Quantitative Regeneration of Carbonyl Compounds from Oximes under Microwave Irradiations using N-bromosuccinimide

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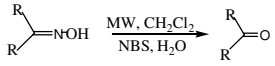
Research Article

Abstract: An efficient, economically viable and operationally simple method was developed for deoximation of oximes (of ketones and aldehydes) to their corresponding carbonyl compounds using N-bromosuccinimide (NBS) has been achieved under microwave irradiations. A new and selective method for the cleavage of oximes by a simple reaction of a ketoxime or an aldoxime with N-bromosuccinimide is an efficient reagent for the oxidative cleavage of oximes to the corresponding aldehydes and Ketones under microwave irradiation in a domestic microwave oven. This procedure features short reaction times, high chemoselectivity (no over-oxidation), easy work-up and high yields.



Ketoxime Ketone

Key Words: N-bromosuccinimide, oximes, aldoxime, ketoxime

Introduction

Nitrogen derivatives of aldehydes and ketones such as oximes are highly crystalline compounds. They constitute a very efficient method for the isolation, purification, and characterization of carbonyl compounds.[1] Protection of aldehydes and ketones is an important transformation in the total synthesis.[2] Oximes are useful in organic chemistry as protecting groups, synthetic intermediates for producing amines[3] and nitriles[4] and also are utilized for purification and characterization of aldehydes and ketones[5]. Regeneration of the carbonyl functionality from oxime, especially under mild reaction conditions, is also an important achievement from the synthetic points of view. This transformation has been achieved by various methods which have been reviewed recently.[6-7] Oximes can be prepared from non-carbonyl compounds[8] and therefore, regeneration of carbonyl compounds from oximes is an important synthetic route. Some of the methods reported earlier for deoximation of carbonyl compounds consist of oxidative or reductive methods[9]. Study of oxidative regeneration of oximes to carbonyl compounds by N- halo compounds such as N-bromophthalimide[10], N-bromosacharin[11], N-bromo-N-phenyl-para-toluene sulfonamide[12] has been reported. We now describe a new method for the selective cleavage of oximes to their carbonyl compounds under microwave irradiation with the use of N-bromosuccinimide as an effective oxidizing agent that overcomes the disadvantages associated with oxidative methods developed so far. Microwave-promoted reactions occur with dramatic decreases in reaction times[13].

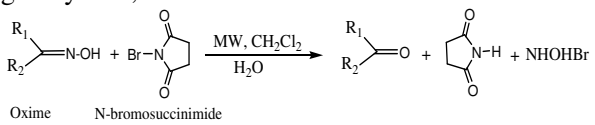
Experimental

The starting materials, aldoxime and ketoxime were prepared according to literature[14,15]. A mixture of the oxime (3 mmol) and NBS (3.5 mmol) in dichloromethane(10 mL) and water (0.1 mL), were introduced in a two necked flask fitted with a reflux condenser and were refluxed under irradiation in a microwave oven at a power output of 200 W for the appropriate times as indicated in Table 1. The reaction was monitored by TLC. After the reaction was completed (TLC), the solvent was removed under reduced pressure, and 20 mL of diethyl ether was added to the mixture, and it was stirred for 10 minutes; then the succinimide, was removed by filtration and the product was purified by column chromatography [(hexane/ diethyl ether : 4/1). Products (aldehydes and ketones) were characterized by their physical constants, by comparison with authentic samples, and the melting points of 2, 4-dinitrophenyl hydrazones derivatives.

Results and Discussion

The application of N-halo compounds in organic chemistry[16] was found a novel and efficient protocol for the deoximation of a variety of oximes using N-bromosuccinimide (NBS) under microwave irradiation conditions. We now report a new oxidative method for deoximation under microwave irradiation using N-bromosuccinimide (NBS), as an oxidizing agent that overcomes the disadvantages associated with oxidative methods developed so far. Dissolution of oximes in dichloromethane with addition of a small amount of water and subsequent reaction with NBS under microwave

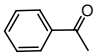
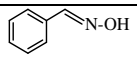
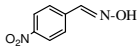
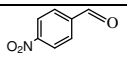
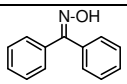
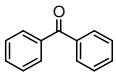
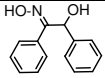
irradiation gave the corresponding carbonyl compounds in good yields, Scheme 1.



Scheme 1

The results of the conversions of various oximes to their corresponding carbonyl compounds are presented in

Table 1: Deoximation of aldoximes and ketoximes with NBS under MW

Entry No.	Substrate	Product	Time (Sec.)	Yield (%)
01	 Acetophenone oxime	 Acetophenone	87	93.%
02	 Benzaldoxime	 Benzaldehyde	83	94%
03	 4-Nitro-Benzaldoxime	 4-Nitro-benzaldehyde	80	94%
04	 Benzophenone oxime	 Benzophenone	90	95%
05	 Cyclohexanone oxime	 Cyclohexanone	94	90%
06	 Benzoin oxime	 Benzoin	98	89%

Even the sterically hindered ketoxime 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 over oxidation of the regenerated aldehyde. This procedure is also useful for the oxidative deoximation of oximes in the presence of alcohols or for oximes that contain -OH functional group. In addition, benzoin oxime was cleaved to the corresponding carbonyl compounds smoothly without affecting the other functionality. Therefore this method is useful for the chemoselective oxidative deoximation of oximes in the presence of alcohols or for oximes that contain an OH functional group. Thus we also used this procedure for the selective deoximation of acetophenone oxime in the presence of an equimolar amount of benzyl alcohol. The only observed product was acetophenone in 93% conversion. As evident from the results, aldehyde derivatives were generally deprotected relatively faster than keto derivatives. It was also interesting to note that by controlling the amounts of the reagent, it was possible to avoid further oxidation of the liberated aldehydes to the corresponding carboxylic acids. On the other hand, after the reaction was completed, N-bromosuccinimide, was converted to the succinimide, so it can be isolated, brominated and reused as a new deoximating reagent.

Conclusions

In conclusion, the striking features of our method are; very short reaction times, formation of no over oxidation products due to high selectivity and mild nature of N-bromosuccinimide, easy work-up procedure, high yields, -OH functional group in the oxime structure does not oxidize to a carbonyl group, and finally, the oxidative reagent (NBS) can be recovered and reused many times. NBS was found to be an efficient reagent for the oxidative cleavage of oximes to the corresponding aldehydes and ketones under microwave irradiation in a domestic microwave oven.

Acknowledgement

The authors are thankful to Principal Vasantrao Naik Mahavidyalaya, Aurangabad for providing laboratory facilities and encouragement for this work.

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