

Red mud catalyzed one-pot synthesis of nitriles from aldehydes and hydroxylamine hydrochloride under microwave irradiation

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Abstract

Red mud (RM) which emerges as a by-product from the alumina producing process has been used as an efficient catalyst for one-pot direct synthesis of nitrile compounds from aldehydes and hydroxylamine hydrochloride under microwave irradiation.

Keywords: Nitrile, red mud, microwave irradiation, aldehyde, hydroxylamine hydrochloride

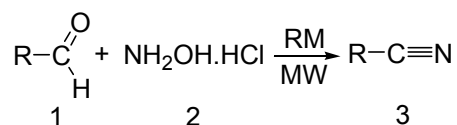
Introduction

Nitrile compounds are important intermediates for the synthesis of pharmaceuticals, pesticides and dyes.¹ There are several methods for synthesis of nitrile compounds such as substitution reactions of alkyl and aryl halides with metal cyanides,² oxidation of primary amines,³ reaction of aldehydes and ammonia using H₂SO₄⁴ and I₂,⁵ reaction of carboxylic acids with tosylamide in the presence of PCl₅⁶ or KSCN,⁷ dehydration of primary⁸ and secondary⁹ amides, dehydration of aldoximes with dehydrating agents such as cetyltrimethylammonium dichromate,¹⁰ 2,4,6-trichloro[1,3,5]triazine,¹¹ chloral (hydrate),¹² thionyl chloride,¹³ PCl₅,¹⁴ orthoester,¹⁵ (CF₃CO)₂O,¹⁶ triethylamine/SO₂,¹⁷ SeO₂,¹⁸ chlorosulfonyl isocyanate,¹⁹ PPh₃/CCl₄,²⁰ Methyl N-(triethylammoniumsulphonyl)carbamate (Burgess reagent),²¹ NaHSO₄/SiO₂,²² MeSO₂Cl,²³ AlCl₃/KCl,²⁴ NaI/MeCN,²⁵ PCl₅/alumina,²⁶ [RuCl₂(p-cymene)]₂/molecular sieves,²⁷ silica gel²⁸ and zeolite.²⁹ It has been reported that N-aminopyridines condense with aldehydes to yield the corresponding Schiff's bases that are converted in the gas-phase into nitriles.³⁰ Conversion of aldehydes into nitriles *via* reaction of the former with hydroxylamine sulfonic acid has also been reported.³¹ Recently, conversion of arylhydrazonals into hydrazononitriles *via* the reaction of hydrazonals with hydroxylamine hydrochloride and sodium acetate has also been reported. The

latter reaction has also been conducted in the microwave oven.³² Another reported method for nitrile compound synthesis is the one-pot reaction of aldehydes and hydroxylamine using pyridine,³³ SeO₂,³⁴ H₃PO₄,³⁵ H₂SO₃,³⁶ formic acid,³⁷ dicyclohexyl carbodiimide(DCC)/CuCl₂,³⁸ MgSO₄/toluenesulfonic acid,³⁹ *N*-tosylimines,⁴⁰ oxalylchloride,⁴¹ acetyl chloride/charcoal,⁴² polymer-supported reagent,⁴³ *N*-methylpyrrolidone,⁴⁴ phthalic anhydride/Et₃N,⁴⁵ NaN₃/AlCl₃,⁴⁶ ClSi(N₃)₃,⁴⁷ (CH₃)₃SiN₃,⁴⁸ anhydrous K₂S₂O₈/alumina⁴⁹ and acetic anhydride.⁵⁰ Some of these methods suffer from limitations such as corrosive, toxic, expensive or commercially unavailable reagents, excess stoichiometric and no reusability of reagents, vigorous reaction conditions, unsatisfactory yields and tedious work up.⁴⁻⁵⁰ Dewan, *et al.* recently reported a one-pot conversion of benzaldehyde and hydroxylamine to nitriles using Na₂SO₄,⁵¹ NaHCO₃,⁵¹ silica gel,⁵² Montmorillonite K-10,⁵³ or KSF⁵³ in dry media under microwave irradiation.

Red mud (RM) emerges as a by-product from the caustic leaching of bauxite to produce alumina. Its major constituents are Fe₂O₃, Al₂O₃, SiO₂, Na₂O, TiO₂, MgO and CaO. It contains small amounts of Zr, Y, Th and U elements and trace amounts of rare earth elements.⁵⁴ The use of RM as an efficient catalyst for various transformations such as hydrogenation,⁵⁵ dehydrochlorination of tetrachloroethylene⁵⁶ and transformation of heavy hydrocarbons to fuel oil⁵⁷ has been well documented in the literature.

Recently, we have reported that RM catalyzes the Knoevenagel and aldol condensation reactions.⁵⁸ The results and importance of one-pot reactions⁵⁹ encouraged us to study the one-pot synthesis of nitrile compounds from aldehydes and hydroxylamine hydrochloride using RM. As part of our research on chemical transformations,⁶⁰ in this paper we report a simple and environmentally benign methodology for the one-pot direct synthesis of nitrile compounds from aldehydes and hydroxylamine hydrochloride using RM as a catalyst. The overall reaction is shown in Scheme 1.



Scheme 1

Results and Discussion

The RM catalyzed one-pot direct synthesis of nitrile compounds was first studied using benzaldehyde and hydroxylamine hydrochloride under microwave irradiation; benzonitrile was isolated in high yield.

To examine the optimal conditions for this reaction using RM as the catalyst, we carried out experiments a-g (Table 1). According to experiments a-c (Table 1) at room temperature the aldoxime was the only product, and an increase in the temperature led to isolation of the nitrile,

but in low yield. Experiments c and g (Table 1) show that microwave irradiation is essential for the best result. Experiments d and g (Table 1) described that the nitrile product was obtained in high yield and short reaction time when the RM was activated (100 °C at oven for 8h). Experiments e-f (Table 1) show the effect of microwave irradiation power; the optimum power of irradiation was determined to be 1000W. Experiment g (Table 1) describes the yields of three consecutive reactions of benzaldehyde and hydroxylamine hydrochloride leading to benzonitrile using RM as catalyst. In these experiments the product was isolated by filtration, the solid residue was washed with ethyl acetate and the remaining RM reloaded with fresh reagent for future runs after reactivation (100 °C at oven for 8h). No considerable decrease in the yield was observed, demonstrating that RM can be reused as a catalyst in the one-pot synthesis of benzonitrile.

Table 1. Optimization of reaction conditions

Entry	Reaction condition	Time(min)	Yield (%) ^a
a	Inactivated RM, r.t.	30	----- ^b
b	Activated RM at 100°C for 8 h, r.t.	30	----- ^b
c	Activated RM at 100°C for 8 h, 80°C(at oven)	30	20
d	Inactivated RM, MW (1000W)	5	38
e	Activated RM at 100°C for 8 h, MW (600W)	10	63
f	Activated RM at 100°C for 8 h, MW (800W)	7	70
g	Activated RM at 100°C for 8 h, MW (1000W)	3	97, 95, 96 ^c
h	Activated RM at 100°C for 8 h, MW (1200W)	3	95

^a Nitrile yield

^b the isolated product is aldoxime

^c Catalyst was used over four runs

Reaction of hydroxylamine hydrochloride with different types of aromatic and aliphatic aldehydes using RM as a catalyst under MW irradiation was then investigated. The results are summarized in Table 2. The data in Table 2 clearly show that the reactions of different aldehydes give the corresponding nitriles in good to high yield with a short reaction time in dry media under MW irradiation.

Conclusions

In summary, it can be concluded that RM, that is the by-product of the Bayer process, can be used as an efficient, excellent and readily available reagent and a very inexpensive catalyst in nitrile synthesis from aldehydes and hydroxylamine hydrochloride under microwave irradiation. Furthermore, the reaction is a green process and the catalyst is recyclable for several uses.

Table 2. One-pot direct synthesis of nitrile compounds from aldehydes and hydroxylamine hydrochloride using RM as a catalyst (Scheme 1).

Product	R	Time(min)	Yield (%)
3a	Ph	3	89
3b	4-ClC ₆ H ₄	4	91
3c	2-ClC ₆ H ₄	5	76
3d	4-FC ₆ H ₄	4	83
3e	4-MeC ₆ H ₄	3	90
3f	3-NO ₂ C ₆ H ₄	5	78
3g	4-NO ₂ C ₆ H ₄	4	97
3h	4-MeOC ₆ H ₄	2	91
3j	4-(Me) ₂ NC ₆ H ₄	2	93
3k	2-furyl	3	82
3l	2-thienyl	4	93
3m	3-pyridyl	3	98
3n	4-pyridyl	3	89
3o	n-butyl	5	71
3p	n-hexyl	5	75
3q	n-octyl	5	63

Experimental Section

General Procedures. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IR-470 spectrometer. ¹H NMR spectra were recorded on a BRUKER DRX-500 AVANCE spectrometer at 500.13. NMR spectra were obtained on solutions in CDCl₃. The mixture of the reaction was irradiated with microwave (MW) laboratory reactor (ETHOS. MR) producing controlled irradiation. The chemicals used in this work were purchased from Fluka (Buchs, Switzerland) and Merck chemical companies. The RM that was used in this work was obtained from Indian gibbsite bauxite and chemical analysis of it was determined with XRF (BRUKER S4 EXPLORER). Table 3 shows these results.

Table 3. XRF analysis of RM used

Species	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	Na ₂ O	TiO ₂	CaO	ZrO ₂
Content (W%)	25.13	19.51	18.5	11.04	3.79	3.06	0.45
Species	K ₂ O	MgO	MnO	SO ₃	Cl	P ₂ O ₅	LOI ^a
Content (W%)	0.39	0.22	0.07	1.23	0.33	0.27	16.01

^a Loss on ignition

General procedure for nitrile preparation

A mixture of an aldehyde (1 mmol) and hydroxylamine hydrochloride (1 mmol) and activated RM (3 g) were mixed thoroughly in a mortar and the mixture was transferred to a beaker and irradiated at 2450 MHz (100% power, 1000 W, 80°C). The progress of the reaction was monitored by TLC using ethyl acetate: n-hexane (20:80, v/v) as solvent. The mixture was extracted with ethyl acetate and then filtered. The solvent was removed under reduced pressure to afford nitrile.

Activation and recovery of RM

RM was activated at 100 °C for 8h and cooled to room temperature in a desiccator under vacuum. For recovery of the RM, after washing twice with ethyl acetate, it was activated again at 100 °C before reuse.

Selected data for compounds 3a-3q

Benzonitrile (3a). Bp 187-190 °C [lit. 190 °C]⁶¹; IR (KBr) (ν_{\max} , cm^{-1}): 3031, 2232; ¹H NMR (CDCl₃, 500MHz): δ_{H} 7.55- 7.61 (5H, m, H-Ar).

p-Chlorobenzonitrile (3b). Mp 91-93 °C [lit. 95-96 °C]⁶²; IR (KBr) (ν_{\max} , cm^{-1}): 3069, 2228; ¹H NMR (CDCl₃, 500MHz): δ_{H} 7.37 (2H, d, $J= 8.4$ Hz, H-Ar), 7.47 (2H, d, $J= 8.4$ Hz, H-Ar).

m-Chlorobenzonitrile (3c). Mp 43-46 °C [lit. 46-47 °C]⁶³; IR (KBr) (ν_{\max} , cm^{-1}): 3032, 2231; ¹H NMR (CDCl₃, 500MHz): δ_{H} 7. 50- 7. 64 (5H, m, H-Ar).

p-Fluorobenzonitrile (3d). Mp 33-36 °C [lit. 35-36 °C]⁶⁴; IR (KBr) (ν_{\max} , cm^{-1}): 3086, 2238; ¹H NMR (CDCl₃, 500MHz): δ_{H} 7.68 (2H, m, H-Ar), 7.19 (2H, m, H-Ar).

p-Tolunitrile (3e). Bp 215-217 °C [lit. 218 °C]⁶¹; IR (KBr) (ν_{\max} , cm^{-1}): 3039, 2229; ¹H NMR (CDCl₃, 500MHz): δ_{H} 7.23 (2H, d, $J= 7.4$ Hz, H-Ar), 7.47 (2H, d, $J= 7.4$ Hz, H-Ar).

m-Nitrobenzonitrile (3f). Mp 115-117 °C [lit. 115 °C]⁶⁵; IR (KBr) (ν_{\max} , cm^{-1}): 3036, 2238; ¹H NMR (CDCl₃, 500MHz): δ_{H} 7.70 (1H, m, H-Ar), 7.90 (1H, d, $J= 9.0$ Hz, H-Ar), 8.46 (2H, m, H-Ar).

p-Nitrobenzonitrile (3g). Mp 146-149 °C [lit. 147 °C]⁶¹; IR (KBr) (ν_{\max} , cm^{-1}): 3076, 2234; ¹H NMR (CDCl₃, 500MHz): δ_{H} 7.92 (2H, d, $J= 8.0$ Hz, H-Ar), 8.37 (2H, d, $J= 8.0$ Hz, H-Ar).

p-Methoxybenzonitrile (3h). Mp 57-59 °C [lit. 62-63 °C]⁶⁶; IR (KBr) (ν_{\max} , cm^{-1}): 3068, 2219; ¹H NMR (CDCl₃, 500MHz): δ_{H} 3.73 (3H, s, Me), 6.95 (2H, d, $J= 9.1$ Hz, H-Ar), 7.40 (2H, d, $J= 9.1$ Hz, H-Ar).

p-Dimethylaminobenzonitrile (3j). Mp 69-71 °C [lit. 75-77 °C]⁶⁷; IR (KBr) (ν_{\max} , cm^{-1}): 2909, 2261; ¹H NMR (CDCl₃, 500MHz): δ_{H} 3.02 (6H, s, Me), 6.63 (2H, d, $J= 8.2$ Hz, H-Ar), 7.43 (2H, d, $J= 8.2$ Hz, H-Ar).

2-Furonitrile (3k). Mp 146-148 °C [lit. 146-147 °C]⁶⁸; IR (KBr) (ν_{\max} , cm^{-1}): 2981, 2236; ¹H NMR (CDCl₃, 500MHz): δ_{H} 6.36 (1H, m, H-furyl), 6.86 (1H, d, $J= 3.6$ Hz, H-furyl), 7.38 (1H, d, $J= 1.8$ Hz, H-furyl).

2-Thiophenecarbonitrile (3l). Mp 125-134 °C (decomp) [lit. 192 °C]⁶⁹; IR (KBr) (ν_{\max} , cm^{-1}): 3067, 2238; ¹H NMR (CDCl_3 , 500MHz): δ_{H} 6.96 (1H, m, H-thienyl), 7.42 (1H, m, H-thienyl), 7.49 (1H, m, H-thienyl).

Nicotinonitrile (3m). Mp 50 °C [lit. 50 °C]⁷⁰; IR (KBr) (ν_{\max} , cm^{-1}): 3036, 2232; ¹H NMR (CDCl_3 , 500MHz): δ_{H} 7.48 (1H, m, H-pyridil), 8.00 (1H, d, $J=1.9$ Hz, H-pyridil), 8.85 (1H, d, $J=1.9$ Hz, H-pyridil), 8.91 (1H, m, H-pyridil).

iso-Nicotinonitrile (3n). Mp 76 °C [lit. 75-77 °C]⁷¹; IR (KBr) (ν_{\max} , cm^{-1}): 3084, 2244; ¹H NMR (CDCl_3 , 500MHz): δ_{H} 7.55 (2H, d, $J=4.1$ Hz, H-pyridil), 8.83 (2H, d, $J=4.1$ Hz, H-pyridil).

Pentanenitrile (3o). Bp 139-141 °C [lit. 142 °C]⁷²; IR (KBr) (ν_{\max} , cm^{-1}): 2742, 2683, 2247; ¹H NMR (CDCl_3 , 500MHz): δ_{H} 0.96 (3H, t, $J=2.8$ Hz, H-Aliph), 1.68 (2H, m, H-Aliph), 1.50 (2H, m, H-Aliph), 2.34 (2H, t, $J=2.8$ Hz, H-Aliph).

Heptanenitrile (3p). Bp 243 °C (decomp) [lit. 253 °C]^{3a}; IR (KBr) (ν_{\max} , cm^{-1}): 2968, 2933, 2247; ¹H NMR (CDCl_3 , 500MHz): δ_{H} 0.90 (3H, t, $J=2.8$ Hz, H-Aliph), 1.32 (4H, m, H-Aliph), 1.46 (2H, m, H-Aliph), 1.65 (2H, m, H-Aliph), 2.34 (2H, t, $J=2.8$ Hz, H-Aliph).

Undecanenitrile (3q). Bp 236 °C (decomp) [lit. 268 °C]⁷³; IR (KBr) (ν_{\max} , cm^{-1}): 2966, 2927, 2247; ¹H NMR (CDCl_3 , 500MHz): δ_{H} 0.89 (3H, t, $J=2.5$ Hz, H-Aliph), 1.27 (14H, m, H-Aliph), 1.65 (2H, m, H-Aliph), 2.32 (2H, t, $J=2.9$ Hz, H-Aliph).

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