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EFFICIENT OLEFIN EPOXIDATION AND ALKANE HYDROXYLATION USING SULFONATED MANGANESE(III) PORPHYRIN SUPPORTED ON IRA-900 ION-EXCHANGE RESIN

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Abstract: Sulfonated manganese(III) tetraphenylporphyrin supported on Amberlite IRA-900 ion exchange resin (MnTPPS-Ad) has been found to be a highly active and stable catalyst for olefin epoxidation and alkane hydroxylation by sodium periodate.

Metalloporphyrins have been used as efficient biomimetic catalysts for oxidation of a wide variety of compounds[1-10].However, difficulty of recovery and instability are two of the major drawbacks of these expensive catalysts. These limitations have prevented practical application of metalloporphyrin catalysts in synthesis. Immobilization of soluble metalloporphyrin complexes on a stable support improve their stability and show other advantages with respect to recovery and reuse[11-14].

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Recently, we have introduced sodium periodate and tetrabutylammonium periodate as effective oxygen atom donors for epoxidation of olefins catalyzed by manganese(III) tetraphenylporphyrin[15-16].

Now we report the use of sodium periodate, in the presencs of sulfonated manganese(III) tetraphenylporphyrin supported on Amberlite IRA-900 (MnTPPS-Ad), in olefin epoxidation and alkane hydroxylation reactions in CH_3CN/H_2O mixture at room temperature. It was found that in this catalytic system, addition of a heterocyclic nitrogen base (Imidazole or 4-methylimidazole) improves the epoxidation rates remarkably. For instance, in the presence of imidazole, the epoxidation of cyclooctene to cyclooocteneoxide is nearly complete, whereas in the absence of the amine only 5% cyclooocteneoxide is produced after 4 h. MnTPPS-Ad in the presence of imidazole, converts different olefins efficiently to their corresponding epoxides(Table 1).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 59% cis- and 9% trans- stilbene oxides, respectively.This catalytic system exhibits a promising regioselectivity in epoxidation of (+)-limonene. The ratio among 1,2 and 8,9-epoxides was found to be 1.7(scheme 1).

In presence of MnTPPS-Ad suspension in CH_3CN/H_2O mixture, reaction of sodium periodate with various alkanes, results in good yields of ketones and alcohols (Table 2).

In conclusion this stable and convenient, periodate-heterogenized metalloporphyrin system expands the scope of utilization of metalloporphyrins in useful organic transformations.

EXPERIMENTAL

All olefins or alkanes were purified prior to use by passage through a column of basic alumina and then checked by gas chromatography. The porphyrin ligand,

Table 1. Epoxidation of Olefins with $NaIO_4$ Catalyzed by MnTPPS-Ad in the Presence of Imidazole

Olefin	Conversion(%)[a]	Epoxide Yield(%)[a]	Reaction Time/h
Cyclooctene	100	95	4
Cyclohexene	88	70	4
Styrene	100	94	4
α–methylstyrene	100	94	4
(+)-Camphene	95	85	4
1-Octene	73	55	8
trans-Stilbene	45	45(trans)	8
cis-Stilbene	68	59(cis)[b] 9(trans)	8
(+)-R-Limonene	54	34(1,2-Epoxide)[b] 20(8,9-Epoxide)	4

a: GLC yield based on starting olefin.
b: Both ^{1}H-NMR and GLC data approved the reported yields.

$TPPSH_2$, was prepared and metalated according to the literature procedures[17-18]. MnTPPS immobilized on Amberlite IRA-900 was prepared according to reported procedure[19]. (9 μ mol of MnTPPS was immobilized on 100 mg of the resin).

General Procedure for Olefin Epoxidations Catalyzed by MnTPPS-Ad.

MnTPPS-Ad (14 μ mol) was added to a solution of olefin (1 mmol) and imidazole (0.2 mmol) in CH_3CN (10 ml). After addition of a solution of sodium periodate (2 mmol) in H_2O (10 ml) the mixture was stirred at room temperature for 4-8 h. The progress of reaction was monitored by GLC. The reaction products were extracted with CH_2Cl_2 (20 ml) and purified by a Silica gel plate or Silica gel column. Pure epoxides were identified by IR and ^{1}H-NMR spectral data.

Scheme 1:

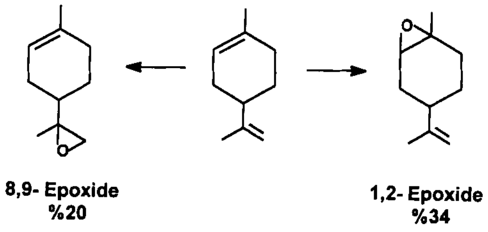

Table 2. Hydroxylation of Alkanes with $NaIO_4$ Catalyzed by MnTPPS-Ad in the Presence of Imidazole

Alkane	Ketone(%)[a]	Alcohol(%)[a]	Reaction Time/h
Cyclooctane	21	35	8
Ethylbenzene	57	-	8
Fluorene	34	-	8
Diphenylmethane	27	-	8

a: GLC yield based on starting alkane

General Procedure for Hydroxylation of Alkanes

CH_3CN (10 ml), alkane (1 mmol) and imidazole (0.2 mmol) were successively added to MnTPPS-Ad (14 μ mol). After addition of a solution of sodium periodate (2 mmol) in H_2O (10 ml), the mixture was stirred at room temperature for 8 h. The progress of reaction was monitored by GLC. The reaction products were extracted with CH_2Cl_2 (20 ml) and purified by a Silica gel plate or Silica gel column. The identities of products were confirmed by IR and ^{1}H-NMR spectral data.

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References

1. Meunier, B., *Chem. Rev.*, **1992,** 92, 1411.
2. Appleton, A. J., Evans, S., Lindsay Smith, J. R., *J. Chem. Soc., Perkin Trans.*, 2, **1996,** 281.
3. Gilbert, B. C., Lindsay Smith, J. R., Macfaul, F., Taylor, P., *J. Chem. Soc., Perkin Trans.*, 2, **1996,** 511.
4. Weber, L., Hommel, R., Behling, J., Haufe, G., Henning, H., *J. Am. Chem. Soc.*, **1994,** 116, 2406.
5. Chen, H. L., Ellis, P. E., Wijesekera, J. T., Hagan, T. E., Groh, S. E., Lyons, J.E., Ridge, D. P., *J. Am. Chem. Soc.*, **1994,** 116, 1086.
6. Zheng, T., Richardson, D. E., *Tetrahedron Lett.*, **1995,** 36, 837.
7. Bhugun, I., Lexa, D., Saveant, J. M., *J. Am. Chem. Soc.*, **1994,** 116, 5015.
8. Solovieva, A. B., Borovkov, V. V., Lukashova, E. A., Grinenko, G. S., *Chem. Lett.*, **1995,** 441.
9. Bailey, A. J., James, B. R., *Chem. Commun.*, **1996,** 2343.
10. Suda, K., Sashima, M., Izutsu, M., Hino, F., *J. Chem. Soc. Chem. Commun.*, **1994,** 949.
11. Leanord, D. R., Lindsay Smith, J. R., *J. Chem. Soc. Perkin Trans.*, 2, **1990,** 1917.
12. Turk, H., Ford, W. T., *J. Org. Chem.*, **1991,** 56, 1253.
13. Barloy, L., Battioni, P., Mansuy, D., *J. Chem. Soc. Chem. Commun.*, **1990,** 1365.
14. Pautet, F., Daudon, M., *Tetrahedron Lett.*, **1991,** 32, 1457.

15. Mohajer, D., Tangestaninejad, S., *J. Chem. Soc. Chem. Commun.*, **1993,** 245.

16. Mohajer, D., Tangestaninejad, S., *Tetrahedron Lett.*, **1994,** 35, 945.

17. Fleischer, E. B., Palmer, J. M., Srinivastava, T. S., Chatterjee, A., *J. Am. Chem. Soc.*, **1971,** 93, 3162.

18. Harriman, A., Porter, G., *J. Chem. Soc. Farady II,* **1979,** 75, 1532.

19. Saito, Y., Mifume, M., Nakashima, S., Nakayama, H., Odo, J., Tanaka, Y., Chikuma, M., Tanaka, H., *Chem. Pharm. Bull.*, **1987,** 34, 2885.

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