

## MILD AND EFFICIENT METHOD FOR OXIDATION OF ALCOHOLS IN IONIC LIQUID MEDIA

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In this study the strong oxidative agent, potassium permanganate, has been moderated with using under ionic liquid media for selective oxidation of some benzylic and aliphatic alcohols to their corresponding carbonyl compounds under mild and green conditions. 1-Butyl-3-methylimidazoliumbromide ([bmim]Br) (BMIM) associated with acetonitrile has been employed as modified media for oxidation of benzylic alcohols. This chemoselective and efficient process produced aldehydes and ketones with higher purity and yields and shorter reaction period in [bmim]Br as ionic liquid than conventional solvents.

(Received August 27, 2010; accepted October 15, 2010)

*Keywords:* ionic liquid, selective oxidation, 1-Butyl-3-methylimidazoliumbromide,  
benzylic and aliphatic alcohols

### 1. Introduction

Carbonyl compounds constitute important class of functional groups in organic chemistry, pharmaceuticals, dyes and industries [1, 2]. One of the basic approaches for preparation of carbonyl compounds is oxidation of alcohols [3]. The oxidation of alcohols to their corresponding aldehydes and ketones is of significant importance in organic chemistry, both for fundamental research and industrial manufacturing [4-6]. The world-wide annual production of carbonyl compounds is over  $10^7$  tones and many of these compounds are produced from the oxidation of alcohols [7]. Whereas the oxidation of alcohols into the corresponding aldehydes and ketones are a fundamental reaction in organic synthesis [8], still many oxidation processes use non-environmentally friendly reagents and solvents. The oxidation of alcohols is traditionally carried out with oxidants such as chromium reagents [9], permanganates [10], ruthenium (VIII) oxide [11] and etc. Unfortunately, these methods often require one or more equivalents of these relatively expensive oxidizing reagents.

There is considerable interest in the use of room temperature ionic liquids as promising substitutes for volatile organic solvents [12]. The ambient-temperature ionic liquids, especially those based on 1,3-dialkylimidazolium cations, have been emerged as promising green solvents in recent decades [13-15]. Ionic liquids have been used as media and catalysts for oxidation reaction since the 1950s [16]. More recently, it has been reported that the bis(acetylacetonato)nickel(II)/tetra-n-butylammonium tetrafluoroborate salt can be used in the liquid phase for oxidation of ethyl benzene in air yielding ethyl benzene hydroperoxide at atmospheric pressure [17]. Low-melting imidazolium and pyridinium ionic liquids are stable toward strong chemical oxidizing agents, such as fuming sulfuric acid [18, 19], and are, therefore, suitable media for oxidation reactions. various aromatic aldehydes were oxidized to the corresponding carboxylic

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acids using bis(acetyl-acetonato)nickel(II) immobilized in (BMI)PF<sub>6</sub> and dioxygen at atmospheric pressure as the oxidant [20]. More recently, classical oxidation of alcohols promoted by tetra-N-propylammonium perruthenate [21] have been performed in tetraethylammonium bromide or 1-ethyl-3-methylimidazolium hexafluorophosphate ionic liquid [22]. In comparison to the conventional solvents ionic liquids can also be used for oxidation reactions with higher yields and more selectivity [23].

One of the most prominent properties of an ionic liquid is its low vapor pressure. Obviously, the use of a nonvolatile ionic liquid simplifies the distillative workup of volatile products, especially in comparison with the use of low-boiling point solvents. Moreover, common problems related to the formation of azeotropic mixtures of the volatile solvents and the product/by-products formed is avoided by use of a nonvolatile ionic liquid. This option may be especially attractive technically, due to the fact that the stabilizing effects could already be observed even with quite small amounts of added ionic liquid [24]. Since the discovery of second-generation ionic liquids in 1992 [25], these novel media have been extensively investigated as solvents [26], and in particular for catalysis [27]. Some of the advantages of using ionic liquids in catalytic reactions are connected with the lack of a measurable vapor pressure. Products can be easily distilled out of the reaction mixture and the impact on the environment and operating personnel is dramatically reduced. In addition, due to the great choice of different ionic liquids, the solvent properties may be tuned to suit a particular application.

According to development of methods which consist of using of environmentally friendly reagents and in continue of our ongoing program to develop environmentally benign methods [28-32] we used 1-Butyl-3-methylimidazoliumbromide (Fig. 1) as ionic liquid in oxidation of alcohols derivatives to corresponding carbonyl compounds.

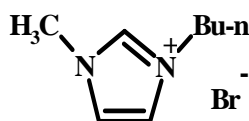


Fig. 1. [bmim]Br

## 2. Experimental

*General:* Yields refer to isolated pure products. The products were characterized by comparison their spectral (IR, <sup>1</sup>H NMR), melting and boiling points with authentic samples. All of the reactions were carried out in a hood with strong ventilation. IR spectra were recorded on Magna-550 IR spectrophotometer. Spectra of solids were carried out using KBr pellets. <sup>1</sup>H NMR spectra were determined on Hitachi R-24, B-360 spectrometers at 60 MHz using CDCl<sub>3</sub> as solvent and TMS as internal standard.

*Typical Procedure for Oxidation of Benzylic Alcohols:* To a mixture of benzyl alcohol (2 mmol), [bmim]Br (1 mmol, 0.219 g) in a round bottomed flask, was added KMnO<sub>4</sub> (1.6 mmol, 0.253 g). The reaction mixture was stirred at 50°C under solvent-free conditions. After completion of the reaction which monitored with TLC (n-hexane:EtOAc 75:25), the reaction mixture was cooled and diluted with diethyl ether (10 ml) and filtered to remove the solids. Ionic liquid phase was recovered for further uses, the solvent was evaporated under reduced pressure and the residue was purified by thick layer chromatography method (EtOAc: petroleum ether, 1:9, & 20 × 20 plate sized).

*Typical Procedure for Oxidation of Aliphatic Alcohols:* The similar procedure was carried out at room temperature for aliphatic alcohols.

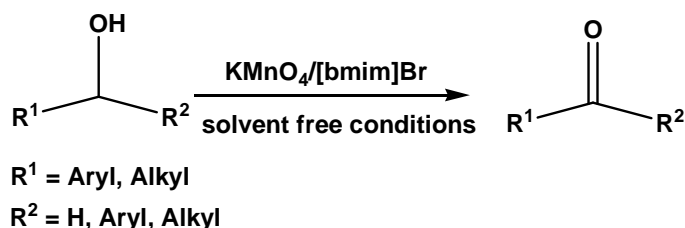
*Typical Procedure for Oxidation of Alcohols in the Mixture of Ionic Liquid and Acetonitril Media:* The similar procedure was carried out under refluxing conditions in ratio of 1: 0.5: 1.5: 0.75 for benzylic alcohol: IL: CH<sub>3</sub>CN: KMnO<sub>4</sub> and in ratio of 1: 0.5: 0.2: 0.65 for aliphatic alcohols: IL: CH<sub>3</sub>CN: KMnO<sub>4</sub>.

### 3. Results and discussion

In this investigation a variety of benzylic and aliphatic alcohols were oxidized by KMnO<sub>4</sub> in ionic liquid [bmim]Br media to the corresponding carbonyl compounds (Scheme 1 and Table 1).

Trying several conditions for optimizing the reaction conditions, the best results were obtained by using alcohol: IL: KMnO<sub>4</sub> in ratio of 1: 0.5: 0.8 mmol at 50 °C. In similar method, optimized parameters were obtained for aliphatic alcohols by using ratio of alcohol: IL: KMnO<sub>4</sub> in 1: 0.5: 0.7 ratio at room temperature. The obtaining results for benzylic alcohols show that derivatives with electron withdrawing substituents have been oxidized faster and in higher yield than others, however in comparison with aliphatic alcohols; benzylic alcohols were oxidized very slowly in higher temperatures. Moreover, compare to the other method [30] in which 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF<sub>4</sub>] was used as ionic liquid, by increasing the steric effect in accordance with the molecular weight of alcohols, the reaction rates and also their yields reasonably are reduced. In other hand, to overcome the mentioned challenge, we tried to change the polarity of the media by addition of acetonitrile to the ionic liquid and optimized the ratio of reagents with choice of benzyl alcohol as substrate. Our attempts showed that the best results can be achieved as alcohol: IL: CH<sub>3</sub>CN: KMnO<sub>4</sub> in ratio of 1: 0.5: 1.5: 0.75 under refluxing conditions. Optimized parameters were obtained for aliphatic alcohols with choosing molar ratio for alcohol: IL: CH<sub>3</sub>CN: KMnO<sub>4</sub> 1: 0.5: 0.2: 0.65 under refluxing conditions.

The results obtained from this modification in Table 1, show that the use of acetonitrile with ionic liquid cause the faster oxidation of benzylic alcohols with higher yields. This modified method did not affect on oxidation of first linear alcohols but was concluded the best, in the case of second ones.



Scheme 1: Conversion of alcohols to the corresponding carbonyl compounds in the presence of IL.

Table 1: Conversion of alcohols to the corresponding carbonyl compounds in the presence of [bmim]Br/KMnO<sub>4</sub> at 50 °C in benzylic alcohols and at room temperature for linear alcohols.

Entry	R <sup>1</sup>	R <sup>2</sup>	Time (hr)	Yields (%) <sup>b</sup>		mp or bp °C/Torr (lit. <sup>28-34</sup> ) <sup>a</sup>
1	C <sub>6</sub> H <sub>5</sub>	H	2	92 <sup>c</sup>	95 <sup>d</sup>	176/690 (179)
2	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	H	1.5	95	>98	105 (106)
3	3-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	H	2	93	>98	55-57 (58)
4	4-MeOC <sub>6</sub> H <sub>4</sub>	H	1	97	98	246/690 (248)
5	3-MeOC <sub>6</sub> H <sub>4</sub>	H	2	93	95	231/690 (232)
6	2,4(MeO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	0.8	94	97	69/690 (67-70)
7	4-ClC <sub>6</sub> H <sub>4</sub>	H	1	94	>98	45-46 (47)
8	4-BrC <sub>6</sub> H <sub>4</sub>	H	0.9	92	>98	57-59 (59-61)
9	2,6-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	1	89	91	70-72 (71)
10	2,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	1	92	>98	72-74 (74.5)
11	4-MeC <sub>6</sub> H <sub>4</sub>	H	1.5	93	95	206/690 (204-205)
12	2-MeC <sub>6</sub> H <sub>4</sub>	H	1	91	94	195/690 (197)
13	3-MeC <sub>6</sub> H <sub>4</sub>	H	1	92	92	200/690 (201)
14	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	1	80	83	47 (47-49)
15	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	1	85	89	18-19 (20)

16	4-ClC <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub>	1.5	80	92	19-21 (20)
17	4-BrC <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> Br	1.5	81	93	108 (110-111)
18	2-HOC <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub>	2	52	62	239-240/690 (243)
19	CH <sub>3</sub> CH <sub>2</sub>	H	1	93	-	46/690 (47-48)
20	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub>	H	1.1	95	-	73/690 (75-76)
21	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub>	H	1.5	91	-	97/690 (102)
22	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub>	H	2	92	-	125-126/690(129-131)
23	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	H	2	90	-	151-152/690 (153)
24	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub>	H	2.5	89	-	163-164/690 (167)
25	CH <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub>	1	81	93	112-113/690 (116.8)
26	CH <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub>	1.5	83	93	78/690 (79.6)
27	CH <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	1.5	82	89	101/690 (102)
28	CH <sub>3</sub> CH <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub>	1	81	87	99-100/690(101.5)
29	CH <sub>3</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub>	1	84	90	150-151/690 (151.45)

<sup>a</sup>Confirmed by comparison with authentic samples.

<sup>b</sup>Yields of isolated pure products after purification.

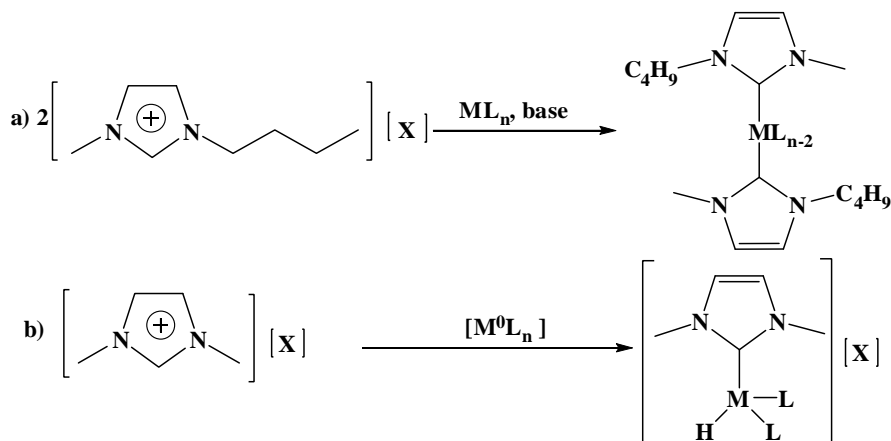
<sup>c</sup>Yields of products in solvent free conditions.

<sup>d</sup>Yields of products in the presence of acetonitrile.

### The Role of Ionic Liquid

Depending on the coordinative properties of the anion and on the degree of the cation's reactivity, the ionic liquid can be regarded as a ligand (or ligand precursor), as a co-catalyst, or as the catalyst itself. Ionic liquids with weakly coordinating, inert anions such as [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N]<sup>-</sup>, [BF<sub>4</sub>]<sup>-</sup>, or [PF<sub>6</sub>]<sup>-</sup> under anhydrous conditions and inert cations can be looked on as "innocent" solvents in transition metal catalysis. In these cases, the role of the ionic liquid is solely to provide a more or less polar, more or less weakly coordinating medium for the transition metal catalyst, but which additionally offers special solubility for feedstock and products [35]. However, the chemical inertness of these media does not necessarily mean that the reactivity of a transition metal catalyst dissolved in the ionic liquid is equal to the reactivity observed in common organic solvents. This becomes understandable from the fact that many organic solvents applied in catalytic reactions do not behave as innocent solvents, but show significant coordination to the catalytic center [35]. In the other hand, ionic liquids formed by treatment of a halid salt with a Lewis acid (such as chloroaluminate or chlorostannate melts) generally act both as solvent and as co-catalyst in transition metal catalysis. The reason is that the Lewis acidity or basicity, which is always present (at least latently), results in strong interactions with the catalyst complex. In many cases, the Lewis acidity of an ionic liquid is used to convert the neutral catalyst precursor into the corresponding cationic active form [36-39]. Both the cation and the anion of an ionic liquid can act as a ligand or ligand precursor for a transition metal complex dissolved in the ionic liquid. An imidazolium moiety as an ionic liquid cation can act as a ligand precursor for the dissolved transition metal. (Scheme 2) [35,40].

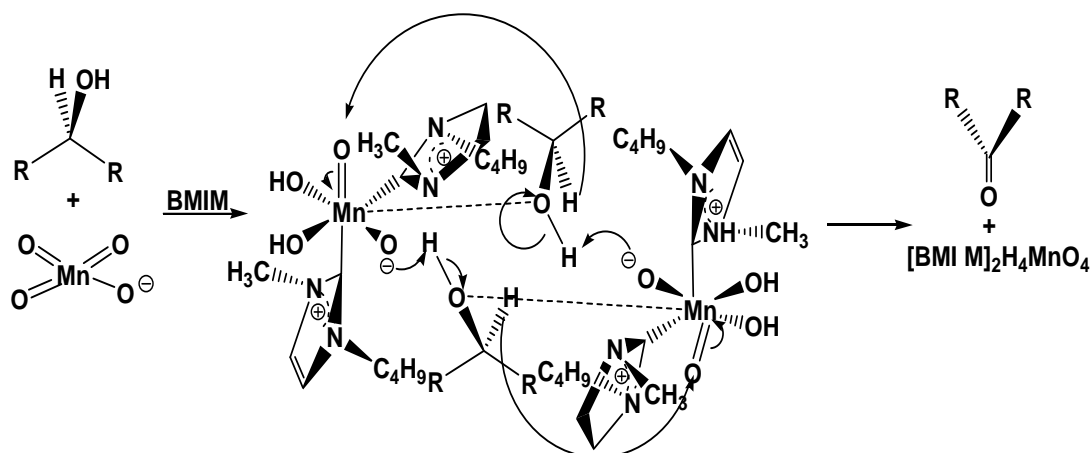
The first reaction pathway for the in situ formation of a metal-carbene complex in an imidazolium ionic liquid is based on the well known, relatively high acidity of the H atom in the 2-position of the imidazolium ion [41-43].



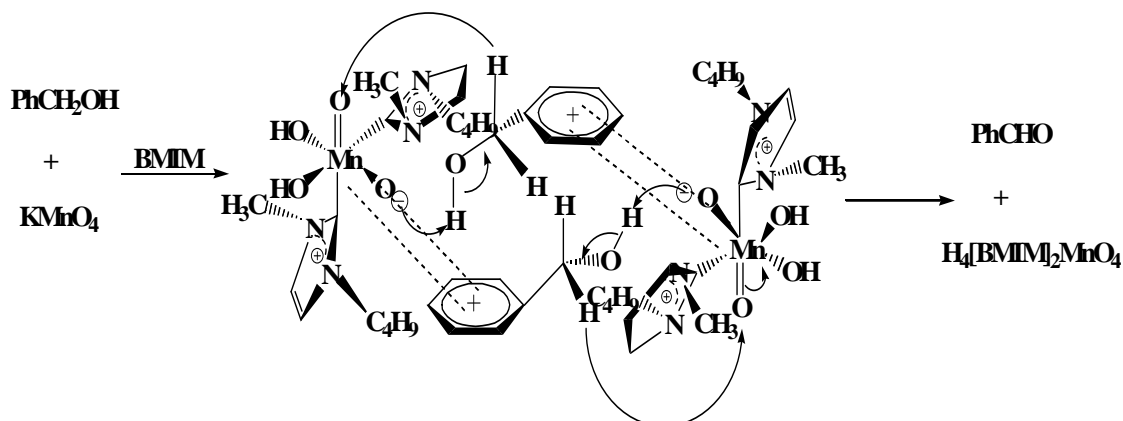
Scheme 2: Different potential routes for in situ ligand formation from an imidazolium cation of an ionic liquid [35].

This can be removed (by basic components in reaction media, for example) to form a metal-carbene complex (see Scheme 2, route a). Xiao and co-workers demonstrated that a Pd imidazolylidene complex was formed when Pd(OAc)<sub>2</sub> was heated in the presence of [BMIM]Br [44]. Mathews et al. were later able to characterize an isolated Pd-carbene complex obtained in this way by X-ray spectroscopy [45]. It should be mentioned that strong bases can also abstract a proton here, to form methyleneimidazoliden species that may also act as a strong ligand to electrophilic metal centers. Another means of in situ metal-carbene complex formation in an ionic liquid is the direct oxidative addition of the imidazolium cation to a metal center in a low oxidation state (see Scheme 2, route b). More recently, it has been reported that stable compounds in the carbene category have been made and definite structural and electronic information is now available [46-48]. Apparently, the stability of these carbenes is derived from a combination of steric and electronic factors that are recorded in the previous literatures [49, 50].

In this attempt, we try to introduce the mechanism according to the passage and the reported mechanism for using the potassium permanganate in the presence of ionic liquid in the oxidation reaction of alcohols [51]. Increasing the steric hindrance surrounding the magnesium atom by imidazolium ligands lead to reduce the rate of reaction (see scheme 3 for formation of carbenic complex with linear alcohols and scheme 4 for formation of carbenic complex with benzylic alcohols).



Scheme 3. Possible mechanism for formation of carbenic complex with linear alcohols.



Scheme 4. Possible mechanism for formation of carbenic complex with benzylic alcohols

As the results show in Table 1, the reactions in more steric hindrances in benzylic alcohols are carried out more slowly than linear ones. In similar reason, the rate of reactions and the yields are reduced in some cases by increasing the molecular weight. However, the reaction times were reduced when we tried to improve the yields using some acetonitrile to optimize the polarity. But, to define exactly how polarity ranges affect the reaction; additional experiments are necessary in future.

#### 4. Conclusions

In conclusion, we developed a mild and efficient method for selective oxidation of some benzylic and aliphatic alcohols to their corresponding carbonyl compounds by the strong oxidative agent, potassium permanganate using under ionic liquid media. This chemoselective and efficient process produced aldehydes and ketones with higher purity and yields and shorter reaction time in [bmim]Br as ionic liquid than conventional solvents. Therefore, developing green and efficient catalysts or solvents for oxidation of alcohols that can use less amounts of oxidant and use of safe and recyclable solvents is of paramount importance for both economic and environmental reasons. Finally oxidation of alcohols to their corresponding carbonyl compounds in ionic liquid media by addition of acetonitrile was achieved in mild reaction conditions without any additional oxidation to acids.

#### Acknowledgements

The authors gratefully acknowledge the financial support of this work by the Research Affairs Office of the University of Kashan, Kashan, I. R. Iran. Dr A H. Bamoniri and Mohammad Esmaeili acknowledged for their helps in the preparation of this paper.

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