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A facile protocol, which uses copper as an effective homogeneous catalyst, has been developed for the oxidative synthesis of nitriles from alcohols and ammonium formate. This system uses air as a green oxidant and produces water as an environmentally benign side product.

 $R = H, OMe, NO_2, CI, Br, OPh, CH_3, CH(CH_3)_2, Ph$

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Nitrile Synthesis

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Copper-Catalyzed Synthesis of Nitriles by Aerobic Oxidative Reaction of Alcohols and Ammonium Formate

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Keywords: Synthetic methods / Homogeneous catalysis / Alcohols / Copper / Oxidation

An efficient methodology has been developed for the synthesis of nitriles through an aerobic oxidative reaction of alcohols and ammonium formate with copper as a homogeneous catalyst under a normal air atmosphere and solvent-free

Introduction

Nitriles are widely used in chemical as well as biological applications as they serve as important building blocks in the pharmaceutical, fine chemical, dye, and agrochemical industries.^[1] Moreover, they are one of the most valuable compounds employed in synthetic organic chemistry for the preparation of amines, amides, carbonyl compounds, and heterocycles.^[2] Traditionally, nitriles were synthesized through the nucleophilic substitution of various leaving groups, such as halogen, hydroxy, alkoxy, diazonium, and sulfonyl functionalities, with inorganic cyanides.^[3] Alternative procedures include the dehydration of amides^[4] and aldoximes,^[5] the elimination of oxime ethers^[6] and oxime esters.^[7] and the oxidative conversion of aldehvdes^[8] and primary amines^[9] into their corresponding nitriles. There are also a few more reports regarding the synthesis of nitriles.^[10] However, despite the potential utility of earlier reported protocols, the use of toxic solvents and expensive reagents along with the production of large amounts of inorganic waste and tedious work-up procedures limits their application from a green chemistry perspective.

The oxidative conversion of alcohols into nitriles is an attractive alternative. In this regard, various protocols were developed, but they required stoichiometric amounts of oxidants and reagents.^[11] Mizuno and co-workers reported the use of the catalysts $Ru(OH)_x/Al_2O_3^{[12]}$ and $Ru(OH)_x/$ TiO₂^[13] for the oxidative synthesis of nitriles from alcohols. Recently, Prabhu and co-workers reported on the direct oxidative synthesis of nitriles by using DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) as the oxidant, TMSN₃ (tri-

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conditions. This protocol uses the air as a green oxidant and ammonium formate as the nitrogen source. A wide range of substrates were well tolerated in the reaction that gave water as a byproduct.

methylsilyl azide) as the nitrogen source, and catalytic amounts of Cu(ClO₄)₂·6H₂O in the presence of DCE (dichloroethane) as the solvent.^[14] However, the use of nongreen TMSN₃ and DDQ requires tedious storage and handling problems. Both of them are air- and moisture-sensitive reagents and produce highly toxic products when they come in contact with water. Thus, the development of a highly efficient and environmentally benign solvent-free protocol for the oxidative conversion of alcohols into nitriles is still a challenging task.

In this work, we have developed a highly efficient protocol for the oxidative synthesis of nitriles from the reaction between alcohols and ammonium formate, an inexpensive nitrogen source (see Scheme 1). This approach employs a copper catalyst and is carried out under air, which serves as a green oxidant.



Scheme 1. Oxidative synthesis of nitriles from alcohols and ammonium formate.

Results and Discussion

A series of experiments were performed to optimize the reaction conditions for the oxidative conversion of benzyl alcohol (1a) into benzonitrile (2a). Initially, we studied the effect of various nitrogen sources with $CuCl_2 \cdot 2H_2O$ as the catalyst and K_2CO_3 as the base (see Table 1, Entries 1–5). Ammonium formate (HCOONH₄) furnished a very good yield of benzonitrile (2a) along with the maximum conversion of 1a, and, thus, it was used for further studies (see

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Table 1, Entry 5). The effect of the HCOONH₄ loading showed that the conversion of **1a** and yield of **2a** increased as the **1a**/HCOONH₄ ratio increased from 1:1 to 1:4 (see Table 1, Entries 5–7). When the reaction was carried out under nitrogen, the desired product was not observed, which indicated the importance of atmospheric air as the oxidant (see Table 1, Entry 8).

Table 1. Effect of the nitrogen source on the oxidative synthesis of nitriles $^{\left[a\right] }$

ĺ	OH CuCl	2 [.] 2H ₂ O (10 mol-% itrogen source		+	СНО
1a (0	(5 mmol) 1	$X_2 C O_3$ (10 moi-%)	~		~
14 (0		55 0, 24 11	Za		3a
Entry	N source	Catalyst	Conv. [%]	Yield	[%] ^[b]
				2a	3a
1	NH ₄ Cl	CuCl ₂ ·2H ₂ O	55	33	22
2	NH ₄ NO ₃	CuCl ₂ ·2H ₂ O	70	43	27
3	$(NH_4)_2HPO_4$	CuCl ₂ ·2H ₂ O	65	39	26
4	$(NH_4)_2SO_4$	CuCl ₂ ·2H ₂ O	68	43	25
5	HCOONH ₄	CuCl ₂ ·2H ₂ O	85	57	28
6 ^[c]	HCOONH ₄	CuCl ₂ ·2H ₂ O	91	79	12
7 ^[d]	HCOONH ₄	$CuCl_2 \cdot 2H_2O$	100	100	_
8 ^[e]	HCOONH ₄	$CuCl_2 \cdot 2H_2O$	0	_	_

[a] Reagents and conditions: **1a** (0.5 mmol), nitrogen source (0.5 mmol), CuCl₂·2H₂O (0.05 mmol), K₂CO₃ (0.05 mmol), 135 °C, 24 h. [b] Yield based on GC analysis. [c] Reaction carried out with **1a**/HCOONH₄ in a ratio of 1:2. [d] Reaction carried out with **1a**/HCOONH₄ in a ratio of 1:4. [e] Reaction carried out under nitrogen.

Thereafter, using the optimum conditions, we studied the effect of various copper catalysts such as CuO, Cu(OAc)₂. 5H₂O, CuI, CuCl, Cu₂O, CuSO₄·5H₂O, and CuCl₂·2H₂O on the nitrile synthesis in the presence of K_2CO_3 as the base (see Table 2, Entries 1–7). Among the screened catalysts, $CuCl_2 \cdot 2H_2O$ was the most effective to provide an excellent yield of the desired nitrile 2a (see Table 2, Entry 7). Furthermore, we studied the effect of the catalyst loading and found that the yield of 2a decreased when the concentration of the catalyst was decreased from 10 to 5 mol-% (80%), and, hence, 10 mol-% of the catalyst was used for further studies. Noting the importance of the base to the reaction outcome, various bases such as K₂CO₃, KOH, KOtBu, and NaOtBu were screened (see Table 2, Entries 7–10), and, hence, further studies were carried out by using K₂CO₃ as it provided the maximum yield of the corresponding nitrile.

Subsequently, the effect of temperature was also investigated, and the yield of 2a decreased as the temperature was lowered (see Table 2, Entry 11). The decrease in the time from 24 to 20 h also resulted in a low conversion of 1a, which indicated that 24 h was the optimum time required for the completion of the reaction. When the reaction was carried out in the absence of catalyst, no conversion of 1awas observed (see Table 2, Entry 13).

With these optimized reaction conditions, the scope of protocol was extended to the synthesis of various nitrile derivatives. As illustrated in Table 3, the reaction proceeded

Table 2. Effect of catalyst screening on the oxidative synthesis of nitriles $^{\left[a\right] }$

OH	catalyst (10 mol-%) HCOONH ₄ (2 mmol)	•	CN		СНО	
	air, K ₂ CO ₃ (10 mol-%)			+		
1a (0.5 mmol)	135 °C, 24 h		2a		3a	

Entry	Catalyst	Base	Yield [%] ^[b]	
			2a	3 a
1	CuO	K ₂ CO ₃	62	38
2	Cu(OAc) ₂ ·5H ₂ O	K_2CO_3	84	16
3	CuI	K_2CO_3	67	33
4	CuCl	K_2CO_3	72	28
5	Cu ₂ O	K_2CO_3	65	35
6	CuSO ₄ ·5H ₂ O	K_2CO_3	78	22
7	CuCl ₂ ·2H ₂ O	K_2CO_3	100	_
8	CuCl ₂ ·2H ₂ O	KOH	77	23
9	CuCl ₂ ·2H ₂ O	KOtBu	70	30
10	CuCl ₂ ·2H ₂ O	NaOtBu	72	28
11 ^[c]	CuCl ₂ ·2H ₂ O	K_2CO_3	90	10
12 ^[d]	CuCl ₂ ·2H ₂ O	K_2CO_3	100	_
13	none	K_2CO_3	_	_

[a] Reagents and conditions: **1a** (0.5 mmol), HCOONH₄ (2.0 mmol), catalyst (0.05 mmol, 10 mol-%), base (0.05 mmol), 135 °C, 24 h. [b] Yield based on GC analysis. [c] Temperature is 125 °C. [d] Temperature is 145 °C.

efficiently with various benzylic and allylic alcohol derivatives to provide a wide range of substituted nitriles in good to excellent yields. The prominent feature of the present protocol is that this system has a significant extent of functional group tolerance, that is, chloro, bromo, and nitro substituents intrinsically remained intact under the reaction conditions (see Table 3, Entries 2–5, 10, and 11). However, the steric effects of the substituents do have an influence on the reaction. For instance, when meta- and para-substituted benzyl alcohols were used, the reaction proceeded smoothly to provide good yields of the corresponding nitriles (see Table 3, Entries 3, 4, 7, 8, and 11). On the other hand, ortho substituents had a negative effect on the transformation (see Table 3, Entries 2, 6, and 10). Benzyl alcohol derivatives with electron-withdrawing and electron-donating groups were smoothly converted into the corresponding nitriles in excellent yields (see Table 3, Entries 7-9 and 11-13). When the simple aromatic ring of benzyl alcohol was replaced with more hindered biphenyl, naphthyl, and 1,3-benzodioxole groups, the corresponding nitriles were also obtained in good yields (see Table 3, Entries 14–16). Cinnamyl alcohol was also converted into the corresponding unsaturated nitrile without isomerization and hydrogenation of the double bond (see Table 3, Entry 17). However, an aliphatic alcohol did not produce the desired nitrile product under the optimized reaction conditions (see Table 3, Entry 18).

When the reaction was carried out in the absence of a nitrogen source (i.e., the ammonium salts), it gave an aldehyde as the major product, which indicates that the first step of the mechanism is the oxidative conversion of an alcohol to an aldehyde. Hence, on the basis of our investigation and literature reports,^[15a,15b] a plausible reaction

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Table 3. Substrate study for oxidative synthesis of nitriles.^[a]



[a] Reagents and conditions: alcohol (0.5 mmol), HCOONH₄ (2.0 mmol), CuCl₂·2H₂O (0.05 mmol, 10 mol-%), K₂CO₃ (0.05 mmol, 10 mol-%), 135 °C, 24 h. [b] Isolated yield. ND = product not detected.

mechanism is proposed (see Scheme 2). The first step involves the aerobic oxidative dehydrogenation of benzyl alcohol to benzaldehyde in the presence of an active copper



Scheme 2. Plausible reaction pathway for the copper-catalyzed oxidative synthesis of nitriles.

catalyst.^[15c] Next, the dehydrative condensation of the aldehyde by treatment with NH₃ (ammonia is generated in situ from the ammonium salt) gives an imine through the formation of a hemiaminal. At last, the imine undergoes an aerobic oxidative dehydrogenation to form the corresponding nitrile product.

Conclusions

We have established a new, efficient, and useful methodology for the direct oxidative synthesis of nitriles from benzylic and allylic alcohols by employing ammonium formate as the nitrogen source along with a copper catalyst. In comparison to earlier reported systems, the developed protocol has significant advantages such as: (i) the use of the inexpensive and easily available CuCl₂·6H₂O catalyst compared to the use of noble metal catalysts, (ii) the solvent- and additive-free reaction conditions, which makes the protocol Date: 24-06-13 16:21:40

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greener than earlier methods, (iii) the present system circumvents the use of oxidants such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), I_2 , H_5IO_6 , and 1,3-diiodo-5,5-dimethylhydantoin (DIH), and (iv) the use of a handy and inexpensive nitrogen source such as ammonium formate. Thus, the developed protocol appears to be highly efficient, green, and economically accepted as well as has a wide substrate applicability, which is appealing for further investigation.

Experimental Section

General Methods: All chemicals were purchased from Lancaster (Alfa-Aesar), Sigma Aldrich, and S. D. Fine Chemical and commercial suppliers. Gas chromatography (GC) and TLC were used to monitor the progress of the reactions. Gas chromatography analysis was carried out with a Perkin-Elmer Clarus 400 GC equipped with a flame ionization detector with a capillary column (Elite-1, $30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \text{ }\mu\text{m}$). GC–MS was carried out with a GC-MS-QP 2010 instrument [Rtx-17, 30 m×25 mm ID, film thickness (df): 0.25 µm, column flow: 2 mLmin⁻¹, 80-240 °C at 10 °Cmin⁻¹ rise]. The ¹H NMR spectroscopic data were recorded with a Bruker 500 MHz spectrometer with CDCl₃ as the solvent and TMS as the internal standard. The ¹³C NMR spectroscopic data were recorded with a Bruker 125 MHz spectrometer with CDCl₃ as the solvent. Chemical shifts are reported in parts per million (δ) relative to TMS as the internal standard. J (coupling constant) values are reported in Hz. Splitting patterns in the ¹H NMR are described as d (doublet) and m (multiplet). The products were purified by column chromatography on silica gel (100-200 mesh). The products were confirmed by comparing the GC-MS, ¹H, and ¹³C NMR data with those of authentic samples.

General Experimental Procedure for Oxidative Synthesis of Aryl Nitriles from Aryl Alcohols: A mixture of aryl alcohol (0.5 mmol), $HCOONH_4$ (2 mmol), $CuCl_2 {\cdot} 2H_2O$ (0.05 mmol, 10 mol-%), and K₂CO₃ (0.05 mmol, 10 mol-%) was stirred at 135 °C under a normal air atmosphere in a sealed 20 mL Schlenk tube for 24 h. The reaction was monitored by TLC and/or GC. After completion of the reaction, ethyl acetate (5 mL) and water (5 mL) were consecutively added to the reaction mixture, and the mixture was then stirred vigorously. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate ($2 \times 5 \text{ mL}$). The combined ethyl acetate layers were dried with anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, 100-200 mesh; petroleum ether/ethyl acetate, 95:5) to afford the pure product. The identity of the compounds was confirmed by using GC-MS, FTIR and ¹H and ¹³C NMR spectroscopic techniques. The purity of the compounds was determined by using GC-MS analysis.

Characterization of Selected Compounds

Benzonitrile (2a):^[16a] Colorless liquid (96% yield). IR (neat): $\tilde{v} = 2224 \text{ cm}^{-1}$. GC–MS (EI, 70 eV): *m/z* (%) = 103 (100) [M]⁺, 76 (43), 50 (16). ¹H NMR (500 MHz, CDCl₃): $\delta = 7.66-7.59$ (m, 3 H, Ar), 7.49–7.45 (m, 2 H, Ar) ppm. ¹³C NMR (125 MHz, CDCl₃): $\delta = 132.7$, 132.0, 129.0, 118.8, 112.3 ppm.

3-Chlorobenzonitrile (2c):^[16b] White solid (75% yield). IR (KBr): $\tilde{v} = 2224 \text{ cm}^{-1}$. GC–MS (EI, 70 eV): *m/z* (%) = 137.0 (100) [M]⁺, 102 (37), 75 (22), 50 (15). ¹H NMR (500 MHz, CDCl₃): $\delta = 7.65-7.55$ (m, 3 H, Ar), 7.45–7.41 (m, 1 H, Ar) ppm. ¹³C NMR (125 MHz, CDCl₃): $\delta = 135.1$, 133.1, 131.8, 130.4, 130.2, 117.3, 113.9 ppm.

4-Chlorobenzonitrile (2d):^[16c] White solid (65% yield). IR (KBr): $\tilde{v} = 2225 \text{ cm}^{-1}$. GC–MS (EI, 70 eV): m/z (%) = 137.0 (100) [M]⁺, 102 (37), 75 (21), 50 (16). ¹H NMR (500 MHz, CDCl₃): $\delta = 7.60$ (d, J = 8.4 Hz, 2 H), 7.47 (d, J = 8.4 Hz, 2 H) ppm. ¹³C NMR (125 MHz, CDCl₃): $\delta = 139.5$, 133.3, 129.6, 117.9, 110.7 ppm.

4-Bromobenzonitrile (2e):^[16d] White solid (60% yield). IR (KBr): $\tilde{v} = 2240 \text{ cm}^{-1}$. GC–MS (EI, 70 eV): m/z (%) = 181.0 (68) [M]⁺, 102 (100), 75 (38), 50 (25). ¹H NMR (500 MHz, CDCl₃): δ = 7.65–7.63 (d, J = 8.5 Hz, 2 H), 7.53–7.52 (d, J = 8.4 Hz, 2 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 133.3, 132.5, 127.9, 117.9, 111.1 ppm.

(2m) 4-Isopropylbenzonitrile;^[16e] Colorless liquid (94% yield). IR (neat): $\tilde{v} = 2226 \text{ cm}^{-1}$. GC–MS (EI, 70 eV): m/z (%) = 145.0 (25) [M]⁺, 130 (100), 103 (25), 77 (10). ¹H NMR (500 MHz, CDCl₃): δ = 7.58–7.57 (d, J = 8.0 Hz, 2 H), 7.33–7.31 (d, J = 8.0 Hz, 2 H), 2.99–2.90 (septet, J = 7.0 Hz, 1 H), 1.27–1.25 (d, J = 7.0 Hz, 6 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 154.2, 132.1, 127.2, 119.0, 109.5, 34.3, 23.4 ppm.

Supporting Information (see footnote on the first page of this article): Characterization data, and copies of the ¹H and ¹³C NMR spectra for selected compounds.

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