N,N-Dibromobenzenesulfonamide as a reagent for oxidative cleavage of oximes to their parent carbonyl compounds under non-aqueous and aprotic conditions

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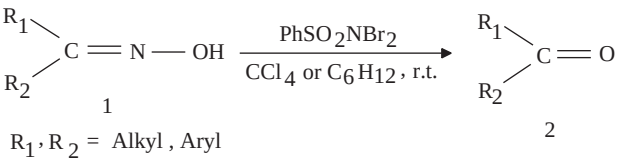
Deprotection of different oximes to their parent aldehydes and ketones in high yields has been carried out by using *N,N*-dibromobenzenesulfonamide(dibromoamine-b) under mild conditions.

Keywords: *N,N*-dibromobenzenesulfonamide, oxidative cleavage of oximes

Oximes are highly crystalline compounds extensively used for the purification and characterisation of carbonyl compounds. These compounds can also be used for the preparation of amides via the Beckman rearrangement.[1] Since oximes can be prepared from non-carbonyl compounds,[2] the regeneration of carbonyl compounds from oximes provides an alternative method for preparation of aldehydes and ketones. The classical recovery of ketones and aldehydes from oximes consists of acid hydrolysis which removes the amine from the equilibrium.[3] This limits the scope of the reaction to exclude acid sensitive ketones and aldehydes. In recent years reagents such as ceric ammonium nitrate on silica gel (CAN-SiO_2),[4] dimethylammonium chlorochromate adsorbed on silica gel (DMCC/SiO_2),[5] quinolinium fluorochromate (QFC),[6] tungsten(VI) chloride (WCl_6) or molybdenum(V) chloride ($MoCl_5$) in the presence of zinc powder,[7] and *N*-methylpiperidinium chlorochromate adsorbed on alumina[8] have been reported for this purpose. Reagents reported for deoximation[9] are often hazardous or very toxic, expensive or not readily available, or need to be freshly prepared or the reactions require drastic conditions, long reaction times and tedious work-up. Thus a milder, more selective, non-hazardous and inexpensive reagent is still required for such transformations.

In connection with some other studies, it was observed that *N*-haloamides serve as effective deoximating agents under mild conditions to give the parent carbonyl compounds in excellent yields. In continuation of our work on deoximation,[10] we recently observed that *N,N*-dibromobenzenesulfonamide can be efficiently utilised for regeneration of aldehydes and ketones



Scheme 1

from the corresponding oximes. *N,N*-Dibromobenzenesulfonamide is a stable crystalline compound easily prepared[11] by brominating directly a sodium carbonate or bicarbonate solution of the benzenesulfonamide, which gives an almost quantitative yield of the pure product. The reaction seems to proceed in two steps, the $C_6H_5SO_2NBrNa$ formed first dissolving to give a yellow solution, then the second step occurs, and the yellow dibromide precipiates. This reagent has been used in many reactions especially in the bromination of alkenes,[12a-h] ethynylbenzene[12i] and tricyclo[4.1.0.02.7]heptan.[12j] The addition of *N,N*-dibromobenzenesulfonamide to unsymmetrical alkenes has been found to lead to products in which the bromine atom took the position expected in a process involving positive bromine.

In this paper we report on *N,N*-dibromobenzenesulfonamide as an efficient and convenient reagent for the cleavage of oximes under non aqueous conditions. We describe a simple method for the regeneration of carbonyl compounds with this reagent from a wide range of aldoximes and ketoximes with varying structural and steric parameters (Scheme 1). The results of some representative transformations are presented in Table 1.

Table 1 Oxidative deprotection of oximes with dibromoamine-b

Entry	Substrate	Product[a]	Time /min	Yield /%	m.p.or b.p.*/°C Found	Lit[14]
1	Benzophenone oxime	Benzophenone	15	94	47	49
2	*p*-Bromoacetophenone oxime	*p*-Bromoacetophenone	10	96	52	51
3	*o*-Methoxybenzaldoxime	*o*-Methoxybenzaldehyde	5	97	37	39
4	*p*-Phenylacetophenone oxime	*p*-Phenylacetophenone	10	92	121	120
5	*o,p*-Dimethoxyacetophenoe oxime	*o,p*-Dimethoxyacetophenone	30	86	41	44
6	*p*-Chloroacetophenone oxime	*p*-Chloroacetophenone	10	97	23	20
7	*p*-Methylbenzaldoxime	*p*-Methylbenzaldehyde	20	88	202	204
8	*p*-Chlorobenzophenone oxime	*p*-Chlorobenzophenone	10	94	79	77
9	*p*-Chlorobenzaldoxime	*p*-Chlorobenzaldehyde	5	91	47	47
10	Benzaldoxime	Benzaldehyde	10	88	180	179
11	2,3-Butanedione monooxime	2,3-Butanedione	10	92	90	88
12	Cyclohexanone oxime	Cyclohexanone	20	91	156	155
13	Camphor oxime	Camphor	20	90	178	179
14	Cinnamaldoxime	Cinnamaldehyde	10	87	255	252
15	4-*tert*-Butylcyclohexanone oxime	4-*tert*-Butylcyclohexanone	40	88	51	49

[a]Products were characterised by their physical constants, comparison with authentic samples and IR spectra.

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Table 2 Comparison of some of the results from dibromoamine-b(I) with those reported with *N*-bromosuccinimide (II)[9c]

Entry	Substrate	Product	Reagent I		Reagent II	
			Time/min	Yield/%	Time/h	Yield/%
1	Benzophenone oxime	Benzophenone	15	94	7	93
2	*p*-Chloroacetophenone oxime	*p*-Chloroacetophenone	10	97	10	93
3	*p*-Chlorobenzaldoxime	*p*-Chlorobenzaldehyde	10	94	1	93
4	Cyclohexanone oxime	Cyclohexanone	20	91	4	89

As indicated regeneration of carbonyl compounds from aliphatic and aromatic aldoximes and ketoximes (entries 1–15) was very fast. The products of these reactions were isolated simply by filtering off benzenesulfonamide and evaporating the solvent from the filtrate. The recovered benzenesulfonamide can be brominated and reused.

It is noteworthy that, α,β-unsaturated oximes such as cinnamaldehyde (entry 14) underwent deoximation with high chemoselectivity without addition of the reagent to the C=C bond. Furthermore, functional groups such as chloro, methoxy, nitro, alkyl were also inert to this reagent and no by product formation was observed.

In order to show the efficiency and applicability of this method, some of the results of our experiments are compared with those reported with NBS (Table 2). As shown in Table 2, deoximation with *N,N*-dibromobenzenesulfonamide is achieved in much shorter reaction time with excellent yields.

In conclusion, in this study we have introduced a simple, convenient and rapid procedure for deoximation of a wide vaiety of acyclic and cyclic aliphatic and aromatic oximes. In addition, high yields of the products, short reaction times, easy work up and regenerability of the reagent are important advantages of this method.

Experimental

The oximes were prepared according to the literature.[13] The purity of the compounds were checked by TLC. Compounds were further characterised by measurement of physical constants.[14] Fluka silica gel plates (F_{245}) were used for TLC. Elemental analyses (CHN) were performed on a Perkin-Elmer 2400 CHN analyser. The IR spectra were recorded on a Perkin-Elmer 1310 spectrophotometer and ^{1}H NMR spectra were recorded in CCl_4 on Varian (60 and 90 MHz) spectrometers using TMS as an internal standard.

*Preparation of N,N-dibromobenzenesulfonamide***:** In a 250ml three-necked flask were placed benzenesulfonamide (5g), KOH (3.6g) and water (25ml); then bromine (10g) was added with vigorous stirring. The resulting precipitate of *N,N*-dibromobenzenesulfonamide was filtered off, washed in water and dried. The yield was 9.8 (98%), m.p. 116°C [reported m.p. 115°C (dec)].[11]

General procedure for the regeneration of carbonyl compounds from oximes with N,N-dibromobenzenesulfonamide: A mixture of oxime (5 mmol), carbon tetrachloride or cyclohexane (15 ml) and *N,N*-dibromobenzenesulfonamide (5 mmol) was stirred at room temperature for the specified time (Table 1). The reaction was monitored by TLC. After completion of the reaction, insoluble sulfonamide was removed by simple filtration and washed with carbon tetrachloride or cyclohexane (2×10 ml). Removal of the solvent under reduced pressure gave the product in good yield.

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