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Polystyrene-bound Manganese(III) Porphyrin as a Heterogeneous Catalyst for Alkene Epoxidation†

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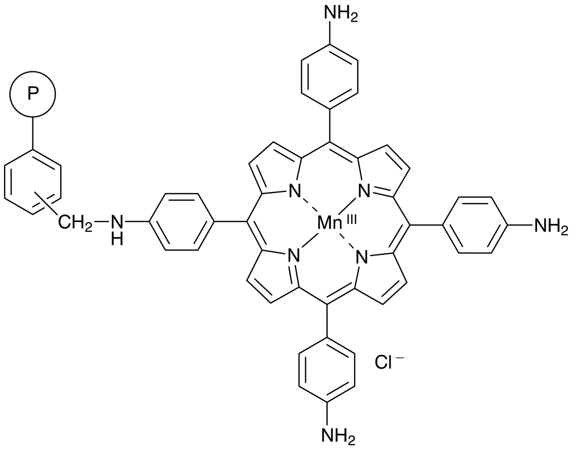
The manganese(III) complex of 5,10,15,20-tetrakis(4-aminophenyl)porphyrin covalently bound to crosslinked chloromethylated polystyrene can act as an efficient heterogeneous catalyst for alkene epoxidation by sodium periodate.

Metalloporphyrins have been found to be efficient biomimetic catalysts for alkene epoxidation using various oxygen atom donors.[1–5] However, difficulty of recovery and instability are two of the major drawbacks of these expensive catalysts. The attachment of metalloporphyrin catalysts to insoluble polymeric supports should prevent intermolecular self-oxidation, and simplifies catalyst recovery by filtration. Furthermore, the support also influences the selectivity of oxidation.[6–10]

This report describes a new polymer-bound manganese porphyrin catalyst which is very easy to prepare and can be used without degradation in the presence of sodium periodate for alkene epoxidation.



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Polymer-bound manganese porphyrin **1** was prepared from cross-linked chloromethylated polystyrene and 5,10,15,20-tetrakis(4-aminophenyl)porphyrin by a slight modification of the previously reported method for non-crosslinked chloromethylated polystyrene.[11] Elemental analysis (Mn) showed that the supported catalysts contained about 15.4% (w/w) of covalently bound manganese porphyrin. The covalent bonding of the polymer and metalloporphyrin is so strong that the manganese porphyrin is not eluted from polymer by water and common organic solvents. The potential of this supported manganese(III) porphyrin as catalyst for epoxidation was initially investigated with cyclooctene in the presence of sodium periodate at room temperature. The reaction was carried out in a 2:1 $CH_3CN–H_2O$ mixture in which higher epoxidation yield was observed.

Table 1 Effect of various axial ligands on epoxidation of cyclooctene with sodium periodate in the presence of polystyrene-bound manganese porphyrin[a]

	Epoxide yield[b] (%)		
Axial ligand	After 1 h	After 2 h	After 3 h
Imidazole	46	80	95
1-Methylimidazole	45	80	95
tert-Butylpyridine	24	29	35
Pyridine	7	10	11
Without axial base	3	6	7

[a]Reaction conditions: cyclooctene (1 mmol), $NaIO_4$ (2 mmol), axial base (0.2 mmol), catalyst (mass equiv. to 0.04 mmol Mn), $CH_3CN–H_2O$ (10 ml–5 ml). [b]GLC yield based on starting cyclooctene.

The effect of different axial ligands upon the rate of epoxidation of cyclooctene was also investigated (Table 1). The epoxidation rates decrease in the order: imidazole ≅ 1-methylimidazole > *tert*-butylpyridine > pyridine.

This heterogeneous catalytic system is very efficient for epoxidation of various alkenes (Table 2). Epoxidation of *trans*-stilbene proceeds with complete stereospecificity and results in *trans*-stilbene oxide, whereas epoxidation of *cis*-stillbene leads to 90% *cis*- and 10% *trans*-stilbene oxide. Epoxidation of (*R*)-(+)-limonene gives a mixture of 1,2- and 8,9-epoxides. The ratio of 1,2- to 8,9-epoxides was found to be 1:1.

Table 2 Epoxidation of alkene with $NaIO_4$ catalyzed by polystyrene-bound manganese porphyrin[a]

Alkene	Conversion (%)[b]	Epoxide yield (%)[b]	Reaction time/h
Cyclooctene	100	95	3
Cyclohexene	100	75	1.25
Styrene	100	93	2
α-Methylstyrene	100	75	2
p-Methoxystyrene	100	70	1.25
(+)-Camphene	84	84	3
(*R*)-(+)-Limonene	70	35 (8,9-Epoxide) 35 (1,2 Epoxide)	3
trans-Stilbene	71	71 (*trans*)	3
cis-Stilbene	100	90 (*cis*) 10 (*trans*)	3

[a]Reaction conditions: alkene (1 mmol), $NaIO_4$ (2 mmol), imidazole (0.2 mmol), catalyst (mass equiv. to 0.04 mmol Mn), $CH_3CN–H_2O$ (10 ml–5 ml). [b]GLC yield based on starting alkene.

The activity of this polymer-bound catalyst was compared to that of the unsupported catalyst in the epoxidation of styrene and cyclohexene. The results showed that the

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homogeneous oxidations are faster but less selective. Commonly observed side reactions such as double bond cleavage and allylic oxidation are minimized with the hetereogeneous catalyst.

The solutions remained colourless during the course of epoxidations and there was no evidence for leaching of the catalyst from the polymeric support into solution. The attachment of metalloporphyrin to the polymer made it possible to remove the stable catalyst by simple filtration at the end of reaction. The stability of the polystyrene-bound manganese porphyrin catalyst was studied in repeated epoxidation reactions of cyclooctene (eight times) by $NaIO_4$. The catalyst was reused after each reaction by simple filtration and washing with acetonitrile. The reused catalyst displayed consistent reactivity and selectivity.

Experimental

The porphyrin ligand, 5,10,15,20-tetrakis(4-aminophenyl)porphyrin, was prepared and metalated according to the literature procedures.[12,13] Alkenes were obtained from Merck or Fluka and were passed through a column containing active alumina to remove peroxidic impurities.

Preparation of Polystyrene-bound Manganese(III) 5,10,15,20-Tetrakis(4-aminophenyl) Porphyrin.—Chloromethylated polystyrene crosslinked with 2% divinylbenzene (2.0 g) (Merck) was suspended in 100 ml of dimethylformamide (DMF) and 1.67 g (2.48 mmol) of manganese(III) 5,10,15,20-tetrakis(4-aminophenyl)porphyrin and 5 ml of triethylamine were added. The mixture was refluxed for 72 h in the dark under N_2 atmosphere while stirring magnetically and then cooled to room temperature. The dark green resin was suction filtered, washed thoroughly with DMF, methanol and acetone, respectively, and dried under vacuum at room temperature for 24 h.

General Procedure for Epoxidation Reactions.—A 25 ml flask was charged with alkene (1 mmol), polystyrene-bound manganese porphyrin (200 mg), imidazole (0.2 mmol) and CH_3CN (10 ml). After addition of sodium periodate solution (2 mmol in 5 ml of H_2O), the mixture was stirred magnetically at room temperature. Progress of the reaction was monitored by GLC. After the reaction was completed, the polymer beads were filtered off and the filtrate was extracted with CH_2Cl_2 and purified by silica gel plate or silica gel column chromatography. The identities of products were confirmed by IR and ^1H NMR spectral data.

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