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Mild and Efficient Alkene Epoxidation and Alkane Hydroxylation by Manganese(III) Porphyrin Supported on IRA-400 Ion-exchange Resin†

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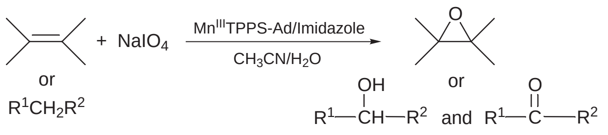
Sulfonated manganese(III) tetraphenylporphyrin supported on Amberlite IRA-400 ion-exchange resin (MnTPPS-Ad), can act as an efficient heterogeneous catalyst for alkene epoxidation and alkane hydroxylation by sodium periodate in the presence of imadazole.

Recently, there has been considerable interest in the synthesis and use of polymer supported catalysts.[1] The high efficiency of some of these catalytic systems makes them potentially useful for large scale oxidation.[2,3] Numerous studies have been carried out employing metalloporphyrins in association with various single oxygen donors for the catalytic oxidation of alkenes,[4] alkanes,[5] amines,[6] phenols,[7] mercaptans[8] and sulfides.[9] Immobilization of expensive metalloporphyrin catalysts on insoluble organic and inorganic supports appears to be a good way to render them practicable and improve their stability, selectivity and show other advantages with respect to recovery and reuse.[9–16]

This report describes a new periodate-heterogenized metalloporphyrin system for alkene epoxidation and alkane hydroxylation in CH_3CN/H_2O mixture at room temperature.

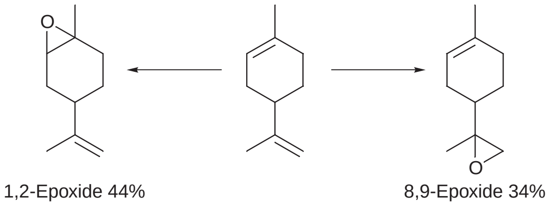


Scheme 1

The effect of different axial ligands upon the epoxidation rate of cyclooctene was also investigated. The epoxidation rates decrease in the order: imidazole = 1-methylimidazole > *tert*-butylpyridine > pyridine. Reactions were performed at room temperature under air in CH_3CN/H_2O containing the alkene, oxidant, imidazole and MnTPPS-Ad in 1 : 2 : 0.2 : 0.0145 ratio, respectively. This catalytic system led to the epoxidation of various alkenes (Table 1, Scheme 1) with good yields (51–100%). Epoxidation of *trans*-stilbene proceeds in a stereospecific manner with complete retention of configuration. In contrast, epoxidation of *cis*-stilbene is associated with some loss of stereochemistry and affords 63% *cis* and 8% *trans*-stilbene oxides, respectively.

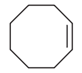
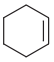
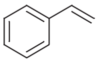
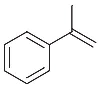
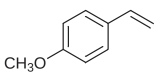
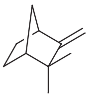
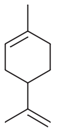
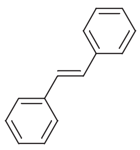
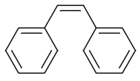
The MnTPPS-Ad/$NaIO_4$ system exhibits regioselectivity for epoxidation of (*R*)-(+)-limonene. The ratio among 1,2- and 8,9-epoxides was found to be 1.29 : 1 (Scheme 2).

Selective partial alkane oxidation is a particularly challenging problem in the organic chemistry. Alkanes were oxidized with sodium periodate by MnTPPS-Ad to the corresponding alcohols and ketones only in the presence of imidazole (Table 2). In the absence of the supported metalloporphyrin catalyst, cyclooctene and cyclooctane remained almost unchanged by $NaIO_4$ in CH_3CN/H_2O after 24 h.



Scheme 2

Table 1 Epoxidation of alkenes with $NaIO_4$ catalysed by MnTPPS-Ad in the presence of imidazole at room temperature

Entry	Alkene	Conversion(%)[a]	Epoxide yield(%)[a]	Reaction time/h
1		100	96	3.5
2		98	82	3.5
3		100	95	3.5
4		100	89	3.5
5		100	90	3.5
6		96	81	4
7		78	44 (1,2-epoxide)[b] 34 (8,9-epoxide)[b]	4
8		51	51 (*trans*-epoxide)[b]	4
9		71	63 (*cis*-epoxide)[b] 8 (*trans*-epoxide)[b]	4

[a]GLC yield based on starting alkene. [b]Both ^1H NMR and GLC data gave reported yields.

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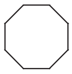
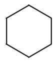
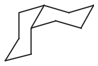
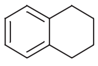
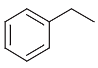
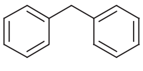
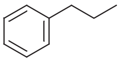
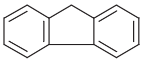
*To receive any correspondence.

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 2 Hydroxylation of alkanes with $NaIO_4$ catalysed by MnTPPS-Ad in the presence of imidazole at room temperature

Entry	Alkane	Ketone(%)[a]	Alcohol(%)[a]	Reaction time/h
1		22	36	8
2		30	14	8
3		—	45	8
4		51	35	8
5		61	—	8
6		34	—	8
7		48	—	8
8		40	—	8

[a] GLC yield based on starting alkane.

The activity of this catalyst (MnTPPS-Ad) was compared to that of unsupported catalyst in epoxidation of cyclooctene and cyclohexene. The results showed that the homogeneous oxidations are faster but less selective. Normally, side reactions such as double bond cleavage and allylic oxidation are minimized with the heterogeneous catalysts.

The solutions remained colorless during the course of epoxidations and there was no evidence for leaching of the catalyst into solution. The attachment of metalloporphyrin to the Amberlite made it possible to remove the stable catalyst by simple filtration at the end of reaction. The stability of MnTPPS-Ad was studied in repeated epoxidation reactions of styrene (5 times) by sodium periodate. The catalyst was removed after, each reaction by simple filtration and washing with acetonitrile. The reused catalyst displayed consistent reactivity and selectivity.

Experimental

Alkene, alkane and alkylaromatic compounds were obtained from Merck or Fluka. All were passed through a column containing active alumina to remove peroxidic impurities. The porphyrin ligand 5,10,15,20-tetrakis(4-sulfonophenyl)porphyrin was prepared and metallated according to the literature procedures.[17,18] MnTPPS immobilized on Amberlite IRA-400) was prepared according to the reported procedure[19] (9 µmol of MnTPPS were immobilized on 100 mg of the resin).

General Procedure for Alkene Epoxidation Catalysed by MnTPPS-Ad.—All of the reactions were carried out at room temperature under air in a 25 mL flask equipped with a magnetic stirring bar. A solution of $NaIO_4$ (2 mmol) in H_2O (5 mL) was added to a mixture of alkene (1 mmol), MnTPPS-Ad (14 µmol) and imidazole (0.2 mmol) in CH_3CN (10 mL). The progress of the reaction was monitored by GLC. The reaction mixture was diluted with CH_2Cl_2 (20 mL) and filtered. The resin was thoroughly washed with CH_2Cl_2 and the combined washings and filtrates were purified on silica gel plates or a silica gel column. IR and ^1H NMR spectra data confirmed the identities of the products.

General Procedure for Alkane Hydroxylation Catalysed by MnTPPS-Ad.—A 25 mL flask was charged with alkane (1 mmol), MnTPPS-Ad (14 µmol), imidazole (0.2 mmol) and CH_3CN (10 mL). After addition of sodium periodate solution (2 mmol in 5 mL H_2O), the mixture was stirred magnetically at room temperature. The progress of the reaction was monitored by GLC. After the reaction was completed, the resin was filtered off and the filtrate was extracted with CH_2Cl_2 and purified on a silica gel plate or silica gel column. IR and ^1H NMR spectral data confirmed the identities of the products.

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