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# Oxidation of sec-Alcohols Catalyzed by Mn(Salen) in Ionic Liquids

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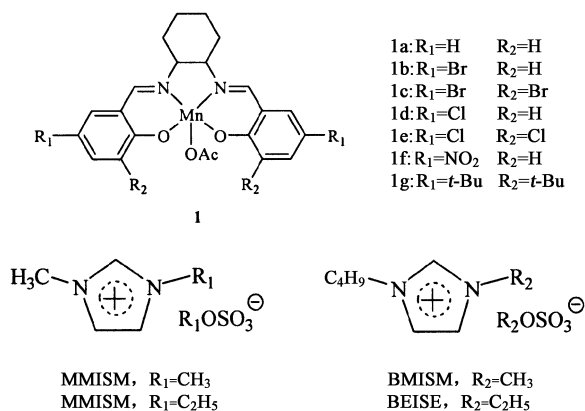
**Key words:** Mn(Salen); Sec-alcohols; Oxidation; Ionic liquids

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Oxidation of alcohols to the corresponding carbonyl compounds plays a central role in organic chemistry<sup>[1]</sup>. Traditionally, the transformation is performed with stoichiometric and toxic oxidants, such as o-iodoxybenzoic acid (IBX), permanganate, chromium reagents, which are cost-ineffective and yield large quantities of noxious waste<sup>[2~4]</sup>. Therefore, it is not surprising that in the area of oxidative transformations one major goal is the replacement of stoichiometric procedure with catalytic procedures<sup>[5~6]</sup>. On the other hand, salen as a kind of ligand shows wide applicability and its metal complexes act as highly selective catalysts for a variety of reactions such as epoxidation<sup>[7~8]</sup>, cyclopropanation<sup>[9]</sup>, asymmetric epoxide ring-opening reactions<sup>[10]</sup>, kinetic resolution of sec-alcohols<sup>[11]</sup> and so on. In our research group, Li Jing-wei employed Mn(Salen) complexes to oxidize sec-alcohols by PhI(OAc)<sub>2</sub> in CH<sub>3</sub>CN with excellent yield in 2004<sup>[12]</sup>.

Room temperature ionic liquids (RTILs) as a novel reaction media are interesting solvents in the last decade due to their unique physical properties such as non-volatility, non-flammability and thermal stability. They have been employed for organic synthesis, catalytic reactions, electrochemistry, extractions and so on<sup>[13~19]</sup>. Additionally in a few catalytic reactions involving the use of ionic liquids, they could provide a

new approach for catalyst separation and recycling by immobilizing the catalyst in RTILs<sup>[5,20]</sup>. In the catalytic oxidation of alcohols, the use of ionic liquids as reaction medium also brought definitive advantages over an organic catalytic phase: the reaction proceeded with high efficiency and the rate was much higher than that of in organic solvent<sup>[21~25]</sup>. In view of the fact that 1,3-dialkylimidazolium sulfate ionic liquids are cheap, stable and not used very much in catalytic oxidation reactions, So herein, we report the oxidation of selected sec-alcohols with iodobenzene diacetate (IBDA) catalyzed by Mn(Salen) complexes in such ionic liquids under gentle reaction conditions.



Scheme 1

Initially for the purpose of comparison, the oxida-

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tion of  $\alpha$ -methylbenzyl alcohol with  $\text{PhI}(\text{OAc})_2$  was chosen as model reaction in the presence of Mn (Salen) complexes **1a-1g** with different substituting groups.  $\alpha$ -methylbenzyl alcohol was oxidated into acetophenone without any other by-products (Table 1).

Table 1 Oxidation of  $\alpha$ -methylbenzyl alcohol by Mn(III) complexes **1a-1g**<sup>a</sup>

Entry	Catalyst	R <sub>1</sub>	R <sub>2</sub>	Yield <sup>b</sup> (%)
1	<b>1a</b>	H	H	95.3 (42.7) <sup>c</sup>
2	<b>1b</b>	Br	H	97.2 (62.5)
3	<b>1c</b>	Br	Br	97.8 (65.4)
4	<b>1d</b>	Cl	H	82.1 (73.2)
5	<b>1e</b>	Cl	Cl	83.8 (40.5)
6	<b>1f</b>	NO <sub>2</sub>	H	87.6 (96.4)
7	<b>1g</b>	<i>t</i> -Bu	<i>t</i> -Bu	59.3 (33.3)


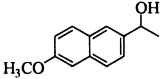
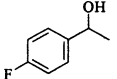

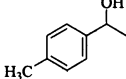

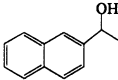
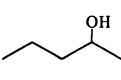
<sup>a</sup> Reaction conditions: molar ratio of Catalyst:  $\alpha$ -methylbenzyl alcohol:  $\text{PhI}(\text{OAc})_2 = 1: 50: 70$ ;

rt; 1 h; MMISM/ $\text{CH}_2\text{Cl}_2$  (1/4, v/v); solvent volume: 2.5 mL

<sup>b</sup> Estimated by GC using decane as an internal standard

<sup>c</sup> The data inside the parentheses are for  $\text{CH}_2\text{Cl}_2$  of 2.5 mL as solvent

Table 2 Oxidation of various sec-alcohols with **1c**-IBDA system in MMISM- $\text{CH}_2\text{Cl}_2$  (1:4, v/v)<sup>a</sup>

Entry	Substrate	Yield (%)	Entry	Substrate	Yield (%)
1		97.8	5		71.3
2		78.7	6		96.3
3		63.4	7		40.3
4		99.0	8		42.7

<sup>a</sup> Reaction conditions: molar ratio of Cat. (**1c**):  $\alpha$ -methylbenzyl alcohol:  $\text{PhI}(\text{OAc})_2 = 1: 50: 70$ ; rt; 1 h; MMISM/ $\text{CH}_2\text{Cl}_2$  (1/4, v/v); solvent volume: 2.5 mL

reaction rate, which was better than that observed in traditional [bmim]BF<sub>4</sub> medium. The oxidation reaction in the presence of MEISE was rather sluggish, which was compared with that of in simple [bmim]PF<sub>6</sub> (due

One can see from the results, that the activities of the catalysts in the presence of MMISM were better than that of in pure  $\text{CH}_2\text{Cl}_2$  except **1f**. Moreover, among these catalysts **1c** was the best one, which may be arise from its strongly electron-drawing effect and high solubility in MMISM.

We employed **1c** as a tentative catalyst to further expand the scope of substrates in the catalytic system. The results obtained are listed in Table 2. The data show that this catalyst system is suitable to a wide range of sec-alcohols. Moreover, the activity of aliphatic sec-alcohols is lower than that of activated aromatic sec-alcohols. In addition, we can also see that the non-substituted aromatic sec-alcohols could convert into corresponding ketones with a quantitative yield.

Further, a series of 1,3-dialkylimidazolium-based ionic liquids containing sulfate anion were tested as immobilizing agents for **1c** in the catalytic oxidation of  $\alpha$ -methylbenzyl alcohols (Fig. 1). Except MEISE, other ionic liquids containing sulfate anion all brought advantages over an organic catalytic phase in accelerating

to insolubility of  $\alpha$ -methylbenzyl alcohols with [bmim]PF<sub>6</sub>).

It was noteworthy that unchanged reactant and product were both easily removed from the reaction

mixture via extraction with n-hexane, which is immiscible with the ionic liquids and that the catalyst was retained in the ionic liquids. We studied the recyclability of the catalytic system in various RTIL-CH<sub>2</sub>Cl<sub>2</sub> (1:4,

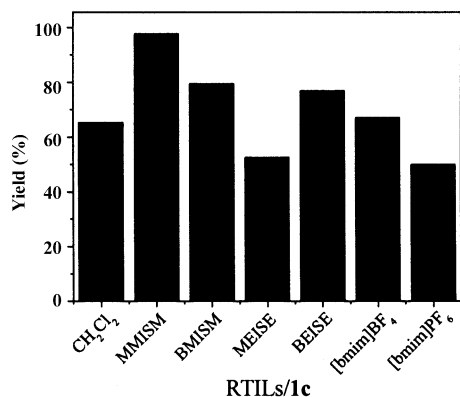


Fig. 1 Influence of the type of ionic liquids on the catalytic performance of **1c**<sup>a</sup>

<sup>a</sup> Reaction conditions: molar ratio of Cat.

(**1c**):  $\alpha$ -methylbenzyl alcohol:  $\text{PhI}(\text{OAc})_2 = 1: 50: 70$ ; rt; 1h; RTIL-CH<sub>2</sub>Cl<sub>2</sub> (1:4, v:v); solvent volume: 2.5 mL

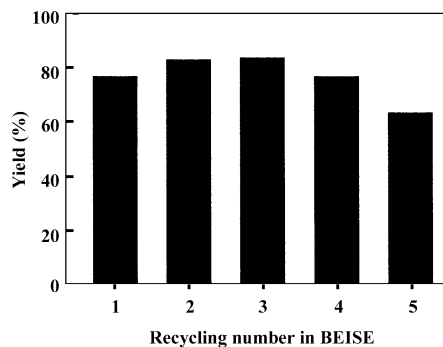
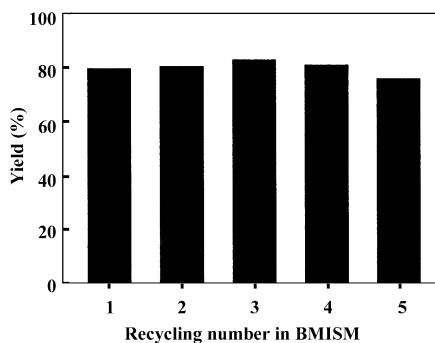


Fig. 2 Recovery and reuse of BMISM or BEISE phase containing catalyst **1c**

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v:v)/**1c**. We found that  $\alpha$ -methylbenzyl alcohol conversion decreased with a different degree when the different RTIL/**1c** system were recycled. Thereinto, the recyclability of catalyst **1c** in BMISM or BEISE was much superior to that observed in other ionic liquids in this paper, which showed that catalyst **1c** is more stable in such two ionic liquids (Fig. 2). Beat all for MMISM, the activity of catalyst **1c** almost remained constant in the first three runs (conversion of  $\alpha$ -methylbenzyl alcohol slightly decreased from 97.8% in the first run to 89.2% in the third run), then decreased dramatically to 62.1% in the forth run.

In summary, we have shown that oxidation of secondary alcohols could be efficiently catalyzed by Mn(salen) in 1,3-dialkylimidazolium sulfate ionic liquids with a well-proportioned CH<sub>2</sub>Cl<sub>2</sub>. The use of such kinds of ionic liquids as medium can not only significantly accelerate reaction rate but also be useful for recycling of catalyst from reaction mixture.

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## 离子液体中 Mn(Salen) 催化仲醇的氧化反应研究

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**摘 要:**以  $\text{PhI}(\text{OAc})_2$  为氧化剂, 考察了 1,3-二烷基咪唑硫酸酯系列离子液体中 Mn(Salen) 催化仲醇氧化的反应. 结果表明, 在  $\text{MMISM}-\text{CH}_2\text{Cl}_2$  (1:4, v:v) 混合溶剂中, 反应条件为  $n(-\text{苯乙醇}): n(\text{醋酸碘苯}): n(\text{催化剂 } \mathbf{1c}) = 50: 70: 1$  时,  $(-\text{苯乙醇})$  的转化率可以达到 97.8%, 产物苯乙酮的选择性为 100%, 远高于在纯  $\text{CH}_2\text{Cl}_2$  中的结果, 也要好于  $[\text{bmim}]\text{BF}_4$  和  $[\text{bmim}]\text{PF}_6$  对该反应的促进作用. 此外, BMISM 及 BEISE 对催化剂 **1c** 有较好的稳定作用, 催化剂可以重复使用.

**关 键 词:** Mn(Salen); 仲醇; 氧化; 离子液体