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Iron Chloride/4-Acetamido-TEMPO/Sodium Nitrite-Catalyzed Aerobic Oxidation of Primary Alcohols to the Aldehydes

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Abstract: A variety of 4-substituted 2,2,6,6-tetramethylpiperidyl-1-oxy (TEMPO) derivatives has been screened for their ability in the oxidation of primary alcohols to the aldehydes with dioxygen under mild conditions. An evaluation of the efficiency of these 4-substituted TEMPO derivatives in the alcohol oxidation may allow an insight into the effect of the structural variations of TEMPO on the oxidation of alcohols, which should facilitate catalyst design and screening efforts. Based on the screening results of 4-substituted TEMPO derivatives, the catalyst comprised of 4-acetamido-TEMPO, iron chloride and sodium nitrite, has been developed for the highly efficient oxidation of a wide range of primary alcohols including primary aliphatic alcohols to the corresponding aldehydes under mild conditions.

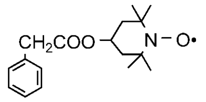
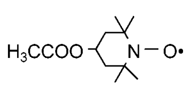
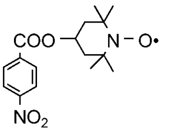
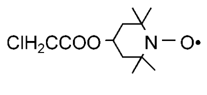
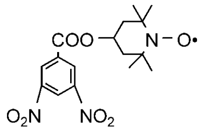
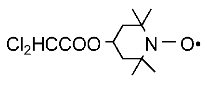
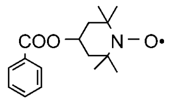
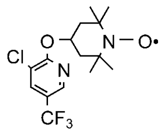
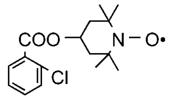
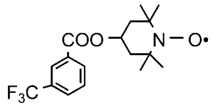
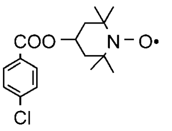
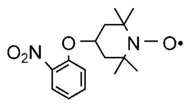
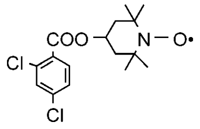
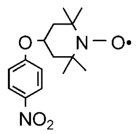
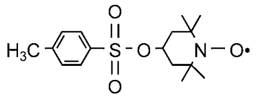
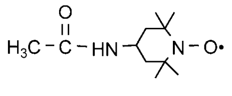
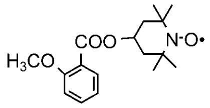
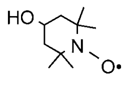
Keywords: aerobic oxidation; iron chloride; primary alcohols; sodium nitrite; TEMPO

Aldehydes are useful compounds in the synthesis of fine chemicals such as pharmaceuticals, fragrances or food additives.[1] The controlled oxidation of primary alcohols is one of the most important approaches to preparation of aldehydes. Recent major efforts in the oxidation of alcohols to carbonyl compounds have been devoted to the discovery and development of catalytic routes using O_2 or H_2O_2 as the terminal oxidant to meet both economic and environmental demands.[2] Among them, interest in the aerobic oxidation of alcohols utilizing TEMPO-based (2,2,6,6-tetramethylpiperidyl-1-oxy) catalysts has been increasing.[3] Notably, a few examples that aimed at oxidative conversion of primary alcohols to the aldehydes with O_2 were reported.[4] However, most reported catalyst systems for the aerobic oxidation of alcohols require toxic metals or expensive transition metals such as palladium[5,6], rhodium or ruthenium[7]. In particular, for pharmaceuticals, fragrances and food additives, these directly human body-related compounds, have been severely restricted in their content of toxic metals.

In this context, we have recently developed a transition metal-free TEMPO-based catalyst for the aerobic oxidation of a wide range of alcohols.[8] However, one limitation of the metal-free catalysis is that primary aliphatic alcohols are oxidized with only moderate selectivity in favor of the formation of aldehydes. Subsequent optimization of our initial catalytic system led to an improved and greener protocol, whereby primary alcohols were selectively oxidized to the corresponding aldehydes in high yields using HCl in place of molecular bromine, but the optimized system required a high TEMPO loading to accomplish the oxidation.[9] On the other hand, the transition metal-catalyzed aerobic oxidation of alcohols has been a field of intensive research due to the inherent advantages of transition metals in dioxygen activation. Therefore, we are also interested in the discovery and development of an innovative transition metal catalyst system for the aerobic oxidation of alcohols, especially for oxidative conversion of primary alcohols to aldehydes. A key criterion was that the metal would be cheap, green, and easily available. Iron is a generally accepted green metal, and iron(III) salts are extremely cheap and readily available. We have reported that $FeCl_3$ in combination with TEMPO and $NaNO_2$ was able to oxidize a wide range of alcohols under mild conditions with dioxygen.[10] However, primary aliphatic alcohols remained elusive. This problem was probably attributed to the catalytic activity of TEMPO, which was not high enough to selectively oxidize primary aliphatic alcohols to the aldehydes. Based on the $FeCl_3$/TEMPO/$NaNO_2$ catalyst system and a systematic appraisal of 4-substituted TEMPOs, we report here an improved catalytic system that is able to efficiently oxidize a variety of primary alcohols to the aldehydes under mild conditions using 4-acetamido-TEMPO in place of TEMPO.

The investigation began with 2-ethylhexanol as a prototypical substrate by screening a variety of 4-substituted TEMPOs for their ability in the oxidation reaction. As shown in Table 1, all the 4-substituted TEMPOs employed provided relatively high selectivities under the conditions of our screen. 4-Hydroxy-TEMPO also provided 99% selectivity, but its conversion is relatively low and it is known to be susceptible to degradation under oxidative conditions. Although the 4-substituent groups of TEMPOs are distant from the oxidative active center (N–O moiety) of TEMPO, 4-substituent groups on TEMPOs have a distinct impact on the catalytic activity of TEMPO for alcohol oxidation, which exceeded our expectations. Electron-withdrawing groups on TEMPO were considered to

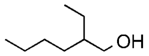
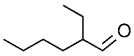
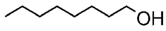
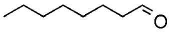
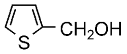
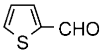
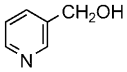
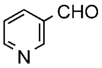
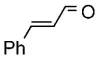
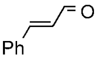
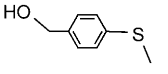
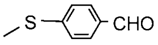
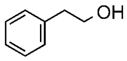
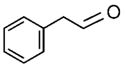
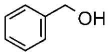
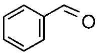
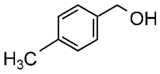
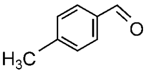
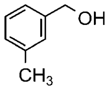
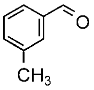
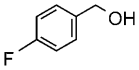
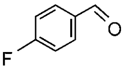
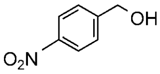
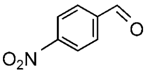
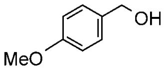
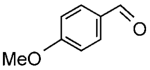
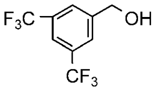
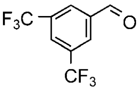
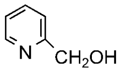
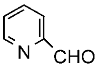
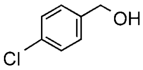
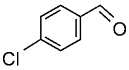
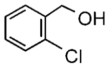
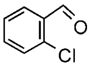
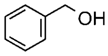
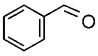
Table 1. Catalytic aerobic oxidation of 2-ethylhexanol in the presence of the 4-substituted TEMPOs.[a]

Entry	4-Substituted TEMPO	Time [h]	Conv. [%][b]	Select. [%][b]	Entry	4-Substituted TEMPO	Time [h]	Conv. [%][b]	Select. [%][b]
1		2	81	90	10		2	59	98
2		2	86	91	11		2	85	92
3		2	90	91	12		2	82	94
4		2	81	92	13		2	79	91
5		2	85	91	14		2	86	91
6		2	81	92	15		2	71	90
7		2	89	90	16		2	81	92
8		2	87	96	17		2	92	98
9		2	75	85	18		2	49	99

[a] Aerobic oxidation conditions are as follows: alcohol (2 mmol), $NaNO_2$ (0.16 mmol), $FeCl_3$ (0.10 mmol), 4-substituted TEMPOs (0.10 mmol), $C_2H_4Cl_2$ (10 mL), 0.4 MPa O_2, room temperature.

[b] Conversion and selectivities are based on gas chromatography (GC) with area normalization.

Table 2. Catalytic aerobic oxidation of primary alcohols in the presence of 4-acetamido-TEMPO, $FeCl_3$ and $NaNO_2$.[a]

Entry	Substrate	Product	Cat. [%]	Time [h]	Conv. [%][b]	Select. [%][b]	Yield [%][d]
1			2	3	100	99	90
2			3	11	100	93	93
3			4	5	100	90	85
4[c]			1	8	100	>99	87
5			3	23	100	98	89
6			1	5	100	>99	86
7			3	10	100	89	–
8			0.1	10	100	>99	87
9			0.5	5	100	96	92
10			0.5	5	100	98	93
11			0.5	5	100	>99	99
12			1	9	100	>99	94
13			3	12	100	94	89
14			1	12	100	95	94
15[c]			2	5	100	92	87
16			0.5	8	100	94	94
17			0.5	10	100	>99	93
18[e]			0.1	14	100	>99	88

[a] Aerobic oxidation conditions are as follows: alcohol (5 mmol), $NaNO_2$ (0.40 mmol), $FeCl_3$ (0.25 mmol), 4-acetamido-TEMPO (0.005–0.15 mmol), $C_2H_4Cl_2$ (10 mL), 0.4 MPa O_2, 50 °C.

[b] Conversions and selectivities are based on gas chromatography (GC) with area normalization.

[c] 1 mL CH_3COOH was added.

[d] Isolated yields.

[e] 0.4 MPa air in place of O_2.

have beneficial effects on the catalytic activity of TEMPO.[11] Interestingly, we observed that such an electronic effect of substituent groups on TEMPO's catalytic activity could also exist at farther distances from substituent groups to the catalytic activity center of TEMPO. For 4-TEMPO-yl acetates, chlorine groups on acetate can also impact on the catalytic activity of the TEMPOs. For example, 4-TEMPO-yl chloroacetates have a higher catalytic activity than 4-TEMPO-yl acetate (entries 11 and 12 *vs.* 10). Although individual examples of 4-substituted TEMPOs have occasionally been used in the alcohol oxidations, the systemic appraisal of 4-substituted TEMPOs for their ability to alcohol oxidation has not been reported previously.

Having examined a variety of 4-substituted TEMPOs, we selected 4-acetamido-TEMPO in combination with $FeCl_3$[12] and $NaNO_2$ as the catalyst to examine the range of primary alcohols to which this catalytic oxidation could be applied with dioxygen. After systematic investigation and optimization of the reaction conditions (temperature, oxygen, pressure, and amount of the catalyst), we developed a highly efficient and green aerobic oxidation of a wide range of primary alcohols to the aldehydes. Several features of this catalytic system are worth noting. As revealed in Table 2, a wide variety of benzylic primary alcohols, which contain electron-donating and electron-withdrawing groups, were completely converted into the desired benzaldehydes in high isolated yields (entries 9–14, 16 and 17). The electronic properties of the substituents on the benzene ring, whether electron-donating groups or electron-withdrawing groups, have not significantly affected the conversions and selectivities of the oxidations, varying only in the reaction rates: the substrates with electron-donating groups (entries 9 and 10) provided a slightly fast reaction compared with those with electron-withdrawing groups (entry 12). The catalyst system showed a relatively high catalytic activity for aromatic alcohol oxidation (entries 8–11, 16 and 17). To our pleasure, primary aliphatic alcohols, which remain elusive in many aerobic oxidation protocols, were smoothly oxidized to the desired aldehydes with high conversions and selectivities (entries 1 and 2). The formation of esters and/or overoxidation is a recurring problem in the aerobic oxidation of primary aliphatic alcohols, whereas this problem did not arise in the newly developed catalytic system. For instance, oxidations of 1-octanol and 2-ethylhexanol could achieve 100% conversion and more than 90% selectivities (entries 1, 2). 2-Phenylethanol and allylic alcohols such as cinnamyl alcohol could also be converted to the expected aldehydes with high selectivity (entries 7 and 5). Interestingly, 2-thiophenemethanol and 4-(methylthio)benzyl alcohol, which are generally considered as difficult substrates in most aerobic oxidation systems involving transition metals because of their strong coordinating ability, could also be very smoothly oxidized to the corresponding aldehydes with high conversions and selectivities (entries 3 and 6). It is noteworthy that 4-(methylthio)benzyl alcohol, which bears a sulfide group that is susceptible to oxidation, was selectively oxidized into the aldehyde, whereas the sulfide group remained unreacted. The selectivity may be of great interest in synthetic organic chemistry. In the case of 3-pyridylmethyl and 2-pyridylmethyl substrates (entries 4 and 15), the oxidative conversions from alcohols to the expected aldehydes could also be accomplished with high selectivity under addition of a small quantity of acetic acid. Acetic acid was envisioned to serve a specific purpose, namely to neutralize the basic pyridine, to enable the catalyst system to operate well. When air was used in place of pure oxygen and benzylic alcohol was used as the substrate, we obtained equally high isolated yields the reactions varying only in a slightly lower conversion rate (Table 2, entry 18 *vs.* entry 8). Overall, when all the facets of this new oxidation system are considered, the use of inexpensive and green $FeCl_3$ in combination with 4-acetamido-TEMPO and $NaNO_2$ and dioxygen as reagents rendered the oxidation very attractive for potential applications on an industrial scale in the preparation of fine chemicals.

In conclusion, a variety of 4-substituted TEMPOs has been systemically estimated for their ability in alcohol oxidation and specific features of their catalytic activities have been revealed, which should facilitate catalyst design and screening efforts. We have further disclosed that the 4-acetamido-TEMPO/$FeCl_3$/$NaNO_2$ catalyst could selectively oxidize a broad range of primary alcohols, which may be primary aliphatic alcohols or substrates containing carbon-carbon double bonds or N or S heteroatoms, under mild conditions with dioxygen.

Experimental Section

General Conditions

All chemicals were of reagent grade and used as commercially supplied without any purification. ^1H NMR spectra were recorded on a Bruker DRX-400 instrument and were referenced to Me_4Si ($\delta = 0$ ppm) and residual $CHCl_3$ ($\delta = 7.26$ ppm). GC analyses for determining the conversions and selectivities of the reactions were performed on an Agilent 7890N GC system. Experimental procedures and spectroscopic data can be found in the Supporting Information.

General Procedure for the Synthesis of 4-Substituted TEMPOs

Esters: A mixture of 4-OH-TEMPO (1.72 g, 10 mmol), dicyclohexylcarbodiimide (DCC) (2.27 g, 11 mmol), 4-dimethylaminopyridine (DMAP) (0.12 g, 1 mmol), and the reactant acid (10 mmol) in 15 mL of anhydrous CH_2Cl_2 was stirred at room temperature and checked by TLC. After the substrate was consumed, 50 mL H_2O were added, and the mixture was extracted with ethyl acetate (50 mL × 3). The combined organic layer was dried over anhydrous sodium sulfate and concentrated under vacuum to obtain crude product, which was purified by flash chromatography or recrystallization from mixture solvent (petroleum ether and ethyl acetate) to afford the desired product. The structures of the final products were confirmed by IR and MS or GC-MS. The preparation procedure for other TEMPO catalysts can be found in the Supporting Information.

General Procedure for 4-Acetamido-TEMPO-Catalyzed Aerobic Oxidation of Alcohols

The oxidation of alcohols were carried out in a Teflon-lined 316L stainless steel autoclave (300 mL), equipped with a magnetic stirrer .Typically, the alcohol (5.0 mmol) and 4-acetamido-TEMPO were dissolved in dichloroethane (10 mL). Anhydrous $FeCl_3$ (0.25 mmol) was added, followed by $NaNO_2$ (0.40 mmol).The resulting mixture was stirred at an oil-bath temperature of 50 °C and oxygen pressure of 0.4 MPa. The conversion and selectivity of the reaction were directly monitored by GC analyses without any purification. When the reactions were completed, the liquid in the autoclave was transferred to a separatory funnel. The organic phase was washed with saturated aqueous $Na_2S_2O_3$ solution to remove the residual oxidant and 4-acetamido-TEMPO. Then the organic layer was dried over anhydrous Na_2SO_4 and concentrated and further purified by flash chromatography to afford the desired product.

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[12] $FeCl_3$ we used was a domestic commercial reagent, with a purity of >99%. According to atom absorption spectroscopy, the copper content was 0.0061%.