



Deep eutectic solvent promoted one-pot synthesis of nitriles from alcohols

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Abstract. Various aryl nitriles were readily synthesized from aerobic oxidation of substituted benzyl alcohols in deep eutectic solvent composed of choline chloride (ChCl) and *p*-toluenesulfonic acid (*p*-TsOH) in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), followed by condensation with hydroxylamine hydrochloride. High yields of corresponding nitriles have been obtained under mild reactions conditions. This strategy belongs to a novel and environmentally benign transition-metal-free one-pot cascade process for the synthesis of nitriles.

Keywords. Deep eutectic solvent; benzyl alcohols; aryl nitriles; hydroxylamine hydrochloride.

1. Introduction

Cyano is a vital group in organic chemistry as it plays a crucial role in pharmaceuticals, agrochemicals, dyes and other fine chemicals.^{1–3} In addition, nitriles can serve as precursors of amides, aldehydes, ketones, carboxylic acids, and heterocycles.^{4–7} Traditionally, aryl nitriles are synthesized through Sandmeyer reaction, which employs diazonium salts and highly toxic metal cyanides as raw materials,⁸ and alkylnitriles are prepared by the nucleophilic substitution of alkyl halides with a stoichiometric amount of alkali metal cyanides. However, there exist risks of poisoning and environmental pollution when using metal cyanides on a large scale. Over the past decades, a variety of procedures for the synthesis of nitriles have been developed, such as the dehydration of amides⁹ and aldoximes,¹⁰ the ammoxidation of aldehydes¹¹ and primary amines,¹² and amination-dehydrogenation of alcohols.^{13,14} Compared to other raw materials, alcohols are inexpensive and easily available, therefore, direct converting alcohols to nitriles has become an

attractive alternative recently. Mizuno *et al.*, reported the synthesis of nitriles from ammoxidation of primary alcohols catalyzed by an alumina supported ruthenium hydroxide catalyst.¹⁵ Hu *et al.*, used silica-supported functionalized ionic liquids as catalysts, such as FeCl₄-IL-SiO₂, to promote the conversion of alcohols with ammonia to nitriles with H₂O₂ as an oxidant.¹⁶ A PS-BHA-Cu system was developed by Molla *et al.*, which permitted aerobic oxidation of alcohols with ammonium formate as nitrogen source to nitriles at 115 °C.¹⁷ Other catalytic oxidation systems were also developed to convert alcohols to nitriles, such as KI/I₂-TBHP,¹⁸ Melamine-Mn(III)-Schiff base complex/O₂,¹⁹ Pt/Bi(NO₃)₃/K₂CO₃/O₂,²⁰ MnO₂/O₂,²¹ NH₄Br/DHPDMDO,²² I₂/DIH.²³ It is important to note that alcohols can be also converted into the corresponding nitriles *via* ammoxidation catalyzed by TEMPO-copper or iron salts based catalyst systems.^{24–27} For instance, a combination of CuI with MeOPEG supported TEMPO developed by Chinnusamy exhibited good to excellent performance in the ammoxidation of

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Initially, several DESs from ChCl with different hydrogen-bond donors were screened. As exhibited in Table 1, all the acidic DESs, in which the hydrogen-bond donors are oxalic acid, citric acid and *p*-TsOH respectively, facilitated the conversion of benzyl alcohol to benzonitrile in good yields (Table 1, entries 1–3). Among them, ChCl/*p*-TsOH showed best result and benzonitrile was obtained in a yield of 86%. ChCl/oxalic acid and ChCl/citric acid were also effective as a component of the catalytic system DES/TEMPO/NaNO₂, but with slightly poor performance compared to ChCl/*p*-TsOH owing to their higher viscosity. In the cases of ChCl/glycol, ChCl/glycerol and ChCl/urea, in which the hydrogen-bond donor is neutral glycol, glycerol or alkaline urea, the aerobic oxidation of benzyl alcohol to benzaldehyde did not take place, indicating the necessity of acid environment in aerobic oxidation process (Table 1, entries 4–6). Then the amount of DES was evaluated. Initially, the yield of benzonitrile increased obviously with the amount of DES (Table 1, entries 3, 7–9). However, with a further increase of the amount of DES from 30 mol% to 50%, the yield of benzonitrile increased only by 2%, therefore, the amount of DES was chosen as 30%. Next, the direct condensation of benzaldehyde with NH₂OH.HCl was performed in the absence of catalyst. In this case benzonitrile was obtained only in a yield of 45.5% (Table 1, entry 10), indicating that acidic DES ChCl/*p*-TsOH also acted as a catalyst to promote the condensation of benzaldehyde with NH₂OH.HCl to benzonitrile. In other words, the acidic DES played a

catalytic role in both steps in the conversion of benzyl alcohol to benzonitrile.

Then the effect of solvent on the reaction was investigated, and CH₃CN gave the best results among the screened solvents (Table 2, entries 1–6). Compared to acetonitrile as the reaction medium, low yield of benzonitrile was obtained due to low solubility of ChCl/*p*-TsOH in 1,4-dioxane and dichloroethane. In the case of CH₂Cl₂ as solvent, only 14% yield of benzonitrile was received, and the main product was benzaldehyde oxime rather than benzonitrile due to low reaction temperature. No benzonitrile was achieved when DMSO and methanol were used as solvent. It was also shown that the temperature in the second step had a great influence on the reaction. With the reaction temperature increased from 100 °C to 130 °C, the yield of benzonitrile increased from 86% to 93% (Table 2, entries 6–9). No big improvement of the yield of benzonitrile was obtained at 130 °C compared to that at 120 °C. So the reaction was conducted at 120 °C in subsequent experiments.

Among the components of the catalytic system TEMPO is most important, therefore, the loading of TEMPO was investigated while keeping NaNO₂ 5 mol%, and DES 30 mol%. As shown in Table 3, the time to finish the aerobic oxidation of benzyl alcohol to benzaldehyde reduced with the increase of the TEMPO loading (Table 3, entries 1–5). When the TEMPO loading was 5 mol%, the time to finish the aerobic oxidation was 7 h. A further increase of TEMPO loading led to an only slight reduction of time (Table 3, entries 3–5). Therefore, the TEMPO loading

Table 1. Screening of DES for the synthesis of nitrile.

Entry	DES (molar ratio)	Catalyst amount/mol%	Solvent	Yield/% ^a
1	ChCl/oxalic acid (1:1)	30	CH ₃ CN	84
2	ChCl/citric acid (2:1)	30	CH ₃ CN	82
3	ChCl/ <i>p</i> -TsOH (1:1)	30	CH ₃ CN	86
4	ChCl/glycerol (1:2)	30	CH ₃ CN	N. D. ^c
5	ChCl/glycol (1:2)	30	CH ₃ CN	N. D.
6	ChCl/urea (1:2)	30	CH ₃ CN	N. D.
7	ChCl/ <i>p</i> -TsOH (1:1)	10	CH ₃ CN	64
8	ChCl/ <i>p</i> -TsOH (1:1)	20	CH ₃ CN	81
9	ChCl/ <i>p</i> -TsOH (1:1)	50	CH ₃ CN	88
10 ^b	–	–	–	45.5

Reaction conditions: (1) benzyl alcohol (5 mmol), NaNO₂ (0.25 mmol), TEMPO (0.25 mmol), CH₃CN (3 mL), DES, and O₂ balloon, room temperature, 2 h; (2) NH₂OH.HCl (6 mmol), reaction temperature 100 °C, reaction time 5 h.

^aThe yields were determined by GC using biphenyl as the internal standard.

^bBenzaldehyde (5 mmol), CH₃CN (3 mL), and then NH₂OH.HCl (6 mmol), 100 °C, 5 h.

^cN. D. = No detected.

Table 2. Screening of temperature and catalyst amount.

Entry	Solvent	T ₂ /°C	Yield/% ^a
1	CH ₂ Cl ₂	50	14
2	DMSO	100	N. D. ^b
3	CH ₃ CH ₂ Cl ₂	100	62
4	1,4-Dioxane	100	79
5	CH ₃ OH	100	N. D.
6	CH ₃ CN	100	86
7	CH ₃ CN	110	89
8	CH ₃ CN	120	92
9	CH ₃ CN	130	93

Reaction conditions: (1) benzyl alcohol (5 mmol), NaNO₂ (0.25 mmol), TEMPO (0.25 mmol), CH₃CN (3 mL), DES (1.5 mmol), and O₂ balloon, room temperature, 2 h; (2) NH₂OH.HCl (6 mmol), T₂, reaction time 5 h.

^aThe yields were determined by GC using biphenyl as the internal standard.

^bN. D. = No detected.

was determined to be 5 mol%. Then, the amount of NH₂OH.HCl in the second step was optimized. It was observed that the yield of benzonitrile increased initially with the increase of the amount of NH₂OH.HCl (Table 3, entries 3, 6, 7). When 1.3 eq. of NH₂OH.HCl was used, benzonitrile was obtained in a yield of 96% (Table 3, entry 3). Instead, a further increase of the NH₂OH.HCl loading led to a slight decrease of the yield of benzonitrile. The above results revealed that 5% of TEMPO and 1.3 eq. of NH₂OH.HCl were appropriate to synthesize aryl nitriles from aryl alcohols by the one-pot two-step strategy.

With optimized reaction conditions in hand, we next investigated the generality of as described catalytic

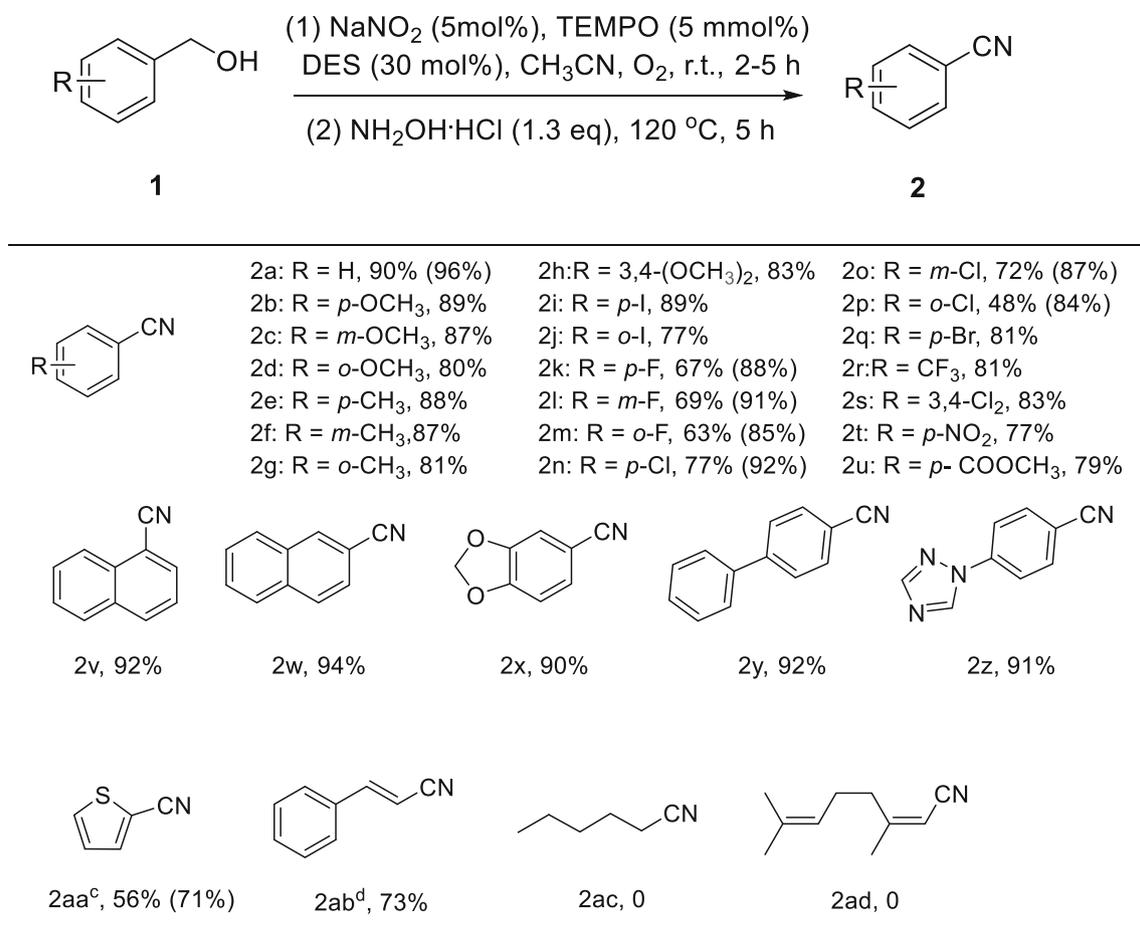
system in the aerobic oxidation of various aryl alcohols, followed by condensation with NH₂OH.HCl to aryl nitriles. As shown in Table 4, various mono- and bi-substituted benzyl alcohols with either electron-donating or electron-withdrawing substituents (2b–2u, 2x–2z) could be transformed into their corresponding nitriles in good to excellent yields. In most cases, the isolated yields were higher than 80%, and up to 89% (2b, 2i). Also, as a result of steric hindrance, *ortho*-substituted alcohols converted into their corresponding nitriles with lower yields compared with *para*- and *meta*-substituted substrates. In some cases (2k, 2l, 2m, 2n, 2o and 2p), the isolated yields were much lower than the GC yield, due to their volatile character leading to losses during the evaporation of solvent in the work-up processes. The catalytic system was also very efficient in the cases of naphthyl carbinols as substrates (2v, 2w). A yield as high as 94% was received in the case of 2-naphthyl carbinol to 2-naphthonitrile (2w). However, in the case of 2-thenyl alcohol as a substrate, the target aldehyde was obtained with low selectivity when the aerobic oxidation reaction was performed at room temperature. The selectivity was increased by decreasing temperature to 10 °C, and moderate yield of 2-cyano thiophene was achieved from 2-thenyl alcohol in this case (2aa). The catalytic system was also tested in the conversion of allyl alcohols to their corresponding nitriles. As shown in Table 4, a yield of 73% of cinnamonitrile (2ab) was received in the case of cinnamyl alcohol as a substrate in 24 h. Unfortunately, no oxidation of geraniol to the corresponding aldehyde took place, therefore, it failed in the synthesis of citronitrile from geraniol over this catalytic system. Besides, this

Table 3. Screening of the loadings of TEMPO and NH₂OH.HCl.

Entry	TEMPO/mol%	NH ₂ OH.HCl/eq.	t/h	Conversion/%	Yield/% ^a
1	3	1.3	11	> 99	95
2	4	1.3	9	> 99	96
3	5	1.3	7	> 99	96
4	6	1.3	6.5	> 99	96
5	7	1.3	6.5	> 99	96
6	5	1.1	7	95	88
7	5	1.2	7	> 99	92
8	5	1.4	7	> 99	95

Reaction conditions: (1) benzyl alcohol (5 mmol), NaNO₂ (0.25 mmol), CH₃CN (3 mL), TEMPO, DES (1.5 mmol), and O₂ balloon, room temperature; (2) reaction temperature 120 °C, reaction time 5 h.

^aThe yields were determined by GC using biphenyl as the internal standard.

Table 4. Synthesis of aryl nitriles from aryl alcohols.^{a,b}

Reaction conditions: (1) benzyl alcohol (5 mmol), NaNO₂ (0.25 mmol), TEMPO (0.25 mmol), CH₃CN (3 mL), DES (1.5 mmol), and O₂ balloon, room temperature, 2–5 h; (2) NH₂OH.HCl (6.5 mmol), reaction temperature 120 °C, reaction time 5 h.

^aIsolated yields.

^bThe yields in the parentheses were determined by GC.

^cThe reaction temperature is 10 °C in the oxidation process.

^dThe reaction time is 24 h.

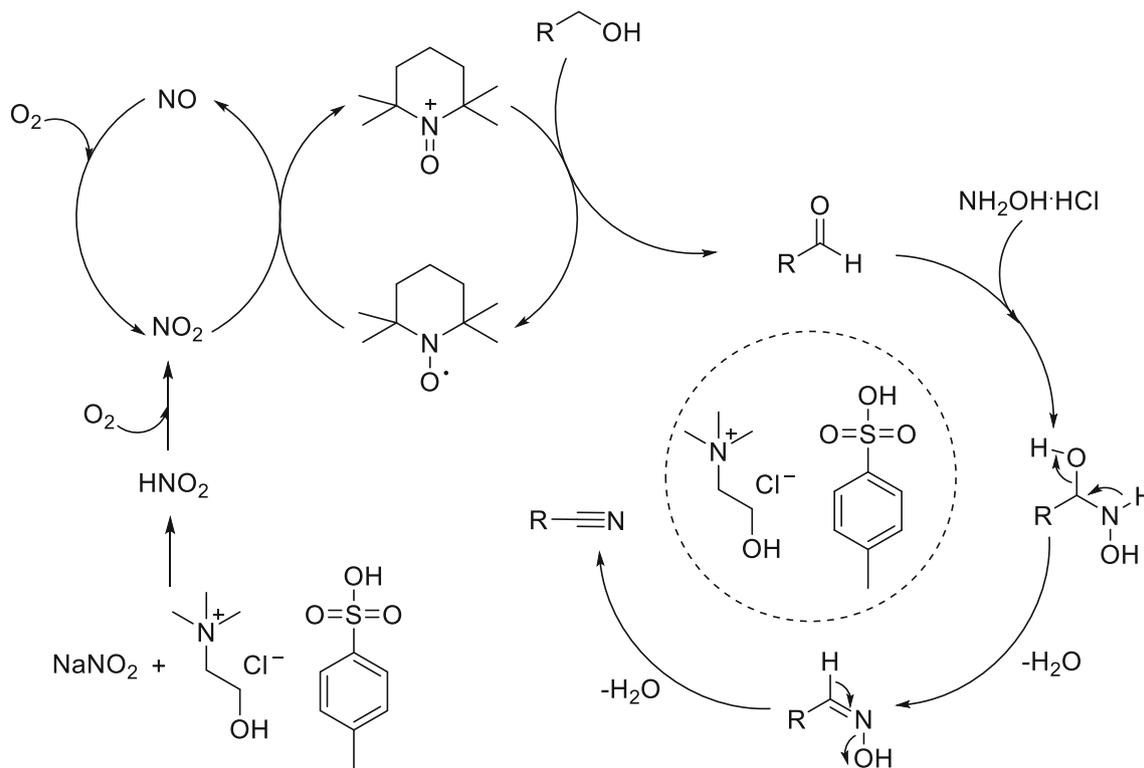
catalytic system was also invalid in the conversion of aliphatic alcohols to nitriles, such as 1-hexanol to hexanenitrile (2ac).

Based on the mechanism proposed for the aerobic oxidation of alcohols with catalytic system HCl/NaNO₂/TEMPO,^{47–49} a possible mechanism for the conversion of aryl alcohols to nitriles was described in Scheme 2. In the transformation of alcohol to aldehyde, ChCl/*p*-TsOH donated H⁺ to NaNO₂ to produce HNO₂ which is oxidized to NO₂ by molecular oxygen; Then TEMPO was oxidized to TEMPO⁺ by NO₂ and TEMPO⁺ acts as an oxidant to oxidize alcohol to aldehyde. At the stage of transformation of aldehyde to

nitrile, hydroxylamine hydrochloride condenses with the aldehyde generated from alcohol to form the oxime firstly catalyzed by DES. Finally, the aldehyde oxime undergoes dehydration promoted also by DES to afford the nitrile (Scheme 2).

4. Conclusions

In summary, various substituted benzyl alcohols and naphthyl carbinols were effectively converted into their corresponding nitriles *via* a novel transition-metal-free one-pot cascade process under the catalysis



Scheme 2. Possible mechanism for the synthesis of nitriles.

of $\text{ChCl}/p\text{-TsOH-TEMPO}/\text{NaNO}_2$. Good to excellent yields of respective products were obtained under mild reaction conditions. This process represents an environmentally-friendly strategy for the synthesis of aryl nitriles from aryl alcohols.

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Supplementary Information (SI)

Supplementary information related to this article is available at www.ias.ac.in/chemsci.

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