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Room Temperature Ionic Liquid: a Powerful Additive of Mn(Salen) Catalyzed Oxidation of *sec*-Alcohols

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Abstract: A simple, mild, efficient Mn(salen)-catalyzed oxidation system of secondary alcohols, in which the ionic liquid [bmim]PF_6 acts as a powerful additive, has been described. The reaction proceeded with higher efficiency. The catalyst was more easier to recycle in ionic liquid [bmim]PF_6 with a well-proportioned CH_2Cl_2 than in the single CH_2Cl_2 or ionic liquid.

Keywords: Salen Mn, ionic liquid, *sec*-alcohols, oxidation.

The oxidation of alcohols to carbonyl compounds is a fundamental reaction in organic chemistry[1]. Traditionally, this transformation is performed with stoichiometric, toxic and expensive inorganic oxidants(such as chromium reagents) and in organic solvents which are of volatility, toxicity and flammability[2]. Today some methods have been described especially in seeking green solvents and efficient catalysts[3]. On the other hand, salen was a ligand that showed wide applicability and its metal complexes were also used as catalysts for a variety of reactions such as epoxidation, cyclopropanation, Diels-Alder reacton and kinetic resolution of sec-alcohols and so on[4]. In 2000, Waldermar Adam employed Cr(III) complexes to oxidize chemoselectively allylic alcohols by PhIO oxidant under catalytic conditions[5]. However, the limitations are that the reaction is time-consuming and the reuse of the catalysts is difficult.

The use of room temperature ionic liquids provided us with wider room in searching environmentally benign catalytic system[6]. Nowadays it has been used in a broad range of chemical processes including manganeseporphyrin catalyzed alkenes epoxidation in [bmim]PF_6 reported by our research group[7]. Herein we describe an extremely effective and reusable oxidation system of sec-alcohols, performed in ionic liquid [bmim]PF_6 with a well-proportioned CH_2Cl_2. And the catalyst is a simple salen Mn complex.

In a previous study[8], we studied the effect of different Mn(salen) complexes **2a-h** as catalysts on the oxidation of DL-*sec*-phenethyl alcohol at room temperatureand found that complex **2e** served as an efficient catalyst, but complex **2a** merely had moderate catalytic activity. Because ionic liquids had the evident rate acceleration effect on some catalytic reactions, for example, scandium triflate catalyzed Fridel-Crafts alkylation of

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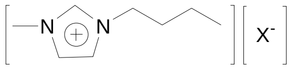
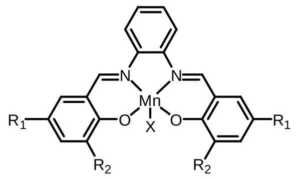
arenes[9], Mn(salen) catalyzed asymmetric epoxidation of olefins[10], we employed **2a** as a tentative catalyst and observed whether there was the same rate acceleration effect on the oxidation of alcohols. Very interestingly, under the same other conditions, the reaction proceeded more rapidly in the ionic liquid [bmim]PF_6 **1a**[11] with a well-proportioned CH_2Cl_2 than in the single solvent, dichloromethane or **1a** and the pure ionic liquid did not give a satisfactory rate acceleration in this reaction. Then we attempted another ionic liquid [bmim]BF_4 **1b**[11] as an additive and found that its effect on the reaction rate is poor.

We chose three kinds of different fractions of **1a** to make a kinetic study, which could clearly illustrates that the remarkable distinction in the rate acceleration of the reaction results from the different mixed proportion. As shown in **Figure 2**, the reaction was almost complete with 30 min in the mixed solvent[**1a**(0.25 equiv.)+CH_2Cl_2], however, there was no obvious rate acceleration effect in the mixed solvent[**1a**(4 equiv.)+CH_2Cl_2].

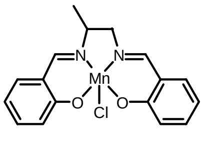
Figure 1



1a: X=PF_6 **1b:** X=BF_4

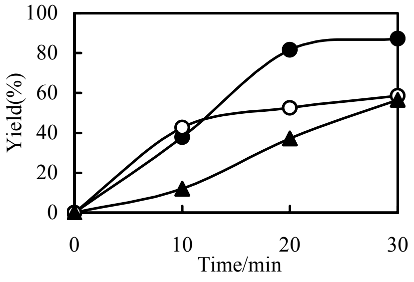


2a: R_1=H; R_2=H; X=OAc **2b**: R_1=H; R_2=t-Bu; X=Cl
2c: R_1=t-Bu; R_2=t-Bu; X=Cl **2d**: R_1=Cl; R_2=H; X=Cl
2e: R_1=Br; R_2=H; X=Cl **2f** : R_1=NO_2; R_2=H; X=Cl
2g: R_1=NO_2; R_2=NO_2; X=Cl



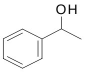
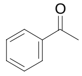
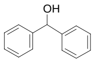
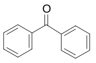
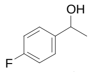
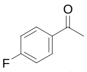
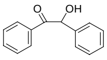
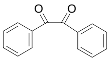
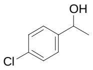
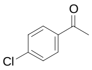
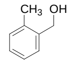
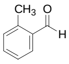
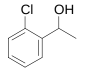
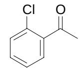
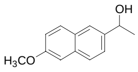
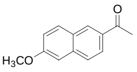
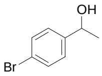
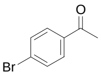
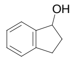
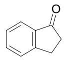
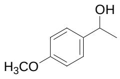
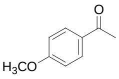
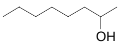
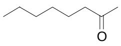
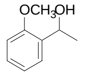
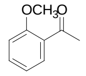
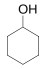
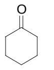
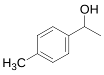
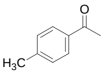
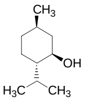
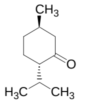
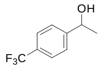
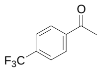
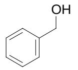
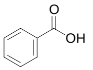
2h

Figure 2 Kinetic studies in the oxidation reaction of DL-*sec*-phenethyl alcohol



○ CH_2Cl_2 (1 mL) ● **1a**(0.25 equiv.)+CH_2Cl_2 ▲ **1a**(4 equiv.)+CH_2Cl_2
DL-*sec*-phenethyl alcohol (0.25 mmol) with $PhI(OAc)_2$(0.35 mmol) in the presence of 2 mol% of Mn(salen) **2a** at room temperature.

Table 1 Mn(salen) complex **2a** catalyzed oxidations of *sec*-alcohols[a]

Entry	alcohol	product	Yield(%)	Entry	alcohol	product	Yield(%)
1			92	**10**			99
2			67	**11**			98
3			95	**12**			22
4			44	**13**			98
5			93	**14**			95
6			93	**15**			59
7			50	**16**			40
8			88	**17**			24
9			93	**18**			60[b]

[a] Reaction conditions: 0.25 mmol of α-phenethyl alcohol, 0.35 mmol of iodobenzene diacetate, 2 mol% of Mn(salen) complex **2a,** 1mL of **1a**(0.25 equiv.)+CH_2Cl_2, 20°C, 1 hr.

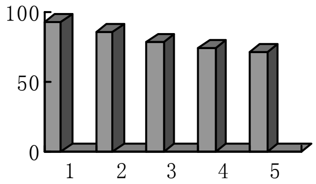
[b] The corresponding carboxylic acid was formed as the major product.

Encouraged by above results, we further examined catalytic oxidations of other substrates in the mixed solvent[**1a**(0.25 equiv.)+CH_2Cl_2]. As shown in **Table 1**, this catalyst system is suitable to a wide range of alcohols including primary and secondary benzylic, aliphatic alcohols. The 4-substituted α-phenethyl alcohols can be conversed to the corresponding ketones in high yield. But for the 2-substituted α-phenethyl alcohols, the yield of the product is moderate(**Table 1**, entries 4 and 7). The best results were obtained for the oxidation of diphenyl methanol in up to 99% yield(entry 10). The activated benzyl alcohols usually react faster than aliphatic alcohols[12], which can be seen from entry 15-17. In addition, from entries 12 and 18 in the **Table 1**, we can see that the oxidized products mainly are the carboxylic acid, not the aldehyde.

Finally, we observed the recyclability of the catalytic system in the reaction system $PhI(OAc)_2$/*sec*-phenethyl alcohol/**2a** at 70/50/1. Upon completion of the reaction, CH_2Cl_2 was distilled off under reduced pressure, then the ionic liquid phase containing [bmim]PF_6 and catalyst Mn(salen) were extracted with *n*-hexane. After five times recycles, the catalyst activity did not reduce obviously (**Figure 3**). The recovered yield was almost quantitative.

In summary, we have demonstrated a simple, mild, effective Mn (salen)-catalyzed oxidation system for secondary alcohols performed in ionic liquid [bmim] PF_6 with a

Figure 3 Recovery of the ionic liquid phase containing catalyst



well-proportioned CH_2Cl_2, in which the ionic liquid acts as a powerful additive. And it can not only accelerate reaction rate but also facilitate recovery of the catalyst.

Acknowledgments

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References and Notes

1. M. Hudlicky, *"Oxidations in Organic Chemistry"*, ACS, Washington, DC, **1990**; J. Muzart, *Chem. Rev.*, **1992**, *92*, 113.
2. S. V. Ley, A. Madin, in: B. M. Trost, I. Fleming, S.V. Ley(Eds.), *"Comprehensive Organic Synthesis"*, Vol. 7, Pergamon, Oxford, **1991**, p.251.
3. R. A. Sheldon, I.W.C.E. Arends, G. J. ten Brink, A. Dijksman, *Acc. Chem. Res.*, **2002**, *35*, 774. G. J. ten Brink, I.W.C.E. Arends, R. A. Sheldon, *Science*, **2000**, *287*, 1636.
4. W. Sun, C. G. Xia, Progress in Chemistry (Chinese), **2002**, *14*, 8.
5. W. Adam, F. G. Gelacha, C. R. Saha-Möller, V. R. Stegmann, *J. Org. Chem.*, **2000**, *65*, 1915.
6. T. Welton, Chem. Rev., 1999, 99, 2071; Z. Li, C. G. Xia, *Tetrahedron Lett.*, **2003,** *44*, 2069; L. W. Xu, L. Li, C. G.. Xia, S. L. Zhou, J. W. Li, *Tetrahedron Lett.*, **2004**, *45*, 1219; L. W. Xu, J. W. Li, C. G. Xia, S. L. Zhou, *New J. Chem.*, **2004**, 183.
7. Z. Li, C. G. Xia, M. Ji, *Applied Catalysis:A.*, **2003**, *252*, 17.
8. J. W. Li, W. Sun, L. W. Xu, H. W. Wang, C. G. Xia, *Acta Chimica Sinica*, **2004**, *62*, 637.
9. C. E. Song, W. H. Shim, E. J. Roh, J. H. Choi, *Chem. Commun.*, **2000**, 1695.
10. C. E. Song, E. J. Roh, *Chem. Commun.*, **2000**, 837.
11. P.A.Z. Suarez, J.E.L. Dullius, S. Einloft, *et al., Polyhedron*, **1996**, *15*, 1217.
12. K. P. Peterson, R. C. Larock, *J. Org. Chem.*, **1998**, *63*, 3185.
13. A typical procedure for the catalytic oxidation of sec-alcohols: Under N_2 atmosphere, to a solution of Mn(salen) (2 mol% to alcohol) and alcohol (0.25 mmol) in a given solvent (1 mL), $PhI(OAc)_2$ (0.35 mmol) was added as an oxidant. The mixture was stirred for 1 hr at room temperature. After the reaction, the yield were determined by internal standard method of gas chromatography (HP 6890, OV-17 capillary column). The products were characterized by GC-MS (Agilent 6890N GC/5973 MS).

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