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Magnesium Sulfate Catalyzed rapid One Pot Synthesis of Nitriles from Aldehydes and Hydroxylamine Hydrochloride

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ABSTRACT

Magnesium sulfate was used as a highly efficient catalyst for a rapid one pot synthesis of nitrilesin 84-91% yields from aldehydes and hydroxylamine hydrochloride.

Graphical abstract:

$$RCHO + H_2NOH.HCl \rightarrow RCN$$

Magnesium sulfate

Keywords: Nitriles, Aldehydes, Hydroxylamine hydrochloride, Magnesium sulfate.

INTRODUCTION

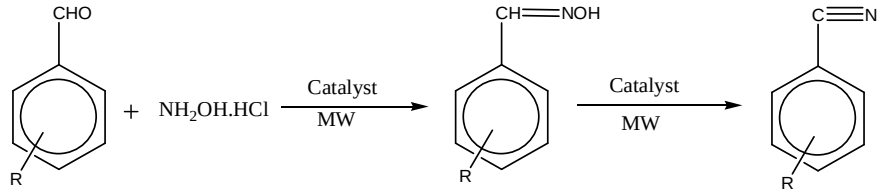
In organic chemistry the nitriles occupy a significant position among functional groups [1]. In fact, they serve as important intermediates in the synthesis of pharmaceuticals, agricultural chemicals, dyes, material sciences as well as in microbial metabolism. They are viable precursors for the synthesis of a variety of nitrogen containing functional compounds. They can be transformed into a number of functional moieties like primary amines upon reduction, amides or carboxylic acids upon hydrolysis, ketones by reaction with organometallics etc. Nitriles are also widely used in petrochemical industry.

$$RCHO + H_2NOH.HCl \rightarrow RCN$$

Magnesium sulfate 85-93%

The nitriles can be synthesized by the reaction of alkyl halides with metal cyanides but the reaction is inconvenient because of the toxicity of the cyanide substrates. Other synthetic methods include the dehydration of oximes and aldoximes. The dehydration of aldoximes has been achieved by using reagents like trimethylamine/sulfurdioxide, sulfurylchloride, sulfurylchloridefluoride, silica gel etc.,

[2]. Recently we reported a one pot synthesis of nitriles from aldehydes and hydroxylamine hydrochloride under microwave irradiation by using sodium sulfate and sodium bicarbonate [3-4]. We now report herein a rapid one pot synthesis from aldehydes and hydroxylamine hydrochloride by using an inexpensive readily accessible sodium chloride.



MATERIALS AND METHODS

Melting points are uncorrected and were determined by open capillary methods. The proton NMR spectra were recorded on a 400MHz NMR Spectrometer. All chemical shifts are expressed in parts per million with respect to tetramethylsilane (TMS) and in CDCl3. The IR spectra were obtained on a FT Nicolet Instrument.

In a typical procedure, 4-hydroxybezaldehyde (122mg, 1mmol), hydroxylamine hydrochloride (105mg, 1.2mmol) and sodium chloride were intimately mixed together in a five 5mL Pyrex beaker and then irradiated at 50^0C for 4 min when the reaction was found to be complete as shown by TLC. The mixture was extracted into dichloromethane (25mL), the solution was filtered off and the solvent evaporated off to give a residue. The crude product was purified by column chromatography (benzene:ethylacetate, 4:1) to give the desired product.

RESULTS AND DISCUSSION

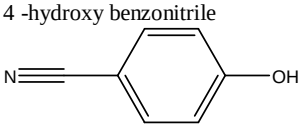
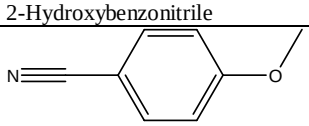
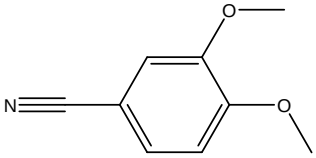
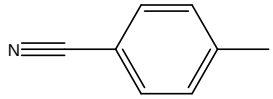
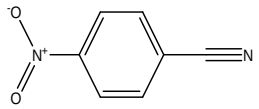
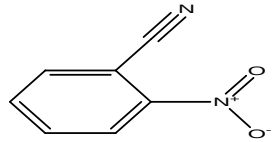
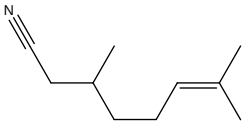
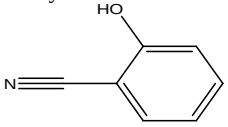
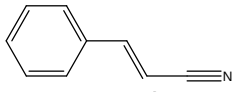
We initiated the investigations with p-hydroxybezaldehyde as that is most readily available in pure form. The mixture of this aldehyde and hydroxylaminehydrochloride taken in 1:1 molar ratio was mixed with sodium chloride and microwaved at a range of temperatures but 50^0C was found to be optimum temperature when it afforded the desired nitrile in 85% yield. Therefore, subsequent reactions were carried out at this temperature. A number of variously substituted arylaldehydes and aliphatic aldehydes and alpha-beta unsaturated aldehydes were converted into corresponding nitriles. Thus, were synthesized 4 - Hydroxybenzonitrile, 2-Hydroxybenzonitrile,3,4-Dimethoxybenzonitrile, 3,4,5-Trimethoxybenzonitrile, 4-Methylbenzonitrile, 4-Nitrobenzonitrile, 2-Nitrobenzonitrile, Decylnitrile, Octylnitrile, Citronellalnitrile, Salicylonitrile, Trans-cinnamonitrile. Table 1 shows the yields of the products obtained. TLC was used to monitor the reactions. All the products were unequivocally identified by their spectroscopic and physical data. As can be seen from table 1, the variously substituted and sterically hindered aldehydes all gave the corresponding nitriles. And the products were obtained in high yields of 85-93%. The yields compare well with our earlier results obtained using sodium sulfate [4].

Thus, the newly developed rapid one pot method is very efficient and cost effective and the catalyst used is readily available in pure form, and is inexpensive as well and should find wide application.

APPLICATION

Compounds related to the title heterocycles have been found to be associated with attractive pharmacotherapeutic profiles such as analgesic, anti-inflammatory and anti-pyretic biological profiles [2-5].

Table 1. Synthesis of nitriles from aldehydes and hydroxylamine hydrochloride in presence of sodium chloride under microwave irradiation.

Entry	Catalyst	% yield Time	Product
1	4 -hydroxy benzonitrile  4 hydroxy benzonitrile	92	4
2	2-Hydroxybenzonitrile	92	3
3	 4-methoxybenzonitrile	96	2
4	3,4-Dimethoxybenzonitrile  3,4 dimethoxy benzonitrile	93	4
5	3,4,5-Trimethoxybenzonitrile	91	3
6	4-Methylbenzonitrile  4 methyl benzonitrile	91	5
7	4-Nitrobenzonitrile  4-nitrobenzonitrile	86	4
8	2-Nitrobenzonitrile  2-nitrobenzonitrile	85	4
9	Decylnitrile	89	5
10	Octylnitrile	90	4
11	Citronellalnitrile  citronellonitrile	88	4
12	Salicylonitrile  salicylonitrile	86	5
13	Trans-cinnamonitrile  cinnamonitrile	88	3

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