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Short Report

Facile Regeneration of Carbonyl Compounds from Oximes Under Microwave Irradiations Using N-Bromophthalimide

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Um método novo e seletivo para clivagem de oximas envolve a reação das oximas derivadas de aldeídos e cetonas com N-bromoftalimida (NBPI) em acetona sob irradiação de microondas.

A new and selective method for the cleavage of oximes has been achieved by a simple reaction of a ketoxime or an aldoxime with N-bromophthalimide (NBPI) in acetone under microwave irradiations.

Keywords: aldoxime, ketoxime, microwave, N-bromophthalimide

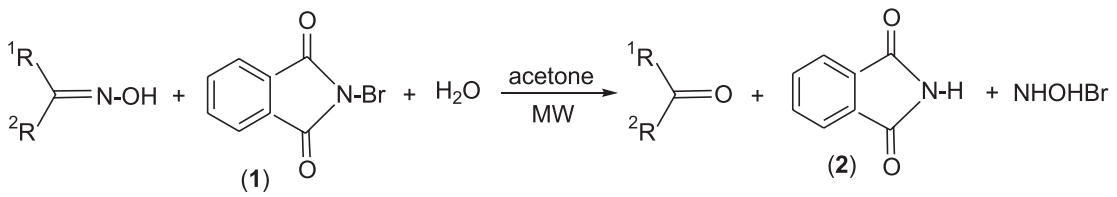
Introduction

The hydrolysis of oximes to the corresponding carbonyl compounds has been of considerable interest in recent years for at least two reasons.[1] Firstly, oxime derivatives are often used to purify, characterise and protect aldehydes and ketones,[2] so the regeneration of the parent carbonyl compounds is important. Secondly, oximes may be accessed by routes not involving the carbonyl function such as the Barton reaction and the reduction of nitro compounds,[3] and so subsequent hydrolysis would define a route to the parent carbonyl compounds. A good number of methods based on hydrolytic,[4] reductive,[5] and oxidative,[6] reactions have been developed for deoximation. In spite of the many reagents available, there is still scope for newer reagents as the existing oxidative methods suffer from one or the other disadvantages like long reaction times,[7] difficulties in isolation of products,[8,9] and formation of over oxidation products leading to low yields. In our preliminary studies we found that microwave-promoted reactions occur with dramatic decreases in reaction times,[10] and in some cases, cleaner reactions with easier work-ups than observed when using conventional heating.[11,12] According to these points, we now report a new oxidative method for deoximation under microwave irradiation using N-bromophthalimide (NBPI), as an oxidising agent, that overcomes the disadvantages associated with oxidative methods developed so far. Dissolution of oximes in acetone with addition of a small amount of water and subsequent reaction with NBPI under microwave irradiation gave the corresponding carbonyl compounds in good yields, Scheme 1.

Results and Discussion

The results of the conversions of various oximes to their corresponding carbonyl compounds are presented in Table 1.

Even the sterically hindered ketone oxime (entry 13)



Scheme 1.

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Table 1. Deoximation with NBPI under MW

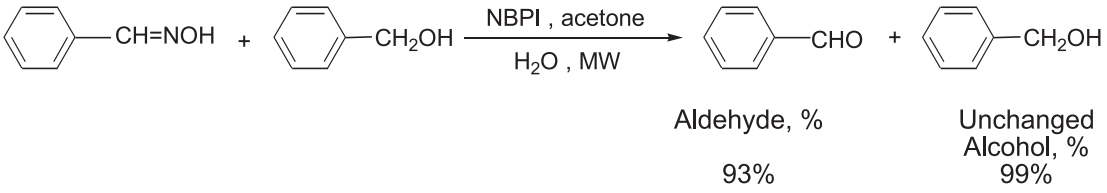
Entry	Substrate	Product	time(min)	Yield(%)[a,b]
1	Cyclohexanone oxime	Cyclohexanone	2.5	96
2	Acetophenone oxime	Acetophenone	2.5	95
3	Benzaldehyde oxime	Benzaldehyde	2.5	94
4	4-Chloro benzaldehyde oxime	4-Chloro benzaldehyde	2.5	94
5	Benzophenone oxime	Benzophenone	2.6	93
6	4-Methyl acetophenone oxime	4-Methyl acetophenone	2.6	93
7	Isobutyraldehyde oxime	Isobutyraldehyde	2.5	92[c]
8	Isobutyl methyl ketone oxime	Isobutyl methyl ketone	3	91
9	Diisopropyl ketone oxime	Diisopropyl ketone	3.2	91
10	2-Chloro benzaldehyde oxime	2-Chloro benzaldehyde	3.2	91
11	Ethyl methyl ketone oxime	Ethyl methyl ketone	3	91[c]
12	Benzoin oxime	Benzoin	3	90
13	Camphor oxime	Camphor	3.2	88
14	Cyclopentanone oxime	Cyclopentanone	3	87
15	Cinnamaldoxime	Cinnamaldehyde	2	84

[a] Products were characterized by their physical constants, comparison with authentic samples and melting points of 2,4-dinitro phenyl hydrazone derivatives and IR and NMR spectra; [b] Isolated yields; [c] CH_2Cl_2/H_2O was used as reaction solvent.

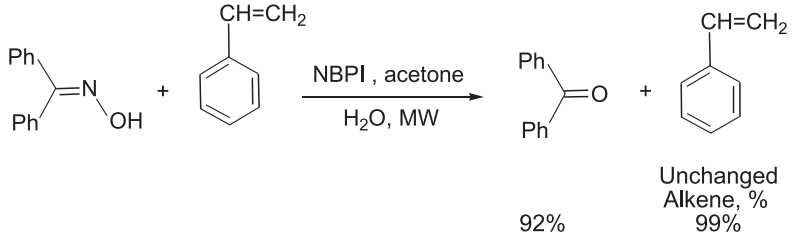
was succesfully oxidatively cleaved to the corresponding ketone in good yield. The aldoximes were converted to the corresponding aldehydes and no acid was formed due to overoxidation of the regenerated aldehyde (entries 3,4,7,10, and 15). This procedure is also useful for the oxidative deoximation of oximes in the presence of alcohols or for oximes that contain -OH functional group (entry 12). Thus, when equimolar mixtures of benzaldoxime and benzyl alcohol in acetone and water were allowed to react with NBPI under MW irradiation,the aldoxime underwent oxidative deoximation giving (93%) benzaldehyde, whereas the benzyl alcohol were recovered unchanged, Scheme 2.

The unsaturated oxime (entry 15) was cleaved to the corresponding unsaturated aldehyde without affecting the double bond. So we observed the competitive oxidation of oximes in the presence of alkene. In a control experiment, when equimolar mixtures of benzophenone oxime and styrene in acetone and water were allowed to react with the title reagent (**1**) under microwave irradiation, the ketone oxime underwent selective oxidative deoximation giving 92% benzophenone, whereas the styrene was recovered unchanged, Scheme 3.

On the other hand, after the reaction was completed, N-bromophthalimide (**1**), was converted to the phthalimide (**2**), so it can be isolated, brominated and reused as a new deoximating reagent.



Scheme 2. Selective deoximation in the presence of benzyl alcohol.



Scheme 3. Selective deoximation in the presence of styrene

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-bromophthalimide, 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 (NBPI.) can be recovered and reused many times.

Experimental

General procedure

A mixture of the oxime (3 mmol) and NBPI (3.5 mmol), in acetone (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 300 W for the appropriate times as indicated in Table 1. After the reaction was completed (TLC), the solvent was removed under reduced pressure, and 20 mL of diethyl ether, ($CHCl_3$ was used for benzoin oxime) was added to the mixture, and it was stirred for 10 minutes; then the phthalimide (2), 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)].

Products (aldehydes and ketones) were characterized by their physical constants, by comparison with authentic samples, and the melting points of 2,4-dinitrophenyl hydrazone derivatives and by their IR and ^1H NMR spectra.

Acknowledgement

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