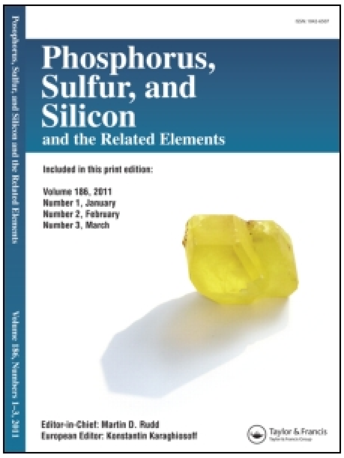

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A NEW APPLICATION OF N-BROMOSACCHARIN AS A SELECTIVE AND EFFICIENT OXIDATIVE REAGENT FOR REGENERATION OF CARBONYL COMPOUNDS FROM OXIMES

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A NEW APPLICATION OF N-BROMOSACCHARIN AS A SELECTIVE AND EFFICIENT OXIDATIVE REAGENT FOR REGENERATION OF CARBONYL COMPOUNDS FROM OXIMES

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A new method for the direct conversion of various oximes into aldehydes and ketones by treatment with N-bromosaccharin is described. N-bromosaccharin can be used for an effective, selective and mild oxidizing agent for the regeneration of carbonyl compounds from oximes in good yield.

Keywords: Aldehydes; ketones; N-bromosaccharin; oximes

Regeneration of carbonyl compounds from the corresponding oximes is a very important reaction because oximes are the preferred derivatives for purification and characterization of carbonyl compounds. Oximes are also useful as protecting group.[1] So far a good number of methods based on hydrolytic,[2] reductive,[3] and oxidative[4] reactions have been developed for deoximation. The methods based on oxidative reactions make use of several oxidizing agents. These include Chromium reagents such as pyridinium chlorochromate,[5] pyridinium chlorochromate-H_2O_2,[6] trimethyl ammonium chlorochromate,[7] and others such as periodic acid,[8] dinitrogen tetroxide,[9] dimethyl dioxirane,[10] manganese triacetate,[11] and N-haloamines.[12] In spite of the many reagents available, there is still a need for newer reagents, because the existing oxidative methods suffer from one or the other disadvantages such as long reaction times,[13] need for refluxing temperature,[11] difficulties in isolation of products,[5–7] and formation of over oxidation products leading to low yields. In this article, we

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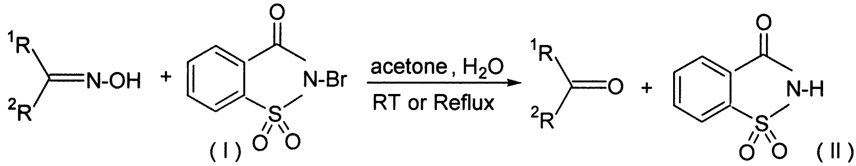
report a new oxidative method for deoximation using N-bromosaccharin (N.B.Sa.) as an oxidizing agent, which overcomes the disadvantages associated with oxidative methods developed so far (Scheme 1).



SCHEME 1

RESULTS AND DISCUSSION

The results of the conversion of various oximes to their corresponding carbonyl compounds are presented in Table I.

Dissolution of oximes in acetone with the addition of a small amount of water and subsequent reaction with N.B.Sa. under stirring at room temperature or reflux gave the corresponding carbonyl compounds in good yields. Even the sterically hindered ketone oxime (Table I,

TABLE I Deoximation with N.B.Sa. at Room Temperature

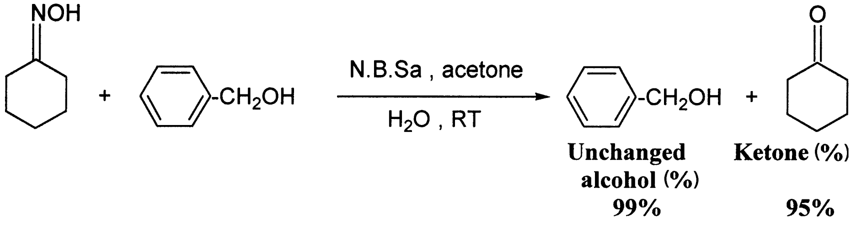
Entry	Substrate	Product	Time (h)	Yield (%)[a,b]
1	Cyclohexanone oxime	Cyclohexanone	1.5	96.52
2	Acetophenone oxime	Acetophenone	1.5	94.7
3	Benzaldehyde oxime	Benzaldehyde	1.5	94.5
4	4-Chloro benzaldehyde oxime	4-Chloro benzaldehyde	1.5	94
5	Benzophenone oxime	Benzophenone	1.5	93.5
6	4-Methyl acetophenone oxime	4-Methyl acetophenone	1.6	93
7	Isobutyraldehyde oxime	Isobutyraldehyde	2	92
8	Isobutyl methyl ketone oxime	Isobutyl methyl ketone	2	91
9	Diisopropyl ketone oxime	Diisopropyl ketone	2.2	91
10	2-Chloro benzaldehyde oxime	2-Chloro benzaldehyde	2.6	90.8[c]
11	Ethyl methyl ketone oxime	Ethyl methyl ketone	2.2	90.3
12	Benzoin oxime	Benzoin	2.6	90[c]
13	Camphor oxime	Camphor	3.8	86[c]
14	Cyclopentanone oxime	Cyclopentanone	2.5	82

[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] Under reflux conditions.

entry 13) was succesfully oxidatively cleaved to the corresponding ketone in good yield. The aldoximes were converted to the corresponding aldehydes, and no acid was formed due to overoxidation of the regenerated aldehyde (Table I, entries 3, 4, 7, 10). 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 (Table I, entry 12). Thus, when equimolar mixtures of cyclohexanone oxime and benzyl alcohol in acetone and water were allowed to react with N.B.Sa. at room temperature, the ketone oxime underwent chemoselectively oxidative deoximation, giving (95%) cyclohexanone, whereas the benzyl alcohol was recovered unchanged (Scheme 2).



SCHEME 2 Selective deoximation in the presence of alcohol.

On the other hand, in this reaction (according to Scheme 1) N-bromosaccharin(I) converted to the saccharin(II), which can be isolated, brominated, and reused as a new deoximating reagent.

CONCLUSION

In conclusion, the striking features of our method are the reaction occurs at room temperature, no formation of overoxidation products due to high chemoselectivity and the mild nature of N-bromosaccharin, easy workup procedure, high yields, and the oxidative reagent (N.B.Sa.) can be recovered and reused many times.

EXPERIMENTAL: GENERAL PROCEDURE

A mixture of the oxime (3 mmol) and N.B.Sa. (3.5 mmol) in acetone (10 ml) and water (1 ml) was stirred at the temperature given in Table I for the specified time. After the reaction was completed (thin layer chromatography (TLC)), the solvent was removed under reduced pressure and 20 ml of diethyl ether was added to the mixture. It was then stirred for 10 min, and then the saccharin was removed by filteration and the product was purified by column chromatography (CCl_4/methanol).

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