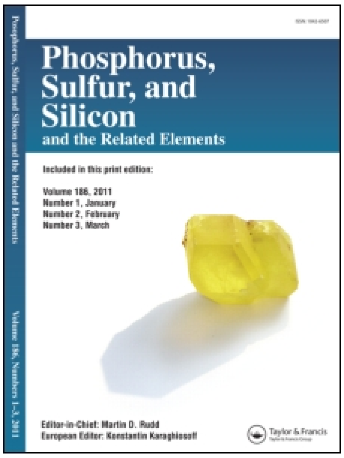

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CONVERSION OF OXIMES INTO CARBONYL COMPOUNDS WITH THALIUM(III) NITRATE SUPPORTED ONTO HZSM-5 ZEOLITE UNDER MICROWAVE IRRADIATION IN SOLVENTLESS SYSTEM

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Oximes are oxidatively deprotected by thalium(III) nitrate supported onto HZSM-5 zeolite to the parent carbonyl compounds in high yields upon exposure to microwave irradiation.

Keywords: Carbonyl compounds; deoximation; microwave irradiation; thalium nitrate; zeolite

INTRODUCTION

Oximes frequently are used to protect carbonyl compounds and hence much attention has been paid to develop methods for their deprotection.[1] Since oximes can be prepared from noncarbonyl compounds, its conversion to carbonyl compounds can be considered a useful method for the synthesis of the latter.[2,3]

The classical recovery of aldehydes or ketones from oximes consists of acid hydrolysis which removes the hydroxylamine from the equilibrium[4] and often results in low yields. Although a large number of reagents are found in the literature for cleavage of oximes to carbonyl compounds,[5] there still appears a need either to improve the existing methods or to introduce newer reagents to permit better selectivity with easy work up procedures.

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Thalium(III) nitrate has been used as an oxidizing agent[6] and Willgerodth-Kindler reaction.[7] Recently, there has been growing interest in the application of microwave irradiation in chemical reaction enhancement,[8] the salient features being improved reaction rates and formation of cleaner products.

When this technique is combined with solvent-free conditions, it would be especially appealing as it provides an opportunity to work with open vessels, thus avoiding the risk of high pressure development, and a possibility of carrying out the reaction on a preparative scale in addition to the associated selectivity and ease of manipulation.[9] The microwave enhanced chemical reactions on mineral supports have gained much attention.[10]

In continuation of our ongoing program to develop environmentally benign reactions under solvent-free conditions using supported reagent combined with microwave,[11] in this article we report the deoximation reaction using thalium(III) nitrate supported onto HZSM-5 zeolite under microwave irradiation in solventless system.

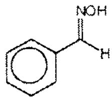
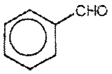
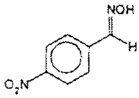
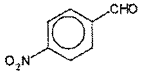
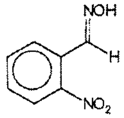
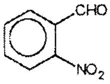
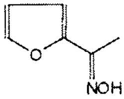
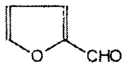
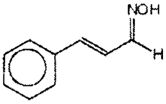
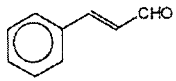
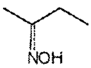
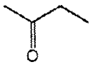
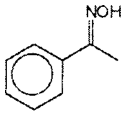
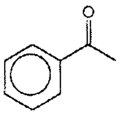
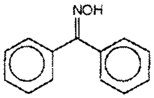
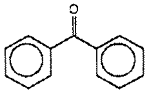
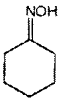
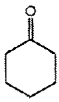
RESULTS AND DISCUSSION

Recently, we reported[12] on the use of HZSM-5 zeolite as a support for the oxidation of alcohols. Among various mineral supports examined such as alumina, clay, silica, and Na-zeolite, we found that HZSM-5 zeolite gives the best results. A weight equivalent of HZSM-5 zeolite and thalium(III) nitrate were crushed using pestle and mortar to give an intimate pair. Two equivalents of this mixture were crushed with the equivalent of neat benzaldoxime and exposed to microwave irradiation.

The progress of the reaction was monitored by TLC using petroleum ether-ethyl acetate, 8:2, as eluents. After 2 min deoximation of benzaldoxime was complete to afford benzaldehyde almost in quantitative yield.

To assess the generality of this deoximation method a variety of aldoximes and ketoximes were reacted under these conditions which yielded to excellent yields (Table I). The interesting feature of this method is the successful deoximation of ketones. As with some other reagents it results in the formation of Beckmann rearrangement[13] products. However, this method is unsuccessful when applied to aryl aldoximes and ketoximes which contain strong electron donating groups such as $-NH_2$ or $-OH$ at *ortho* or *para* position most probably due

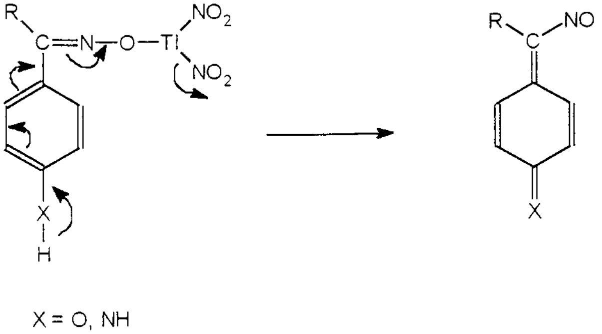
TABLE I Deoximation Reaction Using Thalium(III) Nitrate Under Microwave Irradiation in a Solventless System

Entry	Substrate	Reaction time (sec)	Product[a]	Yield[b] (%)
1		120		98
2		120		83
3		80		85
4		180		82
5		240		80
6		240		85
7		180		92
8		240		83
9		240		90

[a] All products were known and identified by comparison of their physical data with those of authentic sample.

[b] Yields are based on isolated product.

to concomitant oxidation of the aromatic ring to quinone derivatives (Scheme 1).



SCHEME 1

This phenomenon has been noticed previously.[14] This limitation, however, can be circumvented by acetylation of the OH and NH_2 groups before the formation of oximes.[14]

In conclusion we have developed a rapid and solventless method for cleavage of oxime compounds. This high yielding method is manipulatively simple and a selective protocol when compared to the conventional solution phase or heterogeneous reactions.

EXPERIMENTAL SECTION

All substrates were synthesized by a known literature procedure. All products were characterized by comparison of their physical and spectroscopic data with those of authentic samples.

Deprotection of Oximes. Typical Procedure.

Thalium(III) nitrate (4 mmol) and benzylaldoxime (2 mmol) were crushed using a pestle and mortar. This mixture was transferred to a beaker and exposed to microwave irradiation. The progress of the reaction was monitored by TLC using petroleum ether: ethyl acetate 8:2. After completion of the reaction, the product was extracted with dichloromethane and filtered. The filtrate was evaporated to dryness to afford benzaldehyde. Yield 98%.

Caution: Although this reaction worked safely in our hand, using a microwave oven in an efficient hood is highly recommended.

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