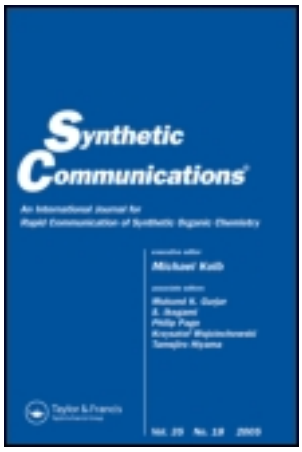

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One-Pot Synthesis of Nitriles from Aldehydes and Hydroxylamine Hydrochloride over Silica Gel, Montmorillonites K-10, and KSF Catalysts in Dry Media Under Microwave Irradiation

Sharwan K. Dewan [a] , Ravinder Singh [a] & Anil Kumar [a]

[a] Department of Chemistry, M.D. University, Rohtak, Haryana, 124001, India

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One-Pot Synthesis of Nitriles from Aldehydes and Hydroxylamine Hydrochloride over Silica Gel, Montmorillonites K-10, and KSF Catalysts in Dry Media Under Microwave Irradiation

Sharwan K. Dewan,* Ravinder Singh, and Anil Kumar

Department of Chemistry, M.D. University, Rohtak, Haryana, India

ABSTRACT

A rapid and facile one-pot synthesis of nitriles has been carried out from the corresponding aldehydes and hydroxylamine hydrochloride in the presence of environmentally benign silica gel (84–95%), Mont K-10 (85–96%), and Mont KSF clay (88–98%) catalysts in dry media under microwave irradiation.

Key Words: Nitriles; Aldehydes; Hydroxylamine hydrochloride; Silica gel; Mont K-10, Mont KSF.

*Correspondence: Sharwan K. Dewan, Department of Chemistry, M.D. University, Rohtak, Haryana 124001, India; E-mail: sharwandewan@rediffmail.com.

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INTRODUCTION

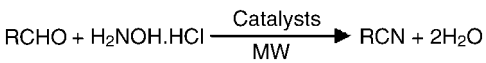
Nitriles form an important functional group from the point of view of organic transformations. They are widely used for conversion into amides amines, esters, carboxylic acids, etc.[1–3] The general method for the synthesis of nitriles is the nucleophilic substitution reaction of alkyl halides with metal cyanides. The dehydration of aldoximes into nitriles has been achieved by using a variety of reagents such as triethylamine/sulfurdioxide,[4] zeolites,[5] sulfuryl chloride fluoride,[6] etc. but many of these transformations suffer from limitations. While ketoximes are undergo Beckman rearrangement over Mont K-10 in dry media under microwave irradiation,[7] we have recently reported that the aldoximes are dehydrated into nitriles under microwave irradiation using silica gel.[8] We have reported the synthesis of oximes from aldehydes and hydroxylamine hydrochloride in high yields using silica gel, Mont K-10, and Mont KSF catalysts under MW conditions.[9] We reasoned that one-pot synthesis of nitriles from aldehydes and hydroxylamine hydrochloride under microwave irradiation in presence of these catalysts (Sch. 1) should be investigated.

3,4-Dimethoxy benzaldehyde was condensed with hydroxylamine hydrochloride in presence of silica gel, Mont K-10, and Mont KSF clay catalysts under varying levels of irradiation (80, 160, 240, 320, 400, 480, 560, 640, 720, and 800 W). The yield between 95% and 98% was observed at 560 W after 4 min of irradiation (TLC monitoring). Subsequent reactions described herein were carried out under these reaction conditions. A variety of substituted aromatic aldehydes have been attempted. These results are indicated in Table 1.

In conclusion, we have shown that one-pot synthesis of nitriles from aldehydes and hydroxylamine hydrochloride can be carried out in high yields in presence of environmentally benign silica gel (84–95%), Mont K-10 (85–96%), and Mont KSF (88–98%) clays as catalysts.

EXPERIMENTAL

Melting points were determined in open capillaries on an electrically heated metal block and are uncorrected. PMR ($CDCl_3$) spectra were recorded



Scheme 1.

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Table 1. One-pot synthesis of nitriles from aldehydes and hydroxylamine hydrochloride in presence of silica gel, Mont K-10, and Mont KSF under microwave irradiation at 560 W.

Serial number	Product[a]	Catalyst (% isolated yield)						M.p. (°C)	
		Silica gel		Mont K-10		Mont KSF			
		(%)	(min)	(%)	(min)	(%)	(min)	Obs.	Lit.
1.	3,4-Dimethoxy benzonitrile	95	4	96	4	98	4	62.5	63[10]
2.	4-Methoxy benzonitrile	92	4	92	4	95	4	58.5	59[10]
3.	2-Hydroxy-4-methoxy benzonitrile	87	5	90	4	94	4	113–114	111–113[10]
4.	4-Nitro benzonitrile	84	5	85	5	88	5	148	148[11]
5.	2-Hydroxy benzonitrile	84	5	86	5	89	4	94.5	95[10]
6.	4-Hydroxy-3-methoxy benzonitrile	85	5	86	5	89	4	87	87–88[10]
7.	4-Hydroxy benzonitrile	92	5	93	5	95	4	110	110[10]
8.	Trans-cinnaminitrile	87	5	89	4	90	4	liq.	liq.[10]
9.	Quinoline-2-carbonitrile	86	4	90	4	94	4	93	94[11]
10.	2-Ethyl-4-cyano pyridine	86	4	91	4	94	4	77	78[12]

[a]Products have been identified based on spectroscopic data.

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on a Jeol FX90Q instrument using TMS as an internal standard. IR spectra were recorded on a Perkin–Elmer 782 spectrophotometer. TLC was done can silica gel G plates with benzene–ethylacetate (4 : 1) system.

Typical Procedure

3,4-Dimethoxy benzaldehyde (166 mg, 1 mmol), hydroxylamine hydrochloride (105 mg, 1.2 mmol) were mixed with silica gel G (1 g) or Mont K-10 (1 g) or Mont KSF (1 g) and taken up in an Earlenmeyer flask and irradiated at 560 W for 4 min in an unmodified domestic microwave oven (Kenstar OM-9925E, 800 W, operating at 2450 MHz). The flask was taken out, cooled, and ether (50 mL) was added. The catalyst was filtered off and the resultant solution evaporated to give a residue, which was purified by chromatography using benzene–ethylacetate (4 : 1) as eluent to afford the desired nitrile (Table 1).

Spectroscopic data for 3,4-dimethoxybenzonitrile (1). ^{1}H-NMR ($CDCl_3$), δ 3.8 (s, 3H, $-OCH_3$), 3.9 (S, 3H, $-OCH_3$), 6.9 (m, 1H, ArH), 7.0 (m, 2H, ArH); IR (neat) 2940 (C–H str.), 2220 (C≡N str.), 1610, 1540, and 1450 (C–C str.); m.p. 62.5°C, reported 63°C.[10]

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