

Investigation of Catalytic Activity of Bis[2-(*p*-tolyliminomethyl)phenolato] Copper(II) Complex in the Selective Oxidation of Alcohols with Hydrogen Peroxide

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In this article, the catalytic activity of bis[2-(*p*-tolyliminomethyl)phenolato] copper(II) complex was studied, for the first time, in the oxidation of various primary and secondary alcohols to the corresponding aldehydes or ketones. The effect of different solvent was studied in the oxidation of benzyl alcohol and methanol was chosen as the reaction medium. Also the effect of different oxidants such as H₂O₂, urea-H₂O₂ (UHP), NaOCl, *tert*-BuOOH (TBHP) and NaIO₄ was studied in the oxidation of benzyl alcohol and H₂O₂ was selected as oxygen donor. In this catalytic system, oxidation of benzyl alcohol required 4 mol% of catalyst for completion and with increasing the reaction temperature to 60 °C, the highest oxidation yield was observed. Results showed that this homogeneous catalyst, exhibited good catalytic activity in the selective oxidation of various alcohols with hydrogen peroxide and gave the corresponding aldehyde without further oxidation to carboxylic acids in good to excellent yields (56-95%).

Keywords: Schiff base, Copper(II) complex, Homogeneous catalyst, Alcohol, Oxidation, Hydrogen peroxide

INTRODUCTION

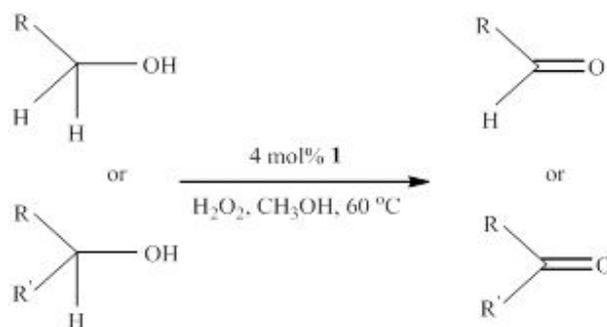
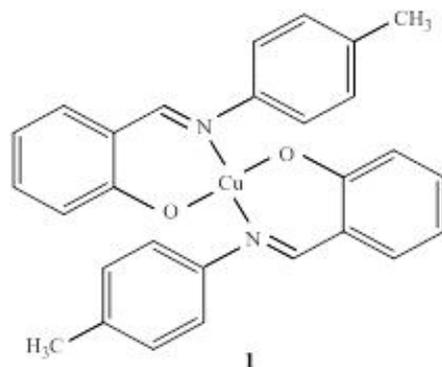
Aldehydes and ketones are important intermediates in the synthesis of other organic compounds both at laboratory and industrial level. Therefore, selective oxidation of alcohols to the corresponding carbonyl compounds is one of the most principle and important progresses in organic chemistry [1].

Oxidation of alcohols with molecular oxygen catalyzed by various metal catalysts such as RuCl₃·3H₂O [2], RuO₂·H₂O [3], combination of cobalt and ruthenium [4,5], Ru-salen [6] and Pd(OAc)₂ [7] has been reported in the articles. Many of these reported methods suffer from drawbacks such as the use of forcing conditions and costly metal catalysts like ruthenium and palladium [8]. Only a few examples of oxidation of alcohols toward carbonyl compounds based on abundant and cheap metals such as Fe, Cu and Co are reported [9,10].

The Schiff base transition metal complexes are interesting oxidation catalysts because of their easy synthesis and their chemical and thermal stability. Transition metal Schiff base complexes known as powerful homogeneous catalysts in the oxidation reaction by different oxygen donors such as NaClO, PhIO, KHSO₅ (Oxone), NaIO₄ and H₂O₂ [11-24]. Along this line, transition metal-catalyzed oxidation of alcohols with hydrogen peroxide has been extensively investigated because the fact that hydrogen peroxide identified as cheap and environmentally mild oxidant, which produces water as the only by-product.

In 1984, Semmelhack described the first efficient Cu-catalyzed aerobic oxidation of alcohols. In this system 10 mol% CuCl and 10 mol% TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) were used to oxidize primary alcohols in DMF under an O₂ atmosphere at room temperature [25]. Also, Punniyamurthy and co-workers disclosed an oxidation that used a salen-type ligand on Cu that chemoselectively oxidized primary alcohols. This system required a pure O₂ atmosphere as well as high temperatures (100 °C) [26].

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Scheme 1. Selective oxidation of alcohols to aldehydes and ketones with H_2O_2 catalyzed by copper(II) Schiff base complex 1.

Here, we wish to report a simple, efficient, eco-friendly and selective process for the oxidation of various alcohols to aldehydes and ketones with hydrogen peroxide catalyzed by bis[2-(*p*-tolyliminomethyl)phenolato]copper(II) complex (Scheme 1).

EXPERIMENTAL

Materials and Methods

All the materials used were commercial reagent grade and obtained from Merck. Alcohols were obtained from Merck or Fluka. Hydrogen peroxide (30%) was stored at 5 °C and titrated with potassium permanganate 0.1 N [27]. The Schiff base ligand was prepared by refluxing ethanolic solutions of salicylaldehyde and *p*-tolylamine in a 1:1 molar ratio for 4 h. The copper(II) Schiff base complex (1) as catalyst was prepared in good yield according to published

procedure and its spectroscopic and analytic data are in according with the reported literature data [28]. For copper(II) Schiff base complex (1): yield 76% and m.p.: 203-205 °C. Anal. Calcd. for $\text{CuC}_{28}\text{H}_{24}\text{N}_2\text{O}_2$ (%): C, 69.49; H, 4.96; N, 5.79. Found: C, 69.10; H, 4.72; N, 5.51.

FT-IR spectra (KBr pellets) were obtained with Nicolet iS10 spectrometer in the range 400-4000 cm^{-1} . The UV-Vis spectra of the ligand and complex were recorded in methanol solutions using a T80 UV-Vis spectrophotometer. Elemental analysis was carried out on a Vario EL III CHNS elemental analyzer. The purity of the products and the progress of the reactions were accomplished by TLC on silica-gel polygram SILG/UV 254 plates. Gas chromatography experiments (GC) were performed with a Philips GC-PU 4600 instrument using 2m column packed with silicon DC-200 with a FID detector.

Table 1. Effect of Solvent on the Oxidation of Benzyl Alcohol Catalyzed by Complex 1^a

| Row | Solvent | Yield (%) |
|-----|------------------------------------|-----------|
| 1 | CH ₃ OH | 90 |
| 2 | CH ₃ CH ₂ OH | 73 |
| 3 | CH ₃ CN | 60 |
| 4 | CH ₃ COCH ₃ | 55 |
| 5 | CHCl ₃ | 47 |
| 6 | CH ₂ Cl ₂ | 35 |
| 7 | H ₂ O | 10 |

^aReaction conditions: Benzyl alcohol (1 mmol), 30% H₂O₂ (0.11 ml, 1 mmol), catalyst (19 mg, 4 mol%), solvent (3 ml), 60 °C, 1 h.

Table 2. Effect of Oxidant on the Oxidation of Benzyl Alcohol Catalyzed by Complex 1^a

| Row | Oxidant | Solvent | Yield (%) |
|-----|---|--------------------|-----------|
| 1 | H ₂ O ₂ | CH ₃ OH | 90 |
| 2 | H ₂ O ₂ /urea (UHP) | CH ₃ OH | 47 |
| 3 | NaOCl | CH ₃ OH | 30 |
| 4 | <i>tert</i> -BuOOH | CH ₃ OH | 65 |
| 5 | NaIO ₄ | CH ₃ OH | 15 |
| 6 | No oxidant | CH ₃ OH | 0 |

^aReaction conditions: Benzyl alcohol (1 mmol), oxidant (1 mmol), catalyst (19 mg, 4 mol%), CH₃OH (3 ml), 60 °C, 1 h.

General Procedure for Oxidation of Alcohols with H₂O₂ Catalyzed by Copper(II) Schiff Base Complex 1

In a typical experiment, copper(II) Schiff base complex 1 (19 mg, 4 mol%) and 30% H₂O₂ (0.11 ml, 1 mmol) were

added to a stirred solution of alcohol (1 mmol) in methanol (3 ml). The reaction mixture was stirred at 60 °C and the reaction progress was monitored by GC or TLC. After completion of the reaction, the reaction products were extracted with CH₂Cl₂ and were purified by a silica-gel

Table 3. Effect of Catalyst Amount on the Oxidation of Benzyl Alcohol Catalyzed by Catalyst 1^a

| Row | Amount of catalyst (mol%) | Yield (%) |
|-----|------------------------------|--------------|
| 1 | 0 | 0 |
| 2 | 1 | 20 |
| 3 | 2 | 45 |
| 4 | 3 | 64 |
| 5 | 4 | 90 |
| 6 | 5 | 91 |

^aReaction conditions: Benzyl alcohol (1 mmol), 30% H₂O₂ (0.11 ml, 1 mmol), CH₃OH (3 ml), 60 °C, 1 h.

Table 4. Effect of Temperature on the Oxidation of Benzyl Alcohol Catalyzed by Complex 1^a

| Row | T (°C) | Yield (%) |
|-----|-----------|--------------|
| 1 | 25 | 20 |
| 2 | 40 | 57 |
| 3 | 50 | 75 |
| 4 | 60 | 90 |

^aReaction conditions: Benzyl alcohol (1 mmol), 30% H₂O₂ (0.11 ml, 1 mmol), catalyst (19 mg, 4 mol%), CH₃OH (3 ml), 1 h.

plate. Also, blank experimental was performed under same experimental conditions in the absence of catalyst or oxidant and only trace amounts of product was detected.

RESULTS AND DISCUSSION

First, oxidation of benzyl alcohol was studied as a template reaction to investigate the effect of solvent, oxidant, catalyst concentration and temperature on catalytic activity of complex 1. Furthermore, at the optimized conditions, the catalyst was used for oxidation of a series of

primary and secondary alcohols.

The Effect of Solvent on the Oxidation of Benzyl Alcohol Catalyzed by Complex 1

In the catalytic oxidation of alcohols the choice of oxygen donor and solvent is crucial [21]. Generally, solvents can affect the reaction rates through many factors, e.g. polarity, differential solvation power, donor ability, electrophilic behavior and the size of the solvent molecule [29]. Although it is difficult to identify the solvent parameters that are responsible for controlling reaction rate,

in the present catalytic system, methanol was chosen as the reaction medium. In this polar protic solvent the highest oxidation yield was observed (Table 1).

The Effect of Various Oxidants on the Oxidation of Benzyl Alcohol Catalyzed by Complex 1

Different oxygen donors such as H₂O₂, urea-H₂O₂ (UHP), NaOCl, *tert*-BuOOH (TBHP) and NaIO₄ were used in the oxidation of benzyl alcohol in the present of complex 1. The results showed that H₂O₂ is the best oxidant, because a higher oxidation yield was observed (Table 2). Also, H₂O₂ is cheap, mild and environmentally benign reagent since water is formed as the only by-product [30].

The Effect of Catalyst Amount on the Oxidation of Benzyl Alcohol Catalyzed by Complex 1

Exploring the effect of catalyst amount on the oxidation of benzyl alcohol was performed at the different amounts of catalyst 1. The results are shown in Table 3. The results indicate that in the absence of catalyst, no conversion of benzyl alcohol was obtained. With the increase in catalyst amount, the conversion of benzyl alcohol increased. This may be due to the availability of more active sites of catalyst that favors the accessibility of large number of molecules of substrates and oxidant to the catalyst [31]. In this catalytic system, the maximum conversion was obtained when 4 mol% (19 mg) of catalyst 1 was used.

The Effect of Temperature on the Oxidation of Benzyl Alcohol Catalyzed by Complex 1

In order to study the effect of temperature, the oxidation of benzyl alcohol was studied at different temperatures while other parameters were kept constant. The results (Table 4) showed that at room temperature (25 °C), the product yield was low and with increasing the reaction temperature to 60 °C, the highest oxidation yield was observed.

Oxidation of Various Alcohols with Hydrogen Peroxide Catalyzed by Complex 1

Oxidation of primary and secondary alcohols was examined in methanol at 60 °C containing the alcohol,

oxidant and catalyst 1 in 1:1:0.04 molar ratios, respectively.

As shown in Table 5, various types of primary benzylic alcohols including those bearing electron-withdrawing and electron-donating groups were selectively converted to their corresponding aromatic aldehydes in good to high yields (entries 1-8). Furthermore, acid sensitive alcohols, such as furfuryl alcohol as a heteroaromatic alcohol underwent smooth oxidation reaction without any decomposition or polymerization under the present reaction conditions (entry 9). In view of the fact that the oxidation of aliphatic alcohols is more difficult than benzylic ones, primary and secondary aliphatic alcohols were oxidized to their carbonyl compounds in low to moderate yields in longer times (entries 10-12). Then, the oxidation of secondary benzylic alcohols was studied. In these cases, the corresponding ketones were obtained in relatively good yields (entries 13-16).

Based on the observations and other related literature [32, 33], a plausible mechanism for the catalytic activity of complex 1 in the oxidation of alcohols is proposed in Scheme 2.

First, the Cu Lewis acid site interacts with H₂O₂ to form I, which reacts with the alcohol to give intermediate II. Two hydration steps convert II to the carbonyl compound, with regeneration of the catalyst.

CONCLUSIONS

In conclusion, copper(II) Schiff base complex (1) was used as homogeneous catalyst for oxidation of a series of alcohols to carbonyl compounds with H₂O₂. The catalyst 1 is a homogeneous catalyst and cannot be recovered, but easy preparation, good to high yields of the products, inexpensive system, eco-friendly and selective oxidation of primary alcohols can be mentioned as advantages of this method for oxidation of alcohols.

ACKNOWLEDGMENTS

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Table 5. Oxidation of Various Alcohols Catalyzed by Complex 1 under the Optimized Reaction Conditions^a

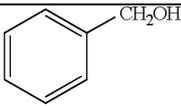
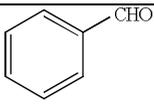
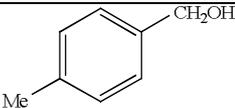
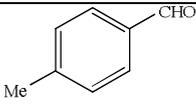
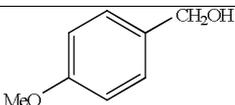
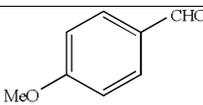
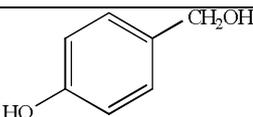
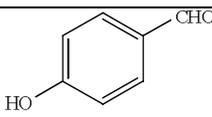
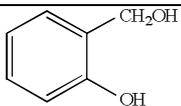
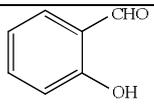
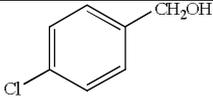
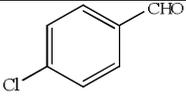
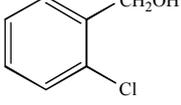
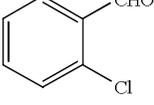
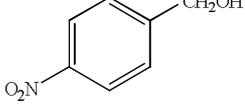
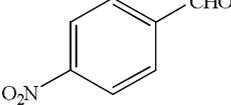
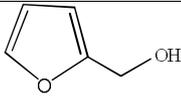
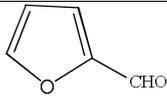
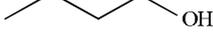
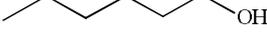
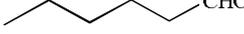
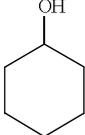
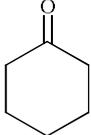
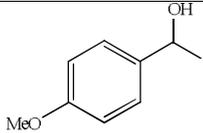
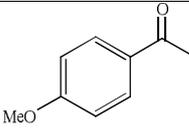
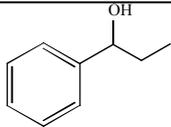
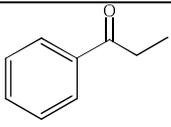
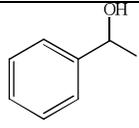
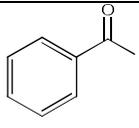
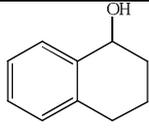
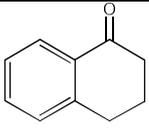
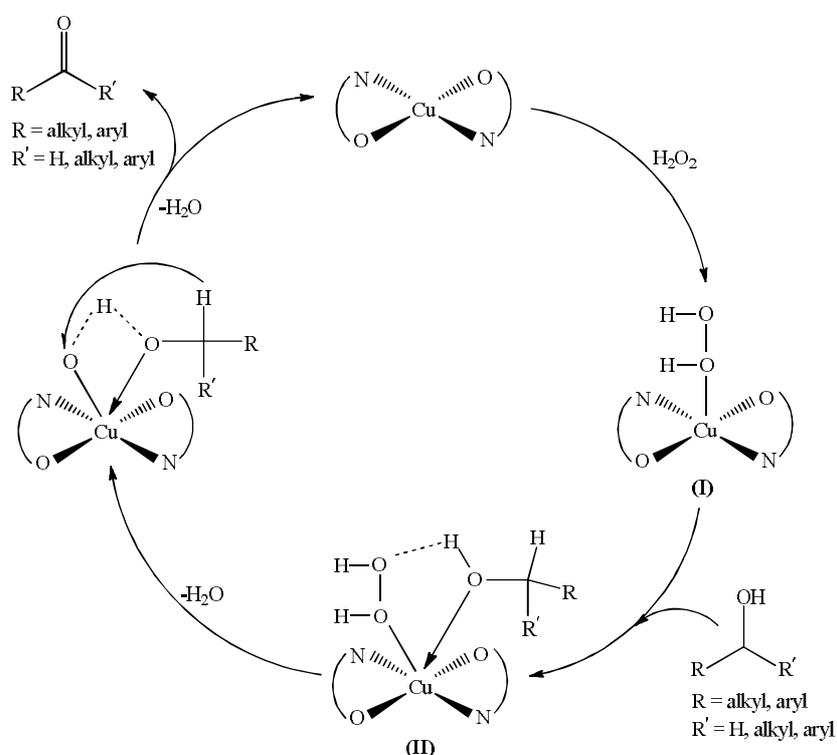
| Entry | Alcohol | Product | Yield (%) ^b | Time (h) |
|-------|---|---|------------------------|----------|
| 1 |  |  | 90 | 1 |
| 2 |  |  | 92 | 1 |
| 3 |  |  | 95 | 1 |
| 4 |  |  | 80 | 1 |
| 5 |  |  | 73 | 1 |
| 6 |  |  | 62 | 1 |
| 7 |  |  | 60 | 1 |
| 8 |  |  | 56 | 1 |
| 9 |  |  | 65 | 2 |
| 10 |  |  | 34 ^c | 2 |
| 11 |  |  | 30 ^c | 2 |
| 12 |  |  | 60 ^c | 2 |

Table 5. Continued

| | | | | |
|----|--|--|-----------------|---|
| 13 |  |  | 65 | 1 |
| 14 |  |  | 55 | 1 |
| 15 |  |  | 48 ^c | 2 |
| 16 |  |  | 45 ^c | 2 |

^aReaction conditions: Alcohol (1 mmol), 30% H₂O₂ (0.11 ml, 1 mmol), catalyst (19 mg, 4 mol%), CH₃OH (3 ml), 60 °C. ^bYields refer to isolated products. ^cGC yields.



Scheme 2. Proposed mechanism for oxidation of alcohols with H₂O₂ catalyzed by copper(II) Schiff base complex 1.

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