ONE POT SYNTHESIS OF NITRILES FROM ALDEHYDES AND HYDROXYLAMINE HYDROCHLORIDE IN PRESENCE OF SUCCINIC ANHYDRIDE

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ABSTRACT:

Succinic anhydride was used as a highly efficient catalyst for a rapid one pot synthesis of nitriles from aldehydes and hydroxylamine hydrochloride in 85-90% yields.

Graphical Abstract

KEYWORDS :Nitriles, Aldehydes, Hydroxylamine hydrochloride, succinic anhydride.

INTRODUCTION

Nitriles occupy a significant position among functional groups in organic chemistry.[1] In fact, they serve as important intermediates in the synthesis of pharmaceuticals, agricultural chemicals, dyes, material sciences as well as in microbial metabolism. Further, 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.

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/sulfur dioxide, sulfur chloride, sulfur chloride fluoride 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.

RESULTS AND DISCUSSION

Studies were initiated with p-hydroxybenzaldehyde as that is a 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°C was found to be optimum temperature when it afforded the desired nitrile in 90% 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, Citronellal nitrile, Salicylonitrile, Trans-cinnamonitrile. The yields of the products are recorded in Table 1. 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 85-90%. These yields compare well with those obtained using sodium sulfate [5].

Therefore, 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.

TABLE 1: Synthesis of nitriles from aldehydes and hydroxylamine hydrochloride in presence of succinic anhydride under microwave irradiation.

Entry	Product	yield %	Time	Catalyst
1	4 -hydroxybenzonitrile	88	7

2	4 hydroxy benzonitrile			
2	2-Hydroxybenzonitrile	90	5	
3		89	6

	4-methoxybenzonitrile			
4	3,4-Dimethoxybenzonitrile	89	5

	3,4 dimethoxy benzonitrile			

5 3,4,5-Trimethoxybenzonitrile 885

6 4-Methylbenzonitrile 906

4 methyl benzonitrile

7 4-Nitrobenzonitrile 886

4-nitrobenzonitrile

8 2-Nitrobenzonitrile 896

2-nitrobenzonitrile

9 Decylnitrile 887

10 Octylnitrile 857

11 Citronellal nitrile 857

citronellonitrile

12Salicylonitrile866

salicylonitrile

13 Trans-cinnamonitrile88 7

cinnamonitrile

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-hydroxybenzaldehyde (122mg,1mmol), hydroxylamine hydrochloride (105mg,1.2mmol) and succinic anhydride were intimately mixed together in a five 5mL Pyrex beaker and then irradiated at 50⁰C 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

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