

Use of ionic liquids as solvents for epoxidation reactions catalysed by a chiral Katsuki-type salen complex: enhanced reactivity and recovery of catalyst

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The Katsuki-type catalyst **2** has been recycled several times following its use in a model epoxidation reaction of 1,2-dihydronaphthalene in an ionic liquid, **3a** or **3b**. The enantioselectivity was comparable to that in dichloromethane, but recovery of the catalyst was easier, activity was higher, and activity and enantioselectivity were retained in recovered ionic liquid fractions to a much greater extent than those for the Jacobsen-type catalyst **1**.

KEY WORDS: ionic liquids; Katsuki-type chiral catalyst; two-phase systems; epoxidation; 1,2-dihydronaphthalene.

1. Introduction

Enantioselective epoxidation catalysed by chiral (salen)Mn(III) complexes has become a useful preparative method in organic synthesis [1,2]. Jacobsen [1] and Katsuki [2] have explored, respectively, several valuable types of epoxidation catalysts in this field. However, although such catalysts offer a high level of activity and enantioselectivity in homogeneous systems, they are not easily separated from the products and are thus difficult to recover. Therefore, much effort has been spent on attempting to support catalysts on solids to generate heterogeneous catalysts, or to use two-phase liquid systems in order to offer a simplified separation of catalyst from product. Thus, for example, attempts have been made to immobilise salen catalysts by: (a) non-covalent immobilisation on a zeolite [3], clay [4] or polydimethylsiloxane (PDMS) membrane [5]; (b) grafting onto silica [6] or MCM-41 [7]; (c) copolymerisation of a functionalised salen ligand or catalyst with other organic monomers [8,9]; and (d) attachment of a salen ligand or catalyst to a preformed polymer [10–14] or dendrimer [15]. However, there are drawbacks with all of these strategies, probably because of the nature of heterogeneous reactions (non-linear kinetic behaviour, unequal distribution of and/or access to the reactive centres, solvation problems, etc. For example, the use of a zeolite “ship-in-a-bottle” catalyst was limited to a narrow range of substrates and gave poor enantioselectivity in some cases [3]; use of a PDMS membrane

led to an unavoidable leaching of catalyst from the membrane [5]; copolymerisation of a salen ligand or catalyst with styrene and divinylbenzene resulted in a cross-linked catalyst which offered a promising yield and recycled catalyst, but showed very poor enantioselectivity [8,9]; and although use of a polymer-supported, singly-bound catalyst was effective and the catalyst could be recycled, synthesis of the specifically-substituted ligand was tedious [14].

Due to the limitations of solid-supported catalysts, a two-phase liquid system, known as Fluorous Biphasic System (FBS), was used by Pozzi and his co-workers [16]. However, in order to take advantage of relatively easy phase separation and catalyst recovery, it was necessary to modify the salen ligand by incorporation of a perfluorinated alkyl chain to help to provide better solvation of catalyst in the FBS solvent. Moreover, a reasonable enantioselectivity was obtained for only one substrate, indene [16]. Therefore, we decided to investigate alternative approaches.

Over the last several years, ionic liquids (called ILs hereafter) have generated much excitement in the field of organic synthesis, particularly for metal complex catalysis, because of their potential as green solvents. Up to date, a number of reactions have been carried out in such solvents, including: Fries rearrangements; Friedel–Crafts, Diels–Alder, nitration, hydrogenation, hydroformylation and Heck reactions; Suzuki cross-coupling; Trost–Tsuji coupling; and so on [17–26].

Recently, Song *et al.* have investigated the epoxidation of 2,2-dimethylchromene with a Jacobsen-type chiral Mn^{III} (salen) complex, [*N,N'* bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine]manganese(III) chloride (**1**), in 4 mol% proportion in a mixture of an IL, 1-butyl-3-methylimidazolium hexafluorophosphate

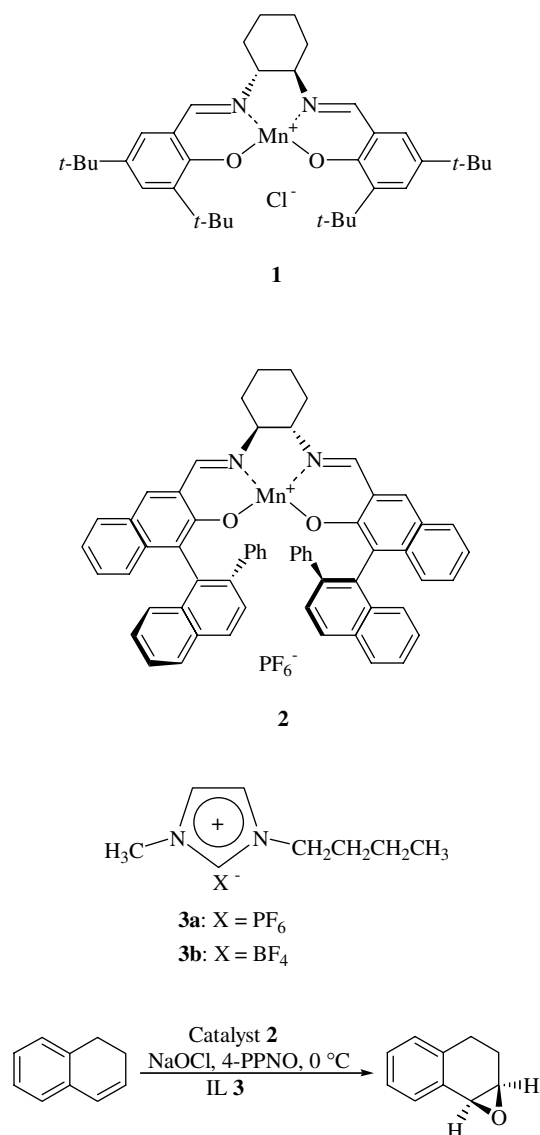
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([bmim]PF₆, **3a**) and CH₂Cl₂(1:4 v/v), providing a good yield, high enantiomeric excess and a recoverable catalyst [27]. Unfortunately, the yield and enantioselectivity became progressively lower with each recovery.

As part of our continuing interest in the development of clean chemical processes [28–37], we became interested in epoxidation of 1,2-dihydronaphthalene catalysed by a Katsuki-type catalyst, **2**, which is more stable and offers higher enantiomeric excess compared to the Jacobsen-type catalyst **1**, in an ionic liquid. We therefore wish to disclose the results of our own epoxidation of 1,2-dihydronaphthalene (1,2-DHN) in two air- and moisture-stable ionic liquids, [bmim]PF₆ (**3a**) and [bmim]BF₄ (**3b**), using commercial sodium hypochlorite as the terminal oxidant and 4phenypyridine *N*-oxide (4-PPNO) as a co-ligand, according to the reaction in Scheme 1.



Scheme 1. Catalytic epoxidation of 1,2-dihydronaphthalene.

2. Experimental

2.1. Materials

1-Methylimidazole, 1-bromobutane, ammonium tetrafluoroborate, sodium hexafluorophosphate, 13% aqueous sodium hypochlorite, 1,2-dihydronaphthalene, 4phenypyridine *N*-oxide and hexadecane were purchased from Aldrich Chemical Company or Lancaster Research Chemicals and used without further purification.

2.2. Analysis and characterisation of the product and ionic liquids **3**

¹H and ¹³C NMR spectra were recorded on an AV400 Bruker spectrometer operating at 400 MHz for ¹H and 100 MHz for ¹³C measurement. ¹¹B, ¹⁹F and ³¹P NMR were recorded on an AC250 Bruker spectrometer. Chemical shifts are reported in parts per million relative to tetramethylsilane. Assignments of signals are based on coupling patterns and expected chemical shift values and have not been rigorously confirmed. Signals with similar characteristics might be interchanged. Electrospray mass spectra were recorded on a Quattro II spectrometer.

Product mixtures from the epoxidation reaction (Scheme 1) were subjected to gas chromatography on a Hewlett Packard HP 5890 (series II) gas chromatograph, fitted with an RTX-1 (100% dimethylpolysiloxane; 30 m, 0.32 mm ID) column. The GC conditions used for analysis were: 100 °C for 2 min, ramped to 250 °C at 10 °C/min and held for 10 min. The injection temperature was 250 °C and the detection temperature 300 °C. Hexadecane was used as an internal standard.

The epoxide 1,2-epoxy-1,2,3,4-tetrahydronaphthalene was characterised by its ¹H and ¹³C NMR spectra, which were identical to those reported in the literature [38].

The ionic liquids **3a** and **3b** were synthesised according to literature procedures [39–41]. Their structures were confirmed by comparison of their ¹H and ¹³C NMR spectra with those reported [39–41] and also by ¹⁹F and ¹¹B or ³¹P NMR spectroscopy and by electrospray mass spectrometry.

Ionic liquid **3a**, NMR (*d*₆-acetone), ppm: ¹H, 8.89 (1 H, s, H2), 7.70 (1 H, d, *J* = 2 Hz, H4), 7.65 (1 H, d, *J* = 2 Hz, H5), 4.33 (2 H, t, *J* = 7 Hz, NCH₂), 4.02 (3 H, s, NCH₃), 1.90 (2 H, apparent pentet, *J* = 7 Hz, CH₂), 1.36 (2 H, apparent sextet, *J* = 7 Hz, CH₂), 0.93 (3 H, t, *J* = 7 Hz, CH₃); ¹³C, 137.3 (d, C2), 124.7 (d, C4), 123.3 (d, C5), 50.1 (t, NCH₂), 36.5 (q, NCH₃), 32.6 (t, CH₂), 19.9 (t, CH₂), 13.6 (q, CH₃); ¹⁹F, −71.4 (d); ³¹P, −90.2 (septet); MS: ES⁺, *m/z*, 139 (M–PF₆[−]); ES[−], *m/z*, 145 (PF₆[−]).

Ionic liquid **3b**, NMR (*d*₆-acetone), ppm: ¹H, 8.91 (1 H, s, H2), 7.71 (1 H, d, *J* = 2 Hz, H4), 7.65 (1 H, d, *J* = 2 Hz, H5), 4.30 (2 H, t, *J* = 7 Hz, NCH₂), 3.99 (3 H, s, NCH₃), 1.88 (2 H, apparent pentet, *J* = 7 Hz, CH₂),