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Efficient oxygenation of hydrocarbons with tetrabutylammonium monopersulfate catalyzed by manganese *meso*-tetraphenylporphyrin in the presence of imidazole

Daryoush Mohajer* and Abdolreza Rezaeifard

Department of Chemistry, Shiraz University, Shiraz 71454, Iran

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Abstract—Oxidation of hydrocarbons, into their corresponding epoxide, alcohol and/or ketone, was achieved with tetrabutylammonium monopersulfate in the presence of manganese(III) *meso*-tetraphenylporphyrin catalyst and axial imidazole ligand in CH_2Cl_2 in low to very high yields (13–100%) and good to excellent selectivities (73–100%) in less than 5 min at room temperature (~25°C). © 2002 Elsevier Science Ltd. All rights reserved.

The challenging selective oxyfunctionalization of hydrocarbons with synthetic models of cytochrome P-450 under mild conditions has been of extreme interest to chemists.[1–6] To achieve this goal a number of biomimetic oxygenation systems composed of a variety of oxygen donors such as PhIO,[7,8] NaOCl,[9,10] H_2O_2,[11–13] and periodates,[14–18] in combination with different metalloporphyrin catalysts have been employed. However, despite the promising employment of $KHSO_5$ (Oxone®, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) in the oxygenation of hydrocarbons in the presence of manganese porphyrins,[19–21] attempts at using Bu_4NHSO_5 (TBAO) as an oxygen source in association with porphyrin catalysts were unsuccessful.[22]

In this report, we describe for the first time the effective activation of TBAO with simple Mn(TPP)OAc (TPP = *meso*-tetraphenylporphyrin dianion) as a single oxygen donor for oxygenation of some hydrocarbons in the presence of imidazole (Im) in CH_2Cl_2. The general procedure for oxidation consisted of adding TBAO[23] (0.3 mmol) to a solution containing hydrocarbon (0.6 mmol), Mn(TPP)OAc (0.006 mmol) and imidazole (0.12 mmol) in CH_2Cl_2 (2 ml). The solution was stirred at a constant speed, under air, at room temperature. The consumption of the starting hydrocarbons and formation of oxidation products were monitored by GLC and the identity of the products were confirmed by IR and ^1H NMR spectral data.

This catalytic system is very efficient for the epoxidation of alkenes in very short times (Table 1). It leads to 95% conversion of cyclooctene with formation of epoxide (92%) in less than 1 min at room temperature. Styrene is 100% converted within 1 min with 95% yield of epoxide. Similarly, conversion and yield of cyclohexene are 100 and 86%, respectively. It seems that the efficiency of oxidation in this catalytic system is very dependent on the steric requirements of the substrates. Epoxidation of *trans*-stilbene proceeds with absolute stereospecificity and the epoxide yield is 55%. Whereas epoxidation of *cis*-stilbene is quantitative (100%) and leads to a mixture of *cis*-stilbene oxide (84%) and *trans*-stilbene oxide (16%) in the same period. The lower activity of *trans*-stilbene relative to the *cis*-stilbene seems to be related to the greater phenyl–phenyl non-bonded interactions between the catalyst and *trans*-stilbene.[7] Formation of *trans*-stilbene oxide in the oxidation of *cis*-stilbene suggests a competition between closure of the epoxide ring and rotation around the C–C bond during the oxygen transfer step from the active oxidizing species to the alkene. Interestingly, in the oxidation of *cis*-stilbene with sterically more demanding Mn(TDCPP)OAc (TDCPP = *meso*-tetrakis (2,6-dichlorophenylporphyrin) dianion) catalyst, a higher yield of *cis*-stilbene oxide (97%) is obtained, thus reflecting the importance of the steric effects of the catalyst. Furthermore, it would be expected that the electron rich 1-methylcyclohexene would be more active towards epoxidation, than cyclohexene.[24] However, a much longer reaction time for the former (5 min) than

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Keywords: hydrocarbons; oxidation; tetrabutylammonium monopersulfate; manganese; catalysis; porphyrin.

* Corresponding author. Tel.: 0711-2284822; fax: 0711-2280926; e-mail: dmohajer@chem.susc.ac.ir

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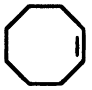
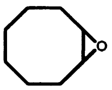
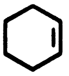
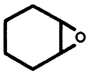
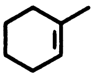
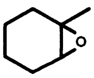
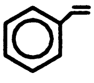
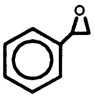
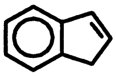
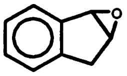
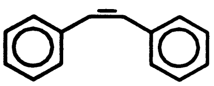
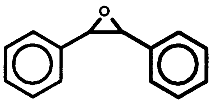
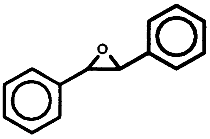
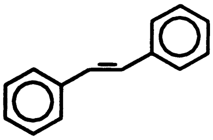
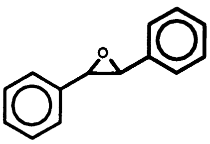
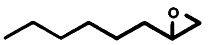
Table 1. Epoxidation of alkenes with TBAO catalyzed by Mn(TPP)OAc in the presence of Im[a]

Alkene	Conversion %^{b}	Epoxide	Yield %^{b}	Selectivity %	Time (min)
	95		92	97	<1
	100		86	86	<1
	98		81	83	5
	100		95	95	<1
	76		76	100	5
	100		84^c	84	<1
			16^c	16	
	55		55^c	100	<1
	41		30	73	<1

[a] Reaction conditions are given in the text, the molar ratio for alkene:oxidant:Im:Mn(TPP)OAc is 100:50:20:1.

[b] GLC yields are based on the starting alkenes.

[c] The organic product(s) and the unreacted alkenes were separated by silica gel column chromatography and isomer ratios were determined by ^{1}H NMR.

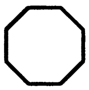
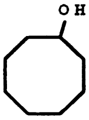
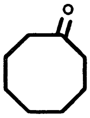
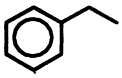
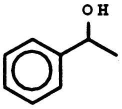
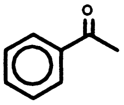
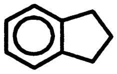
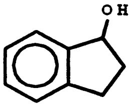
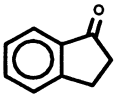
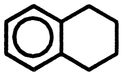
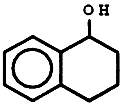
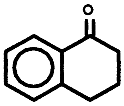
the latter (<1 min) again confirms the influence of steric effects in this catalytic system. Epoxidation of the terminal alkene (oct-1-ene) proceeded in moderate yield (30%) and good selectivity (73%), compared to the oxygenation of the other alkenes. The present catalytic system allows the oxygenation of various saturated C–H bonds to a mixture of their corresponding alcohols and ketones (except for ethylbenzene which produces only acetophenone), with combined yields of 12–72% and excellent selectivities (100%), in less than 3 min at room temperature (Table 2). In all these oxidations much higher yields of ketones rather than alcohols were achieved.

In a similar manner to other biomimetic porphyrin catalytic systems, the presence of an axial ligand dramatically improves the efficiency of the oxidations.[25] The effects of three commonly used axial ligands upon oxygenation of cyclohexene were explored (Table 3). Our results demonstrate that imidazole is by far the best co-catalyst in comparison with pyridines in terms of conversions and epoxide yields.

An increase in the Im/Mn-porphyrin molar ratio up to 20 remarkably improved the rate of conversion and selectivity of cyclohexene epoxidation (Table 4). However, a further increase in the ratio did not affect the results.

In conclusion, the low to excellent yields and good to very high selectivities of hydrocarbon oxidations achieved within a few minutes using the homogeneous TBAO–Mn(TPP)OAc–Im system in CH_2Cl_2 at room temperature, make this simple biomimetic system a very convenient method for rapid monooxygenation of hydrocarbons from a synthetic point of view. A notable

Table 2. Hydroxylation of saturated hydrocarbons with TBAO catalyzed by Mn(TPP)OAc in the presence of Im[a]

Substrate	Conversion %[b]	Alcohol	Yield%[b]	Ketone	Yield%[b]	ol+one %	ol/one
	13		3		9	12	0.33
	22		trace		22	22	0.0
	44		3		41	44	0.07
	72		8		64	72	0.12

[a] All reaction conditions and molar ratios are the same as described in Table 1. All reactions were run at room temperature for 3 min.

[b] GLC yields are based on the starting substrates.

Table 3. Epoxidation of cyclohexene with TBAO catalyzed by Mn(TPP)OAc in the presence of axial ligands[a]

Axial Ligand	Conversion (%)[b]	Epoxide yield (%)[b]	Selectivity (%)
Imidazole	93.5	77	82
Pyridine	66.5	42	63
4-*tert*-Butylpyridine	12	8	67
None	13.8	2	14.5

[a] All reactions were run at room temperature for 5 min. The molar ratio for alkene:oxidant:axial ligand:Mn(TPP)OAc was 100:100:10:1.

[b] GLC yields are based on the starting alkenes.

Table 4. Effect of various Im/Mn(TPP)OAc molar ratios on cyclohexene epoxidation rate and selectivity by TBAO[a]

Im/Mn(TPP)OAc Ratio	Conversion (%)[b]	Epoxide yield (%)[b]	Selectivity (%)
1	22.6[c]	13	57.5
10	93.5[c]	77	82
20	100[d]	86	86
100	100[d]	86	86

[a] All reaction conditions were the same as described in Table 3 except for different Im/Mn(TPP)OAc ratios.

[b] GLC yields are based on the starting alkenes.

[c] Reactions were run for 5 min.

[d] Reaction times were <1 min.

feature of this catalytic system is its relative stability towards oxidative degradation.[26,27] While the total turnover numbers for epoxidation of styrene and cyclohexene are 420 and 460, respectively, the lower yields of oxidation products with the less reactive hydrocarbons were due to competing destruction of the catalyst. Further work with other Mn-porphyrin catalysts is under way in this area.

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23. TBAO was synthesized by the procedure reported in Ref. 22 (a): a sample of potassium monopersulfate (2.0 g, 6.5 mmol) in water (20 ml) was stirred with tetrabutylammonium hydrogen sulfate (2.0 g, 5.9 mmol) for 20 min. The solution was extracted with CH_2Cl_2 (40 ml) and the organic phase was dried over sodium sulfate and filtered. After evaporation of the solvent, the remaining paste was washed with hexane (10 ml) and dried under vacuum. A white powder (1.5 g, 0.97 mmol) was obtained with a purity >90% (determined by iodometration). The freshly prepared TBAO showed much greater oxidizing ability than the commercially available samples, and remained quite active for at least two months. **Caution**: this peroxide should be considered as a potential explosive.
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