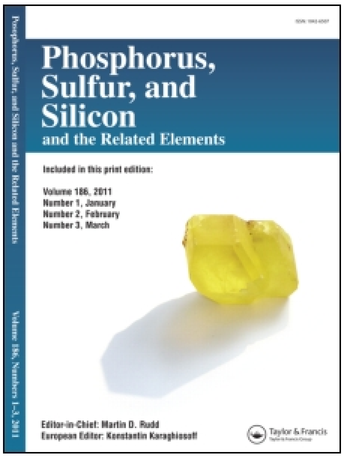

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One-Pot Conversion of Aldoximes Into Nitriles via Aldoxime Tosylates Under Microwave Irradiation

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Silica-gel-supported aldoximes react with tosyl chloride at room temperature to give the corresponding aldoxime tosylates. These supported aldoxime tosylates were directly converted to their corresponding nitriles in high yields under microwave irradiation.

Keywords Aldoximes; tosylates; nitriles; microwave irradiation

INTRODUCTION

Nitriles are versatile functional groups because they can be converted to amides via the nucleophilic addition of water and ketones via hydrolyzing the imine formed by the nucleophilic addition of a Grignard reagent.[1]

The most widely applicable and often the most convenient methods for the formation of a carbon–nitrogen triple bond involve an elimination process.[2] The cyanation of aryl and heteroaryl iodide for the direct introduction of cyano groups to arenes and heteroarenes are known to be classical methods.[3] Direct conversion of aldehydes to nitriles has been also reported.[4] Nitriles can be synthesized from the dehydration of the corresponding oximes using a variety of reagents such as trimethyl

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amine/sulfur dioxide,[5] zeolite,[6] sulphoryl chloride fluoride,[7] and silica gel,[8] etc., each of which has its own merits and drawbacks.

Supported reagents on mineral surfaces have been widely used in organic synthesis.[9] The solventless application of a supported reagent in combination with microwave irradiation provides an ideal reaction condition.[10]

First we thought of using silica gel and zeolite as the acidic, available, and inexpensive catalysts in combination with microwave irradiation in a solvent-free condition.

A variety of aldoximes were mixed with silica gel and zeolite HZSM-5 and put in a microwave oven. All attempts to convert aldoximes to nitriles failed or led to poor yields of nitriles.

After these failures, we planned to expedite o-tosylated oximes, which can be easily synthesized by the reaction of oximes with tosyl chloride in the presence of trimethyl amine. We used silica gel and zeolite HZSM-5 as mineral support in this reaction. The reaction of a silica-gel-supported oximes with tosyl chloride in the presence of trimethyl amine in $CHCl_3$ at room temperature proceeded smoothly to give the corresponding o-tosylated aldoximes, which were not isolated. The solvent was evaporated and the residue was directly subjected to microwave irradiation to obtain the corresponding nitriles in high yields (Table I). The isolation of nitriles was performed by adding methanol to the residue, the evaporation of methanol, and the addition of sodium bicarbonate solution and extraction with ether.

In conclusion, we have developed a simple and one-pot procedure for the conversion of aldoximes to nitriles in high yields.

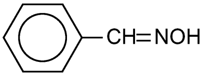
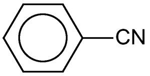
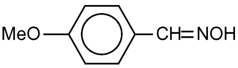
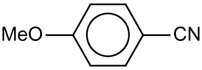
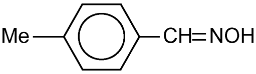
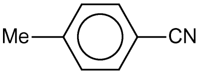
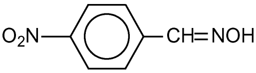
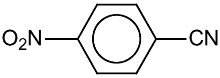
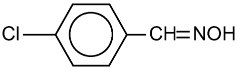
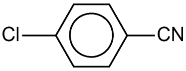
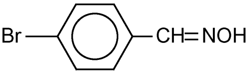
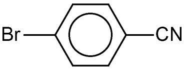
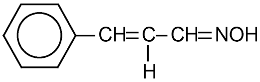
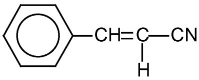
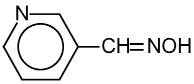
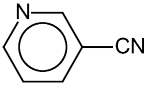
EXPERIMENTAL

Aldoximes were prepared by the reported route.[11] All products were known and their spectroscopic and physical data were compared with those of authentic samples.

Conversion of Aldoximes to Their Corresponding Nitriles (General Procedure)

An appropriate aldoxime (1 mmol) was mixed with silica gel (0.3 g) and tosyl chloride (2 mmol) in $CHCl_3$ (5 mL). To this mixture triethyl amine (3 mmol) was added and stirred at room temperature for a few seconds. The solvent was evaporated under reduced pressure. The crude residue was directly put into an unmodified microwave oven for the indicated time. The progress of the reaction was monitored by TLC.

TABLE I One-Pot Conversion of Aldoxime to Nitrile Under Microwave Irradiation

Entry	Substrate	Time (s)	Product	mp or bp(°C) Found	mp or bp(°C) reported	[a]Yield (%)
1		10		190	191[11]	90
2		12		62	59[3]	92
3		12		63	66[3]	90
4		15		147	148[3]	88
5		15		92	89–90[12]	85
6		15		111	110[12]	82
7		12		255	254[11]	91
8		12		51	—	82

[a]Yeilds are based on weight of oximes used.

After the reaction was completed, methanol was added to the crude residue, filtered, and the filterate was evaporated to dryness. To the residue a saturated solution of sodium bicarbonate was added and the mixture extracted with ether. The ether layer was dried over Na_2SO_4, filtered, and evaporated to afford the corresponding nitrile.

$$\text{Ar–CH=NOH} \xrightarrow[\text{Et}_3\text{N}]{\text{TsCL, silica gel}} \text{Ar–CH=NOTs} \xrightarrow{\text{MW}} \text{Ar–C}\equiv\text{N}$$

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