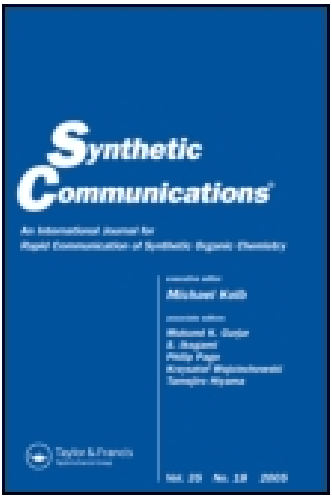

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Oxidation of Benzylic Alcohols to Carbonyl Compounds with Potassium Permanganate in Ionic Liquids

Anil Kumar [a], Nidhi Jain [a] & S. M. S. Chauhan [a]
[a] Department of Chemistry, University of Delhi, Delhi, 110 007, India
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Oxidation of Benzylic Alcohols to Carbonyl Compounds with Potassium Permanganate in Ionic Liquids

Anil Kumar, Nidhi Jain, and S. M. S. Chauhan*

Department of Chemistry, University of Delhi, Delhi, India

ABSTRACT

The selective oxidation of primary and secondary benzylic alcohols with potassium permanganate in ionic liquids to give corresponding aldehydes and ketones in 83–97% yields has been described.

Key Words: Ionic liquid; Potassium permanganate; Benzyl alcohol; Carbonyl compound.

INTRODUCTION

The selective oxidation of alcohols to carbonyl compounds without over oxidation to corresponding carboxylic compounds is of importance in

*Correspondence: S. M. S. Chauhan, Department of Chemistry, University of Delhi, Delhi 110 007, India; E-mail: smschauhan@chemistry.du.ac.in.

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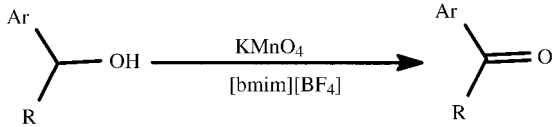
synthesis of natural products.[1] Different reagents, such as DMSO/DCC or oxalyl chloride,[2,3] clayfen,[4] 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3*H*-one (DMP),[5] *o*-iodoxybenzoic acid (IBX),[6] tetravalent chromium oxide™,[7] and hypochlorite/tetrabutylammonium salts,[8] have been used for oxidative transformation of alkyl and benzyl alcohols to corresponding aldehydes and ketones. The activity of $KMnO_4$ has been modified in phase transfer conditions as compared to acidic and basic aqueous conditions where it is non-selective oxidant.[9] Further, the reactivity of $KMnO_4$ has also been modified with the use of solid supports[10] such as $KMnO_4$ supported on $CuSO_4 \cdot 5H_2O$. The use of quaternary ammonium permanganates, like benzyltriethylammonium permanganate and tetra-*n*-butylammonium permanganate in above transformations, is restricted because of violent explosion encountered in their use at high temperature.[11]

1,3-Dialkylimidazolium salts are important class of ionic liquids and have been of considerable interest as environmentally benign, high-tech reaction media due to their unique chemical and physical properties such as excellent chemical and thermal stability with ease of reuse, miniscule vapour pressure, unique miscibilities, and non-flammability.[12–15] They have been employed as reaction media for various organic and enzymatic transformations,[16–18] for liquid–liquid separation[19] and catalyst recovery in organometallic catalysis.[20–23] Recently, the oxidation of alcohols to corresponding aldehydes using IBX in ionic liquid has been reported.[24] In a program towards development of chemical models for enzymes and materials from metallo 5,10,15,20-tetraaryl porphyrins, various types of aromatic aldehydes are needed.[25] Hence, oxidations of different benzylic alcohols to corresponding carbonyl compounds have been studied with potassium permanganate in ionic liquids (Sch. 1).

RESULT AND DISCUSSION

The oxidation of benzyl alcohol with potassium permanganate in 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4] ionic liquid at room temperature gave benzaldehyde in 90% yield in 1 hr. Similarly, other benzylic



Scheme 1.

alcohols were oxidized to the corresponding aldehydes and ketones in excellent yields (Table 1). Primary and secondary aliphatic alcohols, however, required longer time and higher temperature. Further, their conversion to corresponding carbonyl compounds was very low and thus benzylic alcohols could be selectively oxidized to carbonyl compounds in the presence of primary and secondary aliphatic alcohols with potassium permanganate in ionic liquids. In a mixture of benzyl alcohol and 2-phenylethanol, selective oxidation of benzyl alcohol was observed to give benzaldehyde in 88% yield and 97% of 2-phenylethanol was recovered. Further, the oxidation of 4′-(1″-hydroxyethyl)-2-phenylethanol gave 4-(2′-hydroxyethyl)acetophenone in 85% yield (Table 1, entry 12), where only benzylic alcohol is oxidized in presence of both benzylic and aliphatic hydroxyl groups in the same molecule.

The oxidation of benzyl alcohol with potassium permanganate in dichloromethane in presence of cetyltrimethylammonium bromide (CTAB) as phase transfer catalysts gave 58% of benzaldehyde and 23% benzoic acid in 5 hr. The yield of the product was low and reaction time longer as compared with those in ionic liquids. Further, over oxidation of benzaldehyde to carboxylic acid was also observed in phase transfer conditions. The presence of electron withdrawing substituents, such as chloro and nitro, on the benzene ring decreased the reaction rates but not the yields of the products.

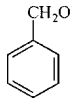
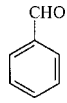
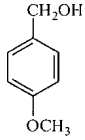
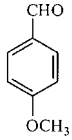
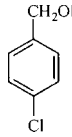
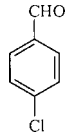
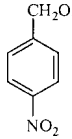
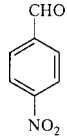
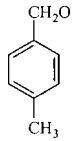
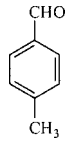
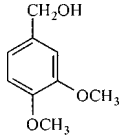
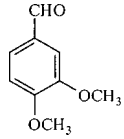
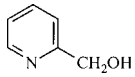
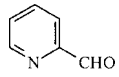
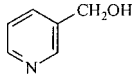
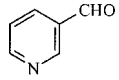
Recycling experiments were examined for the oxidation of benzyl alcohol with potassium permanganate in [bmim][BF_4]. Thus, after first run, which gave benzaldehyde in 90% yields, the ionic liquid was filtered, washed with dichloromethane, and concentrated. The recovered ionic liquid was subjected to a second cycle with addition of 1 equiv. of alcohol and 1 equiv. of potassium permanganate, which gave benzaldehyde in 91% yield. Similarly, in third, fourth, and fifth cycles, yield of benzaldehyde was 88%, 85%, and 84%, respectively (Table 2).

In conclusion, a mild, fast, and efficient method for the chemo-selective oxidation of benzylic alcohols to their corresponding carbonyl compounds in high yields by an environmentally friendly oxidant potassium permanganate in imidazolium ionic liquids has been developed.

EXPERIMENTAL

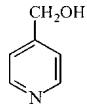
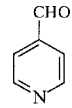
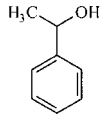
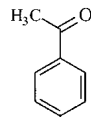
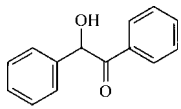
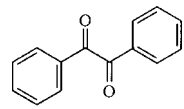
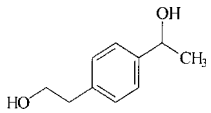
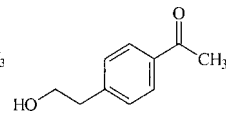
The ^1H and ^{13}C NMR spectra were recorded on Brucker Heaven (300 MHz) spectrophotometer using TMS as internal standard and $CDCl_3$ as solvent and chemical shift were expresssed in ppm. The IR spectra were recorded using KBr pellets on Perkin Elmer Spectrum 2000 infrared and ν_{max} were expressed in cm^{-1}. GC analysis was performed on Shimazdu GC-14B using packed column SE-30. The melting points were taken on

Table 1. Oxidation of benzyl alcohols with potassium permanganate in [bmim][BF_4] at room temperature.[a]

Run	Alcohol	Product	Time (hr)	Yield[b] (%)	Mp/bp (lit.)[26]
1			1	90[c]	177/750 mmHg[d] (179/750 mmHg)
2			1	97	246–249[d] (248)
3			1.5	88	49 (47)
4			2	86	107 (106)
5			1.5	96	202–203[d] (204–205)
6			1	97	46 (44)
7			2	87	63–64/13 mmHg[d] (62–63/13 mmHg)
8			2	85	95–96/26 mmHg[d] (97–99/26 mmHg)

(*continued*)

Table 1. Continued.

Run	Alcohol	Product	Time (hr)	Yield[b] (%)	Mp/bp (lit.)[26]
9			2	83	80–85/16 mmHg[d] (82–83/16 mmHg)
10			1	87	200/760 mmHg[d] (202/760 mmHg)
11			1.5	89	94–96 (95)
12			1	85	128/0.4 mmHg[d] (128–130/ 0.3 mmHg)[27]

[a]Reaction conditions: alcohol (1.0 mmol), $KMnO_4$ (1.0 mmol), and [bmim][BF_4] (2.5 mL).
[b]Yields refer to isolated pure products and the products were characterized by IR and ^{1}H NMR spectral data.
[c]Yield of benzaldehyde is 58% after 5 hr under phase transfer condition and 23% benzoic acid is also formed.
[d]Boiling point.

Thomas HOOVER capillary melting point apparatus and all the melting points and boiling points are uncorrected. The ionic liquid 1-*n*-butyl-3-methylimidazolium tetrafluoroborate {[bmim][BF_4]} was prepared by slight modification of literature procedure[28] and characterized by ^{1}H and ^{13}C NMR data.

Representative Procedure for the Oxidation of Benzyl Alcohol with $KMnO_4$ in Ionic Liquid

Powdered potassium permanganate (1.0 mmol) was added to benzyl alcohol (1.0 mmol) dissolved in [bmim][BF_4] (2.5 mL) and the reaction mixture was stirred at room temperature for 1 hr. The product was extracted with ethyl acetate (3 × 5 mL) and concentrated under reduced pressure to

Table 2. Oxidation of benzyl alcohol with $KMnO_4$ in recycled ionic liquid [bmim][BF_4].

Run	1	2	3	4	5
Yield (%)[a]	90	91	88	85	84

[a]Yields based on GC-analysis.

give benzaldehyde, which was purified by column chromatography over silica gel and characterized by IR, NMR spectroscopic data and comparison of Bp with the authentic sample. Similarly, other benzylic alcohols were oxidized to give corresponding carbonyl compounds and the yields and mp or bp are given in Table 1.

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