	*o*,*p*-Dimethoxyacetophenone oxime	*o*,*p*-Dimethoxyacetophenone	30	86
6	*p*-Chloroacetophenone oxime	*p*-Chloroacetophenone	10	97
7	*p*-Methylbenzaldehyde oxime	*p*-Methylbenzaldehyde	20	88
8	*p*-Chlorobenzaldehyde oxime	*p*-Chlorbenzaldehyde	10	94
9	*p*-Chlorobenzophenone oxime	*p*-Chlorobenzophenone	5	91
10	Benzaldehyde oxime	Benzaldehyde	10	88
11	2,3-Butanedione 2-oxime	2,3-Butanedione	10	92
12	Cyclohexanone oxime	Cyclohexanone	20	91
13	Camphor oxime	Camphor	20	90
14	Cinnamaldehyde oxime	Cinnamaldehyde	10	87
15	4-*tert*-Butylcyclohexanone oxime	4-*tert*-Butylcyclohexanone	40	88

[a] The products were identified by physical constants and IR spectra and by comparison with authentic samples.

* The article was submitted by the authors in English.

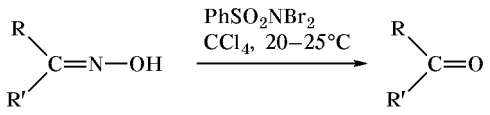
1070-4280/03/3907-1053 $25.00 © 2003 MAIK "Nauka / Interperiodica"

Table 2. Deoximation with *N*,*N*-dibromobenzenesulfonamide (**A**) and *N*-bromosuccinimide (**B**) [9]

Substrate	Product	A		B	
		time, min	yield, %	time, min	yield, %
Benzophenone oxime	Benzophenone	15	94	7	93
p-Chloroacetophenone oxime	*p*-Chloroacetophenone	10	97	10	93
p-Chlorbenzaldehyde oxime	*p*-Chlorobenzaldehyde	10	94	1	93
Cyclohexanone oxime	Cyclohexanone	20	91	4	89

were rapidly and cleanly converted into their parent carbonyl compounds with *N*,*N*-dibromobenzenesulfonamide in excellent yields (Scheme 1). The products were isolated by filtering off benzenesulfonamide and removal of the solvent from the filtrate. Table 2 compares the efficiency and applicability of the proposed procedure with the results obtained with *N*-bromosuccinimide [9].

Scheme 1



R, R′ = Alk, Ar.

It should be emphasized that α,β-unsaturated oximes, e.g., cinnamaldehyde oxime (Table 1, run no. 14), undergo deoximation with high chemoselectivity, with no reagent addition at the double C=C bond. Moreover, such groups as chloro, methoxy, nitro, and alkyl substituents turned out to be inert toward *N*,*N*-dibromobenzenesulfonamide, and no by-products were detected in the reaction mixtures.

Thus we have proposed a simple, convenient, and fast procedure for deoximation of aldehyde and ketone oximes. It is advantageous due to high yields of the products, short reaction time, easy isolation procedure, and the possibility for regeneration of the reagent.

The oximes were prepared by a standard procedure [10]. The purity of the products was checked by TLC. The products were additionally characterized by measuring their physical constants [10]. TLC was performed on silica gel plates F_{245} (Fluka). The elemental analyses were obtained on a Perkin–Elmer 2400 CHN-analyzer. The IR spectra were recorded on a Perkin–Elmer 1310 spectrophotometer. The ^{1}H NMR spectra were obtained on Varian instruments operating at 60 and 90 MHz; CCl_4 was used as solvent, and TMS, as internal reference.

Typical deoximation procedure. A mixture of 5 mmol of appropriate oxime, 15 ml of CCl_4, and 5 mmol of *N*,*N*-dibromobenzenesulfonamide was stirred for a time specified in Table 1. The progress of the reaction was monitored by TLC. Benzenesulfonamide was filtered off and washed with CCl_4 (2×10 ml), and the filtrate was evaporated under reduced pressure.

REFERENCES

1. Donaruma, L.G. and Heldt, W.Z., *Org. React.*, 1960, vol. 11, p. 1; Bosch, A.L., Cruz, P., Diez-Barra, E., Loupy, I., and Langa, F., *Synlett*, 1995, p. 1259.
2. Barry, R.H. and Hartung, W.H., *J. Org. Chem.*, 1947, vol. 12, p. 460.
3. Touster, O., *Org. React.*, 1953, vol. 7, p. 327.
4. Hartung, W.H. and Cressly, F., *Org. Synth. Coll.*, 1943, vol. 1, p. 363.
5. Barton, D.H.R., Beaton, J.M., Geller, L.E., and Pechet, M.M., *J. Am. Chem. Soc.*, 1961, vol. 83, p. 4076.
6. Barton, D.H.R. and Beaton, J.M., *J. Am. Chem. Soc.*, 1961, vol. 83, p. 4083.
7. Greene, T.W. and Wuts, P.G.M., *Protective Groups in Organic Synthesis*, New York: Wiley, 1991.
8. Bandgar, B.P., Shaikh, S.I., and Iyyer, S., *Synth. Commun.*, 1996, vol. 26, p. 1163.
9. Bandgar, B.P., Lalita, B.K., and Thotes, J.L., *Synth. Commun.*, 1997, vol. 27, p. 1149.
10. *Vogel's Textbook of Practical Organic Chemistry, Including Qualitative Organic Analysis*, Furniss, B.S., Hannford, A.J., Rogers, V., Smith, P.W.G., and Tatchell, A.R., Eds., London: Longman Scientific & Technical, 1978, 4th ed.