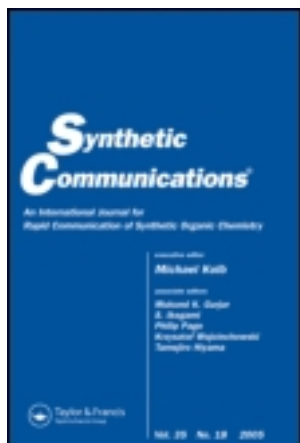


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A. R. Hajipour, S. E. Mallakpour & S. Khoee^a

^a Pharmaceutical Research Laboratory, College of Chemistry, Isfahan University of Technology, Isfahan, IR, 84156, Iran

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**AN EASY AND FAST METHOD
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A. R. Hajipour,* S. E. Mallakpour,* and S. Khoei

Pharmaceutical Research Laboratory,
College of Chemistry, Isfahan University of
Technology, Isfahan, 84156, IR, Iran

ABSTRACT

1-Benzyl-4-aza-1-azoniabicyclo[2.2.2]octane dichromate has been found to be an efficient and new reagent for the conversion of oximes to the corresponding carbonyl compounds. The reaction is performed under microwave irradiation.

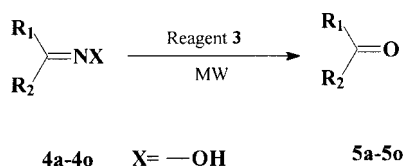
Oximes are highly crystalline and very useful for purification and characterization of carbonyl compounds. These derivatives are also useful as efficient protecting groups for aldehydes and ketones.¹ Conversion of oximes back to their corresponding carbonyl compounds is a very important process in synthetic organic chemistry. Several oxidative deoxygenation methods have been developed and have found some advantages over the classical hydrolysis method.^{2–12}

*Corresponding authors. E-mail: haji@cc.iut.ac.ir

CONVERSION OF OXIMES

11

solvent for both the reagent and the product (3) as a factor for increasing the dielectric constant of the medium. Because by increasing the dielectric constant, the coupling with microwave increased. We tested several solvents such as CCl₄, hexane, toluene, *o*-cresol, acetonitrile and dichloromethane. The reaction was not carried out in hexane and toluene because these solvents are microwave inactive solvents and therefore did not absorb the heat of microwave irradiation. *o*-Cresol and acetonitrile are microwave active solvents but during the reaction, the oximes and solvent are both affected by the reagent and produce several by-products. Since dichloromethane is a microwave active solvent^{1a} and also does not affect by the reagent during the reaction progress, we chose this solvent in these reactions. Therefore 1.5 ml of dichloromethane was added to one equimolar amount of oximes (4a–4o) and reagent (3) and the reaction mixture was irradiated in a domestic microwave oven until TLC showed complete disappearance of starting materials (Scheme 2). Monitoring the reaction by TLC showed that by disappearance of starting material spot, the corresponding carbonyl compound appeared as the only product and no by-product was observed on the TLC plate. The reaction completed within 25–40 s and the pure carbonyl compound was obtained by a simple work-up without further purification.

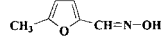
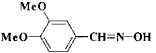
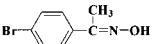


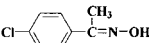
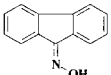
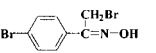
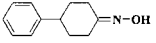


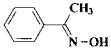
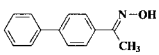
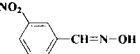
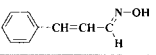


Scheme 2.

Comparing the results obtained from the microwave method by previous catalytic method²⁸ showed that in the latter method aliphatic oximes did not react with (3), even in the presence of AlCl₃, whereas in this new method they react easily (Table 1). Consequently, it seems that under microwave irradiation the reaction loses its selectivity. Therefore, it is interesting to investigate the competitive reaction of aliphatic and benzylic oximes with this reagent. When equimolar amounts of cyclohexanal oxime (4k) and 3,4-dimethoxybenzaldehyde oximes (4b) were treated with (3), only the benzylic oxime (4b) was selectively oxidized to its corresponding aldehyde whereas aliphatic oxime (4k) remained unchanged (Scheme 3). Finally we can say that the selectivity of the reaction did not decrease but its operational domain was extended.



Table 1. Conversion of Oximes to Carbonyl Compounds^a

	Substrate	Time (Sec)	Yield ^b (%)	M.P.(°C) or B.P.(°C)/Torr	
				Found	Reported ⁷
4a		30	89	184-186	187
4b		30	96	41-43	42-45
4c		40	91	49-51	50-52
4d		35	88	49-50	49-51
4e		25	85	121-122/10	113-116/6
4f		40	93	230/760	232/760
4g		45	96	81-83	82-85
4h		52	93	107-108	108-110
4i		43	95	76-79	78-80
4j		30	79	129-131/760	130-131/760
4k		35	85	153-155/760	155/760
4l		20	91	200/760	202/760
4m		27	87	116-118	115-118
4n		40	90	56-59	57-59
4o		26	92	124-127/10	248/760

^a Products were confirmed by comparison with authentic sample (IR, ¹H-NMR, TLC).

^b Yield of isolated pure carbonyl compound.

The compounds (5a–5o) were characterized by ¹H NMR and IR analysis. Notably, aldehydes did not undergo further oxidation to their carboxylic acids under the reaction conditions.

In order to evaluate the effect of microwave irradiation in this reaction, we tried the reaction of acetophenone oxime with reagent (3) without using any microwave irradiation. The reaction did not proceed at all after 60 min

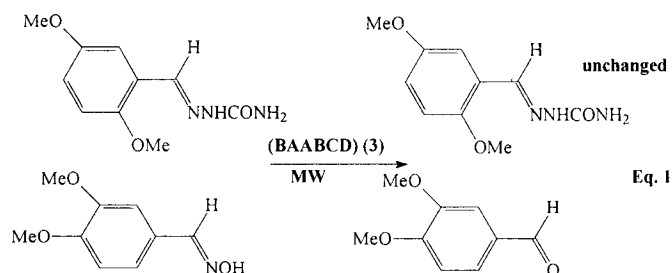


CONVERSION OF OXIMES

13

grinding of the reaction mixture. The mechanism of the reaction is the same, which has been reported by us for the oxidation of alcohols by this reagent.²⁷

Another noteworthy advantage of the reagent lies exclusive oxidation of oximes in the presence of semicarbazone. When a mixture of an equimolar amount of 3,4-dimethoxybenzaldehyde oxime and 2,5-dimethoxy benzaldehyde semicarbazone was treated with reagent (3), only the oxime was selectively oxidized to the corresponding carbonyl compound and the semicarbazone remained unchanged (Eq. 1).



When we treated α,β -unsaturated oxime only the C=N bond was selectively oxidized to the corresponding carbonyl compounds and the reagent was ineffective in oxidizing C=C double bond (Table 1).

In conclusion, we are reporting a new and efficient methodology for the regeneration of aldehydes and ketones from oximes under microwave irradiation. The stability and easy preparation of BAABCD, easy work-up procedure, and high yields of the products, make this method a novel and useful one relative to the reported method for regeneration of carbonyl compounds from their derivatives. These results make BAABCD a bench-top oxidizing agent.

EXPERIMENTAL SECTION

Deprotection of Oximes (4a-4o) with Reagent (3) Under Microwave Irradiation

The deprotection of benzophenone oxime is representative for deprotection of oximes. Benzophenone oxime (0.27 g, 1.39 mmol) was added to 1-benzyl-4-aza-1-azoniabicyclo[2.2.2]octane dichromate (0.87 g, 1.39 mmol)



and the mixture was ground with a pestle in a mortar to form a homogeneous mixture. After transfer of the mixture to an Erlenmeyer flask and adding 1.5 ml CH_2Cl_2 , it was irradiated with microwave oven, until TLC showed complete disappearance of starting materials (Table 1). Then CCl_4 (15 ml) was added to the reaction mixture and after vigorous stirring, the mixture was filtered off and the solvent was evaporated in vacuo. The pure benzophenone was obtained.

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