



# Methyltrioxorhenium-catalyzed epoxidation of olefins with hydrogen peroxide as an oxidant and pyridine N-oxide ionic liquids as additives

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## ABSTRACT

Four ionic liquids (ILs) with both a pyridine N-oxide moiety and an imidazolium moiety combined by an amide spacer were synthesized through a series of reactions including amidation, peroxidation, quaternization and anion exchange reaction. Their structures were fully characterized by  $^1\text{H}$  NMR, FT-IR, UV-vis and HR-MS. The ionic liquids were used respectively as additives in the methyltrioxorhenium (MTO) catalyzed epoxidation of olefins with 30%  $\text{H}_2\text{O}_2$  as an oxidant. The catalytic results displayed that the ILs had excellent performances in suppressing epoxide ring-opening reaction, which led to the significant improvement of the selectivity of the MTO-catalyzed epoxidation with low loadings compared to other substances as additives. The coexistence of the pyridine N-oxide and imidazolium moieties in the structures of ILs is necessary in improving the MTO-catalyzed epoxidation reaction. It was also displayed that the improvement degree on the selectivity of epoxidation depended on the type of anion of the ILs, but not the position of the substituent with imidazolium moiety in the ring of pyridine N-oxide. Meanwhile, the results also showed that the introduction of the ILs caused the decrease of the epoxidation rate, but this side effect was small compared to those of other substances used as additives.

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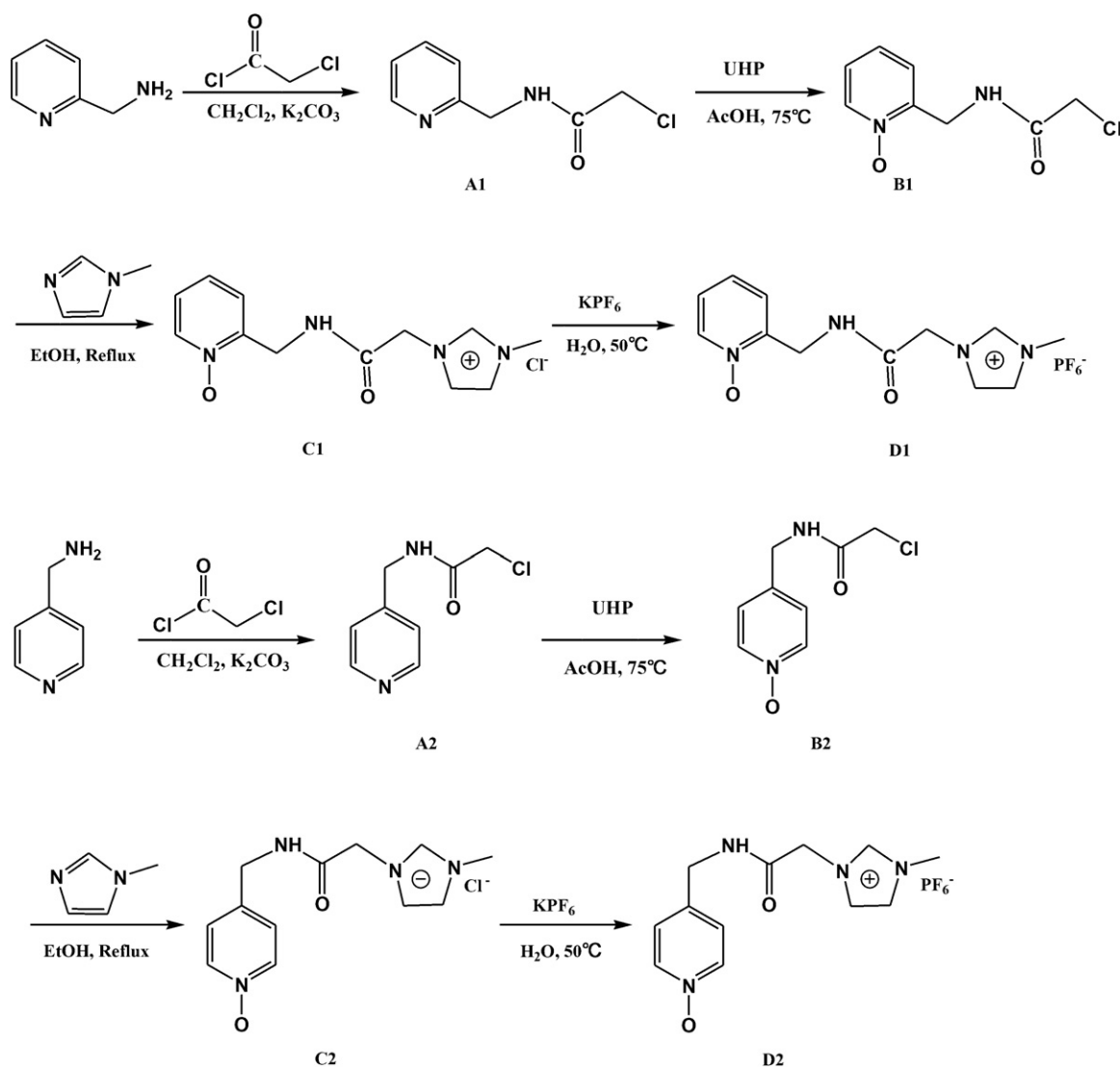
## 1. Introduction

Epoxides are valuable intermediates in organic chemical, fine chemical and pharmaceutical synthesis. The epoxidation of olefins is one of the most efficient strategies for obtaining epoxides [1]. Among all of the procedures the epoxidation of olefins with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) as an oxidant has received special attention due to its high atom efficiency and environment friendliness [2–5]. However, the oxidation activity of  $\text{H}_2\text{O}_2$  is so weak that generally appropriate catalysts such as transition metal complexes are needed to activate it [3,6,7]. In 1991, Herrmann and co-workers [8,9] found that methyltrioxorhenium(VII) ( $\text{CH}_3\text{ReO}_3$ , MTO) as a catalyst was very powerful in the epoxidation of olefins with  $\text{H}_2\text{O}_2$  as an oxidant. However, the MTO/ $\text{H}_2\text{O}_2$  catalytic system is not perfect due to the fact that the strong Lewis acidity of central rhenium atom (Re) can promote the ring opening of epoxides leading to the formation of diols in the presence of water during the reaction, meanwhile, MTO and the active species derived from MTO decompose in the aqueous solutions [10–13]. When trying to overcome both the problems it was found that the addition of Lewis base ligands, containing nitrogen and (or) oxygen donor atoms, could reduce the Lewis acidity of MTO and increase the selectivity of the epoxides. Therefore, a wide range of ligands has been chosen or

synthesized to evaluate their improvement on the MTO-catalyzed epoxidation [14–37]. We also synthesized some Schiff-bases as ligands for the MTO-catalyzed epoxidation of olefins with 30%  $\text{H}_2\text{O}_2$  as an oxidant, which showed excellent selectivity for the formation of epoxides with moderate or poor catalytic activity [38–41]. All previous results have shown that pyridine and its derivatives are among the most efficient additives at increasing the selectivity of the reaction. However, generally significant excess of the Lewis base additives is necessary to achieve excellent catalytic performance in such cases [17,21,27], which is unfavorable from the viewpoints of cost and separation. Besides, if the additives are too basic, then, MTO will decompose to catalytically inert perrhenic acid and methanol [11,25,26,32]. Much efforts have been made to seek additives that can suppress the ring opening side reaction in low loading, while not promote the decomposition of MTO or its derivatives. It was found that some oxygen donor ligands can coordinate with MTO to form stable complexes [19,31,33–37]; the complexes pre-prepared or generated in situ not only suppressed the ring opening side reaction, but also showed long lifetime compared to the cases with nitrogen donor ligands as additives in epoxidation of olefins. Moreover, in contrast to N-donor adducts, no pronounced ligand excess is necessary to achieve high yields and selectivity in olefin epoxidation catalysis.

On the other hand, MTO-catalyzed epoxidations carried out in ILs were reported in literature [42–44]. Several olefinic substrates with different structure characters were oxidized at room temperature (RT) to the corresponding epoxides with fair to excellent

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**Scheme 1.** Synthesis of pyridine N-oxide ionic liquids.

yields. In most cases, the epoxidation rates are at least comparable, if not higher than those reported previously. For example, the epoxidation of cyclooctene in four different water-equilibrated ILs, [BMIM]NTf<sub>2</sub>, [BMIM]PF<sub>6</sub>, [BMIM]BF<sub>4</sub>, and [C<sub>8</sub>MIM]PF<sub>6</sub>, with H<sub>2</sub>O<sub>2</sub> as an oxidant and Schiff- and Lewis-base adducts of MTO acting as active catalytic species gave higher yields compared to the solvent-free systems [43]. Recently, we found that 1-methyl-3-(butyl-4-sulfonate) imidazoliumbetaine (MBSIB), a zwitter ionic compound similar to ILs in structure, showed good performances as an additive in enhancing the MTO-catalyzed epoxidation of alkenes with 30% H<sub>2</sub>O<sub>2</sub> as an oxidant [45]. The introduction of 10-fold excess MBSIB significantly improved the selectivity of epoxide without reducing the reaction rate. Furthermore, the MTO–MBSIB system was stable throughout the entire catalytic run and increased the TON of the epoxidation of alkenes. Our work in combination with the literature described above encourages us to design some new type ligands with both oxygen donor and ionic liquid moieties as shown in Scheme 1. As expected, the catalytic results showed that low loadings of the ligands can suppress the ring opening of epoxides and extend the lifetime of MTO in the MTO-catalyzed epoxidation of olefins with 30% H<sub>2</sub>O<sub>2</sub> as an oxidant. Besides, the high stability and solubility of the ligands in water make them easy

separation with the organics and recycling. Herein, we reported the results.

## 2. Experimental

### 2.1. Materials and reagents

2-Aminomethyl pyridine and methyltrioxorhenium (MTO) were purchased from Alfa Aesar. Cyclohexene (99%), 1-octene (99%) and styrene (99%) were purchased from Acros. Pyridine N-oxide (PyNO) was prepared according to a previously reported method [46]. 1-n-Butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF<sub>6</sub>) was prepared as described in literature [47]. 4-Aminomethyl pyridine was prepared by us in high purity. All of the other reagents and solvents were obtained from commercial sources and used as received without further purification.

### 2.2. Physical measurements

The <sup>1</sup>H NMR spectra were recorded on a Bruker AC-P400 instrument using CDCl<sub>3</sub>, DMSO or D<sub>2</sub>O as solvent and TMS as internal

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