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Base-free copper-catalyzed aerobic oxidation of benzylic alcohols with *N*-benzylidene-*N*,*N*-dimethylthane-1,2-diamine and TEMPO

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ABSTRACT

Selective oxidation of alcohols using *N*-benzylidene-*N*,*N*-dimethylthane-1,2-diamine, CuBr₂ and TEMPO as the catalytic system was developed. Catalyzed by this simple catalytic system in the absence of any external base, various benzylic alcohols could be oxidized to their corresponding aldehydes with excellent yields in CH₃CN/H₂O (v/v = 1/1) under 0.2 MPa O₂ at 80 °C.

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1. Introduction

Oxidation of alcohols to their corresponding carbonyl products is one of fundamental transformations in organic chemistry [1]. Various investigations have showed that 2,2,6,6-tetramethyl-piperidyl-1-oxyl (TEMPO) could efficiently and selectively catalyze the oxidation of alcohols with molecular oxygen [2-4]. Its catalysis always relied on the assistance of various co-catalysts, especially the transition metal compounds [5-7]. Among them, Cu(II) complexes with N-donor ligands, including bipyridine [8,9], 1,10-phenanthroline [10], 2-Narylpyrrolecarbaldimine [11], 3-(2-hydroxy-4-nitrophenylhydrazo) pentane-2,4-dione [12], triethanolamine [13], pyrazole-pyridine [14], DMAP [15], N,N-bis-(2-pyridylmethyl)-1,3-diaminopropan-2-ol [16], 1,4-diazabicyclo[2.2.2]octane [17] and N-alkyldiethanolamine [18], etc., proved to be the prime catalysts. Recently, this Cu/TEMPO system was extended interestingly to the use of bifunctional catalysts bearing both TEMPO and Cu complex moieties in a 1,3,5-triazine ring [19,20]. For these catalytic oxidations, a new mechanism was proposed, in which the key step was the simultaneous coordination of TEMPO and the deprotonated alcohol on the Cu center [10,11,21,22]. However, an additional base was always needed for alcohol deprotonation. So t-BuOK [8,9,14,19,20], NaOH [10,16,23], K₂CO₃[11-13,18], etc., were used in different systems, respectively.

In continuation of our interest in exploring green oxidation methods [24,25], our attention was focused on developing a new Cu/TEMPO system by using simple ligands and also attempting to avoid additional base. It was encouraging to find that in the absence of additional base a three-component catalytic system consisting of *N*benzylidene-*N*,*N*-dimethylthane-1,2-diamine, CuBr₂ and TEMPO could catalyze effectively the selective aerobic oxidation of alcohols under mild conditions. As far as we are aware, the catalytic properties of such Cu complexes for aerobic oxidation of alcohols have not been studied yet. Moreover, it was notable that this type of Schiff base was easily prepared and inexpensive. Herein, the catalytic performance of this catalytic system was investigated.

2. Experimental

2.1. Generals

The chemical reagents used were of analytical grade. Elemental analyses were carried out with a Perkin-Elmer 2400 elemental analyzer. FT-IR spectra were recorded on a PE-SPECTRUM ONE Spectrometer in KBr pellets. ¹H NMR spectra were acquired on a Bruker Biospin-AVANCE III 400 MHz Digital NMR Spectrometer. Mass spectra were collected on a JEOL JMS-SX 102 mass spectrometer. UV spectra were recorded with a PE-lamada-35 spectrophotometer in CH₃CN/ water (1/1). Perkin-Elmer Clarus 500 GC-MS detector equipped with a PE-5MS capillary column was used to identify reaction products. GC measurements were conducted using an Agilent 7890 gas chromatograph equipped with a flame ionization detector and a KB-Wax capillary column. Quantitation



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of components was performed by using acetophenone as an internal standard.

2.2. Synthesis and characterization of ligands and complexes

All ligands were synthesized by condensation reaction of *N*,*N*-dimethylethylenediamine and the corresponding aldehydes [26,27]. Two equivalent ligand (typically, 1.76 g L^1) reacted with CuBr₂ (1.12 g) in 10 mL CH₃CN under refluxing for 3 h to give the deposited corresponding Cu complex, which was collected by filtration, washed by ether, and then vacuum dried. They were characterized by ¹H NMR, IR, Elemental analyses, MS and UV, respectively, and were presented in Fig. 1 where the ligands were described as typified by L^1 , and the complexes as Cu(L^1)₂, respectively.

- $\begin{array}{ll} L^1 & \mbox{Brown oil (yield 90\%). Anal. Calc. (\%): C 74.96, H 9.15, N 15.89; \\ found: C 74.86, H 9.23, N 15.92. IR (cm^{-1}): \nu_{(C=N)} 1628 (s), \\ \nu_{(C-N)} 1332 (s). \ ^{1}\mbox{H NMR} (d-DMSO, ppm): 2.26 (s, 6H, CH_3); \\ 3.39 (t, 2H); 3.63 (t, 2H); 7.29 (d, 1H); 7.61(d, 1H); 8.27 (s, 1H). UV (\lambda, nm): 267, 321. \end{array}$
- $\begin{array}{ll} Cu(L^1)_2 & \mbox{Blue solid (yield 87\%). Mp 151-152 °C. Anal. Calc. (\%): C 45.88, \\ H 5.60, N 9.73; found: C 45.92, H 5.71, N 9.66. IR (cm^{-1}): \\ \nu_{(C = N)} 1604 (s), \nu_{(C N)} 1328 (s), \nu_{(Cu N)} 533 (s). m/z (\%): 416 \\ (20, M^+-1), 239 (48, M^+-L^1), 176 (100, L^1). UV (\lambda, nm): 265, \\ 310, 571. \end{array}$
- $$\begin{split} L^2 & \quad \mbox{Yellow oil (yield 86\%). Anal. Calc. (\%): C 69.87, H 8.80, N 13.58; \\ found: C 69.53, H 8.98, N 13.43. IR (cm^{-1}): \nu_{(C=N)} 1638 (s), \\ \nu_{(C-N)} 1342 (s). \ ^1\mbox{H NMR} (d-DMSO, ppm): 2.18 (s, 6H, CH_3); \\ 3.71 (s, 3H, CH_3); 2.72 (t, 2H); 3.64 (t, 2H); 6.92 (d, 1H); 7.61 (d, 1H); 8.12 (s, 1H). UV (\lambda, nm): 270, 324. \end{split}$$
- $\begin{array}{ll} \mbox{Cu}({\bm L}^2)_2 & \mbox{Blue solid (yield 89\%)}. \mbox{ Mp 160-161 °C. Anal. Calc. (\%): C 45.33, } \\ & \mbox{H 5.71, N 8.81; found: C 45.23, H 5.78, N 8.43. IR (cm^{-1}): } \\ & \mbox{$\nu_{(C=N)}$ 1624 (s), $\nu_{(C-N)}$ 1334 (s), $\nu_{(Cu-N)}$ 542 (s). m/z (\%): 477 (22, M^+-1), 269 (47, M^+-{\bm L}^2), 206 (100, {\bm L}^2). UV (λ, nm]: 269, $315, 582. $ \end{array}$
- $\begin{array}{ll} L^{3} & \mbox{Yellow oil (yield 88\%). Anal. Calc. (\%): C 75.74, H 9.53, N 14.72; \\ found: C 75.58, H 9.68, N 14.41. IR (cm^{-1}): \nu_{(C=N)} 1634 (s), \\ \nu_{(C-N)} 1336 (s). \ ^{1}\mbox{H NMR} (d-DMSO, ppm): 2.17 (s, 6H, CH_3); \\ 2.33 (s, 3H, CH_3); 3.39 (t, 2H); 3.63 (t, 2H); 7.24 (d, 1H); 7.61 \\ (d, 1H); 8.28 (s, 1H). UV (\lambda, nm): 268, 323. \end{array}$
- $\begin{array}{ll} \text{Cu}(\boldsymbol{L^3})_2 & \text{Blue solid (yield 84\%). Mp 159-160 °C. Anal. Calc.: C 47.73; H} \\ & \text{6.01; N 9.28; found: C 47.52, H 6.23, N 9.41. IR (cm^{-1}): } \\ & \nu_{(C=N)} \\ & \text{1623 (s), } \nu_{(C-N)} \\ & \text{1328 (s), } \nu_{(Cu-N)} \\ & \text{538 (s). } m/z \ (\%): \\ & \text{444 (20, M^+-1), 253 (50, M^+-L^3), 190 (100, L^3). UV (\lambda, nm): 267, 314, 580.} \end{array}$
- Cu(**L**⁴)₂ Blue solid (yield 86%). Mp 135–136 °C. Anal. Calc. (%): C 40.98, H 4.69, N 8.69; found: C 40.82, H 4.53, N 8.85. IR (cm⁻¹):



Fig. 1. Schematic structures of Cu(L)₂ complexes.

 $\nu_{(C=N)}$ 1608 (s), $\nu_{(C-N)}$ 1339 (s), $\nu_{(Cu-N)}$ 547 (s). m/z (%): 485 (20, M^+-1), 275 (49, M^+- L^4), 212 (100, L^4). UV (λ , nm): 270, 312, 585.

2.3. Oxidation experiments

Typically, benzyl alcohol (3 mmol), TEMPO (0.09 mmol), CuBr₂ (0.06 mmol), L^1 (0.12 mmol) and CH₃CN/H₂O (v/v = 1/1, 6 mL) were added into a 70-mL Teflon-lined stainless-steel reactor. After the air was replaced with O₂ for three times, the reactor was heated to 80 °C under stirring, and then charged by 0.2 MPa O₂. After reaction ended, the reaction mixture was cooled to room temperature, and extracted with ethyl acetate. The organic phase was measured by GC analysis.

3. Results and discussion

3.1. Comparison of the activities of catalysts

The oxidation of benzyl alcohol in CH₃CN/H₂O (v/v = 1/1) was chosen as a model reaction to test initially the catalytic potential of the Cu(**L**)₂ s (Table 1). As could be seen, all of *pre*-made Cu(**L**)₂ s in combination with TEMPO gave above 83% conversions in 2 h, and benzaldehyde was the sole product (entries 1–5). In particular, Cu (**L**¹)₂ realized a complete transformation. Since the Cu(**L**)₂ s could be easily prepared just by heating CuBr₂ and **L**s, CuBr₂ and **L**s were directly employed in the oxidation, which realized approximate conversions to those of the *pre*-made Cu(**L**)₂ s under the same conditions (entries 6–10). It was reasonably thought that Cu(**L**)₂ s could be *in situ* formed during the oxidations when CuBr₂ and **L**s were used directly.

 Table 1

 Oxidation of benzyl alcohol using different Cu catalysts ^a.

Entry	Catalyst	Conv. (%)
1	$Cu(L^1)_2$	100
2	$Cu(\mathbf{L}^2)_2$	86
3	$Cu(L^3)_2$	99
4	$Cu(L^4)_2$	93
5	$Cu(L^5)_2$	83
6	$CuBr_2 + L^1$	100
7	$CuBr_2 + L^2$	95
8	$CuBr_2 + L^3$	99
9	$CuBr_2 + L^4$	94
10	$CuBr_2 + L^5$	85
11	CuBr ₂	<1
12	L ¹	2
13 ^b	$CuBr_2 + L^1$	4
14 ^b	$Cu(L^1)_2$	<1
15 ^c	$CuBr_2 + L^1$	98
16 ^d	$CuBr_2 + L^1$	35, 100 ^e

^a Reaction conditions: 3 mmol benzyl alcohol, 3 mol% TEMPO, 2 mol% Cu(L)₂ or the combination of 2 mol% CuBr₂ and 4 mol%L, 3 mL CH₃CN, 3 mL H₂O, 80 °C, 0.2 MPa O₂, 2 h.

^b TEMPO-free.

c with 2 mmol K₂CO₃.

 $^{\rm d}\,$ Air instead of ${\rm O_2}.$

e for 12 h.

L

In sharp contrast, the reaction occurred barely in the absence of any component (entries 11–14), displaying that all three components were indispensable. Moreover, both L^2 bearing a strong electron-donating substituent and L^5 bearing a strong electron-withdrawing substituent gave relatively low conversions (entries 2, 5, 7, 10), showing the substituents in the ligands had no obvious electronic effects on their catalytic activities.

In general, the Cu/TEMPO system needs an additional base for better activity. Actually, in the presence of K_2CO_3 our oxidation realized 98% conversion (entry 15). S. Mannam et al. found that when 1,4-diazabicyclo[2.2.2]octane was used as the ligand, the conversion of the oxidation of alcohol without any base was similar to the data of using K_2CO_3 as a base [17]. They assumed that the ligand might display dual roles: as a base to deprotonate the hydroxy and as an *N*donor ligand to coordinate Cu. So it might be supposed that the amino group of **L**s had adequate basicities for deprotonation, and the oxidation could occur without any external base.

In addition, when air was used as the oxidant instead of O_2 , only 35% benzyl alcohol converted under the same conditions, however, a complete conversion was obtained by prolonging time to 12 h (entry 16). This implied that for the present system the efficient oxidation relied on the considerable concentrations of O_2 in the reaction solution.

3.2. Influence of the solvent

The oxidations of the Cu/TEMPO systems reported before were conducted in various solvents, in particular CH₃CN/H₂O (2/1) [8,9,16,19,20]. And the solvent showed obvious influences on the activities. When pyrazole-pyridine was used as ligand, H₂O led to precipitation of the Cu catalysts and thus the oxidation was retarded, whereas a much higher conversion was obtained in neat CH₃CN [14]. In contrast, for the oxidation in water using 2-N-arylpyrrolecarbaldimine as ligand, even small amounts of organic solvents, such as CH₃CN, EtOH, MeOH, or CH₃COCH₃, could deactivate the catalytic system [11]. Hence, in order to explore which solvent would be suitable for the present Cu/L¹/TEMPO, different solvent pairs were studied (Table 2). The results showed that the rate of CH₃CN and H₂O influenced the catalytic activity, and the preferable ratio was 1/1 (entry 2). However, no matter whether neat CH₃CN or H₂O was used as solvent, the oxidations slowly took place (entries 3 and 4). The external tests indicated that the *pre*-made $Cu(L^1)_2$ was dissoluble in H₂O but less dissoluble in CH₃CN, whereas benzyl alcohol was miscible in CH₃CN but less dissoluble in H₂O. These meant that a more homogeneous reaction system was obtained and the oxidation proceeded faster when CH₃CN/H₂O (1/1) was used. Interestingly, using methanol, ethanol or acetone as cosolvents with the ratio from

Table 2	
Oxidation of benzyl alcohol with Cu(L ¹) ₂ /TEMPO in different solvent ^a .	

Entry	Solvent (v/v)	Conv. (%)
1	Acetonitrile/Water (2/1)	81
2	Acetonitrile/Water (1/1)	100
3	Acetonitrile/Water (1/2)	94
4	Acetonitrile	32
5	Water	59
6	Methanol/Water (1/1)	92
7	Methanol/Water (1/2)	81
8	Methanol/Water (2/1)	87
9	Ethanol/Water (1/1)	90
10	Ethanol/Water (2/1)	94
11	Ethanol/Water (1/2)	94
12	Acetone/Water (1/1)	96
13	Acetone/Water (1/2)	95
14	Acetone/Water (2/1)	81

^a The reaction conditions were as described in Table 1.

2/1 to 1/2, the oxidation of benzyl alcohol achieved moderate or excellent conversions (entries 6–14). The decrease of catalytic activity, as previously reported [11], was not observed.

3.3. Effect of temperature

Fig. 2 displayed the influence of reaction temperature on catalytic activity of Cu/L¹/TEMPO. The conversions were found to have corresponding responses with the rise of temperatures. At ambient temperature, only 44% of benzyl alcohol was oxidized. The conversion could be up to 78% when the temperature was increased to 50 °C. The preferable temperature was 80 °C, which resulted in 100% conversion. Moreover, according to GC-MS analysis, no overoxidation occurred as benzoic acid was not identified in all cases.

3.4. Oxidation of various alcohols

Cu/L¹/TEMPO was further employed to catalyze the aerobic oxidation of various alcohols in CH₃CN/H₂O (1/1) (Table 3). It was notable that the corresponding carbonyl compounds were the sole products in all cases. As could be seen, cinnamyl alcohol and all primary benzylic alcohols with either electron-donating or electronwithdrawing substituents could be oxidized efficiently to the corresponding aldehydes with excellent conversions (entries 2-9). However, in the series of the methoxy-substituented benzyl alcohols, the *p*-substituted one gave the lowest conversion (83%) (entries 2–4). This phenomenon was also found in the oxidation using 2-Narylpyrrolecarbaldimine as ligand before [11]. In conjunction with the relatively low conversions of other *p*-substituted benzylic alcohols, such as *p*-methylbenzyl alcohol, *p*-chlorobenzyl alcohol and *p*-nitrobenzyl alcohol, the author proposed that the influence of the remote *p*-substituent appeared to be more related to steric effects than electronic ones. When $Cu/L^1/TEMPO$ was employed, the complete oxidation of *p*-chlorobenzyl alcohol was achieved (entry 5). Meanwhile, the conversion of *p*-methylbenzyl alcohol was even higher than that of *m*-methylbenzyl alcohol (entries 6–7). It could be suggested that the reactivity of benzylic alcohols had unobvious relationships with both steric and electronic effects of the substituents when Cu/L¹/TEMPO was used. However, aliphatic alcohols could not be oxidized effectively, which was similar to the previous Cu/TEMPO systems [8-18].



Fig. 2. Oxidation of benzyl alcohol at a different temperature. The reaction conditions were as described in Table 1.

Table	3
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Aerobic oxidation of va	rious alcohols b	$y Cu(L^1)$) ₂ /TEMPO ^a .
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Entry	Alcohol	Product	Conv. (%)
1	Benzyl alcohol	Benzaldehyde	100
2	o-Methoxylbenzyl alcohol	o-Methoxylbenzaldehyde	95
3	m-Methoxylbenzyl alcohol	m-Methoxylbenzaldehyde	99
4	p-Methoxylbenzyl alcohol	p-Methoxylbenzaldehyde	83
5	p-Chlorobenzyl alcohol	p-Chlorobenzaldehyde	100
6	m-Methylbenzyl alcohol	<i>m</i> -Methylbenzaldehyde	88
7	p-Methylbenzyl alcohol	p-Methylbenzaldehyde	93
8	p-Nitrobenzyl alcohol	p-Nitrobenzaldehyde	92
9	Cinnamyl alcohol	Cinnamaldehyde	97
10	1-Octanol	1-Octanal	9
11	Cyclohexanol	Cyclohexanone	7

^a The reaction conditions were as described in Table 1.

4. Conclusion

In summary, a new catalytic system consisting of L^1 , CuBr₂ and TEMPO was developed for the efficient aerobic oxidation of various benzylic alcohols to their corresponding aldehydes under mild conditions. The CH₃CN/H₂O (1/1) was the preferable solvent. Interestingly, unlike most of the previously reported Cu/TEMPO systems, $Cu/L^{1}/L^{1}$ TEMPO could perform well without any external base. The easy synthesis of L¹ makes the present system an attractive candidate for oxidation of benzylic alcohols.

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