Journal of Molecular Catalysis A: Chemical 391 (2014) 1–6

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Transition metal-free catalytic oxidation of aromatic alcohols with molecular oxygen in the presence of a catalytic amount of *N*-bromosuccinimide

Xinli Tong[a,*], Yongfa Sun[a], Yongtao Yan[a], Xuan Luo[b], Jinbiao Liu[a], Zhidong Wu[a]

[a] Tianjin Key Laboratory of Organic Solar Cells and Photochemical Conversion, School of Chemistry and Chemical Engineering, Tianjin University of Technology, No. 391 Binshuixi Road, Tianjin 300384, PR China
[b] Technical Center for Safety of Industrial Products, Tianjin Entry-Exit Inspection and Quarantine Bureau, No. 33 Youyi Road, Tianjin 300201, PR China

ARTICLE INFO

Article history:
Received 25 April 2013
Received in revised form 6 March 2014
Accepted 8 March 2014
Available online 25 March 2014

Keywords:
Oxidation
Aromatic alcohols
Oxygen
Transition metal-free
N-Bromosuccinimide

ABSTRACT

A highly efficient *N*-bromosuccinimide (NBS)-mediated transition metal-free catalytic system has developed for the efficient aerobic oxidation of aromatic alcohols. Various aromatic alcohols are successfully oxidized to the corresponding aldehydes or ketones under mild condition. For instance, benzyl alcohol is oxidized to benzaldehyde with 99% conversion in 94.5% selectivity with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)–$NaNO_2$–NBS system under 0.3 MPa of O_2 at 90 °C for 2 h. The effects of reaction time, catalyst amount and solvents are investigated in detail, and a possible reaction mechanism is proposed.

1. Introduction

The selective oxidation of alcohols into carbonyl compounds is one of the most important transformations in both laboratory and industrial synthetic chemistry [1–3]. Many oxidizing reagents including permanganate and dichromate have been traditionally employed in order to accomplish this transformation [4–7]. For instance, Helquist's group reported that catalytic 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (20 mol%) catalyzed alcohol oxidation with 6 equiv of $Mn(OAc)_3$ as oxidant [7]. Electron-rich benzylic alcohols are oxidized efficiently to their corresponding carbonyls, but less electron-rich benzylic alcohols remain unchanged. However, these are all hazardous reaction process and produce a large amount of toxic waste. From both economic and environmental point of view [8,9], the catalytic and selective oxidation with H_2O_2 or molecular oxygen as the oxidant becomes a promising orientation in this research field. Up to now, several efficient catalytic oxidation systems have been developed using molecular oxygen as the terminal oxidant [10–12]. Therein, catalysts containing transition metal Ru [13–15], Cu [16–21], Pd [22–39], Co [30] were widely used in the catalytic aerobic oxidation of alcohols under mild conditions. Though these catalyst systems could efficiently perform oxidation, transition metal ions were not easily removed and produce new toxic waste. They are referred as being not green from the point of environment. Recently, the recyclable heterogeneous catalyst and transition metal-free catalytic systems are considered as the promising and environment-friendly catalytic technology in the oxidation processes. For example, in the heterogeneous catalytic process, the supported Au nanoparticle catalysts has been reported as highly active, selective and recyclable catalysts for the oxidation of alcohols into corresponding aldehydes and ketones [31,32]. On the other hand, several transition metal-free catalyst systems based on the organic radical 2,2,6,6-tetramethyl piperidine-*N*-oxide (TEMPO) have been used for the oxidation of alcohols [33–37]. Particularly, Liu et al. [33] reported using TEMPO–$NaNO_2$–Br_2 as the catalytic system for the efficient oxidation of aromatic alcohols. Galli's group [34] described laccase/TEMPO mediator system as the catalyst, in which the primary benzyl and allyl alcohols were converted into the corresponding aldehydes in high yields. Notably, secondary benzyl alcohols were also efficiently oxidized to ketones, while tertiary benzyl alcohols kept unchanged. Tromp et al. [35] further reported the kinetic parameters and the catalytic reaction mechanism for oxidation of benzyl alcohol with laccase/TEMPO system. Hu's group [36] found a TEMPO-based catalyst system that could oxidize benzylic alcohols and hetero- aromatic analogues in water. Therein, 88–98%

* Corresponding author. Tel.: +86 22 6024259; fax: +86 22 60214259.
E-mail addresses: tongxinli@tju.edu.cn, tongxli@sohu.com (X. Tong).

http://dx.doi.org/10.1016/j.molcata.2014.03.011
1381-1169/

yields of benzylic aldehydes and ketones were obtained when a catalytic amount of TEMPO, 1,3-dibromo-5,5-dimethylhydantoin and $NaNO_2$ was employed. In addition, Hu's group [37] further reported using TEMPO-HBr-*tert*-butyl nitrite (TBN) as the catalytic system for the aerobic alcohols oxidation, in which up to a 16,000 turnover number could be achieved for oxidation of benzylic alcohol to benzaldehyde. Moreover, using the catalytic amounts of DDQ and TBN, selective oxidations of non-hindered benzylic alcohols were also successfully performed under mild conditions [38].

Through the careful considerations on the present "new" catalyst systems for oxidation of alcohols with molecular oxygen, it can be found that the numerous catalysts have an unavoidable relationship with the stoichiometric oxidant in the past oxidation systems. For example, metallic manganese salt has been developed as the catalyst for aerobic oxidation process while it was initially employed as an oxidant long years ago [7,39,40]. Besides, the occurrence of TEMPO as a catalyst is closely related to the oxoammonium cation that can directly oxidize primary alcohols to the corresponding aldehydes as a stoichiometric oxidant [41,42]. Herein, the TEMPO can be converted to oxoammonium cation *via* the single electron oxidation by the molecular halides [43]. So, it can be concluded that the extensive development of these new oxidation catalyst should be attributed to the continuous research on stoichiometric oxidation reaction systems in the recent years.

As inspired by the above progress of catalyst, we consider *N*-bromosuccinimide (NBS) can be employed as a catalyst component for the oxidation of alcohols with molecular oxygen though it or it analogues was always regarded as an oxidant for the oxidation reaction [44–47]. Thus, we have investigated the oxidation of aromatic alcohols with NBS as a catalyst in the presence of DDQ and $NaNO_2$. It is found that primary alcohols can be efficiently and selectively converted to the corresponding aldehydes under mild condition.

2. Experimental

2.1. Reagents

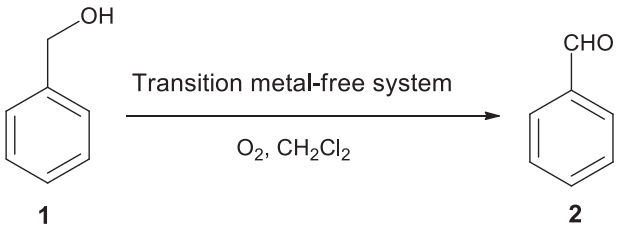
Benzyl alcohol (**1**), Succinimide, benzaldehyde (**2**), NBS, NCS, NIS, DDQ, and $NaNO_2$ are of analytical grade and purchased from Alfa Aesar, A Johnson Matthey Company. Dichloromethane and other solvents are purified by distillation. All other reagents are analytical grade and obtained from commercial. Oxygen (purity of 99%) supplied in a high-pressure cylinder was used through a reducing valve without further treatment.

2.2. General procedure for oxidation of aromatic alcohols

All oxidation experiments are performed in a 120 mL autoclave equipped with the magnetic stirring and automatic temperature control. A typical procedure for the oxidation of **1** is as follows: a CH_2Cl_2 (10 mL) solution of **1** (1.0 g, 9.2 mmol), NBS (3.0 mol%), DDQ (7.0 mol%), and $NaNO_2$ (10.0 mol%) is charged into the reactor, and the atmosphere inside is replaced with the pure oxygen after the reactor is sealed. Under stirring, oxygen is charged to 0.3 MPa at room temperature and the autoclave is preheated to 90 °C, and then kept for 2 h. After reaction, the autoclave was cooled and the mixture is analyzed by GC and GC–MS after the excess gas (unreacted oxygen and little nitrogen oxide) is purged.

2.3. Analysis and separation of reaction products

The products are analyzed with the internal standard technique by gas chromatography using a flame ionization detector (all products are determined on GC–MS). Moreover, for oxidation of **1**, the product is separated from the product solutions as follows: the reaction mixture is first distilled to remove the solvent CH_2Cl_2, and then is transferred into a flask and a saturated aqueous $NaHSO_3$ solution is added. The obtained liquid mixtures were stirred for 2 h under N_2 atmosphere and left in a refrigerator for 3 h, and then the resulting solid was collected by filtration. The solid mixtures are washed with an aqueous solution of sodium chloride to remove **1** and by-products. In the following, the washed solid was transferred into a two-neck flask and the HCl solution is added under N_2 atmosphere. The reaction is performed with stirring for 1 h at room temperature and for 2 h at 50 °C. The product is regenerated and extracted with diethyl ether. After being dried, the diethyl ether layer was distilled to obtain pure **2** as a liquid. As a result, the purity is more than 99% from GC analysis. The difference between the GC yield and separated yield is less than 10%.



Scheme 1. The aerobic oxidation of **1** with transition metal-free catalytic systems.

3. Results and discussion

3.1. Oxidation of benzyl alcohol with different catalysts

Initially, the oxidation of **1**, as shown in Scheme 1, is selected as a model to investigate the catalytic performance of different catalyst systems. As a result, it is found that the conversion of **1** is only 2.7% for 2 h in the absence of any catalyst at 90 °C under 0.3 MPa of O_2 in dichloromethane (CH_2Cl_2) (Table 1, entry 1). The conversion is elevated to 4.5% when 3 mol% NBS is added in the reaction (Table 1, entry 2).

Moreover, the conversion of **1** is 14.3% or 23.1% when the NBS–DDQ or NBS–$NaNO_2$ is used as the catalyst, respectively (Table 1, entries 3 and 4). To our surprise, 99% conversion and 94.5% selectivity for **2** are obtained under similar reaction conditions when a catalytic amount of NBS–DDQ–$NaNO_2$ is employed as the catalyst system (Table 1, entry 5). Furthermore, the combination of DDQ–$NaNO_2$ and single DDQ are also investigated, and it is found that only 11.8% and 9.2% conversions of **1** are obtained for 2 h (Table 1, entries 6 and 7). Besides, the oxidation process is studied with a sole and large amount of NBS (10 mol%, 20 mol%, 30 mol% or 50 mol%) in order to further reveal the character of NBS as the catalytic component, and the conversions of **1** are 13.7%, 67.4%, 60.8% and 80.3%, respectively (Table 1, entries 8–11), in which the highest selectivity for benzaldeyde is only 86.2% in the presence of 50 mol% NBS. This exhibited that the combination of NBS, DDQ and $NaNO_2$ is most efficient to the oxidation of **1** with molecular oxygen, which is superior to large amount of single NBS in oxidation. Also, the catalytic systems including analogues of NBS and $NaNO_2$–DDQ were investigated for the oxidation of **1**. It is found that a 37.6%, 73.8% and 21.0% conversions of benzyl alochol are obtained at 90 °C for 2 h when NBS is replaced by *N*-iodosuccinimide (NIS), *N*-chlorosuccinimide (NCS) and succinimide, respectively (Table 1, entries 12–14). All these results show that NBS plays an important role for obtaining a good catalytic activity.

3.2. The effect of reaction time and kinetic investigations

The effect of reaction time is investigated and presented in Fig. 1. The time is recorded once the temperature adds up to 90 °C, in which the conversion and selectivity for **2** are 22.9% and 68.9%.