Manganese/Bicarbonate Catalyzed Epoxidation of Lipophilic Alkenes with Hydrogen Peroxide in Ionic Liquids

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Supporting Information

Experimental Procedure

All chemicals were purchased from Aldrich and used as received.

Instrumentation

¹H NMR spectral measurements were carried out on a Bruker DPX-400MHz NMR spectrometer. An unmodified household microwave oven (SHARP R342D M/OVEN 34L 1100W T; microwave frequency 2450 MHz) was used for the preparation of [bmim][Br].

Preparation of 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄])

[bmim][BF₄] was prepared from the bromide which was in turn prepared from bromobutane and N-methylimidazole using the recently reported microwave-assisted

procedure.^{1a} The [bmim][BF₄] was purified using the same procedure reported by Park and Kazlauskas.^{1b}

Preparation of tetramethylammonium hydrogencarbonate (TMAHC)²

A 25% w/w tetramethylammonium hydroxide in water (10g) was dried by rotatory evaporator and diluted with methanol (40mL). The solution was bubbled with carbon dioxide at room temperature for 4 hours. Methanol was distilled off under reduced pressure and pale brown solid was obtained, 3.65g, 99%. IR (KBr, cm⁻¹) 1655, C=O.

Typical procedure for the epoxidation of alkene with TMAHC/Mn²⁺/H₂O₂ in

[bmim][BF₄]

To [bmim][BF₄] (300uL) was add TMAHC (0.02g), followed by alkene (20uL, 0.15mmol), MnSO₄ (0.2 mol%), and hydrogen peroxide (200uL, 35%). The reaction mixture was stirred vigorously at room temperature. When the reaction was completed, the mixture was extracted by pentane (5 x 2mL)³, dried over sodium sulfate, filtered, and the solvent was removed by a rotary evaporator to give the

¹ For the preparation of 1, see (a) Law, M. C., Wong, K. Y., Chan, T. H. *Green Chem.* **2002**, 4, 328. (b) Park, S.; Kazlauskas, R. J. *J. Org. Chem.* **2001**, 66, 8395-8401.

² Venturello, C.; Dalosio, R. *Synthesis-Stuttgart* **1985**, 33-34.

³ It is generally assumed that, if necessary, pentane can be replaced by supercritical carbon dioxide for the extraction of lipophilic substrates. See (a) Blanchard, L. A., Hancu, D., Beckman, E. J., Brennecke, J. F. *Nature*, **1999**, 399, 28. (b) Blanchard, L. A., Brennecke, J. F. *Ind. Eng. Chem. Res.* **2001**, 40, 287.

desired product. The percentage yields were determined by GC-MS or ^1H NMR with internal standard.

*Recycling of [bmim][BF₄] in the epoxidation of styrene (**1a**)*

To [bmim][BF₄] (1200uL) was add TMAHC (0.08g), followed by **1a** (80uL, 0.6mmol), MnSO₄ (0.2 mol%), and hydrogen peroxide (800uL). The reaction mixture was stirred vigorously at room temperature. When the reaction was completed, the mixture was extracted by pentane (5 x 3mL), dried over sodium sulfate, filtered, and the solvent was removed by a rotary evaporator to give the desired product. The percentage yields were determined by GC-MS with internal standard. The residual pentane in the [bmim][BF₄] was removed by rotary evaporator. The recovered oily yellowish liquid was then reused for the same epoxidation of **1a** as described by Table 2.