Catal Lett (2008) 125:52–56
DOI 10.1007/s10562-008-9486-5

Catalytic Oxidation of Alcohols by a Novel Copper Schiff Base Ligand Derived from Acetylacetonate and L-Leucine in Ionic Liquids

Meizhu Rong · Chong Liu · Jinyu Han · Wenbo Sheng · Yufei Zhang · Hua Wang

Received: 14 December 2007 / Accepted: 14 April 2008 / Published online: 17 June 2008

Abstract A selective oxidation of alcohols to corresponding carbonyl compounds in room temperature ionic liquid (IL) [bmim]BF4 was achieved by using novel amino acid Schiff base copper ligand. The catalytic system can be recycled and reused for five runs without any significant loss of catalytic activity.

Keywords Oxidation · Ionic liquid · Schiff base · Amino acid · Catalysis

1 Introduction

Oxidation of alcohols to the corresponding carbonyl compounds is one of the important reactions in the organic chemistry both at the laboratory and industry [1]. Traditionally, this transformation is performed with stoichiometric, toxic and expensive inorganic oxidizing agents (i.e., $KMnO_4$, Cr(VI) compounds, HNO_3, etc.) and in organic solvents which are of volatility, toxicity, and flammability [2]. Moreover, purification of the reaction products is often demanding and laborious. Due to the industrial importance of this process and the ever-growing environmental concerns. The development of effective, greener catalytic systems that use inexpensive oxidants is an important challenge.

As one of the alternative approaches for tackling these problems, ambient temperature ionic liquids (ILs) have been employed as the promising alternative green solvents for the above reactions because of their solvating ability, negligible vapor pressure, easy recyclability and reusability. Over the last several years, many transition metals such as palladium [3], ruthenium [4], manganese [5], tungsten [6], rhenium [7], iron [8] and vanadium [9] have been used as catalysts for alcohol oxidation with ILs as green solvents [10].

The Schiff base transition metal complexes are attractive oxidation catalysts because of their cheap, easy synthesis and their chemical and thermal stability. Considerable attention has been paid to the preparation of transition metal complexes of Schiff bases derived from amino acids because they are considered to constitute new kinds of potential antibacterial and anticancer reagents [11]. However, to the best of our knowledge, no amino acid Schiff base compounds were used for the oxidation in ILs ever before.

Copper is an abundant metal on the earth's crust and is found in various metalloproteins, especially in enzymes [12]. However, the cheap and "green" Cu catalytic systems for oxidation of alcohols in ILs have received less attention, especially copper metal ligands. Recently aerobic oxidation of alcohols to the corresponding aldehydes or ketones using Cu-TEMPO systems in ILs have been reported [13]. However, the limitations are that the transformation of *sec*-alcohols is time-consuming for Cu(I), with Cu(II) no reaction occurs, and both systems are complex.

Recently, we reported a commercially available copper acetylacetonate/*tert*-butylhydroperoxide system that can be recycled and reused in IL 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6) for secondary alcohols to corresponding ketones [14]. In continuation of our interest in exploring green oxidation of alcohols in ILs by

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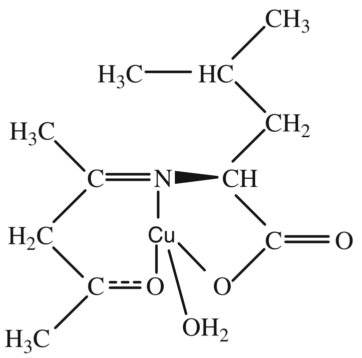
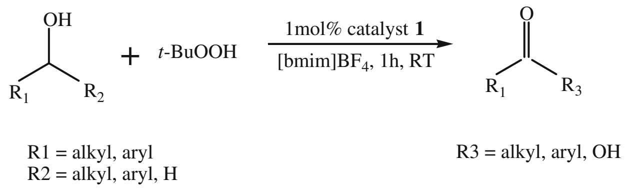
M. Rong · C. Liu · J. Han (✉) · W. Sheng · Y. Zhang · H. Wang
Key Laboratory for Green Chemical Technology of State Education Ministry, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, People's Republic of China
e-mail: hanjinyu@tju.edu.cn



Catalyst 1



Scheme 1 Amino acid Schiff base copper complex catalyzed oxidation of alcohols

metal ligands, we herein report a mild and effective procedure for the selective oxidation of alcohols to the corresponding carbonyl compounds using a novel amino acid Schiff base copper ligand/*tert*-butylhydroperoxide system with an IL 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4) as the solvent (Scheme 1).

2 Experimental

2.1 General

Chromatographic analyses were performed on an Hp-4890 gas chromatograph, a flame ionization detector, equipped with an Hp-Innowax capillary column (polyethylene glycol, 30 m long, 0.32 mm i.d., and 0.25 µm film thickness). The ^1H NMR measurements were carried out on an Inova 500 MHz high-resolution liquid nuclear magnetic resonance spectrometer. IR spectra were obtained with Nicolet Magna-IR 560 SXB and expressed in cm $^{-1}$. Elemental analyses were performed with a Vanio-EL analyzer and VISTA-MPS. TGA data were recorded on a SHIMADZU TA-50.

2.2 Chemicals

ILs and other chemicals used without further purification in the present study were of analytical grade and procured from and Acros Organics, respectively.

2.3 Synthesis of Copper Amino Acid Schiff Base Catalyst 1

Sodium hydroxide (10 mmol) and L-leucine (10 mmol) were stirred in ethanol (100 mL). When the L-leucine and sodium hydroxide were dissolved, ethanol (20 mL) which dissolved 10 mmol acetylacetone was added. After refluence for 4 h, aqueous $Cu(OAc)_2 \cdot H_2O$ (30 mL) solution was slowly added. The color of solution changed to blue, and the solutions was continuously refluent for 3 h. Left out for a night, the complex settled out. The precipitate of copper complex was collected by filtration, washed with ethanol and ether, respectively, and dired under vacuum. IR (KBr): 3437 cm^{-1}(–OH), 1623 cm^{-1} (C=N), 1573 cm^{-1} (COO^-), 1394 cm^{-1} (COO^-), 569 cm^{-1} (Cu–N), 460 cm^{-1} (Cu–O). Anal. Calcd for $C_{11}H_{20}NO_4Cu$: C, 44.89; H, 6.80; N, 4.76; Cu, 21.77. Found: C, 44.75; H, 6.98; N, 4.81; Cu, 22.04. The thermal behavior of catalyst 1 was characterized by thermogravimetric analysis (TGA). The sample was analyzed in a platinum pan under N_2 and the temperature was linearly increased at 10 °C min^{-1} over a temperature range 25–800 °C. Thethermal decomposition profile shows a slight weight loss about 6.08% around 75–218 °C, but no visible pick on DTA curve. Then two peaks occurs at 250 °C and 276 °C on DTA curve, which correspond to the two catastrophic weight losses on TGA curve. Constant weight is finally gained at about 340 °C.

Table 1 Optimization of the reaction conditions for oxidizing benzyl alcohol to benzoic acid[a]

Entry	Ionic liquid	Conversion (%)	Selection (%)[b]
1	[bmim]BF_4	94	>98
2	[bmim]PF_6	40	22
3	[bmim]$CCOOF_3$	63	50
4	[bmim]BF_4	28[c]	20
5	[bmim]BF_4	52[d]	62
6	[bmim]BF_4	66[e]	55
7	[bmim]BF_4	81[f]	75
8	[bmim]BF_4	76[g]	71

[a] 2 mmol benzyl alcohol, 1 mol% catalyst 1, 5 equiv *t*-BuOOH, 1 mL [bmim]BF_4, room temperature for 1 h

[b] Based on the benzoic acid

[c] 30% aqueous H_2O_2 as the oxidant

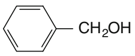
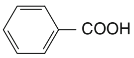
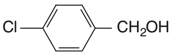
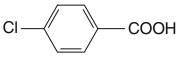
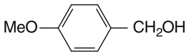
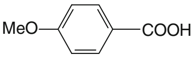
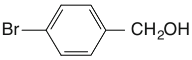
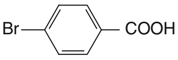
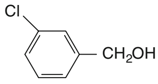
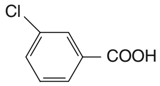
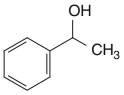
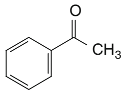
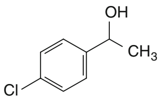
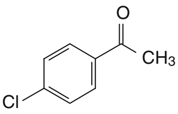
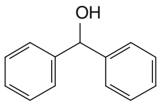
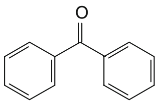
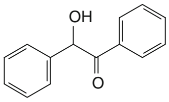
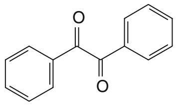
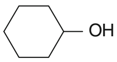
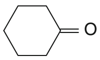
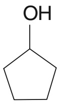
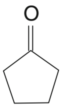
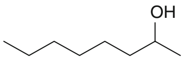
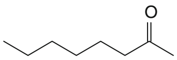
[d] 10% aqueous NaClO as the oxidant

[e] 3 equiv *t*-BuOOH was used

[f] 4 equiv *t*-BuOOH was used

[g] The reaction time was 30 min

Table 2 Oxidation of alcohols in [bmim]BF_4[a]

Entry	Substrate	Products	Time (h)	Con[b]/Yield (%)[c]
1			1	94/88
2			1	96/89
3			1	99/92
4			1	95/87
5			1	95/88
6			1	92/88
7			1	93/88
8			1	99/94[d]
9			1	99/94[d]
10			1 10	53/42 72/63
11			1 10	58/50 74/64
12			1 10	22/– 40/30

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[a] 2 mmol benzyl alcohol, 1 mol% catalyst 1, 5 equiv *t*-BuOOH, 1 mL [bmim]BF_4, room temperature for 1 h

[b] Conversion by GC of the crude product complex

[c] Isolated yield by flash chromatography

[d] CH_2Cl_2 (2 mL) was added to help dissolve the substrate

2.4 Representative Procedure for the Oxidation of Alcohols

A mixture of benzyl alcohol (2 mmol), cataylst 1 (0.02 mmol) and [bmim]BF_4 (1 mL) was added in a microreactor under magnetic stirring for 1 min, and *tert*-butylhydroperoxide (10 mmol) was added to the mixture. After several seconds of stirring, the purple color of the reaction mixture turned into colorless and then change into green color after next several seconds stirrng. The reaction mixture was stirred under room temperature for 1 h and then extracted with ethyl ether (3 × 5 mL). It is noted that the color of the solvent changed back purple color after extraction. The combined ethyl ether phase was concentrated in vacuo and monitored by GC. Then the residue was purified by flash chromatography to afford benzoic acid (yield 88%).

3 Results and Discussion

The initial study was carried out using benzyl alcohol as the substrate to optimize the reaction conditions, and the results are summarized in Table 1. At first, three different ILs [bmim]PF_6, [bmim]BF_4, 1-butyl-3-methylimidazolium trifluoroacetate ([bmim] CF_3COO) were tested with the compound 1 as the catalyst for the oxidation. Generally, oxidation rapidly in BF_4-type IL while far slower rate occured in PF_6-type and CF_3COO-type ILs (Table 1, Entry 1–3). Next, various types of oxidants were tested as oxygen resource in [bmim]BF_4. It was clear that all the oxidants gave comparable conversions and selections, but *t*-BuOOH showed to be optimal (Table 1, Entry 1, 4, 5). It was noted that the increment of load of *t*-BuOOH and reaction time led to the increment of selections of benzoic acid (Table 1, Entry 1, 6, 7, 8).

Having optimized the reaction condition, the oxidation of other alcohols were then examined (Table 2). It was clear that all primary alcohols and secondary alcohols have been selectively oxidized to carboxylic acids and ketones, respectively. In addition, the reaction of aromatic alcohols to the corresponding carbonyl compounds was fast and efficient, whereas aliphatic alcohols all reacted more slowly.

Subsequently, the recyclability of the used ILs solution containing the catalyst was demonstrated for the oxidation of benzyl alcohol to benzoic acid. The catalytic system could be reused directly for a new cycle, after full extraction of the product three times with 5 mL ethyl ether per extraction. The results shown in Table 3 demonstrated that this oxidative system was readily recyclable for five runs without any significant loss of catalytic activity.

Table 3 Recycling of the catalytic system for the oxidation of benzyl alcohol to benzoic acid[a]

Run	Conversion (%)	Yield (%)[b]
1	94	88
2	92	85
3	92	84
4	91	84
5	90	83

[a] 2 mmol benzyl alcohol, 1 mol% catalyst 1, 5 equiv *t*-BuOOH, 1 mL [bmim]BF_4, room tempture for 1 h

[b] Isolated yield by flash chromatography

4 Conclusion

In summary, a novel, very mild and efficient protocol for oxidation of alcohols to corresponding carbonyl compounds with excellent conversions using an amino acid Schiff base copper ligand as the catalyst has been developed in the IL [bmim]BF_4. Most importantly, this catalytic system is very simple and easy to handle, and can be recycled and reused for five runs without any significant loss of catalytic activity.

Acknowledgments This research was supported by the Special Program for Key Basic Research of the Ministry of Science and Technology of China (Grant No. 2005CCA06100) and the National Natural Science Foundation of China (Grant No. 20776109).

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