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N-Bromo-(4-methylphenyl) Sulfonimide: A Mild and Efficient Reagent for Oxidative Deoximation of Oximes Under Microwave Irradiations

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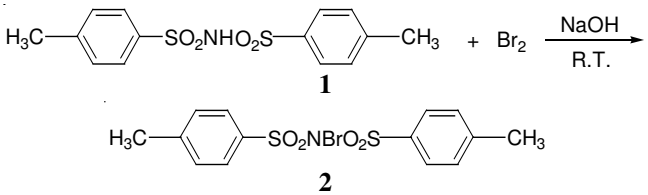
Aldoximes and ketoximes are converted to the parent carbonyl compounds in good yields when treated with N-bromo-(4-methylphenyl) sulfonimide (**2**), under microwave irradiations. The simple work-up minimizes the loss of product and oximes have been selectively oxidized in the presence of alcohols and alkenes.

Key Words: Aldoxime, Ketoxime, Microwave, Sulfonimide, Selective.

INTRODUCTION

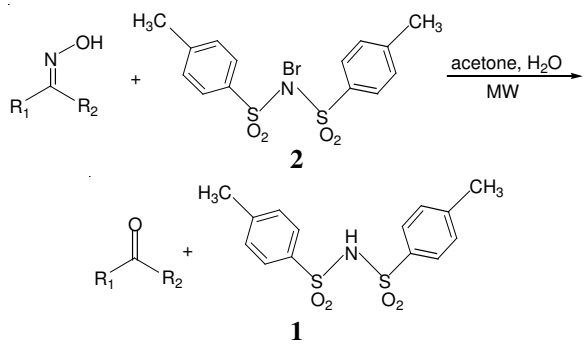
Carbonyl compounds derivatives such as oximes, phenylhydrazones and semicarbazones are used not only for isolation, purification and characterization[1] but also for protection of carbonyl compounds[2]. Oximes are important for organic synthesis[3-6]. Their synthesis from non-carbonyl compounds offers an alternative route to aldehyde and ketones[7,8]. So regenaration of carbonyl compounds from the corresponding oximes is a very important reaction.

Many oxidative deoximations have used for oxidation of oximes[9]. Many reagents are not selective for oximes in the presence of alkenes[9c], or their selectivity patterns have not yet been explored[9d]. Advantages such as cleaner reactions, short reaction times and ease in work-up have kindled a special interest in microwave chemistry[10]. During the course of our systematic study and researches on oxidation of funcional groups with N-halo reagents[11], we wish to report a convenient method for selective conversion of oximes to their carbonyl compounds by using N-bromo-(4-methylphenyl) sulfonimide (**2**), as an effective oxidizing agent. The title reagent was prepared from (4-methyl phenyl) sulfonimide (**1**) (**Scheme-I**).



Scheme-I

Dissolution of oximes in acetone : water mixture (10:0.1) and subsequent reaction with N-bromo-(4-methylphenyl) sulfonimide (**2**) under microwave irradiations gave the corresponding carbonyl compounds in good yields (**Scheme-II**).



Scheme-II

EXPERIMENTAL

Melting points were uncorrected. IR and ^{1}H NMR spectra were recorded using a Shimadzu 435-U-04 spectrophotometer (KBr pellets) and a 90 MHz Jeol FT-NMR spectrometer, respectively. ^{1}H NMR chemical shifts were measured relative to TMS (int; 1H).

Solvent-free synthesis of (4-methylphenyl)sulfonimide (1): A mixture of 15.03 g (78.84 mmol) 4-methylbenzene sulfonyl chloride and 9.00 g (52.57 mmol) of 4-toluene sulfonamide were placed in a beaker. The beaker was heated on an oil bath (140 ºC) until the mixture changed to a liquid. The mixture was stirred with a glass rod for 5 h. Then it was

cooled to room temperature and the product was recrystallized from ethanol, m.p. 136-137 ºC, yield, 13.70 g (80 %). IR (paraffin), ν cm^{-1}: 3317, 3242, 3125, 1575, 1461, 1325, 1152, 808 cm^{-1}. ^{1}H NMR (acetone-d_6/TMS), δ (ppm): 2.34 (s, 6H), 6.36 (br., 1H), 7.34-7.70 (dd, 8H). ^{13}C NMR (acetone-d_6/TMS), δ (ppm): 21.72, 127.23, 130.56, 142.48, 143.62. Mass calcd. for $C_{14}H_{15}NO_4S_2$: 325.39. Found : 325.10.

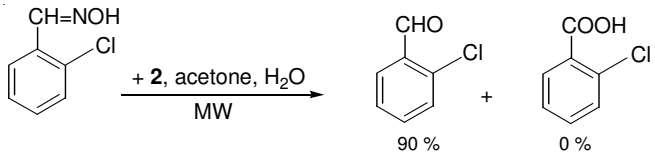
Synthesis of N-bromo-(4-methylphenyl)sulfonimide (2): 6.0 g (18.44 mmol) of (4-methylphenyl) sulfonimide (**1**), was dissolved in a slight molar excess of chilled aqueous sodium hydroxide solution (of approximately 2 M) in room temperature and transfer the solution to a beaker. 0.95 mL (18.44 mmol) of Br_2 dissolved in 2 mL of tetrachloromethane was added to the solution with vigorous stirring and immediately yellow precipitate was formed. The yellow precipitate was collected by suction on a Büchner funnel, washed with cold distilled H_2O (30 mL) and then dried in a vacuum desicator at room temperature for 6 h. The yield of **2**, was 5.70 g (76.46 %). The product was stable at room temperature and not sensitive to air. IR (paraffin), ν cm^{-1} : 2919, 2864, 1599, 1461, 1330, 1161, 815. ^{1}H NMR (acetone-d_6/TMS), δ (ppm): 2.36 (s, 6H), 7.35-7.70 (dd, 8H).

General procedure for deoximation: A mixture of the oxime (3 mmol) and N-bromo-(4-methylphenyl) sulfonimide (**2**), (3.5 mmol, 1.14 g) in acetone[a] (10 mL) and water (0.1 mL) was introduced in a two necked flask and irradiated in a domestic microwave oven at a power output of 300 W for the appropriate times as indicated in Table-1. After the reaction was completed (TLC)[b], the solvent was removed under reduced pressure and diethyl ether or *n*-hexane* (10 mL) was added to the mixture and it was stirred for 10 min, then the (4-methylphenyl) sulfonimide (**1**) was removed by filtration and the product was purified by column chromatography (hexane/diethyl ether).

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 over oxidation of the regenerated aldehyde (entries 3, 10, 11, 14 and 15) (**Scheme-III**).



Scheme-III: Selective formation of aldehyde from aldoxime

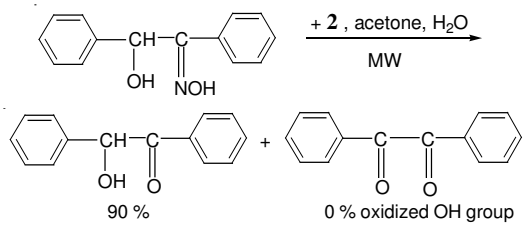
Even the sterically hindered ketone oxime (entry 4) was succesfully oxidatively cleaved to the corresponding ketone in good yield. This procedure is also useful for the chemoselective oxidative deoximation of oximes in the presence of alcohols or for oximes that contain -OH functional group (entry 2) (**Scheme-IV**).

[a]CH_2Cl_2 was used for isobutyraldehyde and ethyl methyl ketone.
[b]Every 20 s microwave oven was turned off and progress of the reaction was monitored by TLC.
*[For benzoin oxime; after the reaction was completed, the solvent was removed under reduced pressure and product was purified by column chromatography (hexane/Et_2O)].

TABLE-1
DEOXIMATION WITH N-BROMO-(4-METHYLPHENYL) SULFONIMIDE (**2**) UNDER MICROWAVE

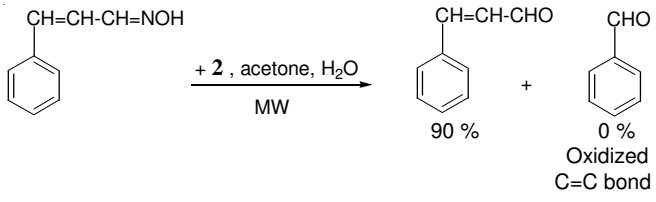
Entry	Substrate	Product	Time (min)	Yield (%)[a,b]
1	Benzophenone oxime	Benzophenone	2.0	91
2	Benzoin oxime	Benzoin	3.0	90
3	Isobutyraldehyde oxime	Isobutyraldehyde	2.5	90[c]
4	Camphor oxime	Camphor	3.0	87
5	Cyclohexanone oxime	Cyclohexanone	2.0	94
6	Ethyl methyl ketone oxime	Ethyl methyl ketone	2.8	88[c]
7	Diisopropyl ketone oxime	Diisopropyl ketone	2.6	90
8	Isobutyl methyl ketone oxime	Isobutyl methyl ketone	2.5	90
9	Acetophenone oxime	Acetophenone	2.0	94
10	Cinnamaldehyde oxime	Cinnamaldehyde	2.5	90
11	2-Chloro benzaldehyde oxime	2-Chloro benzaldehyde	2.7	90
12	Cyclopentanone oxime	Cyclopentanone	3.0	86
13	4-Methyl acetophenone oxime	4-Methyl acetophenone	2.0	91
14	Benzaldehyde oxime	Benzaldehyde	2.0	94
15	4-Chloro benzaldehyde oxime	4-Chloro benzaldehyde	2.0	93

[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.
[c]CH_2Cl_2/H_2O was used as reaction solvent.

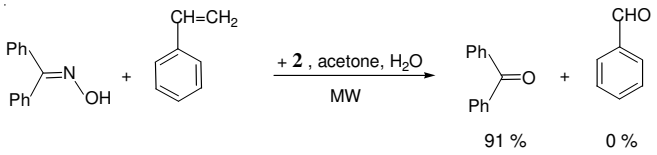


Scheme-IV: Selective deoximation in the presence of OH functional group

The unsaturated oxime (entry 10) was cleaved to the corresponding unsaturated aldehyde without affecting the double bond (**Scheme-V**). So we observed the competitive oxidation of oximes in the presence of alkenes. In a control experiment, when equimolar mixtures of benzophenone oxime and styrene in acetone and water were allowed to react with title reagent, under microwave irradiations, the ketone oxime underwent chemoselectively oxidative deoximation giving (91 %) benzophenone, whereas the styrene does not get oxidized to benzaldehyde (**Scheme-VI**) (was checked by TLC).



Scheme-V: Selective deoximation in the presence of C=C functional group



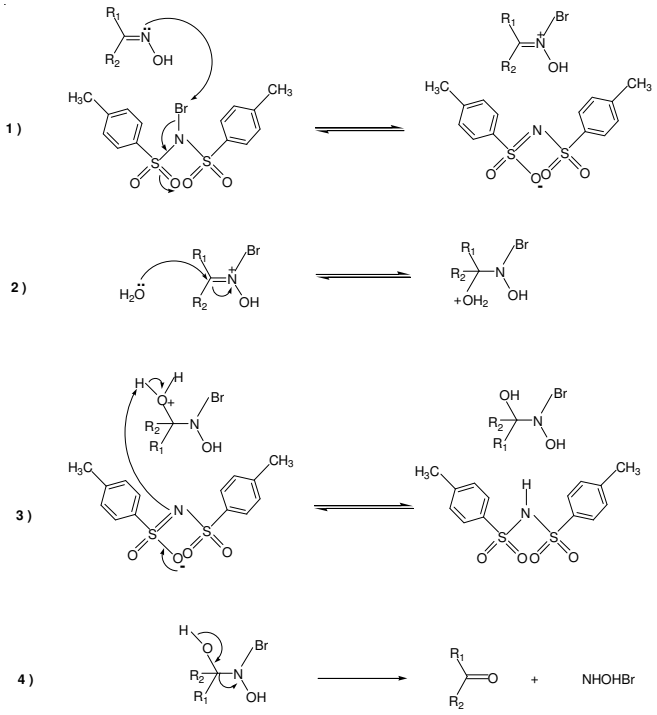
Scheme-VI: Chemoselective deoximation in the presence of styrene

After the reaction was completed, according to **Scheme-II**, N-bromo-(4-methylphenyl) sulfonimide (**2**), was converted to the (4-methylphenyl)sulfonimide (**1**), thus **1** can be isolated, brominated and reused many times as deoximating reagent.

Conclusion

The striking features of present method are (a) short reaction times, (b) no formation of over oxidation products due to high chemoselectivity (c) mild nature of the title reagent **2**. The OH and C=C functional groups in the oxime structure do not get oxidized to other functional groups, there is an easy work-up procedure, good yields and finally, the debrominated product **1** can be converted to **2** and reused several times.

The proposed mechanism for deoximation by title reagent is shown in **Scheme-VII**[11i].



Scheme-VII

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