



Epoxidation of olefins catalyzed by manganese(III) porphyrin in a room temperature ionic liquid

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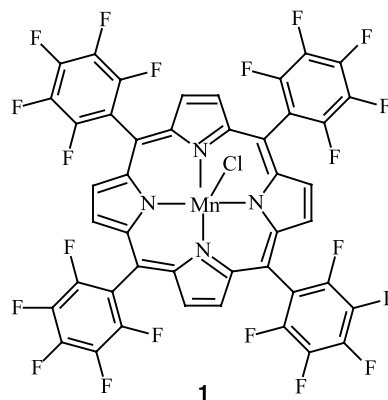
Abstract—The epoxidation of several alkenes catalyzed by (*meso*-tetrakis(pentafluorophenyl)porphinato) manganese(III) chloride (MnTFPPCl) was carried out in a 3:1 [bmim]PF₆ ionic liquid/CH₂Cl₂ mixed solvent. The conversion and the yield of epoxide are excellent. It was also found that [bis(acetoxy)iodo]benzene [PhI(OAc)₂] is a more efficient oxidant than PhIO. The catalyst in the ionic liquids can be recycled for several runs without substantial diminution in the catalytic activity. © 2003 Elsevier Science Ltd. All rights reserved.

The use of ionic liquids as solvents for a broad range of chemical processes is potentially one of the most significant developments in the last decade.¹ In contrast to molten salts that have very high melting points and are highly corrosive, ionic liquids are organic salts that are liquid under ambient conditions. Ionic liquids with tetrafluoroborate or hexafluorophosphate ions, for example, are considered as inert solvents in most reactions. In these cases the role of the ionic liquid is mainly to provide a polar, weakly coordinating medium for a transition metal catalyst that additionally offers special solubility for starting materials and products. Moreover, the use of an ionic liquid solvent allows an easy catalyst recycle without the need of any catalyst modification. Recently results published by Song and Roh indicate that the use of ionic liquids is also of advantage in selective oxidation reactions.²

The epoxidation of alkenes and hydroxylation of alkenes catalyzed by metalloporphyrin complexes is the subject of many investigations. A variety of oxygen donors such as iodosylarenes, hypochlorites, alkylhydroperoxides, hydrogen peroxide and periodates have been used for these transformations.³ Homogeneous sterically hindered metalloporphyrin catalysts, and those containing sophisticated chiral auxiliaries, or strongly electron-withdrawing groups can exhibit high regio-,^{3b,4} stereo-,^{4b,c,5} and enantioselectivity,⁶ and high

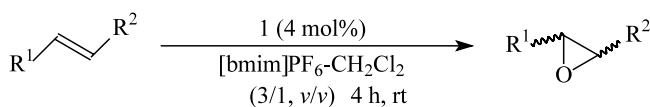
catalyst turnovers.⁷ However, the difficulty in recovery and the high cost of the catalysts outweigh these appealing features and so far have made their applications to synthesis impractical.

This report describes the use of manganese(III) porphyrin **1**, (*meso*-tetrakis(pentafluorophenyl) porphinato)manganese(III) chloride, for the epoxidation of alkenes with PhI(OAc)₂ in a [bmim]PF₆/CH₂Cl₂ mixture at room temperature. We selected 1-butyl-3-methylimidazolium hexafluorophosphate [bmim]PF₆ for our model system since this liquid is stable in the presence of both oxygen and water. To dissolve fully the reactants in [bmim]PF₆, it was essential to add a small volume of CH₂Cl₂ to the ionic liquid. The CH₂Cl₂ improves the solubility of the substrates and product.



Keywords: epoxidation; ionic liquid; manganese porphyrin.

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Table 1. Catalytic epoxidation of different olefins with **1**^a

Entry	Substrate	Oxidant	Conversion ^b (%)	Yield ^b (%)
1	Styrene	PhIO	81	58
		PhI(OAc) ₂	95	89
			66 ^c	65 ^c
2	Cyclohexene	PhI(OAc) ₂	98	74
3	Cyclooctene	PhI(OAc) ₂	96	57
4	1-Undecene	PhI(OAc) ₂	83	79
5	Hept-1-ene	PhI(OAc) ₂	96	74
			97 ^c	88 ^c
6	Indene	PhI(OAc) ₂	99	97
			100 ^c	20 ^c
7	1,2-Dihydro-naphthalene	PhI(OAc) ₂	95	95
			95 ^c	69 ^c

^a All reactions were performed in capped vials in 2 mL mixed solvent using a 50:25:1 oxidant/substrate/catalyst ratio.

^b Determined by capillary GC integration against an internal quantitative standard.

^c In CH₂Cl₂.

Epoxidations were carried out in the presence of 4 mol% of **1** with several alkenes as substrates in [bmim]PF₆/CH₂Cl₂ (3:1, v/v) using PhI(OAc)₂ as the oxidant at room temperature. The results obtained are given in Table 1. It was found that when the reactions were carried out in pure CH₂Cl₂, the yield of the epoxide was lower than that in the mixed solvent system (entries 1, 6 and 7). However, it seems that CH₂Cl₂ was a better solvent for hept-1-ene epoxidation (entry 5). Moreover, the catalyst seemed to be very active in the epoxidation of aromatic olefins (entries 6 and 7). Although PhIO is a common oxidant, generally used as the oxygen source in metalloporphyrin catalytic

systems, it was found that the use of PhI(OAc)₂ under the same conditions led to the epoxides in higher yields and substrate conversion.

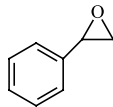
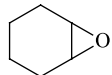

The unchanged reactants and products were both easily removed from the reaction mixture via extraction with *n*-hexane, which is immiscible with the ionic liquid used in this work. The brown-red oily ionic liquid phase containing the catalyst was reused five times using PhI(OAc)₂ as oxidant. The results are shown in Table 2. One can see from the results that the recovered catalyst gave comparable catalytic activity. In the case of styrene and cyclohexene epoxidation, both catalytic activity and selectivity fall slightly after five reuses. For hept-1-ene, the reused catalyst shows the same efficiency (activity and selectivity) with that of fresh catalyst. After the catalytic reaction, the UV-vis spectrum of the remaining ionic liquid containing the catalyst showed the presence of undecomposed MnTFPPCl by the presence of an unchanged Soret band at 473 nm, which indicated that the catalyst is stable during the reaction.

In summary, we have shown that ionic liquids can be used as solvents in the metalloporphyrin catalyzed olefin epoxidation and that PhI(OAc)₂ is an efficient oxygen donor. The use of an ionic liquid provides for simple recycling of the catalyst. Further research including the determination of the epoxidation mechanism involved in the [bmim]PF₆ and characterization of the kinetics is in progress. We also hope to expand the use of this oxidation approach to amines, alcohols, hydrocarbons, and aromatics.

Acknowledgements

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Table 2. The recycling experiment for the epoxidation of three substrates using PhI(OAc)₂ as oxidant catalyzed by MnTFPPCl in [bmim]PF₆/CH₂Cl₂^a

Entry	Cycle						
		Yield ^b (%)	Selectivity (%)	Yield ^b (%)	Selectivity (%)	Yield ^b (%)	Selectivity (%)
1	Fresh	89	94	74	75	74	77
2	1	94	97	75	76	78	79
3	2	92	97	74	70	82	94
4	3	90	92	72	84	82	90
5	4	87	89	57	66	88	89
6	5	84	88	56	65	86	88

^a All reactions were carried out in 2 mL of [bmim]PF₆/CH₂Cl₂ (3:1, v/v) at room temperature for 4 h with 4 mol% catalyst, 0.05 mmol substrate and 0.1 mmol PhI(OAc)₂.

^b Determined by capillary GC integration against an internal quantitative standard.

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