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Methyltrioxorhenium-catalyzed epoxidations in ionic liquids

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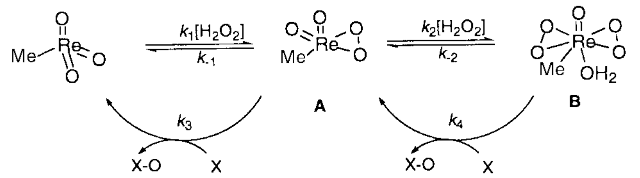
Alkenes and allylic alcohols have been epoxidized in an ambient-temperature ionic liquid for the first time using methyltrioxorhenium (MTO) and urea hydrogen peroxide; excellent conversions and selectivities for the epoxides of a wide number of substrates were observed.

One of the pressing issues for chemists in the twenty-first century is the pursuit of 'clean' or 'green' chemical transformations.[1] A particular source of chemical waste that is often taken for granted is the use of volatile molecular solvents.[2,3] The use of non-volatile ionic liquids, or molten salts, in chemical synthesis and catalysis has received attention in recent years;[2] however, the utility of these compounds remains largely unexplored. We report the first catalytic epoxidation system that makes use of a room-temperature ionic liquid as the solvent. Alkenes and allylic alcohols have been oxidized to their corresponding epoxides using the well studied methyltrioxorhenium (MTO) catalyst and urea hydrogen peroxide (UHP) with the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate, [emim]BF_4, as the solvent.

Numerous low-melting ionic salts are known, including chlorocuprates, halogenoaluminates, and alkylphosphonium, *N*-alkylpyridinium, alkylammonium, and *N*,*N′*-alkylimidazolium cations with various anions.[2] Chlorocuprates are not suitable for catalytic oxidations because of their oxygen sensitivity, and halogenoaluminates are difficult to work with because of their instability in the presence of water. We chose to use the 1-ethyl-3-methylimidazolium cation because: (i) its synthesis is facile,† and (ii) it is neither oxygen nor water sensitive (but is hygroscopic). Furthermore, with BF_4^- as the counteranion, the salt melts at 15 °C.[4]

The discovery by Herrmann in 1991 of MTO's ability to catalyze the epoxidation of olefins has led to a wealth of information regarding the efficiency and versatility of this catalyst.[5] This discovery has also fueled many efforts aimed at developing 'environmentally friendly' oxidation systems, as the only byproduct of the MTO–peroxide system is water. The creation of two active oxygen-transfer complexes, a monoperoxo- and a diperoxorhenium species, during the catalytic cycle has been well established, as have the mechanisms of oxygen transfer (Scheme 1). We refer the reader to the many reviews that have been written on the subject of MTO-catalyzed oxidations, for further information.[6–9]

Urea hydrogen peroxide has been shown to be a water-free peroxide source for MTO-catalyzed epoxidations.[10] The only disadvantage, thus far, to using UHP is that it is insoluble in organic solvents, such as chloroform, methylene chloride, and acetonitrile. Hence, the MTO–UHP system in organic media is heterogeneous.

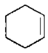
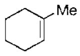
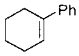
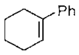
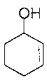
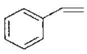
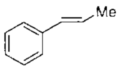
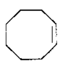
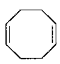
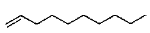


Scheme 1

In this work, the advantageous properties of the MTO–UHP oxidation system and [emim]BF_4 have been combined to give an exceptionally clean environment for catalytic oxidations. One major advantage of this system is that both UHP and MTO are soluble in the ionic liquid, as are the peroxorhenium species. This gives an oxidation solution that is completely homogeneous. The formation of the peroxorhenium species is evident by the appearance of an intense yellow color in the solution; this color is attributable to the monoperoxo- and the diperoxorhenium intermediates. UV–Vis experiments have confirmed the presence of the diperoxorhenium complex, as indicated by its absorption maximum at 360 nm.

The results in Table 1 show that several different olefinic substrates have been oxidized to epoxides, with yields ranging from fair (in the case of 1-decene) to excellent. Aqueous hydrogen peroxide (30%) was used in one experiment (entry 4) to illustrate the ring-opening of sensitive epoxides in the presence of large amounts of water, as previously reported in molecular solvents.[5,11,12] In contrast, the reaction in entry 3 was performed with molecular sieves to ensure the complete removal of water from the system. As a result, only the epoxide

Table 1 Epoxidations of various substrates with MTO–peroxide in [emim]BF_4[a]

Entry	Substrate	Oxidant	Conversion (%)[b]	Epoxide yield (%)[b]
1		UHP	⩾95	⩾99
2		UHP	⩾95	⩾95
3		UHP	⩾95	⩾95
4		H_2O_2 (30%)	⩾95	⩽5[c]
5		UHP	> 99	95[d]
6		UHP	95	⩾95
7		UHP	⩾95	⩾95
8		UHP	⩾95	⩾95
9		UHP	> 99	85[e]
10		UHP	46[f]	> 99

[a] *Reaction conditions*: 0.5 mol substrate, 1.0 mol oxidant, 2% MTO, room temperature, 8 h. [b] Yields determinded by ^1H NMR and GC–MS. [c] The majority of the product is the diol. [d] Major products are 2,3-epoxycyclohexanol (62%) and 2,3-epoxycyclohexanone (32%). [e] This yield represents the diepoxide. The remainder of the product is the monoepoxide. The same results are obtained when 2.0 mol oxidant is used. [f] This conversion was obtained after 72 h.

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was obtained. It is also interesting to note the poor conversion in the reaction of 1-decene (entry 10). Better conversions for this reaction have been obtained with other MTO–peroxide epoxidation systems;[11–13] however, after 72 h, we observed that the reaction mixture was still intensely yellow, indicating that the catalyst is still active and, apparently, highly stable in this ionic medium. The poor conversion of 1-decene may be the result of heterogeneity in the solution; 1-decene was the least soluble substrate in the ionic liquid. The results in Table 1 also indicate that the time required for the epoxidation of these substrates is quite comparable to that required for previously reported results.[5,11,12] Additionally, as shown in previous work,[10] the use of UHP eliminates the epoxide ring-opening that is commonly observed when using aqueous hydrogen peroxide. This is because the urea that is produced during the consumption of UHP modulates the pH of the solution and prevents acid-catalyzed ring opening.

As shown in Table 1, two equivalents of UHP were used relative to the substrate. Although two equivalents of oxidant leads to faster epoxidation rates, only a single equivalent is required, as evidenced by experiments with 1,5-cyclooctadiene using one and two equivalents of UHP per double bond, which yield the same product distributions.

Remaining reactants and products are both easily removed from the reaction mixture *via* extraction with diethyl ether, which is immiscible with the ionic liquid used in this work. This method of removing reactants and products is also advantageous because MTO, the peroxorhenium species, and the urea byproduct are insoluble in diethyl ether. Careful evaporation of the ether extracts gives the reactant–product mixture, which can then be analyzed by NMR and GC–MS.

In summary, the advantages of this oxidation system are numerous: (i) urea hydrogen peroxide and MTO are completely soluble in [emim]BF_4, giving a homogeneous oxidation solution. (ii) The oxidation solution is nearly water-free, so conversion of the substrates yields only the epoxides and not the diols. (iii) Left-over reactants, if any, and products are easily separated from the oxidation solution by extraction with an immiscible solvent. (While it is true that molecular solvents have been used for isolation of the reactants/products in this work, one can easily imagine a large-scale system in which the reactants and products are distilled from the reaction mixture, thereby completely eliminating the use of organic solvents.) (iv) Most rates of epoxidation in this system are at least comparable to previously published data. Current work in progress includes the determination of equilibrium constants K_1 and K_2 (Scheme 1) in [emim]BF_4 and characterization of the kinetics. We also hope to expand the use of this oxidation solution to substrates other than olefins, such as amines, alcohols, hydrocarbons, and aromatics.

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Notes and references

† The 1-ethyl-3-methylimidazolium cation is readily synthesized from 1-methylimidazole and bromoethane. Subsequent metathesis with sodium tetrafluoroborate gives the desired ionic liquid, which is purified by passage through neutral alumina.[14] The conversion in the metathesis step is rather important, as bromide competes with alkenes for oxidation to hypobromite.[15]

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