



Oxidation of benzyl alcohols to the corresponding carbonyl compounds catalyzed by copper (II) meso-tetra phenyl porphyrin as cytochrome P-450 model reaction

Rahmatollah Rahimi*, Ensieh Gholamrezapor, Mohammad Reza Naimi-jamal

Department of Chemistry, Iran University of Science and Technology, Tehran, Iran

ARTICLE INFO

Article history:

Received 30 January 2011

Accepted 31 May 2011

Available online 12 June 2011

Keyword:

Cytochrome P-450

Copper (II) tetra phenyl porphyrin

Benzyl alcohols

Molecular oxygen

Isobutyraldehyde

Oxidation

ABSTRACT

The oxidation of benzyl alcohols has been studied in the presence of isobutyraldehyde as co-catalyst, molecular oxygen as oxidant and copper (II) meso-tetra phenyl porphyrin (CuTPP) as catalyst. The CuTPP catalyst exhibits good activity and high selectivity under mild conditions. The effects of temperature and solvents have also been investigated in this catalyst system.

© 2011 Published by Elsevier B.V.

Introduction

Various synthetic metalloporphyrins have been studied as cytochrome P-450 model and the catalyst for oxidation of alcohols, hydrocarbons and epoxidation of alkenes since last three decades [1–3]. The cytochrome P-450 can be as a mono oxygenase enzyme and as active catalyst in oxidation of benzyl alcohols to the corresponding carbonyl compounds [4]. Metalloporphyrins have been attended as synthetic models of cytochrome P-450 in catalytic oxidation of hydrocarbons, epoxidation of olefins and sulfoxidation by different oxygen sources but they have been attended fewer to oxidation of alcohols to their corresponding carbonyl compounds [5–14]. The oxidation of benzyl alcohols to the corresponding carbonyl compounds is a vital, usual and catalytic conversion in laboratory and industry chemistry for synthesis of many medicinal compounds [5–16]. In this study, the copper (II) porphyrin (CuTPP) was used useful catalyst for the aerobic oxidation of benzyl alcohols to the corresponding carbonyl compounds in normal condition oxygen (1 atm) [17]. Oxidative catalytic conversion of organic compounds has been done with environmentally clean oxidants such as molecular oxygen or peroxide hydrogen since the recent years. Because of they are not deadly or dangerous oxidants. Using from green oxidants has been increased in oxidation of benzyl alcohols recently. Molecular oxygen is a selective oxidant because of it produces only water as a byproduct in oxidation of benzyl alcohols [18,19]. Using from molecular oxygen have others advantageous such as inexpensive,

secure and available amount [16,20]. In addition, a simple and comfortable system has been reported for the oxidation of benzyl alcohols in present copper (II) porphyrin as catalyst, isobutyraldehyde as co-catalyst and molecular oxygen as oxidant [21]. Jung and et al reported for the first time that iron porphyrin complexes could catalyze oxidation benzyl alcohols to the carbonyl compounds effectively [22]. The electron withdrawing groups in phenyl ring of the benzyl alcohols have lower yield in oxidation processes usually [23–25]. In this article, homogeneous oxidation of benzyl alcohols has been done under atmospheric pressure of oxygen. The electronic effect of the substituents in the benzyl alcohols and reaction behavior has been compared. Also it was found that the yield of reaction was rather low in the absence of the catalyst [26].

Results and discussion

In order to finding optimum conditions of reaction, the oxidation of benzyl alcohol was utilized for model reaction. The reaction was performed in the absence and the presence of the CuTPP catalyst. The reaction was proceeding in the absence catalyst slowly and benzaldehyde yield was obtained low but yields of products were obtained excellent in the presence CuTPP and *O*-xylol solvent after 37 h. In order to studying the solvent effects in these reactions, solvents such as acetonitrile, toluene, benzene and *O*-xylol were utilized. The *O*-xylol was recognized the best solvent (Table 1). A wide range of benzyl alcohols have been oxidized that various substitutions containing electron-donating or electron-withdrawing groups had high and excellent yields (Table 2) without any carboxylic acids as byproducts. It seems that the efficiency of oxidation in these catalytic

* Corresponding author. Tel.: +98 21 7724 0290; fax: +98 21 7749 1204.

E-mail address: rahmatolla.rahimi@gmail.com (R. Rahimi).