

## Iron-Catalysed Selective Aerobic Oxidation of Alcohols to Carbonyl and Carboxylic Compounds

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A method for aerobic alcohol oxidation catalysed by  $Fe(NO_3)_3/2$ , 2,2'-bipyridine/TEMPO has allowed highly selective conversion of primary alcohols into either aldehydes or carboxylic acids in one-step. The oxidation of primary alcohols proceeded selectively to aldehydes, as TEMPO was present in the reaction. Nevertheless, the aldehydes were further oxidized into carboxylic acids as the reaction time was extended. Detailed investigation of the reaction suggested, that the deoxygenation of TEMPO into TMP enabled the auto-oxidation of aldehydes to carboxylic acids, which was initially inhibited in the presence of TEMPO. The procedure was also efficient in oxidation of secondary alcohols when TEMPO was replaced by the less sterically hindered ABNO.

Oxidation of alcohols into the corresponding carbonyl and carboxylic compounds is among the most studied chemical reactions.<sup>[1,2]</sup> These transformations are traditionally carried out using stoichiometric amounts of oxidants, such as CrO<sub>3</sub>,<sup>[3]</sup> MnO<sub>2</sub>,<sup>[4]</sup> activated DMSO and hypervalent iodine,<sup>[5]</sup> which are all expensive and produce equimolar amounts of hazardous waste. Lately, environmentally benign oxidation processes have been the subject of intensive research, including the metal-catalysed aerobic methods that are now routinely used for converting alcohols into aldehydes and ketones on a laboratory scale.<sup>[6–8]</sup> However, direct aerobic oxidation of primary alcohols into carboxylic acids remains a great challenge. To date, only a handful of noble metals, such as Pd, Ru, Pt, Rh and Au, have been reported as catalysts for this transformation.<sup>[9–13]</sup>

In the search for novel catalytic systems, Fe has great potential owing to its fundamental role in enzymatic reactions and its high catalytic activity in aerobic alcohol oxidation reactions.<sup>[14, 15]</sup> Particularly efficient for alcohol oxidation are the systems involving simple Fe salts together with NO<sub>x</sub> and nitroxyl radicals, such as 2,2,6,6-tetramethyl-piperidyl-1-oxy (TEMPO).<sup>[16]</sup> These catalytic systems are most often used under homogeneous conditions without any acid or base co-catalysts.<sup>[17–21]</sup> Also, heterogeneous and ionic-liquid-bound variants have been developed.<sup>[22–24]</sup> A common factor for these Fe-based catalytic systems is their ability to selectively convert primary and secondary alcohols into aldehydes and ketones.

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Supporting information for this article can be found under http:// dx.doi.org/10.1002/cplu.201600240. Carboxylic acids are highly valuable synthons in chemistry and readily available through aerobic oxidation of aldehydes.<sup>[25-29]</sup> So far, direct aerobic oxidation of alcohols into carboxylic acids have proven challenging, even though the oxidation pathway proceeds through aldehyde intermediates.<sup>[2]</sup>

Herein, we introduce a one-step aerobic alcohol oxidation procedure catalysed by  $Fe(NO_3)_3$ /TEMPO for the selective conversion of primary alcohols into either the corresponding aldehydes or carboxylic acids (Scheme 1; TEMPO=2,2,6,6-tetra-

$$R \frown OH \xrightarrow{\begin{array}{c} O_2 \\ Fe(NO_3)_3/TEMPO \text{ catalyst} \\ \hline \text{one-step} \\ \text{time-controlled selectivity} \end{array}} R \frown O \text{ or } R \frown OH$$

Scheme 1. Oxidation of primary alcohols either into aldehydes or carboxylic acids catalysed by  $Fe(NO_3)_3$ /TEMPO in one step.

methyl-piperidyl-1-oxy). Initially, aerobic oxidation of primary alcohols was investigated using 1-octanol (**1a**) as a model compound. Conversion of **1a** into octanal (**2a**) was attempted in various solvents using 5 mol% of  $Fe(NO_3)_3$ /TEMPO catalyst formed in situ (for details see Scheme S1 in the Supporting Information). Promising results were obtained in solutions of MeCN and AcOH, as **1** was converted into **2a** in 45 and 48% yields, respectively (Table 1, entries 1 and 2).

The impact of different organic ligands on the oxidation of **1a** was then studied (Table 1, entries 3–8; for full details see Table S3). Of the ligands employed, 2,2'-bipyridine (bpy) showed the highest catalytic amplification; **1a** was converted into **2a** in an excellent 96% yield after 6 h (Table 1, entry 3). A similar positive effect was detected with 1,10-phenanthroline and 4,4-di-*tert*-butyl-2,2-bipyridine ligands (Table 1, entries 4 and 5), whereas 4,4-di-nitro-2,2-bipyridine, di-(2-picolyl)amine and 1-methylimidazole gave poor outcomes, resulting in low yields of **2a** (Table 1, entries 6–8). Although *N*-heterocyclic ligands are commonly used in transition-metal-catalysed oxidation chemistry,<sup>[7,30–32]</sup> such auxiliaries have not attracted substantial interest in Fe/TEMPO-catalysed aerobic oxidation of alcohols and therefore their exact role is still undisclosed.

Notably, high reactivity was only observed in AcOH solution (Table 1, entry 3). The reactions conducted in other solvents, such as commonly used MeCN<sup>[17,21,33]</sup> or 1,2-dichloroethane<sup>[18,19,34,35]</sup> (DCE), resulted in significantly lower yields of **2a** (Table 1, entries 9 and 10; for full details see Table S2). This outcome indicates that the active oxidant is the oxoammonium ion of TEMPO that is formed via acid-catalysed disproportionation of the nitroxyl radical.<sup>[36–40]</sup> Furthermore, control ex-



Table 1. Screening of the aerobic 1-octanol oxidation conditions <sup>[a]</sup>						
(√) <sub>6</sub> ⊂ 1a	0H <u>5 mol %</u>	( metal precursor, TEMPC Ambient air, 25 °C	D, ligand) ►	. *	†€0 2a	
Entry	Metal precursor	Ligand	Solvent	t [h]	Yield [%] <sup>[b]</sup>	
1 <sup>[c]</sup>	Fe(NO <sub>3</sub> ) <sub>3</sub>	-	MeCN	23	45	
2	Fe(NO <sub>3</sub> ) <sub>3</sub>	-	AcOH	23	48	
3	$Fe(NO_3)_3$		AcOH	6	96	
4	Fe(NO <sub>3</sub> ) <sub>3</sub>		AcOH	6	94	
5	Fe(NO <sub>3</sub> ) <sub>3</sub>	tBu tBu	AcOH	6	93	
6	Fe(NO <sub>3</sub> ) <sub>3</sub>	O <sub>2</sub> N NO <sub>2</sub>	AcOH	6	18	
7	Fe(NO <sub>3</sub> ) <sub>3</sub>	K K K K K K K K K K K K K K K K K K K	AcOH	23	8	
8	Fe(NO <sub>3</sub> ) <sub>3</sub>	$N \gg N$	AcOH	23	8	
9	Fe(NO <sub>3</sub> ) <sub>3</sub>		MeCN	23	29	
10	Fe(NO <sub>3</sub> ) <sub>3</sub>		DCE	23	18	
11 <sup>[d]</sup>	NaNO <sub>2</sub>		AcOH	23	2	
12 <sup>[e]</sup>	Fe(NO <sub>3</sub> ) <sub>3</sub>		AcOH	23	0	
13	FeCl <sub>3</sub>		AcOH	23	2	
[a] Reaction conditions: solvent (2 mL), $Fe(NO_3)_3$ ·9H <sub>2</sub> O/TEMPO/bpy (1:1:1, mol/mol/mol) catalyst formed in situ (5 mol%), 1-octanol (1 mmol), open test tube (20 mL), 25 °C, 1200 rpm stirring. [b] Yields were determined by GC-FID analysis using the area normalization method [c] catalyst was not						

completely soluble. [d] NaNO<sub>2</sub> (15 mol%). [e] Reaction without TEMPO.

periments showed that all catalyst components (ligand,  $Fe^{3+}$ , TEMPO and  $NO_3^-$ ) were crucial for the catalysis under our conditions (Table 1, entry 3 vs. entries 2 and 11–13; for detailed results see Figure S5).

As the Fe(NO<sub>3</sub>)<sub>3</sub>/bpy/TEMPO catalyst exhibited the highest activity in the oxidation of **1a** into **2a**, this system was investigated in more detail. The studies revealed that **2a** was further converted into octanoic acid (**3a**) when the reaction time was prolonged from 6 to 23 h. This outcome was surprising because TEMPO and other persistent nitroxyl radicals are known to inhibit the aerobic oxidation of aldehydes into carboxylic acids.<sup>[41-43]</sup>

Gas chromatography–Flame Ionization detector (GC-FID) analysis of the **1a** oxidation reaction (aliquots taken every 2 h) showed that conversion of the starting alcohol into **2a** occurred during the first 6 h, and was followed by a 10 h period when the oxidation of **2a** into carboxylic acid **3a** was very slow (Figure 1a). After 16 h, the colour of the reaction solution



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**Figure 1.** Aerobic oxidation of 1-octanol. Reaction conditions: a) Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O/TEMPO/bpy (1:1:1, mol/mol) catalyst formed in situ (5 mol%). b) Catalyst molar ratio of 1:3:1, TEMPO added in three portions at 0 h, 8 h and 16 h. Yields were determined by GC-FID analysis using the area normalization method. Reaction conditions: AcOH (2 mL), 1-octanol (1 mmol), open test tube (20 mL), 25 °C, 1200 rpm stirring.

suddenly changed from deep red to brown, and the turnover rate of **2a** into **3a** increased significantly, leading to completion of the reaction in the following 2 h. We reasoned that the observed colour change and the subsequent rapid oxidation of aldehyde **2a** resulted from quenching of TEMPO, which then allowed the auto-oxidation to the carboxylic acid **3a**.<sup>[44,45]</sup> The hypothesis was confirmed by GC-MS analysis, which showed complete degradation of TEMPO during the first 16 h of the reaction. The major decomposition product detected was 2,2,6,6-tetramethylpiperidine (TMP), which was presumably formed via Fe-catalysed N–O bond cleavage.<sup>[46,47]</sup> Furthermore, the gradual addition of TEMPO (5 mol%) to the oxidation reaction of **1a** every 8 hours completely inhibited the oxidation of the formed aldehyde **2a** into carboxylic acid **3a** (Figure 1b), thus supporting the proposed auto-oxidation pathway.

The effect of the Fe(NO<sub>3</sub>)<sub>3</sub>/bpy catalyst on aldehyde oxidation was investigated in the absence of TEMPO. With 5 mol% of Fe(NO<sub>3</sub>)<sub>3</sub>/bpy, **2a** was converted into **3a** in 1 h (Figure 2a), whereas 12 h was required without the catalyst (Figure 2b). This outcome demonstrates that Fe(NO<sub>3</sub>)<sub>3</sub>/bpy catalyses the oxidation of aldehydes into carboxylic acids without TEMPO and thus, explains the sudden conversion of **2a** into **3a** after complete decomposition of TEMPO during the catalytic oxidation of **1a**.

The oxidation of benzylic alcohols was investigated using 4methoxybenzyl alcohol (**1b**) as a model compound. The initial experiment was conducted applying the same conditions used for the oxidation of **1a** (5 mol% of  $Fe(NO_3)_3$ /bpy/TEMPO catalyst formed in situ in AcOH and under ambient condition in air). Under these conditions, **1b** was rapidly converted into the respective aldehyde (**2b**), but no further oxidation into the carboxylic acid (**3b**) occurred within 23 h. To increase the reactivi-

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**Figure 2.** Aerobic oxidation of octanal. Reaction conditions: a) a)  $_{3,9}H_2O/$  bpy (1:1, mol/mol) catalyst formed in situ (5 mol%). b) No catalyst. Yields were determined by GC-FID analysis using the area normalization method. Reaction conditions: AcOH (2 mL), octanal (1 mmol), open test tube (20 mL), 25 °C, 1200 rpm stirring.



**Figure 3.** The effect of catalyst loading on 4-methoxybenzyl alcohol oxidation rate. a) Formation of 4-methoxybenzaldehyde. b) Formation of 4-methoxybenzoic acid. Yields were determined by GC-FID analysis using the area normalization method. Reaction conditions: AcOH (2 mL), 4-methoxybenzyl alcohol (1 mmol), open test tube (20 mL) fitted with O<sub>2</sub> balloon, 80 °C, 1200 rpm stirring.

ty, the reaction temperature was raised from ambient to  $80 \,^{\circ}$ C and an O<sub>2</sub> atmosphere (1 atm) was used instead of air. Now, **1 b** was converted into **2 b** in 30 min and further into **3 b** in 5 h, in 99 and 60% yields, respectively.

The influence of catalyst loading (0.5 to 5 mol%) on the oxidation rate of **1b** was examined (Figure 3). Fast and almost quantitative conversion of the starting alcohol into aldehyde

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Table 2. Substrate scope of the aerobic alcohol oxidation with protocol A.							
Protocol A: 5 mol% Fe(NO <sub>3</sub> ) <sub>3</sub> , 2,2'-bipyridine, TEMPO or ABNO <sup>[a]</sup>							
OH R <sup>1</sup> R <sup>2</sup> open air, 25 <b>1a, c-I</b> AcOH		$ \xrightarrow{\mathbf{N}} \overset{\mathbf{O}}{\overset{\mathbf{O}}}{\overset{\mathbf{O}}{\overset{\mathbf{O}}}{\overset{\mathbf{O}}{\overset{\mathcal{O}}{\overset$		R <sub>2</sub> = H	$\begin{array}{ccc} H & O \\ \downarrow \\ tended \\ & \mathbf{R}^1 & OH \\ & \mathbf{3a, c-h} \end{array}$		
Entry	Sub	ostrate	<i>t</i> [h]	Pro	duct	Conv. <sup>[b]</sup> (sel.) [%]	Yield <sup>[c]</sup> (isolated) <sup>[d]</sup> [%]
1 2	1a	M <sub>6</sub> OH	6 23	2a 3a	-CHO -COOH	97 (99) >99 (93)	96 (87) 93 (89)
3 4	1 c	₩Ĵ <sub>9</sub> ОН	8 24	2c 3c	-сно -соон	99 (98) 99 (95)	97 94
5 6	1 d	HO	6 26	2 d 3 d	-CHO -COOH	99 (94) 95 (94)	93 (88) 89 (85)
7 8	1 e	СІ∽(+)₄ОН	6 24	2e 3e	-CHO -COOH	92 (98) 94 (91)	90 86
9 10	1 f	/он	6 24	2 f 3 f	-CHO -COOH	>99 (96) 98 (91)	94 89
11 12	1 g	М	6 24	2 g 3 g	-CHO -COOH	98 (87) >99 (77)	85 76
13 14	1 h	HO HO	6 24	2 h 3 h	-CHO -COOH	99 (90) 96 (76)	89 73
15	1i	но∕(-∕}_он	24	4i	lactone	99 (63)	62
16 17	1j	OH	8 1	2j 2j	$R_1$ -C(=O)- $R_2$	> 99 (99) > 99 (> 99)	99 >99 <sup>[a]</sup>
18 19	1 k	OH 5	10 4	2 k 2 k	$R_1$ -C(=O)- $R_2$	72 (99) >99 (99)	71 99 <sup>[a]</sup>
20 21	11	ОН	26 1	21 21	$R_1$ -C(=O)- $R_2$	94 (99) > 99 (99)	93 99 <sup>[a]</sup>

[a] ABNO used as nitroxyl radical. [b] Conversion of alcohol is presented for aldehyde and ketone products, conversion of aldehyde is presented for carboxylic acid products. [c] Yields were determined by GC-FID analysis using the area normalization method. [d] Yield of isolated product. Reaction conditions: alcohol (1 mmol), AcOH (2 ml), test tube (20 mL), 1200 rpm stirring.



**2b** was observed using amounts of catalyst as low as 1 mol% (Figure 3 a). The formation of **2b** was followed by further oxidation into carboxylic acid **3b**, and which was most efficient using 1.5 mol% of catalyst (Figure 3 b). Formation of carboxylic acid was clearly delayed with higher catalyst amounts because of the increased amount of TEMPO, which had to be consumed before the Fe-catalysed auto-oxidation of the aldehyde initiated (Figure 3 b). Likewise with **1a**, full conversion of the alcohol into the aldehyde took place before the formation of the carboxylic acid began, thus enabling selective oxidation.

After optimisation of the reaction conditions the substrate scope was explored. Under the best conditions used for 1-octanol oxidation (Protocol A, Table 2), undecanol (1 c) and 3-phenyl-1-propanol (1 d) were smoothly converted into the corresponding aldehydes (2c and 2d, respectively). This was followed by further conversion into the carboxylic acids (3c and 3d) in very good yields. Also alcohols bearing functional groups, such as chlorine (1e), a double bond (1 f), a triple bond (1 g), and ether (1 h) were oxidised into the respective aldehydes (2e-h) and further to carboxylic acids (3e-h) in good yields. Almost complete oxidation of alcohols into aldehydes was observed with all substrates before the formation of carboxylic products began, thus enabling excellent control of selectivity and high yields. Oxidation of 1,5pentanediol (1 i) resulted in the formation of  $\delta$ -valerolactone in fair yield.

Oxidation protocol A was also employed for the conversion of secondary alcohols into ketones. Diphenyl methanol (**1j**) was transformed into diphenylketone (**2j**) in excellent yield in 8 h, whereas oxidation of 2-octanol (**1k**) and borneol (**1l**) into the corresponding ketones (**2k** and **2l**, respectively) was slow and low yielding. To enhance the reactivity, the catalyst system was modified by replacing sterically hindered TEMPO with a less bulky nitroxyl radical, 9-azabicyclo[3.3.1]nonane *N*-oxyl (ABNO), which has been proven to be an efficient catalyst in the oxidation of secondary alcohols.<sup>[21,48]</sup> Pleasingly, this change led to enhanced reactivity and ketones **2j**–**I** were obtained from the respective alcohols in quantitative yields in 1 to 4 h.

The use of ABNO was also applied to the oxidation of primary alcohols. This resulted in superior reaction

rates, yet lower selectivities compared with the  $Fe(NO_3)_3/bpy/TEMPO$  system (see Table S4).

Notably, applying the conditions optimised for the oxidation of benzylic primary alcohols (Protocol B, Table 3) to the oxidation of aliphatic primary alcohols resulted in incomplete substrate conversion and poor product selectivities.

Benzylic, heteroaromatic and allylic alcohols were subjected to oxidation using the conditions optimised for 4-methoxybenzyl alcohol (Protocol B, Table 3). With all the substrates (1 b, 1 m-x), the corresponding aldehydes (2 b, 2 m-x) were ob-

Table 3. Substrate scope of aerobic alcohol oxidation with protocol B.								
Protocol B:								
OH 1.5 mol% □↓ Fe(NO <sub>3</sub> ) <sub>3</sub> , 2,2'-bipyridine, TEMPO				0		R' = H		
<b>1b, 1m-x</b> O <sub>2</sub> (1 atm), 80 °C, AcO			OH	•	2b, 2m-x	reaction exten	ded 3b, 3m-r	
Entry Substrate		<i>t</i> [h]	Product		Conv. <sup>[a]</sup> (sel.) [%]	Yield <sup>[b]</sup> (isolated) <sup>[c]</sup> [%]		
1 2	1 b	О-С_У-ОН	0.5 3	2 b 3 b	-CHO -COOH	>99 (99) 79 (96)	99 76	
3 4	1 m	С	0.5 4	2 m 3 m	-CHO -COOH	>99 (>99) 89 (97)	>99 (98) <sup>[d]</sup> 86 (84) <sup>[d]</sup>	
5 6	1 n	- С- ОН	0.5 3	2 n 3 n	-CHO -COOH	>99 (>99) 81 (96)	>99 78	
7 8	10	CF3-	0.5 4	20 30	-CHO -COOH	>99 (>99) 93 (98)	>99 91 (87)	
9 10	1p		0.5 4	2 p 3 p	-CHO -COOH	> 99 (99) 84 (96)	99 81	
11 12	1q	СІСІОН	0.5 4	2 q 3 q	-CHO -COOH	> 99 (96) 65 (92)	96 60	
13 14	1r	Вгорон	0.5 3	2r 3r	-CHO -COOH	>99 (99) 96 (95)	99 (97) 91 (88)	
15 16	1 s	ОТОН	0.5 5	2 s 3 s	-CHO -COOH	93 (99) <5 (0)	92 0	
17 18	1t	Он	0.5 5	2t 3t	-CHO -COOH	>99 (>99) <5 (0)	>99 (96) 0	
19 20	1 u	€утон	0.5 5	2 u 3 u	-CHO -COOH	quant. (99) >5 (0)	99 0	
21 22	1 v	ОН	1 5	2 v 3 v	-CHO -COOH	96 (96) < 5 (0)	92 <sup>(e)</sup> 0 <sup>(e)</sup>	
23 24	1 x	←→→→ OH	1 5	2 x 3 x	-CHO -COOH	95 (86) < 5 (0)	82 <sup>[e]</sup> 0 <sup>[e]</sup>	

[a] Conversion of alcohol is presented for aldehyde and ketone products, conversion of aldehyde is presented for carboxylic acid products. [b] Yields were determined by GC-FID analysis using the area normalization method. [c] Yield of isolated product. [d] Reaction conducted on a 100 mmol scale. [e] catalyst (3 mol%). Reaction conditions: alcohol (1 mmol), AcOH (2 ml), test tube (20 mL), 1200 rpm stirring. quant.= quantitative.

tained in high yields in 0.5–2 h. By extending the reaction time to 3-4 h, benzylic substrates **1b** and **1m–r** were further oxidised into the respective carboxylic acids (**3b**, **3m–r**). Partial amenability to oxidation was observed with 3,4-(methylenedioxy)benzyl alcohol **1s** as well as with heteroaromatic **1t– u** and allylic alcohols **1v–x**, as aldehydes **2s–x** were the final oxidation products. To demonstrate the applicability of the catalyst system for preparative scale synthesis, 100 mmol of **1m** was oxidised into the corresponding aldehyde **2m** and carboxylic acid **3m** in 98 and 84% yields, respectively.

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Scheme 2. Proposed mechanism for the catalytic aerobic oxidation of primary alcohols into carboxylic acids.

Based on the pertinent literature, a plausible reaction mechanism for conversion of the alcohol and subsequent aldehyde oxidation is presented in Scheme 2. It is known that TEMPO disproportionates into the respective hydroxylamine (TEMPOH) and oxoammonium ion (TEMPO<sup>+</sup>) under acidic conditions (step 1),<sup>[36-38]</sup> the latter of which is reported as the active species in the oxidation of alcohols into aldehydes while simultaneously undergoing reduction into TEMPOH (step 2).<sup>[17,23,39,40,49,50]</sup> TEMPOH is most likely oxidised back into radical TEMPO by Fe<sup>III</sup> (step 3), which has been proposed to oxidise TEMPO derivatives via reduction to  $Fe^{II}$ .<sup>[17, 19, 23]</sup> NO<sub>3</sub> has a catalytic role as a source of NO<sub>x</sub> species that have been suggested to mediate the aerobic oxidation of Fe<sup>II</sup> into Fe<sup>III</sup>.<sup>[19,23,51]</sup> Although the exact role of bpy is unknown, it plausibly coordinates to Fe and enhances the reactivity by affecting the electronic properties and bonding of the metal centre.<sup>[52,53]</sup> Together the above-mentioned reactions form a cascade of redox reactions that convert alcohols into carbonyl compounds and  $H_2O$  is formed as a side product.

As discussed above, further oxidation of the formed aldehyde is inhibited by the presence of TEMPO, thus allowing highly selective oxidation of primary alcohols into aldehydes.<sup>[44,45]</sup> However, slow decomposition of TEMPO into TMP, through N–O bond cleavage (step 4), eventually initiates the Fe-catalysed aldehyde auto-oxidation leading to the formation of carboxylic products (steps 5–8).<sup>[44,45,54–56]</sup>

In conclusion, we have developed a sustainable, highly efficient and practical  $Fe(NO_3)_3/bpy/TEMPO$ -catalysed method for the selective aerobic oxidation of aliphatic and benzylic primary alcohols into either aldehydes or carboxylic acids in onestep. The system is compatible with a wide range of functionalities including halogens, double bonds, triple bonds, ethers and esters. Moreover, the method is also effective in the oxidation of secondary alcohols into ketones when TEMPO is replaced with ABNO. It was demonstrated that reactions are easily scalable to ten grams.

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**Keywords:** aerobic oxidation • alcohols • iron • synthetic methods

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## COMMUNICATIONS

$$R \frown OH \xrightarrow{\begin{array}{c} O_2 \\ Fe(NO_3)_3/TEMPO \text{ catalyst} \\ \hline \text{one-step} \\ time-controlled selectivity} \end{array} R \frown O \text{ or } R \frown OH$$

A highly selective aerobic oxidation of primary alcohols into either aldehydes or carboxylic acids has been developed. This mild and practical method used  $Fe(NO_3)_3/TEMPO/2,2'$ -bipyridine as a catalyst in aerobic conversion of alcohols into aldehydes (see figure). Further oxidation into carboxylic acids was achieved in extended reactions where TEMPO was de-oxygenated into TMP. The procedure was also efficient for the oxidation of secondary alcohols when TEMPO was replaced by the less sterically hindered ABNO. K. Lagerblom, P. Wrigstedt, J. Keskiväli, A. Parviainen, T. Repo\*

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Iron-Catalysed Selective Aerobic Oxidation of Alcohols to Carbonyl and Carboxylic Compounds