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Selective oxidation of oximes to carbonyl compounds using *N*-bromo-*N*-benzoyl-4-toluenesulfonamide

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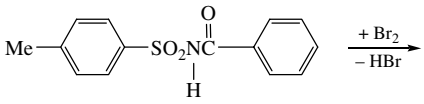
Oximes were converted to parent carbonyl compounds in good yields by treating with *N*-bromo-*N*-benzoyl-4-toluenesulfonamide.

Oximes are extensively used for the purification and characterization of carbonyl compounds.[1] Their syntheses from non-carbonyl compounds, such as the nitrosation of an active methylene group[2] and the condensation of a nitro alkene with an aldehyde,[3] provide alternative pathways to carbonyl compounds. Therefore, the regeneration of carbonyl compounds from the corresponding oximes is a very important reaction.[4] Currently available, oxidative methods suffer from disadvantages like long reaction time,[5] need for refluxing temperature,[6] difficulties in isolation of products,[7] and formation of overoxidation products leading to low yields. Many reagents are not selective for oximes in the presence of alkenes,[8] or their selectivity patterns have not been explored.[9] Previously, we studied the oxidation of organic compounds with *N*-halo reagents.[10] Here, we report a convenient method for the selective conversion of oximes into carbonyl compounds using *N*-bromo-*N*-benzoyl-4-toluenesulfonamide **2**[†] as an effective oxidising agent.

The dissolution of oximes in acetone with the addition of a small amount of water and the subsequent reaction with reagent **2** under stirring at room temperature or reflux gave the corresponding carbonyl compounds in good yields (Scheme 1).[‡]



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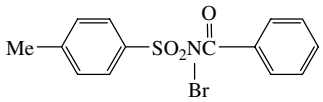

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The results of the conversion of oximes into corresponding carbonyl compounds are presented in Table 1.

The aldoximes were converted into the corresponding aldehydes and no acid was formed due to overoxidation of the regenerated aldehyde (entries 3,4,7,8 and 11) (Scheme 2).

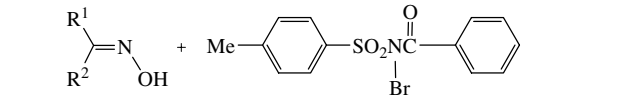
A sterically hindered ketone oxime (entry 14) was successfully oxidatively cleaved to the corresponding ketone in good yield. This procedure is also useful for the chemoselective oxidative deoximation of oximes in the presence of alcohols or for oximes that contain the OH group (entry 13). Thus, when

Table 1 Deoximation with *N*-bromo-*N*-benzoyl-4-toluene sulfonamide at room temperature.

Entry	Substrate	Product	Time/h	Yield (%)[a,b]
1	Cyclohexanone oxime	Cyclohexanone	1.5	93
2	Acetophenone oxime	Acetophenone	1.5	93
3	Benzaldehyde oxime	Benzaldehyde	1.5	93
4	4-Chlorobenzaldehyde oxime	4-Chlorobenzaldehyde	1.5	93
5	Benzophenone oxime	Benzophenone	1.5	92
6	4-Methylacetophenone oxime	4-Methylacetophenone	1.5	92
7	Isobutyraldehyde oxime	Isobutyraldehyde	2	90[d]
8	Cinnamaldehyde oxime	Cinnamaldehyde	2.25	80
9	Isobutyl methyl ketone oxime	Isobutyl methyl ketone	2	88
10	Diisopropyl ketone oxime	Diisopropyl ketone	2.3	87
11	2-Chlorobenzaldehyde oxime	2-Chlorobenzaldehyde	2.5	84[c]
12	Ethyl methyl ketone oxime	Ethyl methyl ketone	2.5	84[d]
13	Benzoin oxime	Benzoin	2.5	83[c]
14	Camphor oxime	Camphor	3.3	83[c]
15	Cyclopentanone oxime	Cyclopentanone	3	81

[a]Products 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. [b]Isolated yields. [c]Under reflux conditions. [d]CH_2Cl_2/H_2O was used as a solvent.

equimolar mixtures of camphor oxime and benzyl alcohol in acetone and water were allowed to react with *N*-bromo-*N*-benzoyl-4-toluenesulfonamide at room temperature, the ketone oxime underwent chemoselectively oxidative deoximation giving (82%) camphor, whereas benzyl alcohol was not oxidised to benzaldehyde (Scheme 3).



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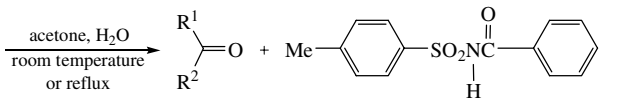

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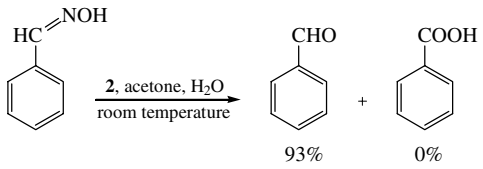
Scheme 1

† IR and ^{1}H NMR spectra were recorded using a Shimadzu 435-U-04 spectrophotometer (paraffin) and a 90 MHz Jeol FT-NMR spectrometer, respectively. ^{1}H NMR chemical shifts were measured relative to TMS.

Solvent-free preparation of N-*benzoyl-4-toluene sulfonamide* **1**. A mixture of 10.0 g (58.4 mmol) of 4-toluene sulfonamide and 10.2 ml (87.6 mmol) of benzoyl chloride was placed in a beaker. The beaker was heated in an oil bath (140 °C). The mixture was stirred with a mechanical stirrer for 1 h. Then, it was cooled to room temperature, and the product was recrystallised from ethanol. The yield of pure compound **1** was 15.1 g (94%), mp 147–149 °C. ^{1}H NMR ([$^2H_6$]acetone) δ: 2.34 (s, 3H), 7.31–7.95 (m, 9H), 10.9 (s, 1H). ^{13}C NMR ([$^2H_6$]acetone) δ: 21.88, 129.22, 129.50, 129.79, 130.54, 133.02, 134.31, 137.94, 145.84, 166.14. IR (paraffin, ν/cm^{-1}): 3309, 1709, 1597, 1493, 1335, 1235, 1165, 1059, 888, 841, 791, 678. Found (%): C, 61.32; H, 4.62; N, 5.22. Calc. for $C_{14}H_{13}NO_3S$ (%): C, 61.07; H, 4.76; N, 5.09.

Preparation of N-*bromo*-N-*benzoyl-4-toluene sulfonamide* **2**. 5.0 g (18.2 mmol) of *N*-benzoyl-4-toluene sulfonamide **1** was dissolved in a chilled aqueous sodium hydroxide solution (~2 M) at room temperature, and the solution was transferred to a beaker. 0.93 ml (18.2 mmol) of bromine dissolved in 2 ml of tetrachloromethane was added to the solution with vigorous stirring, and a yellow precipitate was immediately formed. The yellow product was separated from the aqueous layer and recrystallised from acetone. The yield of pure **2** was 5.2 g (80%), mp 204–207 °C. ^{1}H NMR ([$^2H_6$]acetone) δ: 2.28 (s, 3H), 7.13–8.00 (m, 9H). ^{13}C NMR ([$^2H_6$]acetone) δ: 21.81, 127,44, 128.45, 129.09, 130.00, 130.64, 132.49, 138.22, 143.21, 165.28. IR (paraffin, ν/cm^{-1}): 1697, 1596, 1456, 1333, 1231, 1128, 895, 860, 719, 663. Found (%): C, 47.78; H, 3.25; N, 4.10. Calc. for $C_{14}H_{12}BrNO_3S$ (%): C, 47.47; H, 3.41; N, 3.95.

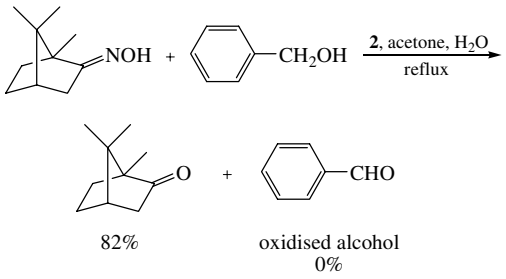
‡ *General procedure for deoximation.* A mixture of an oxime (3 mmol) and reagent **2** (4.5 mmol) in acetone (10 ml) and water (0.1 ml) was stirred at a temperature specified in Table 1. After the reaction was completed (TLC), the solvent was removed under reduced pressure, and diethyl ether (20 ml) was added to the mixture, which was stirred for 10 min; then, sulfonamide **1** was removed by filtration, and the product was purified by column chromatography (hexane–diethyl ether, 4:1, CH_2Cl_2 was used for isobutyraldehyde and ethyl methyl ketone).



Scheme 2

An unsaturated oxime (entry 8) was cleaved to the corresponding unsaturated aldehyde without affecting the double bond. Thus, we observed the competitive oxidation of oximes in the presence of alkenes (Scheme 4).

After the reaction was completed, according to Scheme 1, compound **2**, was converted into *N*-benzoyl-4-toluenesulfonamide **1**, which can be isolated, brominated and reused many times as a deoximating reagent.



Scheme 3

In conclusion, the test reaction occurs at room temperature without the formation of overoxidation products due to high chemoselectivity of reagent **2**. The OH and C=C functional groups in the oxime structure were not oxidised to other functional groups. Finally, the oxidative reagent can be recovered and reused many times.

Reagent **2** is a competitor to the known reagents NBS and *N*-bromophthalimide with the advantage of easier preparation.

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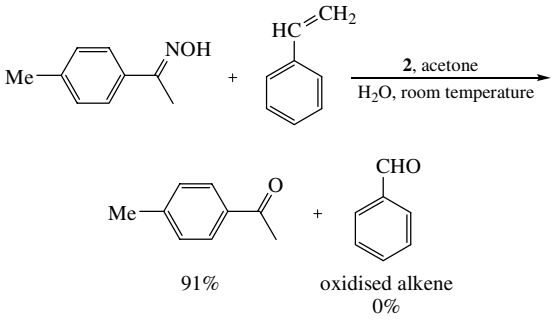

Scheme 4

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