Iron Nitrate/TEMPO: a Superior Homogeneous Catalyst for Oxidation of Primary Alcohols to Nitriles in Air

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Abstract: A highly practical, one-step, facile synthesis of aromatic, heteroaromatic, allylic and aliphatic nitriles from primary alcohols catalyzed by ferric nitrate $[Fe(NO_3)_3 \cdot 9H_2O]$ in the presence of TEMPO, aqueous ammonia and air at room temperature is described.

Keywords: aerobic oxidation; alcohols; homogeneous catalyst; iron; nitriles

The nitrile group is considered to be a vital functional group in organic chemistry as it not only forms part of many important fine chemicals, pharmaceuticals, materials and agrochemicals, but also serves as an intermediate in the preparation of several functional groups.^[1,2] The classical methods of synthesis of nitriles include Sandmeyer reaction and halide/CN exchange or C-H functionalization of arenes,^[3] oxidation of amines,^[4] and dehydration of amides and oximes.^[5] However as these strategies utilize stoichiometric amounts of toxic reagents coupled with high temperature and pressure and often lead to generation of wastes, more practical methodologies for nitrile synthesis from inexpensive and readily available starting materials are desirable. As a consequence, many new approaches such as use of DMF as the CN source for C-H functionalization of arenes,^[6] oxidative dehydrogenation of benzylic alcohols,^[7] azides,^[8] or methylarenes,^[9] have been developed. In particular, the direct synthesis of nitrile from alcohol and aqueous ammonia under oxidative conditions is considered to be an attractive strategy. Initially such oxidative reactions were conducted in the presence of reagents such as $I_2/$ DIH or TBHP, $(Bu_4N)_2S_2O_8/Cu(HCO_2)_2/Ni(HCO_2)_2/$ KOH, $MnO_2/MgSO_4$ and $NiSO_4/K_2S_2O_8/NaOH$,^[7] but the use of stoichiometric amounts of expensive oxidants and generation of large amount of wastes, made these protocols unsuitable for large scale synthesis.

Nevertheless, with the increasing applications of molecular oxygen as an oxidant which offers remarkable advantages such as abundance, low cost and benign by products like H₂O, direct transformation of alcohols to nitriles was accomplished via catalytic aerobic oxidation,^[10] either under the influence of heterogeneous or the homogeneous catalysts. Amongst heterogeneous catalysts, Mizuno and co-workers used $Ru(OH)_x/Al_2O_3$,^[11] while Ishida et al. and Hou et al. employed MnO₂ or MnO₂-supported on graphite for conversion of alcohols to nitrile.^[12,13] During compilation of the present work, Beller et al. reported the use of novel nitrogen-doped graphene-layered cobalt or iron oxides (nanocatalyst) under oxygen at 130°C for transforming diverse alcohols to nitriles.^[14] On the other hand homogeneous catalysts generally comprise of Cu/TEMPO systems which have been demonstrated earlier to oxidize alcohols to aldehydes under aerobic conditions at ambient temperature.^[6a-c,15] Tao and co-workers employed Cu(NO₃)₃/TEMPO in DMSO in a sealed tube flushed with oxygen whereas Huang et al. used CuI/TEMPO/bipyridine in ethanol or acetonitrile in the presence of oxygen to prepare nitriles from alcohols.^[16,17] Muldoon et al. reported an open flask procedure for this transformation using Cu(OTf)₂/TEMPO/bipyridine in the presence of air instead of pure oxygen (presence of NaOH increased the rate of reaction).^[18] As the reaction was performed in open flask the ammonia was added slowly though placing an air balloon could obviate this continuous addition. However for aliphatic alcohols they switched to [Cu(MeCN)₄][OTf] in the absence of base. Further they also reported when reactors were

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used (with limiting oxygen mixtures) $1 \mod \%$ of CuCl₂ is sufficient for the transformation. Kim and Stahl also demonstrated that Cu(OTf)/TEMPO in



Figure 1. Comparison of previous works with this work.

Table 1. Results of the optimization^[a] with Fe/TEMPO catalyst system for the synthesis of benzonitrile from benzyl alcohol



entry	Fe source (mol%)	TEMPO (mol%)	solvent	Yield ^[b] (%)
1	FeCl ₃ ·6H ₂ O (10)	10	DCE	12
2	$Fe(acac)_3(10)$	10	DCE	24
3	$Fe(NO_3)_3 \cdot 9H_2O(10)$	10	DCE	54
4	$Fe(NO_3)_3 \cdot 9H_2O(10)$	10	MeCN	92
5	$Fe(NO_3)_3 \cdot 9H_2O(10)$	10	PhMe	62
6	$Fe(NO_3)_3 \cdot 9H_2O(10)$	10	EtOH	30
7	$Fe(NO_3)_3 \cdot 9H_2O(10)$	10	DMSO	-
8	$Fe(NO_3)_3 \cdot 9H_2O(5)$	5	MeCN	93
9 ^[c]	$Fe(NO_3)_3 \cdot 9H_2O(5)$	5	MeCN	93
10	$Fe(NO_3)_3 \cdot 9H_2O(5)$	-	MeCN	-

[a] All reactions were carried out using 1a (0.2 g, 1.85 mmol), aq. NH₃ (25%) 0.157 mL (9.2 mmol), MeCN (5 mL), air balloon.

^[b] Isolated yields after column chromatography.

^[c] The reaction was performed using NaCl (10 mol%) as additive.

DMSO in the presence of oxygen efficiently transforms alcohol to nitriles.^[19] These methodologies represent a major advancement in transformation of alcohols to nitriles but have their own drawbacks. Reactions with heterogeneous catalysts require high temperature and pressure while the reactions with Cu/ TEMPO system often require ligands and additives, long reaction time under heating or are substrate selective. We, therefore, believe that there is a need for developing a catalytic system which can function at room temperature with broad substrate scope. Like Cu/TEMPO system, the Fe/TEMPO system has been well studied for the aerobic oxidation of alcohols to aldehydes.^[20] This homogeneous catalytic system is benign with minimal safety concern and avoids the use of any ligand and base. Therefore we considered exploring the iron- catalyzed direct transformation of alcohols to nitriles. Herein, we disclose the Fe/ TEMPO-catalyzed aerobic oxidative synthesis of nitriles from primary alcohols (Figure 1). The protocol with this catalytic system is practical and superior to the ones reported to date as it is performed at room temperature in the presence of air, requires less time, does not require slow addition of ammonia, and accommodates a broad range of substrates including aliphatic, allylic, aromatic and heteroaromatic systems.

Our study commenced with screening the transformation of benzyl alcohol to benzonitrile in the presence of different Fe(III) salts and TEMPO using liquid ammonia and air. As the best performance of the Fe/TEMPO system is obtained in a weakly coordinating solvent such as dichloroethane (DCE),^[10a] we initially used different Fe(III) salts (10 mol%) with TEMPO (10 mol%) in DCE (Table 1). In order to prevent the evaporation of ammonia, the flask was capped with rubber septum and the air atmosphere was maintained using a balloon. We observed that all the three salts successfully catalyzed the conversion,

Table 2. Scope of substituted benzyl alcohols^[a] for aerobic double dehydrogenation

	$R \xrightarrow{II} \qquad OH \qquad \frac{TEMPO (5 \text{ mol}\%)}{\text{NH}_3 (\text{aq.}), \text{ MeCN},} \qquad R \xrightarrow{II} \qquad CN$ air balloon, rt, 12 h				
entry	R	yield ^[b] (%)	entry	R	yield ^[b] (%)
1	2b , 2-Cl	91	8	2i , 4-NO ₂	92
2	2c , 2-OMe	87	9	2j , 4-OMe	82
3	2d , 3-OMe	89	10	2k , 4-OCF ₃	90
4	2e , 4-Me	84	11	21 , 2,6-Cl ₂	88
5	2 f , 4-F	82	12	$2m, 3.4-(OMe)_2$	78
6	2 g, 4-Cl	93	13	$2n, 3, 4, 5-(OMe)_3$	71
7	2h , 4-Br	98	14	20 , 2,3-(OCH ₂ O)-6-NO ₂	92

 $E_{0}(NO_{2}) = 9H_{2}O_{1}(5 \text{ mol})/2$

^[a] All reactions were carried out using substituted benzyl alcohol (0.2 g, 1.0 equiv), Fe(NO₃)₃·9H₂O (0.05 equiv), TEMPO (0.05 equiv), aq. NH₃ (25 %, 5.0 equiv), MeCN (5 mL), air balloon.

^[b] Isolated yields after column chromatography.

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Table 3. Scope of polyaromatic, allylic, aliphatic and heteroaromatic alcohols for aerobic double dehydrogenation $^{[a]}$

R∕ОН	Fe(NO ₃) ₃ ·9H ₂ O (5 mol%) TEMPO (5 mol%)		
	NH ₃ (aq.), MeCN, air balloon, rt, time	R-CN	

entry	reactant	reaction time (h)	Product 3	yield ^[b] (%)
1	CH ₂ OH	12		91
2	CH2OH	12		94
3	CH ₂ OH	12		80
4	O ₂ N Me	8	O ₂ N Me	86
5	СН2ОН	12	CN	80
6	HOH ₂ C	12	TT DIA	68
7	но	12	NC Me	77
8	HOH ₂ C CH ₂ OH	12	NC	58
9	Me L S CH ₂ OH	4	Me L _S L _{CN}	76
10	Ph CH ₂ OH	4	Ph CN	84
11	Br N-O CH ₂ OH	5	Br N-O CN	86
12	N·N Ph CH ₂ OH	5	Ph Ph CN	90
13	CH ₂ OH	5		89
14	CH2OH N N MeO OMe	5	N N H MeO OMe	90
15	CH2OH N CH2OH	8		86

but the best yield (58%) of benzonitrile was obtained using Fe(NO₃)₃·9H₂O/TEMPO (entries 1-3). Optimization of the solvent system revealed that MeCN gave a superior yield (92%) of the product (entries 4-7). Optimization of the amount of the catalyst and TEMPO revealed that $5 \mod \%$ of $Fe(NO_3)_3 \cdot 9H_2O$ and 5 mol% of TEMPO is sufficient for the transformation of benzyl alcohol to benzonitrile (entry 8). In our hands the addition of NaCl (10 mol%) as additive as reported by Ma et al. did not influence the yield of the product (entry 9). The reaction was unsuccessful in the absence of TEMPO (entry 10). Thus the optimized reaction conditions which worked efficiently for us were benzyl alcohol (1 equiv), 25% NH₃ (aq.) (5equiv), $Fe(NO_3)_3 \cdot 9H_2O$ (5 mol %), TEMPO (5 mol%), MeCN as solvent under an air balloon at room temperature for 12 h.

Having defined the optimum conditions for the reaction, we then investigated the generality of the methodology employing diverse benzyl alcohols. It was observed that all the substituted benzyl alcohols gave the respective products (2b-2o) in excellent yields in 12 h of reaction time (Table 2). The electronic nature of the substituent did not influence the outcome. Unlike the observation of Huang et al.,^[17] the protocol was found to be efficient for the electron deficient benzyl alcohol, since 4-nitrobenzyl alcohol gave product 2i in 92% yield (entry 8). Even for 2,3methylenedioxy-6-nitro benzyl alcohol the corresponding nitrile 20 was isolated in 92% yield (entry 14). We observed that only 3,4,5-trimethoxybenzyl alcohol furnished the corresponding benzonitrile **2n** in only 71 % yield (entry 13).

Next we investigated the scope with a range of alcohols which included polyaromatic, allylic, aliphatic and heteroaromatic systems. To our delight the catalytic system could transform all alcohols to their corresponding nitriles efficiently (Table 3). The reaction of polyaromatic, allylic and aliphatic alcohols required 8-12 h for completion whereas the transformations for heteroaromatics were completed in less than 5 h. The relative stereochemistry of the allylic alcohols was maintained in the nitriles (entries 3,4). In contrast to the Cu(NO₃)₃/TEMPO which failed to afford the nitrile with aliphatic alcohols,^[16] this catalytic system efficiently transform the different aliphatic alcohols investigated in this study to the respective nitriles (**3g-h**) (entries 5-8). The protocol when ap-

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 [[]a] All reactions were carried out using polyaromatic, aliphatic or heteroaromatic alcohols (0.2 g, 1.0 equiv), Fe(NO₃)₃.9H₂O (0.05 equiv), TEMPO (0.05 equiv), aq. NH₃ (25%) (5.0 equiv), MeCN (5 mL), air balloon.

^[b] Isolated yields after column chromatography.

^[c] Minor amount of amide was observed if the reaction was allowed to proceed for 5 h.



Scheme 1. Transformation of a heteroaromatic alcohol into an amide via the nitrile.

plied to 1,6-hexanediol afforded adiponitrile (3h) in 58% yield in 18 h. The low yield and longer reaction time for this substrate may be attributed to the use of only 5 mol% each of $Fe(NO_3)_3$ ·9H₂O and TEMPO for oxidizing two hydroxyl groups. For heteroaromatics, it was noticed that if the reactions of (5-methylthiophen-2-yl)methanol and (3-phenylisoxazol-5-yl)methanol to the respective nitriles (3i and 3j) were allowed to continue beyond 4 h, polar side products, which were identified to be the amides, were formed in minor quantities (entries 9,10). Such an observation for heteroaromatic alcohols was also reported by Muldoon et al.^[18] In a model experiment therefore the progress of oxidation of (3-phenylisoxazol-5-yl)methanol in the presence of Fe/TEMPO system was closely monitored. The transformation of alcohol to nitrile **3j** (84%) was completed in 4 h, but if the reaction was prolonged to 8 h, the corresponding amide 4 was isolated in 92% yield (Scheme 1). Other heteroaromatics also gave the products (3k-n) within 5 h (entries 11-15). Unlike 1,6-hexanediol, the β -carboline derivative bearing two hydroxymethyl groups at 1and 3-positions was transformed into bisnitrile derivative **3o** in 86% yield in 8 h with the use of 5 mol% of the catalyst (entry 15).

The plausible mechanism of the formation of nitrile from Fe/TEMPO-catalytic system is presented in Figure 2. In the first step the alcohol is transformed into the aldehyde via an oxidative dehydrogenation. The aldehyde then forms an imine which also undergoes oxidative dehydrogenation under the influence of the catalytic system in step 2. It has been already suggested by Ma et al. that the NO₂ generated by the



use of nitrate salts could oxidize the nitroxyl radical such as TEMPO into an oxoammonium salt, which is the active oxidant and could also assist the reoxidation of Fe(II) to Fe(III).^[20e] We assume that a similar mechanism operates here to transform the alcohol to a nitrile.

In summary, we have demonstrated that Fe/ TEMPO is a very effective homogeneous catalyst system for direct conversion of alcohols to nitriles using aqueous ammonia and air as oxidant. As this catalytic system uses iron and air and does not require the use of any ligand or additive or higher temperature and pressure, it offers a cheaper and more practical option than the methods reported to date. As this protocol accommodates a wide range of alcohols and in general requires less time, it offers a superior and sustainable option for the synthesis of nitriles via aerobic oxidation. This work therefore updates the repertoire of the homogeneous catalysts for the oxidative transformation of primary alcohols to nitriles.

Experimental Section

General Procedure for the synthesis of nitriles from primary alcohols as exemplified for benzonitrile 2a

To a stirred solution of benzyl alcohol **1a** (0.2 g, 1.85 mmol) and NH₃ (aq, 25–30% w/w, 0.157 mL, 9.2 mmol, 5.0 equiv) in MeCN (5.0 mL) was added Fe(NO₃)₃·9H₂O (0.037 g, 0.092 mmol) and TEMPO (0.014 g, 0.092 mmol) at room temperature. The flask was capped with a septum and air was introduced via a balloon; the reaction was allowed to continue for 12 h at the same temperature. After the reaction was complete (as determined by TLC), the solvent was removed and the residue was purified by column chromatography on silica gel using hexanes/EtOAc (9.5:0.5) as eluent to afford **2a** (92%, 0.175 g) as a colorless oil. R_f = 0.77 (hexanes/EtOAc, 8:2, v/v); ¹H NMR (400 MHz, CDCl₃): δ (ppm)=7.45–7.49 (m, 2H), 7.58–7.66 (m, 3H).

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Figure 2. Plausible mechanism for the formation of nitrile from primary alcohol.

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UPDATES

6 Iron Nitrate/TEMPO: a Superior Homogeneous Catalyst for Oxidation of Primary Alcohols to Nitriles in Air

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