Efficient Catalytic Epoxidation of Alkenes by a Manganese Porphyrin and Periodate in the Presence of Imidazole

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Different alkenes are epoxidized with high selectivity in the presence of manganese(III) tetraphenylporphyrin–imidazole–sodium periodate–tetrabutylammonium bromide system in CH_2Cl_2–H_2O media, with high yields (80–100%) at room temperature.

The development of synthetic models of cytochrome P-450 for the selective oxygenation of hydrocarbons has been the focus of continuous attention in recent years.[1] Considerable progress in attaining this goal has been achieved with various metalloporphyrin catalysts and a variety of oxygen sources.[1] Despite all these efforts, there are still some questions regarding the stability of porphyrin systems under oxidising conditions. Assessment of the factors which influence the chemical stability of metalloporphyrins in catalytic systems,[2] particularly the effect of the nature of oxidants,[3] prompted us to explore the potential of $NaIO_4$ as an oxygen source. As far as periodate is concerned, only a few limited reports on epoxidation with low to moderate yields and low selectivity have been presented with Fe or Mn porphyrins as catalysts.[4]

In this report we describe a highly efficient catalytic system for the epoxidation of alkenes which employs [Mn^{III}(tpp)(Cl)] (tpp = tetraphenylporphyrin), an axial imidazole ligand, a phase-transfer catalyst (tetrabutylammonium bromide) and sodium periodate as the oxygen atom donor in a two-phase (CH_2Cl_2–H_2O) system.

In a typical experiment, tetrabutylammonium bromide (0.025 mmol) was added to a solution of [Mn(tpp)(Cl)] (0.006 mmol) in dichloromethane (2 ml) and then imidazole (0.125 mmol) and alkene (0.5 mmol) were added successively. After addition of a solution of $NaIO_4$ (1 mmol) in H_2O (10 ml) the two phases were mixed and stirred for the required time at room temperature. Formation of epoxides and disappearance of the alkenes were monitored by gas-liquid chromatography. Some significant results for several substrates are listed in Table 1.

This catalytic system is very efficient for alkene epoxidation (Table 1). It leads to 100% conversion of cyclooctene with the formation of epoxide (100%) within less than 2 h at room temperature. Cyclohexene is also 100% converted in less than 3 h with 90% yield of epoxide while the more electron rich, 4-acetyl-1-methylcyclohex-1-ene is completely converted to epoxide in 2 h. Similarly, the conversion and yield of epoxide for α-methylstyrene are 100 and 94.6%, respectively, and the less electron rich styrene affords lower conversion (94%) and epoxidation (88%) under identical conditions. Expoxidation of *trans*-stilbene proceeds with absolute stereospecificity and results in *trans*-stilbene oxide. Whereas epoxidation of *cis*-stilbene leads to 85% of *cis*-stilbene oxide and 15% of *trans*-stilbene oxide.

Our results show that $NaIO_4$–[Mn(tpp)(Cl)]–imidazole is a very efficient system for the epoxidation of alkenes under mild conditions and could be introduced as an efficient methodology for organic synthesis. We believe a notable feature of this catalytic system is its relative stability towards oxidative degradation.[2,3] In all of the oxygenation reactions presented in this report there is not much loss of activity of the Mn catalyst and reactions could be repeated with little decrease in the total catalyst activity. Under similar conditions but without imidazole the epoxidation rate is very low and only minute amount of products are obtained. Further work in this area is under way.

Table 1 Catalytic epoxidation of alkenes by $NaIO_4$ in the presence of [Mn(tpp)(Cl)] and imidazole[a]

Alkene	Conversion (%)[b]	Epoxide yield (%)[b]	Reaction time/h
Cyclooctene	100	100	2¼
Cyclohexene	100	90	2¾
4-Acetyl-1-methyl-cyclohex-1-ene	100	100	2
Styrene	94	88	3
α-Methylstyrene	100	94.6	3
trans-Stilbene	80	80 (*trans*)[c]	5
cis-Stilbene	100	85 (*cis*)[c] 15 (*trans*)[c]	3
Indene	94.6	94.6	3

[a] All of the reactions are carried out at ambient temperature and under air, with a 83.6 : 177.2 : 1 : 21 alkene: oxidant: [Mn(tpp)(Cl)]: imidazole molar ratio. [b] GLC yield based on the starting alkene. [c] The organic products and unreacted alkene are separated by silica gel columns and the ratio of isomers are determined by ^{1}H NMR.

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