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Aerobic, Chemoselective Oxidation of Alcohols to Carbonyl Compounds Catalyzed by a DABCO-Copper Complex under Mild Conditions

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This paper is dedicated to Prof. Dr. Dr. h.c. Lutz F. Tietze on the occasion of his 65th birthday.

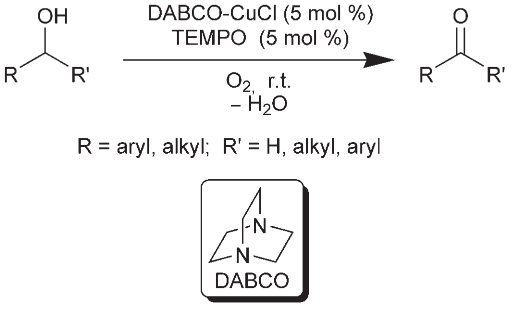
Abstract: A DABCO-copper(I) chloride complex (5 mol%) together with TEMPO (5 mol%) in nitromethane as solvent has been used as an efficient catalytic system for the selective oxidation of benzylic and allylic alcohols into the corresponding carbonyl compounds at room temperature where molecular oxygen acts as an ultimate, stoichiometric oxidant and water is the only by-product. The solid-state structure determination of the DABCO-copper complex shows that the copper is in the +II oxidation state with trigonal bipyramidal geometry and exists in a linear polymeric structure due to strong hydrogen bonding.

Keywords: aerobic oxidation; alcohols; aldehydes; copper catalyst; diamine ligand; ketones

The selective oxidation of alcohols is a fundamental transformation in organic synthesis.[1] In particular, the conversion of primary alcohols to aldehydes is crucial in the total synthesis of natural products and fine chemicals such as fragrances or food additives.[2] A variety of reagents has been developed to achieve this oxidation process which is testimony for the importance of this reaction. Unfortunately, these reagents turned out to involve stoichiometric or super-stoichiometric amounts of toxic or hazardous oxidizing agents such as CrO_3, $KMnO_4$, MnO_2, SeO_2, etc.[3] So a catalytic oxidation process is thus extremely useful from economic and environmental points of view, and those employing molecular oxygen or air as stoichiometric oxidant are particularly attractive. In the last decade several transition metal salts such as Cu,[4] Co,[5] V,[6] Pd,[7] Ru,[8] Rh,[9] and Mo[10] have been used as catalyst for the oxidation of alcohols together with molecular oxygen.

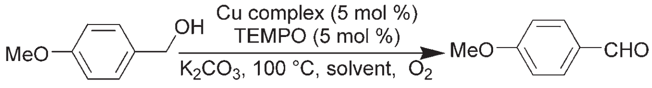
Among the above-mentioned metal salts, Cu is more attractive as it is a biomimetic functional model of the mononuclear copper enzyme galactose oxidase.[11] As copper salt alone is an inefficient catalyst, a variety of ligands is used with copper salts to increase the catalytic activity.[12] Unfortunately, most of these Cu complexes need higher temperature and an external base for efficient oxidation.[13] In this communication, we report an oxidation reaction that can be performed under very mild conditions (room temperature) in the presence of commercially available, inexpensive 1,4-diazabicyclo[2.2.2]octane (DABCO) as ligand with CuCl without use of an external base, where molecular oxygen acts as an ultimate, stoichiometric oxidant and water is the only by-product (Scheme 1).

To find the optimal conditions for the alcohol oxidation, 4-methoxybenzyl alcohol was dehydrogenated under various conditions and the results are summarized in Table 1. Initially, commercially available nitrogen-containing ligands such as 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), DABCO and (−)-sparteine were used with CuCl and the DABCO-CuCl complex provided the highest yield for the oxidized product (entry 3). A variety of copper salts was screened with DABCO in



Scheme 1. DABCO-Cu complex-catalyzed oxidation of alcohols.

Table 1. Optimizing the oxidation of 4-methoxybenzyl alcohol.



Entry	Ligand	Cu salt	Solvent	Time [h]	Yield [%][a]
1	DBN	CuCl	Toluene	4	69
2	DBU	CuCl	Toluene	12	51
3	DABCO	CuCl	Toluene	2	84
4	(-)-sparteine	CuCl	Toluene	12	53
5	DABCO	$Cu(ClO_4)_2 \cdot 6\,H_2O$	Toluene	24	52
6	DABCO	$CuCl_2 \cdot 2\,H_2O$	Toluene	20	59
7	DABCO	$Cu(OAc)_2 \cdot H_2O$	Toluene	20	30
8	DABCO	$CuSO_4 \cdot 5\,H_2O$	Toluene	20	38
9	DABCO	$Cu(OTf)_2$	Toluene	7	78
10	DABCO	CuI	Toluene	20	22
11	DABCO	$CuNO_3 \cdot 3\,H_2O$	Toluene	20	35
12	DABCO	CuCl	benzene	24	40
13	DABCO	CuCl	CH_2Cl_2	24	42
14	DABCO	CuCl	xylene	3	74
15	DABCO	CuCl	THF	24	60
16	DABCO	CuCl	EtOAc	24	60
17	**DABCO**	**CuCl**	**Toluene**	**2**	**89**[b]
18	DABCO	CuCl	Toluene	2	00[c]
19	----	----	Toluene	24	02
20	----	CuCl	Toluene	24	09

[a] Isolated yield.
[b] Without K_2CO_3.
[c] Without TEMPO.

toluene at 100 °C and DABCO-CuCl turned out to be the best Cu complex in terms of reaction rate and conversion (entry 3). Then the reaction was carried out in several organic solvents and toluene became the first choice of solvent (entry 17).

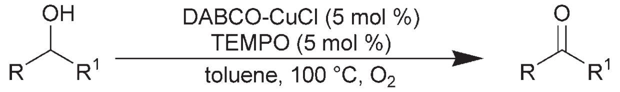
There was almost no reaction when the DABCO-CuCl complex was not used (entry 19). Without DABCO the reaction gave only 9% yield (entry 20). So it is clear that the CuCl alone is not an active catalyst and DABCO is needed to increase its catalytic activity. Similarly, the oxidation reaction did not provide any oxidized product when the reaction was carried out without TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxyl free radical) (entry 18). Although the exact role of TEMPO is unclear, we assume that the TEMPO might act as a hydrogen acceptor during the catalytic cycle. In general, the Cu complex needs an external base for better activity. In contrast to this observation, the yield was increased from 84% to 89% when K_2CO_3 was not used (entry 17 *vs.* 3). We assume that the DABCO might have dual roles: as a base to deprotonate the hydroxy group and as an N-donor ligand to CuCl.

To probe the efficiency of the DABCO-CuCl catalyst, a series of alcohols was oxidized to the corresponding carbonyl compounds under the optimized condition and the results are summarized in Table 2. It is clear that all the primary alcohols have been selectively oxidized to aldehydes and over-oxidized carboxylic acids were not observed. The reaction was faster for the benzylic primary alcohols and allylic primary alcohols but it took only a slightly longer time for benzylic secondary alcohols. In the case of aliphatic alcohol the reaction takes an even longer time (entry 16).

The DABCO-Cu catalytic system can be used for selective oxidation of one alcohol over another (Table 3). When a mixture of 4-methoxybenzyl alcohol and 1-phenylethanol (1 mmol each) was reacted with molecular oxygen in the presence of 5 mol% catalytic system for 2 h, 4-methoxybenzyl alcohol was fully consumed (85% isolated yield) and only 9% of acetophenone was isolated from the 1-phenylethanol oxidation (Table 3; entry 1). Similarly, when a mixture of 4-methoxybenzyl alcohol and *trans*-cinnamyl alcohol (1 mmol each) was oxidized, 4-methoxybenzyl alcohol was selectively oxidized (entry 2). The cinnamyl alcohol was fully converted to corresponding aldehyde in the presence of 1-phenylethanol whereas the secondary alcohol was fully recovered as unreacted material (entry 3). Similarly, the competing reaction between 4-methoxybenzyl alcohol and 1-octanol showed complete consumption (87% isolated yield) for 4-methoxybenzyl alcohol but 1-octanol was left intact (entry 4). Interestingly, when both the primary and secondary benzylic alcohols are present in the same molecule, only the primary alcohol was selectively oxidized and the secondary alcohol was left intact and the reaction produced the corresponding aldehyde with 81% yield (entry 5). The reactivity of the alcohols is as follows: benzylic primary alcohols > allylic primary alcohols > benzylic secondary alcohols > aliphatic alcohols. These results clearly demonstrate the excellent selectivity of the DABCO-CuCl complex as an efficient catalyst in the aerobic oxidation of alcohols providing considerable advantages for synthetic organic chemistry.

If we consider the DABCO-Cu complex, both the nitrogen atoms of one DABCO molecule cannot coordinate with one copper atom since the lone pair of electrons of both the nitrogens are 180° away from each other. So we assume that the DABCO-Cu complex may be a dimer or an oligomer where two copper atoms are linked through a DABCO molecule as bridge.[14] The X-ray single crystal analysis of the DABCO-Cu complex $[(DABCO)_2CuCl_2 \cdot HCl]$ shows that copper exists in the Cu(II) oxidation state and that two DABCO molecules are coordinated to Cu(II) using one nitrogen atom of each (Figure 1). The complex crystallizes in a rhombohedral crystal system with space group *R*32 and with unit cell dimensions $a = 10.6777(2)$ Å, $b = 10.6777(2)$ Å, $c = 12.0487(2)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$. The Cu(II) center has a perfect trigonal bipyramidal geometry (TBP). Copper and three chlorine atoms lie in one plane. The Cl−Cu−Cl bond angle is 120°, the Cl−Cu−N bond angle is 90°, and the N−Cu−N bond angle is

Table 2. Oxidation of alcohols using the DABCO-CuCl complex.[a]



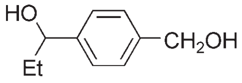
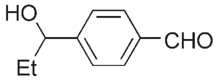
Entry	Alcohols	Products	Time [h]	Yield [%][b]
1	$C_6H_5CH_2OH$	C_6H_5CHO	02	85
2	*o*-Cl-$C_6H_4CH_2OH$	*o*-Cl-C_6H_4CHO	02	96
3	*p*-Cl-$C_6H_4CH_2OH$	*p*-Cl-C_6H_4CHO	02	87
4	*p*-OMe-$C_6H_4CH_2OH$	*p*-OMe-C_6H_4CHO	02	89
5	3,4,5-$(OMe)_3C_6H_2CH_2OH$	3,4,5-$(OMe)_3C_6H_2CHO$	02	98
6	$C_6H_5CH{=}CHCH_2OH$	$C_6H_5CH{=}CHCHO$	03	84
7	$C_6H_5CH(OH)CH_3$	$C_6H_5COCH_3$	24	69
8	$C_6H_5CH(OH)C_6H_5$	$C_6H_5COC_6H_5$	24	66
9	*p*-Cl $C_6H_4CH(OH)C_6H_5$	*p*-Cl-$C_6H_4COC_6H_5$	24	85
10	*p*-OMe-$C_6H_4CH(OH)C_6H_5$	*p*-OMe-$C_6H_4COC_6H_5$	24	78
11	*o*-OH-$C_6H_4CH_2OH$	*o*-OH-C_6H_4CHO	02	85
12	*o*-NO_2-$C_6H_4CH_2OH$	*o*-NO_2-C_6H_4CHO	02	92
13	*p*-OMe-$C_6H_4CH(OH)CH_3$	*p*-OMe-$C_6H_4COCH_3$	24	90
14	*m*-NO_2-$C_6H_4CH_2OH$	*m*-NO_2-C_6H_4CHO	02	91
15	*p*-NO_2-$C_6H_4CH(OH)CH_3$	*p*-NO_2-$C_6H_4COCH_3$	24	51
16	$CH_3(CH_2)_6CH_2OH$	$CH_3(CH_2)_6CHO$	72	20
17	furfuryl alcohol	furfuryl aldehyde	02	88
18	4-(hydroxymethyl)-2-methoxyphenol	4-hydroxy-3-methoxybenzaldehyde	10	56
19	1,4-phenylenedimethanol	terephthalaldehyde	02	81[c]
20	(2-amino-5-chlorophenyl)-(phenyl)methanol	(2-amino-5-chlorophenyl)-(phenyl)methanone	24	58

[a] In all the cases, the primary alcohols were selectively oxidized to corresponding aldehydes and over oxidized carboxylic acids were not observed. All the products gave satisfactory spectral data.

[b] Isolated yield.

[c] 10 mol% of catalyst was used.

Table 3. Selective oxidation of alcohols by the DABCO-CuCl complex in toluene.[a]

Entry	Alcohols	Products	Time [h]	Yield [%][b]
1	4-methoxybenzyl alcohol + 1-phenyl ethanol	4-methoxybenzaldehyde + acetophenone	2	85 09
2	4-methoxybenzyl alcohol + cinnamyl alcohol	4-methoxybenzaldehyde + cinnamaldehyde	1	72 05
3	cinnamyl alcohol + 1-phenyl ethanol	cinnamaldehyde + acetophenone	2	68 00
4	4-methoxybenzyl alcohol + 1-octanol	4-methoxybenzaldehyde + 1-octanal	2	87 00
5			2	81

[a] 1 mmol each of both the alcohols were treated with 5 mol% of DABCO-CuCl, 5 mol% of TEMPO in toluene at 100 °C.

[b] Isolated yield.

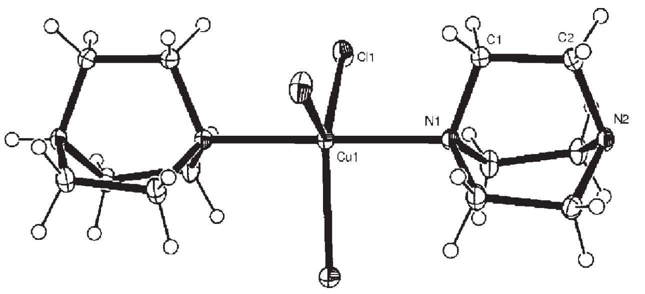


Figure 1. Solid-state structure determination of the DABCO-Cu complex (30% probability; CCDC No.: 633455).

180°. The three Cu–Cl distances are equivalent with a bond distance of 2.377 Å. The Cu–N bond distance is 2.120 Å. Out of the two DABCO molecules attached to copper, one nitrogen is with tetrahedral geometry due to protonation and the other nitrogen is having pyramidal geometry and a proton of one DABCO molecule is linked to the nitrogen of the other DABCO through a strong H-bond resulting in the crystal packing in the form of a linear polymer (Figure 2). The hydrogen bond length between N···H is 1.76 Å which is shorter than the typical hydrogen bond length of 2.4 Å. Because of this strong hydrogen bonding the Cu-DABCO complex is stable.

Since the DABCO-Cu complex exists in linear polymeric structure due to strong intermolecular hydrogen bonding, we thought that if we break the intermolecular hydrogen bond by a polar solvent, the DABCO-Cu complex may exist in monomeric form and its catalytic activity will be enhanced, thus the reaction may be carried out at room temperature. Also, in monomeric form one nitrogen atom of the DABCO-Cu complex (the nitrogen which is not protonated) will be free from hydrogen bonding and will be able to act as internal base to deprotonate the alcohol molecule. To check this assumption, we tried the reaction using polar solvents such as CH_3CN, DMSO, DMF, 1,4-dioxane and nitromethane and the results are summarized in Table 4. Surprisingly, as per our prediction the reaction took place at room temperature in polar solvents. The reaction was faster in

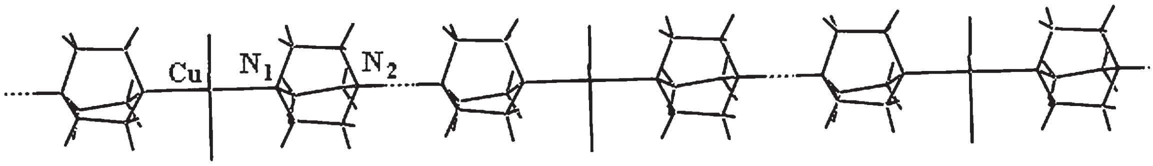
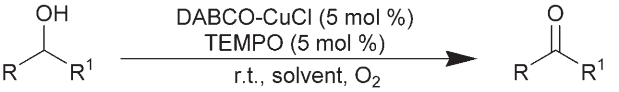


Figure 2. Linear polymeric structure of the DABCO-Cu complex due to strong intermolecular hydrogen bonding.

Table 4. DABCO-CuCl-catalyzed oxidation of alcohols at room temperature in nitromethane.



Entry	Alcohols	Products	Solvent	Time [h]	Yield [%][a]
1	p-OMe-$C_6H_4CH_2OH$	p-OMe-C_6H_4CHO	CH_3CN	5	59
2	p-OMe-$C_6H_4CH_2OH$	p-OMe-C_6H_4CHO	DMSO	5	64
3	p-OMe-$C_6H_4CH_2OH$	p-OMe-C_6H_4CHO	DMF	2	84
4	p-OMe-$C_6H_4CH_2OH$	p-OMe-C_6H_4CHO	1,4-dioxane	4	51
5	p-OMe-$C_6H_4CH_2OH$	p-OMe-C_6H_4CHO	CH_3NO_2	5	93
6	p-OMe-$C_6H_4CH_2OH$	p-OMe-C_6H_4CHO	CH_3NO_2	24	0[b]
7	p-OMe-$C_6H_4CH_2OH$	p-OMe-C_6H_4CHO	CH_3NO_2	24	0[c]
8	p-OMe-$C_6H_4CH_2OH$	p-OMe-C_6H_4CHO	CH_3NO_2	5	24[d]
9	$C_6H_5CH_2OH$	C_6H_5CHO	CH_3NO_2	5	92
10	3,4,5-trimethoxy-$C_6H_2CH_2OH$	3,4,5-trimethoxy-C_6H_2CHO	CH_3NO_2	4	94
11	p-Cl-$C_6H_4CH_2OH$	p-Cl-C_6H_4CHO	CH_3NO_2	8	78
12	p-NO_2-$C_6H_4CH_2OH$	p-NO_2-C_6H_4CHO	CH_3NO_2	5	89
13	$C_6H_5CH{=}CH$-CH_2OH	$C_6H_5CH{=}CH$-CHO	CH_3NO_2	10	80
14	furfuryl alcohol	furfuraldehyde	CH_3NO_2	10	87

[a] Isolated yield.
[b] Without CuCl and TEMPO.
[c] Without TEMPO.
[d] Without DABCO.

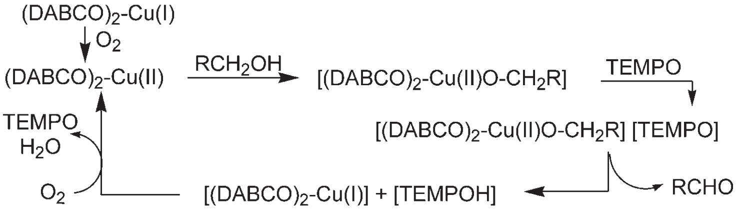


Figure 3. Proposed catalytic cycle for the oxidation of alcohols using DABCO-CuCl-TEMPO complex.

DMF and gave 84% yield in just 2 h. Nitromethane gave the highest isolated yield of 93% in 5 h at room temperature. Highest yield and easy work-up procedure in nitromethane encouraged us to expand its scope with other alcohols. In all the cases, the reaction took place at room temperature in shorter time with excellent yields (entries 9–14). The procedure is very simple, and it has to be noted that the reaction is performed directly under oxygen atmosphere by using O_2 balloon and bubbling of oxygen is not necessary.

Based on our experimental results and the solid state structure determination of DABCO-Cu complex, we are proposing the catalytic cycle as shown in Figure 3.[15] However, studies on the full scope of the DABCO-Cu complex as catalyst in alcohol oxidation, detailed mechanistic studies, increasing the catalyst's activity towards aliphatic alcohol oxidation and the chiral version of this oxidation (non-enzymatic kinetic resolution) using chiral Cu complex are under progress.

In conclusion, we have developed a new catalytic system (5 mol% of DABCO-CuCl-TEMPO in nitromethane) for the aerobic, selective oxidation of alcohols to corresponding carbonyl compounds with excellent yield under very mild conditions. In all the cases, the primary benzylic and allylic alcohols were selectively oxidized to corresponding aldehydes and over oxidized products carboxlylic acids were not observed. Solid state structure determination of DABCO-Cu complex shows that the Cu is in the Cu(II) oxidation state with TBP geometry and exists in a linear polymeric structure due to strong hydrogen bonding. We have increased the catalytic activity of DABCO-Cu complex by using nitromethane, and thus we could accomplish the oxidation reaction at room temperature with very good yield.

Experimental Section

General Remarks

All oxidation reactions were performed under oxygen atmosphere using an oxygen balloon. All the solvents (used in Table 1) were obtained from Merck, India and dried by Vogel's procedure. Reactions were monitored by TLC plates (silica gel 60 F_{254}, obtained from Merck) using appropriate mixture of ethyl acetate and hexane. Product purification was done by silica gel (100–200 mesh) column chromatography and hexane and ethyl acetate mixture as eluent. $Cu(OTf)_2$, CuI, DABCO, DBN, DBU, (−)-sparteine, TEMPO, *p*-methoxybenzyl alcohol, 3,4,5-trimethoxybenzyl alcohol, cinnamyl alcohol, 1-phenylethanol, furfuryl alcohol, and *p*-nitrobenzyl alcohol were obtained from Aldrich chemicals. Benzyl alcohol, *o*-chlorobenzyl alcohol, *p*-chlorobenzyl alcohol, and *n*-octanol were obtained from SRL chemicals, India. *o*-Hydroxybenzyl alcohol, *o*-nitrobenzyl alcohol, *m*-nitrobenzyl alcohol, benzhydrol, (4-chlorophenyl)-(phenyl)methanol, (4-methoxyphenyl)(phenyl)methanol, 1-(4-methoxyphenyl)ethanol, 1-(4-nitrophenyl)ethanol, 4-(hydroxymethyl)-2-methoxyphenol and (2-amino-5-chlorophenyl)(phenyl)methanol were prepared from corresponding carbonyl compounds by reduction using $LiAlH_4$ or $NaBH_4$. 1-(4-(Hydroxymethyl)phenyl)propan-1-ol was synthesized from terephthalic acid. All the products were fully characterized by ^{1}H and ^{13}C NMR, IR, and mass spectroscopy.

Typical Experimental Procedure in Nitromethane at Room Temperature

A mixture of CuCl (4.95 mg, 0.05 mmol) and DABCO (5.7 mg, 0.05 mmol) in 2 mL of nitromethane was stirred at room temperature for 10 min, TEMPO (7.82 mg, 0.05 mmol) was added to the reaction mixture. After stirring for 5 min 4-methoxybenzyl alcohol (138 mg, 1 mmol) was added and stirred for 5 h at room temperature under O_2 atmosphere (using balloon). After completion of reaction (followed by TLC), the reaction mixture was concentrated and the resulting residue was directly purified by silica gel column chromatography (hexane-ethyl acetate) to obtain corresponding pure aldehyde; yield: 126.5 mg (93%); $R_f=0.69$ (20% ethyl acetate in hexane); IR (neat): $\nu=1690$ cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=9.79$ (s, 1H), 7.7 (d, $J=8.65$ Hz; 2H), 6.9 (d, $J=8.64$ Hz; 2H), 3.8 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta=190.7$, 164.6, 131.9, 130, 114.3, 55.5; HR-MS: $m/z=137.0602$, calcd mass: 137.0603 (M^+).

Typical Experimental Procedure in Toluene at 100 °C

A mixture of CuCl (4.95 mg, 0.05 mmol) and DABCO (5.7 mg, 0.05 mmol) in 2 mL toluene was stirred at room temperature for 10 min, then TEMPO (7.82 mg, 0.05 mmol) was added to the reaction mixture. After stirring for 5 min, 4-methoxybenzyl alcohol (138 mg, 1 mmol) was added and then heated to 100 °C under an O_2 atmosphere (using O_2 balloon) for two hours. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate, washed with dilute HCl followed by water. The organic layer was dried over sodium sulfate, concentrated and the resulting residue was purified by silica gel column chromatography (hexane-ethyl acetate) to give the aldehyde; yield: 121 mg (89%).

Synthesis of the DABCO-Cu Complex

To a solution of CuCl (9.9 mg, 0.1 mmol) in acetonitrile (10 mL), DABCO (11.3 mg, 0.1 mmol in 10 mL acetonitrile) was added. The resulting solution was slightly warmed to give clear solution. The reaction mixture was filtered through Whatman filter paper. The filtrate was kept at room temperature for slow evaporation which gave slightly green-colored needle-like crystals whose solid state structure determination shows that the copper is in the Cu(II) oxidation state with the molecular formula [(DABCO)$_2$CuCl$_2$·HCl].

Crystallographic data: $C_{12}H_{25}Cl_3CuN_4$, $M=395.25$, rhombohedron, $a=10.6777(2)$ Å, $\alpha=90°$, $b=10.6777(2)$ Å, $\beta=90°$, $c=12.0487(2)$ Å, $\gamma=120°$, $V=1189.67(4)$ Å^3, $T=293(2)$ K, space group $R32$, $Z=3$, $\mu=1.878$ cm, $R_{\text{int}}=0.0215$ (for 3006 measured reflections), $R1=0.0208$ [for 1032 unique reflections with $I>2\sigma(I)$], $wR2=0.0470$; CCDC No: 633455.

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[13] There are only very few reports for Cu complex-catalyzed oxidations of alcohols at room temperature. In these reports, they have used ionic liquid,[12d] an external base such as *t*-BuOK[12f] or DABCO[12b] is used.

[14] Since the lone pair electrons of both the nitrogens in DABCO are 180° away from each other, it gives binuclear or polynuclear complex. For a similar kind of Cu-DABCO complex structure, see: J. K. Clegg, J. K. Gloe, M. J. Hayter, O. Kataeva, L. F. Lindoy, B. Moubaraki, C. J. McMurtrie, K. S. Murray, D. Schilter, *Dalton Trans.* **2006**, 3977–3984.

[15] Formation of the copper alkoxide with an alcohol will be easier for Cu(II) than for Cu(I) as Cu(II) is a stronger Lewis acid. Similarly, if Cu(I) is the catalyst, it will be reduced to Cu(0) during the course of the catalytic cycle and reoxidized to Cu(I) which is not facile under the reaction conditions. If Cu(II) is the catalyst, it will be reduced to Cu(I) during the reaction and Cu(I) will be easily oxidized back to Cu(II) under the reaction conditions. So we assumed that, in this reaction, Cu(I) is getting oxidized to Cu(II) in the presence of O_2 during the initial stage. This phenomenon is also supported by the X-ray crystal structure of the DABCO-Cu complex.