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Efficient Olefin Epoxidation with Tetrabutylammonium Periodate Catalyzed by Manganese Porphyrin in the Presence of Imidazole

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Abstract: Epoxidation of various olefins is achieved by *tetra*-n-butylammonium periodate in the presence of manganese (III) *meso*- tetraphenylporphyrin and imidazole in CH_2Cl_2, with high selectivity and yield under mild conditions.

The modeling of cytochrome P-450 class of enzymes with synthetic metalloporphyrin complexes accompanied by various oxygen sources, for oxyfunctionalization of hydrocarbons, has received the immense attention of different research groups for over a decade [1]. Considerable effort has been aimed at introducing new catalytic systems with higher degree of chemo-and stereoselectivity and with greater stability under oxidizing conditions[1]. Recently, it was demsonstrated that $NaIO_4$ can be employed as an effective oxygen atom donor for the epoxidation of olefins, catalyzed by [MnIII(TPP)(Cl)] (TPP=*meso*-tetraphenylporphyrin) in a two-phase medium[2].

Now we wish to report on the use of *tetra*-n-butylammonium periodate, $n\text{-}Bu_4NIO_4$, as a very convenient and effective source of oxygen for efficient epoxidation of different olefins in the presence of catalytic amounts of [MnIII(TPP)(Cl)] and imidazole (Im) in a single phase, CH_2Cl_2, at room temperature.

The general procedure for epoxidation consisted of adding olefin (1 mmol) to a solution of [MnIII(TPP)(Cl)] (0.012 mmol) in dichloromethane (4 ml) and then imidazole (0.12 mmol) and tetra-n-butylammonium periodate (2 mmol) were added successively. The solution was stirred at a constant speed under air, at ambient temperature for 5 hrs. The consumption of the starting olefins and formation of epoxides were monitored by gas-liquid chromatography. The identity of pure epoxides were confirmed by IR, ^1H NMR spectral data.

The present catalytic system manifests a high efficiency for olefin epoxidation. Example reactions are listed in Table 1. The epoxide yield for oxygenation of cyclooctene, 4-acetyl-1-methyl-cyclohex-1-ene,α-methylstyrene, *trans*-stilbene, and indene is within 75 to 98%, but selectivity for all these reactions is 100%. Epoxidation of *trans*- stilbene proceeds in a stereospecific manner with complete retention of the configuration. Whereas, oxidation of *cis*- stilbene is associated with some loss of stereochemistry and affords 86% of *cis*-stilbene and 14% of *trans*- stilbene oxides, respectively. The conversion of these olefins ranges between 75-98% in 5 hrs.

In this catalytic system, similar to other biomimetic catalysts based on synthetic metalloporphyrins, presence of an axial ligand remarkably improves the rate of epoxidation[3]. The influence of a number of ligands upon oxygenation of cyclooctene is examined. The epoxidation rate decreases in the order imidazole >pyridine>DMF>triethylamine, although the pKa's of the protonated bases are 6.95, 5.72,-2.0 and 10.75, respectively. It seems clear that simple σ-donor strength does not correlate with the observed trend. However, the π–bonding capabilities of the aromatic axial amines and DMF, may be responsible for their behavior[4].

Table 1. Epoxidation of olefins with n-Bu_4NIO_4 catalyzed by [MnIII(TPP)(Cl)]-imidazole system[a]

Olefin	Conversion (%)[b]	Epoxide Yield (%)[b]
Cyclooctene	98	98(88)[c]
Cyclohexene	95	93(87)[c]
4-Acetyl-1-methyl-cyclohex-1-ene	98	98
Styrene	80	77(72)[c]
α–Methylstyrene	85	85
trans-Stilbene	75	75(*trans*)[d]
cis-Stilbene	95	82(*cis*)[d] 13(*trans*)[d]
Indene	88	88(80)[c]

a. Reaction conditions are given in the text, the molar ratio for olefin: oxidant: [MnIII(TPP)(Cl)]: imidazole is 83.3: 166.6: 1: 10. All the reactions are run at room temperature for 5 hrs.

b. GLC yield is based on the starting olefin.

c. Isolated yield.

d. The organic product(s) and the unreacted olefins are separated by silica gel columns and isomer ratios are determined by ^1H NMR.

The effect of different Mn-porphyrin/Im molar ratios upon the rate of epoxidation of cyclooctene was also investigated (Table 2). When the Mn-catalyst/Im=1:0.5 the epoxide yield (%) is between 13-31% less than that of the 1:1 molar ratio.Whereas, for 1:1 and 1:10 molar ratios the epoxide yields are very close. Thus, it appears that for both 1:1 and 1:10 molar ratios the formation of 1:1 Im-Mn porphyrin complex, which is of prime importance in the catalytic cycle, is nearly complete[5]. Furthermore, these experiments imply that the imidazole ligand is quite stable towards oxidative demolition in the present catalytic system and a 1:1 Mn-catalyst/Im molar ratio is sufficient to ensure an effective epoxidation.

Table 2. Effect of various Mn-catalyst/Im molar ratios on cyclooctene epoxidation rate by n-Bu_4NIO_4[a].

Reaction time(min)	30	60	90	120	150	180	210
Epoxide yield (%)for:							
Mn-catalyst/Im=1:0.5	15	28	40	52	60	64	65
Mn-catalyst/Im=1:1	28	55	68	78	87	92	96
Mn-catalyst/Im=1:10	34	56	70	81	89	94	97

a. All reaction conditions are the same as described in Table 1 except for different Mn-catalyst/Im ratios.

The Mn-catalyst decomposition, both under the oxidizing conditions and in the absence of olefin, was followed by measuring the percentage decrease of the absobance at 478 nm (λ_{max} of Mn III(TPP)(Cl)) referred to the sample taken at zero time of reaction, see Table 3.The slow reduction of the absorption with time is indicative of the stability of the manganese porphyrin in this catalytic system. It is noteworthy that the Mn-catalyst is reasonably stable even in the absence of any substrate.

Our study demonstrates that [MnIII(TPP)(Cl)] bearing an imidazole axial ligand is an extremely efficient catalyst for the activation of n-Bu_4NIO_4 for the epoxidation of olefins under neutral and homogeneous conditions. The present homogeneous single phase catalytic system has some obvious advantages over our previously reported two-phase system[2]. The high selectivity and stability of this mild and effective catalytic system suggests a promising and convenient methodology for synthetic purposes.

Table 3. Change of percent absorption at 478 nm in electronic spectra of MnIII(TPP)(Cl) with n-Bu_4NIO_4 in CH_2Cl_2 at room temperature.

Time (min)	30	60	90	120	150	180
Percent absorption						
Olefin present	100	99	98	95	93	90
Olefin absent	95	90	84	79	74	71

a. The molar ratio is the same as described in Table 1, and percent absorption = (absorption/absorption at zero time) X100.

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