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A non-cyanide route for glutaric acid synthesis from oxidation of cyclopentene in the ionic liquid media

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ABSTRACT

The current work deals with the catalytic application of bis(1-butyl-3-methylimidazolium) tungstate ([BMIm]₂WO₄) for green synthesis of glutaric acid (GA) through oxidative cleavage of cyclopentene. In this method, 30% hydrogen peroxide (H₂O₂) was used as oxidant with water as the sole by-product of the reaction. Compared to the current synthetic procedures, this protocol is significantly improved in the environmental point of view. Moreover, the effect of the various parameters was investigated on the reaction efficiency. It was found that high yield of GA could obtain without using special methodologies or precautions. The catalytic system is reusable for several times.

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1. Introduction

Owing to the better environmental capability, ionic liquids (ILs) are gradually finding their ways into the various chemical industries (Plechkova and Seddon, 2008). They have some unique properties such as negligible vapor pressure, low toxicity and non-flammability (Wasserscheid and Welton, 2008). A significant property of the ILs refers to the miscibility of these compounds in both aqueous and non-aqueous mediums. This characteristic made the ILs as an alternative solvent for both organic and inorganic reactions (Rogers and Seddon, 2003). Additionally, the hydrophobicity and hydrophilicity of ILs can tune by manipulating the side chain hydrocarbon length of these compounds. The major drawback of the ILs is that they are expensive reagents for solely utilizing as solvent, especially in large scale synthesis. In this regards, the term of the task-specific IL was introduced (Visser et al., 2001) which refers

to an IL with particular functions (Yue et al., 2011; Karimi and Vafaezadeh, 2012).

Glutaric acid (GA) or 1,5-pentanedioic acid is an important chemical which has been used in the production of polymers such as polyester polyols and polyamides. 1,5-Pentanediol which is a common plasticizer and the precursor for synthesis of polyesters is typically prepared by hydrogenation of GA (Werle et al., 2008). In some industries, GA can be obtained from adipic acid by-product recovery (Cavani and Teles, 2009). The most common way to synthesis of GA is through the ring-opening of the butyrolactone with potassium cyanide following by hydrolyzing to produce GA (Paris et al., 2003). It can be also prepared from the reaction of 1,3-dibromopropane with sodium or potassium cyanide to obtain the dinitrile derivative which undergoes hydrolysis to form GA. Unfortunately, in both of the mentioned methods the highly toxic source of cyanide (CN⁻) compounds are

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used. Another serious drawback refers to releasing poisonous hydrogen cyanide (HCN) which evolves during this reaction. Moreover, recovery of GA from the by-product of the adipic acid is not an inherently safe process. The reason is that adipic acid itself produces via nitric acid oxidation of KA oil (a mixture of cyclohexanone and cyclohexanol). The major environmental concern of this method is attributed to releasing stoichiometric amount of highly toxic N_2O gas which contributes to global warming, ozone depletion and contributes to acid rain.

In this work we wish to report a green protocol for preparation of GA by oxidation of cyclopentene (CyP) with 30% H_2O_2 as an alternative way to avoid participating and releasing hazardous cyanide wastes during the reaction. The applied bis(1-butyl-3-methylimidazolium) tungstate ($[BMIm]_2WO_4$) IL bears tungstate (WO_4^{2-}) species which is necessary to improve the oxidation efficiency of the H_2O_2 (Noyori et al., 2003). Another role of the IL is to act as a phase transfer catalyst (PTC) to provide a suitable media for better miscibility of both aqueous oxidant and organic phase of the starting materials.

2. Experimental

2.1. General

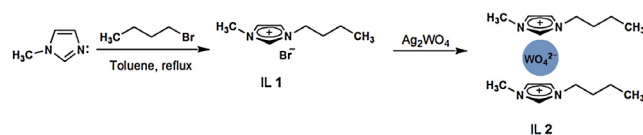
All chemicals and solvents were purchased from the Fluka and Merck and used without further purification. 1H and ^{13}C NMR spectra were recorded by Bruker 500 MHz spectrometer. FT-IR spectra were recorded with ABB Bomem MB100 Fourier Transform Infrared Analyzer.

2.2. Preparation of the $[BMIm]_2WO_4$

In a round-bottom flask equipped with a condenser, 1-methylimidazole (0.252 mol, 1 eq.) was added to 1-bromobutane (0.277 mol, 1.1 eq.). The mixture was heated to 70 °C for 24 h. After the completion of the reaction, the mixture was cooled to room temperature and the IL was washed by diethyl ether and then dried in vacuum to afford $[BMIm]Br$ (IL 1). For anion exchange, at the first step, Ag_2WO_4 was synthesized as a pale yellow solid by the reaction between 0.05 molar solution of $AgNO_3$ (8.49 g) and 0.025 molar solution of $Na_2WO_4 \cdot 2H_2O$ (8.25 g) in a dark place. The precipitated Ag_2WO_4 was washed with deionized water for three times. An aqueous solution of 0.05 mol $[BMIm]Br$ (10.96 g) was added to the freshly prepared Ag_2WO_4 at room temperature. After 1 h stirring, the mixture was filtrated and the liquid was concentrated and dried in vacuum to afford $[BMIm]_2WO_4$ (IL 2) as a yellow liquid. $[BMIm]_2WO_4$: 1H NMR (500 MHz, $DMSO-d_6$): 0.78–0.81 (t, 3H), 1.15–1.19 (m, 2H), 1.66–1.72 (m, 2H), 3.89 (s, 3H), 4.19–4.22 (t, 2H), 7.81 (s, 1H), 7.82 (s, 1H) and 9.97 (s, 1H). ^{13}C NMR (125 MHz, $DMSO-d_6$): δ = 14.17, 19.65, 32.48, 36.61, 49.36, 123.12, 124.55 and 139.15. FT-IR (liquid film): 3515, 3071, 2865, 2189, 1657, 1571, 1464, 1168 and 843.

2.3. General procedure for oxidation of CyP to GA

A mixture of CyP (10 mmol), 30% H_2O_2 (5.00 g–45 mmol), PTSA (95 mg) and 150 mg of the $[BMIm]_2WO_4$ were added into a round-bottomed flask equipped with a reflux condenser. The mixture was heated at 50 °C for 1 h and then at 80 °C for 10 h. After the reaction completion, it was cooled to room temperature. The product was extracted with diethyl ether. Then, the



Scheme 1 – Synthesis pathway of the IL 2.

organic phase was dried by Na_2SO_4 and the solvent was evaporated to afford pure GA: 1H NMR (500 MHz, $DMSO-d_6$): 1.67–1.71 (q, 2H), 2.23–2.26 (t, 4H) and 12.06 (broad, 2H).

2.4. Reusability of the IL 2

The resulted filtrated aqueous phase from the first reaction was concentrated in the reduced pressure. The remained light brown liquid was re-charged with starting materials and the reaction was conducted at the next reaction runs with identical conditions.

3. Results and discussion

As shown in Scheme 1, $[BMIm]_2WO_4$ IL (IL 2) was synthesized via anion exchange of the $[BMIm]Br$ (IL 1) with freshly prepared Ag_2WO_4 in water. The Br content of the IL 2 was determined using standard method (Volhard titration) to be less than 2 wt%.

1H NMR and ^{13}C NMR analyses demonstrated the high purity of the IL 2. To obtain pure IL 2 after the first step, IL 1 should wash with diethyl ether (3×20 mL) to remove unreacted starting materials. The residual starting materials are the major source of impurity in the IL. The anion exchange was performed in dark and Ag_2WO_4 should be freshly prepared and wash with deionized water before treatment for anion exchange with IL 1 (Fig. 1).

Comparative FT-IR spectra of IL 1 and IL 2 are shown in Fig. 2. A characteristic band which observed at 843 cm^{-1} is belonged to the W–O stretching frequency of the WO_4^{2-} species and confirms the successful anion exchange of the IL 1 (Takai et al., 2004).

To study the effects of the reaction parameters, the effect of the amount of IL 2 on the GA yield was investigated. In all cases the reaction was heated in two stages. First, it was heated at 50 °C (near to the boiling point of CyP) for 1 h and then at 80 °C for 10 h. The catalyst amount was of great importance for oxidation of CyP to yield GA. Hence, the reaction was conducted in various amounts of IL 2. The results are shown in Fig. 3a.

The effect of the amounts of the IL 2 to GA yield illustrated that there were not sufficient conversion to GA when the catalyst amount was low (50 and 100 mg). The conversion increased to 87% (isolated yield) when the amount of IL 2 was reached to 150 mg. However, when the amount of catalyst was exceeds to 200 and 250 mg, the yields of GA increased very slightly.

By considering the cost of the catalyst, the optimum amounts of IL 2 for the reaction was considered to be 150 mg.

The reaction time had a significant effect on the amount of GA. The results of the effect of the reaction time on the reaction yield are shown in Fig. 3b. In each case, the reaction mixture was heated at 50 °C and then the flask was immediately transferred into the second oil bath which its temperature was adjusted at 80 °C and was heated for times indicated in Fig. 3b. It was found that a significant conversion could be observed with an increase of the reaction time to 10 h. However, further increase of the reaction time to 12.5 h and

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