



Copper catalyzed oxidation of benzylic alcohols in water with H₂O₂

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ARTICLE INFO

Article history:

Received 15 June 2011

Received in revised form 6 October 2011

Accepted 26 October 2011

Available online 3 November 2011

Keywords:

Oxidation

Alcohols

Copper

Hydrogen peroxide

Water

ABSTRACT

A straightforward, efficient and sustainable copper catalyzed method was developed for oxidation of benzylic alcohols with 30% H₂O₂ in water. The reaction proceeded with CuSO₄ catalyst (1 mol%) at 100 °C without additional base or ligand. Primary benzylic alcohols were converted almost quantitatively to aldehydes with 70–90% selectivity, corresponding acids being the major side products. Also secondary benzylic alcohols afforded the corresponding ketones in high conversion with selectivities greater than 90%. It was demonstrated that the CuSO₄ catalyst can be recycled and reused at least for three runs, even though with some loss of catalytic activity. Selectivity of the CuSO₄ based catalyst system could be further increased by using 2-*N*-(*p*-fluorophenyl)-pyrrolocarbaldimine (**1**) as a ligand in combination with TEMPO in K₂CO₃ solution. The catalyst system was individually optimized (1 mol% CuSO₄, 2 mol% **1**, 0.1 M K₂CO₃ and 5 mol% TEMPO) for a wide range of benzylic and allylic alcohols, which were quantitatively and selectively converted into the corresponding aldehydes with 3 eq. of H₂O₂ in 1 h.

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1. Introduction

Aldehydes and ketones are important intermediates in the synthesis of other organic compounds and they are utilized particularly in the manufacture of medicines, flavors, fragrances and aniline dyes [1]. Therefore selective oxidation of alcohols toward carbonyl compounds by transition metal catalysts is a broadly studied field and various catalytic methods have been developed [2]. Regarding sustainable systems, O₂ and H₂O₂ are preferred oxidants. H₂O₂ is easy to handle and it has higher oxidation potential than O₂. Only a few examples of catalytic systems based on Mn, Fe, Mo, W and Re with H₂O₂ are reported [3]. Reports in respect of Cu and H₂O₂ are still sparse [4] even though a system based on Cu–diphenoxydiamine complex is encouraging [5].

Our interest lies in developing green catalytic systems for alcohol oxidation [6]. We have recently reported aerobic oxidation of benzylic alcohols catalyzed by Cu(II)–2-*N*-arylpyrrolocarbaldimino complexes in combination with TEMPO in alkaline water solution under mild reaction conditions [7]. These catalysts could employ both O₂ and H₂O₂ as an oxidant. Related to this finding, herein are reported detailed studies on oxidation of benzylic alcohols in water using several copper salts as catalyst and H₂O₂ as an end oxidant (Scheme 1). The influence of various additives, such as acids or bases, radical scavengers and N-containing ligands, on the efficiency/selectivity of the catalyst system is demonstrated as well.

2. Experimental

2.1. General

All reagents were purchased from commercial suppliers and used as received. The ligands (**1**–**2**) used in this work were synthesized by published procedures [6(b),7] and purities were confirmed by ¹H NMR and melting point measurements. UV–vis spectra were recorded with a Hewlett Packard 8453 spectrophotometer. The oxidation products were quantitatively analyzed by GC (Agilent 6890 chromatograph, Agilent 19091J-413 capillary column 0.32 mm × 30 m × 0.25 μm, FID detector) using internal standards. GC–MS method was used for identification of the products (Agilent 6890N equipped with Agilent 5973 mass selective detector, HP 19091 L-102 capillary columns, 200 mm × 24 m × 0.31 μm).

2.2. Oxidation experiment

The catalytic oxidation reactions were carried out in a 100 mL two-neck round-bottomed flask equipped with a condenser and a magnetic stirring bar. Typically, 0.03 mmol of CuSO₄·5H₂O (stock solution of 50 mg/mL in H₂O) and a ligand in 1:2 molar ratio, respectively, were loaded to the flask and diluted with 5 mL of 0.1 M K₂CO₃ water solution. The reaction mixture was heated at 80 °C for 30 min to ensure complex formation and then cooled to room temperature. TEMPO (0.15 mmol), a substrate and 30% H₂O₂ (1 mL, 3 eq. to substrate) were introduced. The reaction was performed at the selected temperature, ranging from ambient temperature to 80 °C, for 1.5 h after which the reaction mixture was first allowed to cool to room temperature and then it was acidified with 1 M HCl solution (1 mL).

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