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Ultrasound-Promoted Rapid Oxidative Cleavage of Oximes with NaBrO₃/Ion Exchange Resin

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Ultrasound-Promoted Rapid Oxidative Cleavage of Oximes with NaBrO₃/Ion Exchange Resin

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Abstract: The oxidative cleavage of oximes has been studied under solvent-free ion exchange resin (IER) catalysis by sodium bromate using ultrasonic irradiation. Both aldoximes and keto-oximes selectively converted to the corresponding carbonyl compounds in high yields within short times at room temperature.

Keywords: NaBrO₃/ion exchange resin, oxidation, oxime, ultrasound

INTRODUCTION

Because of their hydrolytic stability, oximes are used as carbonyl protectors^[1,2] from which the parent carbonyl compounds must be regenerated at the completion of a synthetic procedure. Regeneration of the carbonyl compound requires the use of mild reagents and reaction conditions that will cleave the C==N bond without modification to the rest of the molecule.

Furthermore, because oximes can also be prepared from noncarbonyl compounds, the generation of carbonyl compounds from them provides an alternative method for the preparation of aldehydes and ketones.^[3–6]

Because of their low price and versatility, halogens and halogenated compounds (bromine, iodine, hypoclorite, *N*-bromoamides, percholoric acid, percholorates, periodic acid) have been used in reactions of deoximation and have delivered good results.^[2]

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Sodium bromate is commercially available as a stable solid, which potentially is an interesting candidate for the oxidation of organic compounds because of its capability in multi-electron transfer. Thermodynamically sodium bromate is a strong oxidant, but according to the literature, bromate itself is not able to oxidize organic compounds. It is usually used in aqueous media in the presence of coreactants such as NaHSO₃,^[7] HBr,^[8] Br₂,^[9] NH₄Cl,^[10-12] FeCl₃,^[13] cerium(IV) ammonium nitrate (CAN),^[14] H₂SO₄,^[15] KHSO₄,^[16] [CH₃(CH₂)₃]₄NHSO₄,^[17] and HClO₄.^[18] In most of these oxidation systems, not only the reaction conditions are hard, but the removal of excess sodium bromate from the coreactant is difficult.

In continuation of our studies on the oxidation of organic compounds with sodium bromate^[10-13,17] and deoximation of keto-oximes with KMnO₄,^[19] we have used a combination of a solvent-free reaction strategy and solid ion-exchange resin (IER) catalysis using ultrasound irradiation in the oxidative cleavage of oximes for the first time by sodium bromate, which not only overcomes the previously mentioned disadvantages but also has other advantages: easy and quick separation of the products from the oxidant and catalyst, better selectivity because of lower activity of H^+ in the solid state, high yields, and faster reaction.

In addition, because of the higher concentration of oxidant and lower reaction temperature, less toxic effluent can be used, and other waste problems can be minimized. The catalyst is regenerable and does not have the problem of the limited use of bromate resluting from its insolubility in almost all organic solvents.

As shown in Table 1, a wide variety of aryl aldoximes and aryl and alkyl keto-oximes could be easily oxidized to corresponding carbonyl compounds using ultrasound irradiation in high yields at room temperature (Scheme 1).

Comparisons of the time and yield of this method with our previous method using KMnO₄ supported on MnSO₄ or MnO₂ under solvent-free conditions are indicated in Table 1. The current procedure is usually much faster in a similar range of yields. In addition, most standard oxidants of aldoximes result in the formation of acids;^[19,20] however, by controlling the times, aldehydes librated via deprotective reaction are not further oxidized to the corresponding acids (entries 15-22).

In conclusion, both sodium bromate and IER are cheap and commercially available reagents, and not only is ion-exchange resin is regenerable but also excess bromate ions are easily separated from the reaction mixture and recycled.

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. The results were in agreement with the calculated values. Mass

Entry Reactant Product $\%$ Time (min) $\%$ Time (min) 1 $\downarrow \downarrow \downarrow \downarrow \downarrow$ $\downarrow \downarrow \downarrow \downarrow$ $\downarrow \downarrow \downarrow \downarrow$ 79 10 75 90 2 $\downarrow \downarrow \downarrow \downarrow \downarrow \downarrow$ $\downarrow \downarrow \downarrow \downarrow$ 78 15 73 100 3 $\downarrow \downarrow \downarrow \downarrow \downarrow \downarrow$ $\downarrow \downarrow \downarrow \downarrow$ 83 25 70 120 4 $\downarrow \downarrow \downarrow \downarrow \downarrow$ $\downarrow \downarrow \downarrow \downarrow$ $\downarrow \downarrow \downarrow \downarrow$ 84 35 83 110 5 NOH Q 81 60 81 150					Isolated Yield		Ref. [19] Yield		GC Yield	
$1 \qquad \qquad$	Reactant	Reactant	Product	Product	%	Time (min)	%	Time (min)	%	Time (min)
2 4 4 4 4 4 4 4 4 4 4	[NOH			79	10	75	90	78	45
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	с́	NOH		H.C.	78	15	73	100	85	55
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		NOH			83	25	70	120	75	75
$Br' \sim Br' \sim$ 5 NOH Q 81 60 81 150	- 	NOH			84	35	83	110	85	90
O_2N	,N	NOH		Br O	81	60	81	150	84	75

Table 1.	Oxidation of oximes by	v NaBrO ₃ /ion exchange	resin under ultrasonic	irradiation at room temperature
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			Isolated Yield		Ref. [19] Yield		GC Yield	
Entry	Reactant	Product	%	Time (min)	%	Time (min)	%	Time (min)
6	NOH		80	15	71	85	79	45
7			76	30			—	
8	HON Ph Ph		71	20	—	_	—	_
9	NOH		97 ^a	15		—		
10	NOH		84 ^{<i>a</i>}	20	—	—		—
11	NOH		72 ^{<i>a</i>}	20		_		
12	NOH		63	5		_	—	_
13	NOH	° L	54 ^{<i>a</i>}	20	_	_	_	_

Table 1. Continued



Table 1	 Continued 	
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			Isolated Yield		Ref. [19] Yield		GC Yield	
Entry	Reactant	Product	%	Time (min)	%	Time (min)	%	Time (min)
20	CI NOH H	CI O H	68	45		_		_
21	NOH H	С	71	25	_	_		_
22	HO H	но	74	10	_	_		_

^aGC yield.

Oxidative Cleavage of Oximes



Scheme 1. R^1 and R^2 = aryl and alkyl; R^1 = aryl and R^2 = H.

spectra were recorded on a Finnigan-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV. IR spectra were recorded on a Shimadzu IR-470 spectrometer. ¹H and ¹³C NMR spectra were recorded on a Bruker DRX-300 Avance spectrometer at 300.13 and 75.47 MHz. NMR spectra were obtained on solutions in CDCl₃. All products are known compounds, which were identified by IR and ¹H NMR spectral data, and their melting points were compared with literature reports.

General Procedure for Oxidation of Oximes

A mixture of oxime (1 mmol), IER (0.2 g), and sodium borate (0.5 g, 3.3 mmol) was ground and then successively charged into a screw-capped vial. The mixture was irradiated in a water bath of the ultrasonic cleaner (Eyela-92303, Tokyo Rikakikai Co.) at $25-30^{\circ}$ C for 15-30 min. Then, the reaction mixture was washed with 25 cm³ of chloroform. The crude product was purified by column chromatography on silica gel using *n*-heptane–ethyl acetate (9:1) as eluent to afford the pure product.

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