

A Facile and Efficient Oxidation of α,β -Unsaturated Alcohols with Manganese Dioxide in Ionic Liquids under Mild Conditions

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Abstract: The oxidation of α,β -unsaturated primary and secondary alcohols to corresponding aldehydes and ketones by manganese dioxide in ionic liquids as a safe recyclable and accelerative reaction medium under mild conditions are described. The rate of the oxidation reaction is faster and the yield is higher than that with conventional procedures.

Keywords: Ionic liquids, manganese dioxide (MnO_2), α,β -unsaturated alcohols, oxidation.

Recently, studies of the application of neoteric solvents¹⁻² such as supercritical CO_2 ³⁻⁴, aqueous biphasic systems⁵, and ionic liquids⁶⁻⁷ have attracted the attention of many peoples. Especially ionic liquids have an important impact on organic reactions because of their unique properties such as negligible vapor pressure, high solvating but low coordinating properties and recyclability *etc.*⁷⁻⁸. Some papers have demonstrated that ionic liquids is a valuable solvent for reactions between organic compounds and inorganic salts⁹.

The oxidation of alcohols to carbonyl compounds is an important transformation that is encountered at all levels of organic synthesis. The past investigation has shown active manganese dioxide (MnO_2) to be a reliable selective oxidising reagent for allylic¹⁰⁻¹¹, polyene¹², allyl¹³ and benzylic¹⁴⁻¹⁵ alcohols. The oxidation of organic compounds with MnO_2 has been performed in many solvents. The choice of the solvents is important. Most of the reactions described in the literatures were carried out in aliphatic or aromatic hydrocarbons, chlorinated hydrocarbons, diethyl ether, THF, ethyl acetate, acetone, and acetonitrile. In the past case of the oxidation of benzylic¹⁵ and allylic¹¹ alcohols, the best results have been obtained using diethyl ether. However, many of these conventional methods are deficient in some respects, for example, a large of solvents, long reaction time and comparatively high temperature¹⁶ were needed. Recently, some new protocols were reported. S. Varma and

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co-workers described a method that alcohols are oxidized to the corresponding aldehydes and ketones by silica supported active MnO_2 under microwaves conditions¹⁷. Lou and Xu reported the oxidation of alcohols to corresponding carbonyl compounds by MnO_2 under solvent free conditions¹⁸. But still there are some drawbacks in the above protocols, for example, reaction temperature for solid substrates must be near or higher than their melting points¹⁸.

In some cases the room temperature ionic liquids can result in enhanced rates of chemical processes and can provide higher yield compared to conventional solvents¹⁹. In view of high polarity and the ability to solvate both inorganic and organic compounds, we wish to introduce the ionic liquids into the oxidation of alcohol with MnO_2 . Here we disclose the results in the following **Table 1**. It can be seen in the **Table 1** that the oxidation of α,β -unsaturated primary and secondary alcohols to corresponding aldehydes and ketones in room temperature ionic liquids using MnO_2 is a facile and very efficient procedure.

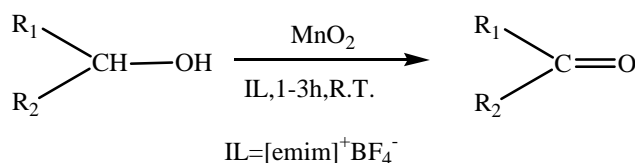


Table 1 Oxidation of α,β -unsaturated primary and secondary alcohols with manganese dioxide in room temperature ionic liquids

Entry	R ₁	R ₂	Time(h)	m.p./b.p.(°C)	Lit.m.p./b.p.(°C)	Ref.	Yield(%) ^{a,b}
a	C ₆ H ₅ CH ₂	H	1	80	79	20	95
b	<i>p</i> -CH ₃ OC ₆ H ₄ CH ₂	H	1	0	0	23	90
c	<i>p</i> -CH ₃ C ₆ H ₄ CH ₂	H	1	105/10mm	106/10mm	20	92
d	<i>p</i> -HOC ₆ H ₄ CH ₂	Ht	1.5	118	117	20	87
e	<i>p</i> -ClC ₆ H ₄ CH ₂	H	2	45-46	47	20	85
f	<i>p</i> -BrC ₆ H ₄ CH ₂	H	2	68	67	20	83
g	<i>p</i> -O ₂ NC ₆ H ₄ CH ₂	H	3	106-108	107	20	80
h	2-HO-5-Cl-C ₆ H ₃ CH ₂	H	2.5	99-100	100	20	85
i	C ₆ H ₅ CH=CH	H	1	132/20mm	130/20mm	23	92
j	C ₆ H ₅	CH ₃	1.5	200-202	202	20	90
k	C ₆ H ₅	C ₆ H ₅	2	47	48-49	23	87
l	C ₆ H ₅ C=C	C ₆ H ₅	2	45-46	44	22	85

^aIsolated yield after chromatographic purification;

^bAll the product characterized by b.p., m.p., elemental analyses, IR and NMR spectroscopy;

We chose more popular [emim]⁺[BF₄]⁻ (1-ethyl-3-methylimidazolium tetrafluoroborate) as the reaction media and obtained carbonyl compounds from corresponding alcohols at room temperature in high yield. The reaction can proceed facilely at room temperature in ionic liquids whereas conventional methods require high temperature (for example, refluxed in water¹⁶) or microwave activation¹⁷. A variety of α,β -unsaturated primary and secondary alcohols are converted into corresponding aldehydes and ketones in excellent yield (**Table 1**). We found that the presence of an electron-withdrawing group on the benzene ring have adverse effect on the rate and yield of the reaction (**Table 1**, Entry **d-g**). However, yields are as good as with conventional solvents. In addition, the method has two distinct merits. First, the rate of reaction is faster compared with conventional methods^{14-15,18}, most of reactions were completed in less than 3 h (for example, for benzylic alcohol 1 h in [emim]⁺BF₄⁻ (**Table 1**), 94 h in ether¹⁵ and 23 h in chloroform¹⁴). Furthermore, the recycling of the solvent is another merit of the reaction. We found that the ionic liquids could almost be quantitatively recovered with simple procedure. After the product was extracted with ether, the rest of the ionic liquid was filtrated, concentrated *in vacuo* (10.0 torr for 6 h at room temperature). The same procedure was repeated up to 4 times using recovered ionic liquids. The recycled ionic liquid has little effect on the reaction rate and yield of the product (**Table 2**).

Table 2 The yield with reused of the ionic liquids [emim]⁺BF₄⁻

cycle	yield(%)	cycle	yield(%)
1	95	4	94
2	93	5	92
3	92	6	90

^a Isolated yield based on benzyl alcohol

In summary, at room temperature the oxidation of α,β -unsaturated primary and secondary alcohols to corresponding aldehydes and ketones by MnO₂ in ionic liquids is a novel, efficient method. The products were readily separated from the ionic liquids *via* extraction. The reactions with recycled solvents were found no obvious decrease in yield.

General Procedure: To a 25 mL flask, the solution of benzyl alcohol (0.20 g, 1.85 mmol) and manganese dioxide (0.32 g 3.70 mmol) in [emim]⁺BF₄⁻ (3 mL) was stirred at room temperature for 1 h. The reaction mixture was extracted with ether (3×5 mL). The ether layer was separated. The ionic liquid phase can be reused. The product was further purified by column chromatography (10:1, petroleum ether/ethyl acetate), yield: 95%. Active MnO₂ is prepared from potassium permanganate (KMnO₄) under basic conditions according to the literature²¹. All the compounds were characterized by NMR, MS and physical constants.

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