



Facile open air oxidation of benzylic alcohols in distilled water by in situ made copper(II) complexes

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ABSTRACT

A highly efficient, selective and green catalytic protocol for open air oxidation of primary benzylic alcohols into aldehydes by in situ made *N*-isopropyl-3,5-di-*tert*-butylsalicylaldimine (HL3)–Cu(II) complexes and TEMPO (2,2,6,6-tetramethyl-piperidinyloxy radical) is introduced herein. Distilled water as a solvent the reaction proceeds at 80 °C temperature without any auxiliaries such as base and/or co-solvent. For example, benzyl alcohol is quantitatively and selectively oxidized to benzaldehyde within a few hours under optimized reaction conditions [80 °C, open air, 0.3 mol% CuBr₂, 2 mol% HL3, 3 mol% TEMPO and 5 mL of distilled water]. Under anaerobic conditions, the catalyst decomposes to a free ligand and Cu₂O nanoparticles (diameter >50 nm) via anticipated Cu(I)-hydroxo complex. On the basis of these observations and deuteration studies, a plausible reaction mechanism is proposed for the catalytic system.

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1. Introduction

Selective oxidation of alcohols into corresponding carbonyl compounds is highly important and the topic is ceaselessly gaining large amount of interest [1,2]. Especially benign catalytic methods for activation of oxygen or hydrogen peroxide are sought-after [3]. With these oxidants water is formed as a by-product and thus water-tolerant catalysts are in the focus of research. In this respect, and being environmentally benign solvent [4], water can be considered as the most attractive reaction medium for alcohol oxidation. When considering reactions under high oxygen pressure, water provides also a distinct advantage over organic solvents by being safe medium. In general, sensitivity of catalysts and low solubility of alcohols in water can be seen as major limitations in development of such oxidation systems [5].

Attractive examples of heterogeneous catalysts working in aqueous media using oxygen or air as oxidant include Fe [6], Ru [7], Au [8], Pt [9] and Pd [10] nanoparticles, bimetallic [11] clusters, polymer-stabilized Au nanoclusters [12] and even bulk gold [13]. However, examples of homogeneous transition metal catalysts are rather rare [14,15] and the most studied systems are based on Cu(II) complexes and 2,2,6,6-tetramethyl-piperidinyloxy (TEMPO) [16–18]. Remarkably, these catalysts can convert

selectively primary benzylic alcohols into corresponding aldehydes in air.

For efficient oxidation, the homogeneous catalysts mentioned above need auxiliary substances like base and/or co-solvent. In general, base is used in catalytic protocols for deprotonation of alcohol which makes it more susceptible to coordination to a catalyst [16–22]. Water miscible organic solvents are often employed as co-solvents to improve homogeneity of the system or to ensure the dissolution of the substrate into aqueous phase [16,18–20]. However, when following the green chemistry principles [4], additional auxiliaries should be avoided. In this sense TEMPO/CuCl-1,4-diazabicyclo[2.2.2]octane (DABCO) catalyst, although it worked in toluene, is attractive as it provided similar oxidation activities with and without base [23]. Apparently, the applied ligand had adequate basicity to deprotonate alcohol and thus oxidation occurred without auxiliary base [23,24]. In continuation of our interest in developing green catalytic methods for alcohol oxidation [22,25–28], we report herein in situ made salicylaldiminato-Cu(II) catalysts for highly efficient and selective open air oxidation of benzylic alcohols into corresponding aldehydes in distilled water.

2. Experimental

2.1. General methods and chemicals

Reagents were purchased from commercial suppliers and were used as received. UV–vis and ¹H NMR spectra were recorded with

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