

Oxidation of Hydrocarbons with Tetrabutylammonium Oxone Catalyzed by β -Tribrominated *meso*-Tetraphenylporphyrinato-manganese(III) Acetate in the Presence of *N*-Bases

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β -Tribrominated meso-tetraphenylporphyrinato-manganese(III) acetate (Mn(TPPBr₃)OAc) as an electron-deficient metalloporphyrin shows high catalytic activity in the oxidation of less hindered conjugated double bonds and cycloalkenes by tetrabutylammonium monopersulfate.

Keywords: Tetraphenylporphyrin, catalyst, epoxidation, oxidation, alkenes, saturated hydrocarbons.

Introduction

Different manganese porphyrins and related systems such as Schiff bases have been used extensively in chemical modeling of biological monooxygenation reactions. The biomimetic oxidation of hydrocarbons and nitrogen- and sulfur-containing compounds with different oxygen donors such as PhIO, NaOCl, H₂O₂, periodate, amine *N*-oxides and ⁿBu₄NHSO₅ (TBAO) have been extensively studied.^[1-20] Iron and manganese porphyrins bearing halogen substituents on the periphery of the porphyrin ring have been shown to be particularly efficient for epoxidation and hydroxylation reactions.^[21-23] Such porphyrins are also more resistant to degradation *via* free-radical attack or direct oxidation of porphyrin ring than those containing electron-donating substituents.^[1,24-25] The employment of nitrogenous donors in metalloporphyrin systems for mimicking the oxygenation function of P-450 has led to marked improvement in selectivities and turnover rates in the epoxidation of alkenes.^[18,26-27]

Despite the favorable employment of Oxone® (2KHSO₅·KHSO₄·K₂SO₄) in the Mn porphyrin catalyzed oxygenation of hydrocarbons,^[28-29] attempts at using TBAO as an oxygen source in association with porphyrin catalysts has been unsuccessful until 2002.^[18] Oxidation of hydrocarbons with TBAO in the presence of different electron-rich and electron-deficient Mn^{III} *meso*-tetra(halogensubstituted aryl)porphyrins have been reported. The present work is the first report on using electron deficient Mn porphyrins bearing halogen atoms at β -positions (β -tri-brominated *meso*-tetraphenylporphyrinato-manganese(III) acetate, Mn(TPPBr₃)OAc, as catalyst for oxidation of hydrocarbons with TBAO in the presence of different nitrogen donors as co-catalyst.

Experimental

All of the materials and solvents were purchased from Merck. ¹H NMR spectra were obtained in CDCl₃ solutions on a Bruker FT-

NMR 250 (250 MHz) spectrophotometer. The residual CHCl₃ in conventional 99.8 atom% CDCl₃ gives a signal at δ = 7.26 ppm, which was used for calibration of the chemical shift scale. A double beam spectrophotometer (Shimadzu, UV-240) was used for the UV-vis absorption determination. The reaction products of oxidation were determined and analyzed by HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (phenyl methyl siloxane 30 m $\times$ 320 μ m $\times$ 0.25 μ m) and flame-ionization detector.

Preparation of H₂TPPBr₃. β -Tri-brominated *meso*-tetraphenylporphyrin (H₂TPPBr₃) was prepared from H₂TPP and freshly recrystallized *N*-bromosuccinimide (NBS) according to the method reported by Bhyrappa *et al.* with some modification.^[30] H₂TPP (300 mg, 0.49 mmol) was dissolved in CHCl₃ (80 ml). To this solution, freshly recrystallized NBS (270 mg, 1.47 mmol) was added (recrystallized from hot water and dried at 80°C under vacuum). The reaction mixture was stirred for 24h and then CHCl₃ was evaporated to dryness. The residue was washed with methanol (2 $\times$ 20 ml) to remove any soluble succinimide impurities. UV-vis (CH₂Cl₂) $\lambda_{\max}$ nm: 427, 523, 599, 658. ¹H NMR (CDCl₃, 250 MHz) δ_{H} ppm: 8.70-8.86 (5H, m, β pyrrole), 8.07-8.21 (8H, m, *o*-phenyl), 7.73-7.77 (12H, m, *m*- and *p*-phenyl).

Preparation of Mn(TPPBr₃)OAc. Mn(TPPBr₃)OAc was also prepared and purified according to the previously reported method.^[31]

Preparation of ⁿBu₄NHSO₅. The synthesis of ⁿBu₄NHSO₅ was based on the procedures given by Compestrini *et al.*^[18,28] Freshly prepared ⁿBu₄NHSO₅ was a much stronger oxidant than commercially available samples. Since the oxidizing ability of ⁿBu₄NHSO₅ samples reduces with time, in order to obtain reproducible results, the freshly prepared oxidant was refrigerated and used within three days.

General Oxidation Procedure. The general procedure for oxidation consisted of adding ⁿBu₄NHSO₅ (0.57 mmol) to a CH₂Cl₂ solution containing the alkene (0.3 mmol), the catalyst (0.003 mmol) and nitrogenous bases as co-catalysts (0.06 mmol). The reaction solutions were stirred for 2 min at room temperature and analyzed immediately by GLC.

Results and Discussion

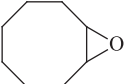
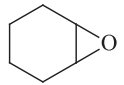
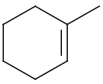
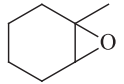
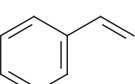
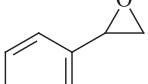
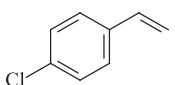
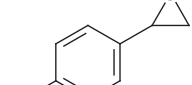
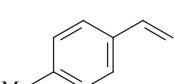
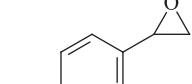
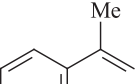
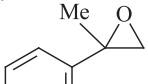
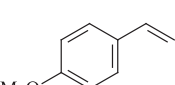
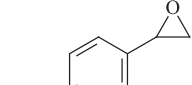
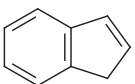
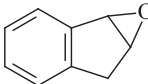
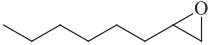
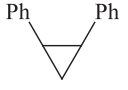
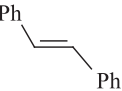
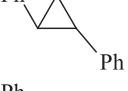
Mn(TPPBr₃)OAc catalyzed oxidation of cyclooctene with ⁿBu₄NHSO₅ in the presence of imidazole leads to

cyclooctene oxide as the sole product (Table 1). Styrene, α -methylstyrene and *para*-substituted styrenes are 100% converted within 2 min with 100% selectivity for epoxide products except for α -methylstyrene which gives 25% acetophenone as the by-product. Electron-donating (entries 6, 8 in Table 1) as well as electron-deficient substituents (entry 5) on the *para* position of the aryl ring of styrene were compatible with the reaction conditions, and gave the corresponding epoxide. With the exception of cyclooctene, terminal double bonds and unconjugated ones (Table 1, entries 2, 3 and 10) are less reactive than the conjugated double bonds and show lower selectivities.

Decreased reactivity of α -methylstyrene relative to styrene (entries 4 and 7) seems to be due to the steric hindrance of methyl group. Also, the comparison of *cis*- and *trans*-stilbene (entries 11 and 12) shows the importance of steric effects. The enhanced stability of Mn(TPPBr₃)OAc relative to Mn(TPP)OAc towards the oxidant and higher yields of epoxide make this electron-deficient Mn-porphyrin more efficient than Mn(TPP)OAc in the epoxidation of olefins.

Coordination of nitrogen donors to the metal center of metalloporphyrins usually increases the catalytic activity of the metalloporphyrin.^[1,9-20] In this work, co-

Table 1. Epoxidation of alkenes with ⁿBu₄NHSO₅ catalyzed by Mn(TPPBr₃)OAc in the presence of ImH.^a

Entry	Alkene	Conversion %	Epoxide	Yield%	Selectivity %	Time (min)
1		100		100	100	2
2		100		91	91	2
3		93		71	76	2
4		100		97	97	2
5		100		100	100	2
6		100		100	100	2
7		100		75	75 ^b	2
8		100		100	100	2
9		100		100	100	2
10		40		30	75	2
11		100 ^c		89	100	2
12		70 ^c		11	100	2

^aThe molar ratio for oxidant: alkene:ImH:catalyst is 190:100:20:1.

^bAcetophenone is the by product.

^cThe organic product(s) and unreacted alkenes were determined by ¹H NMR spectroscopy.

catalytic activities of a selected series of nitrogen donors, in the presence of Mn(TPPBr₃)OAc as catalysts, in the epoxidation of cyclohexene with ⁿBu₄NHSO₅ were studied (Table 2).

Table 2. Epoxidation of cyclohexene with ⁿBu₄NHSO₅ catalyzed by Mn(TPPBr₃)OAc in the presence of different nitrogen donors.^a

Axial Ligand	Conversion (%) ^b	Epoxide yield (%) ^b	Selectivity (%)
ImH	100	92	92
2-MeImH	89	83	93
BzImH	88	79	89
Py	88	83	94
2,6-Cl ₂ Py	30	27	90
4-CNPy	16	16	100
3-CNPy	22	22	100
Piperidine	63	54	85
Et ₃ N	41	32	78
Et ₂ NH	62	50	80
None	9	7	77

^aAll reactions were run at room temperature for 2 min. The molar ratio for oxidant: alkene:ImH:catalyst is 190:100:20:1.

It is observed that imidazole with ring size smaller than the other nitrogen donors is the best one. The introduction of π -electron-withdrawing substituents at different positions of pyridine dramatically decreases the activity of pyridine as a nitrogen donor. It seems that the activity of nitrogen donors is strongly depends on the π -donor ability of axial base. In accordance with the explanation, co-catalytic activity of

benzimidazole is almost equal to that of imidazole, although the size of the former is much larger than that of the latter.

It is also observed that simple amines which may be considered as pure σ -donors are less effective than those with both σ - and π -donor abilities.

Table 3 shows the effect of Im to catalyst molar ratio in the cyclooctene epoxidation. It is observed that an increase in the ImH to catalyst molar ratio up to 20 remarkably improves the epoxidation rate.

Table 3. Effect of various ImH/Mn(TPPBr₃)OAc molar ratios on Cyclooctene epoxidation rate and selectivity by ⁿBu₄NHSO₅^a.

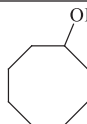
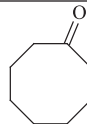
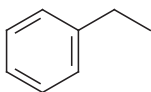
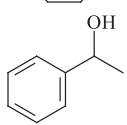
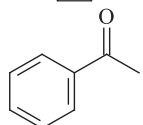
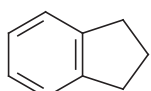
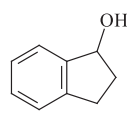
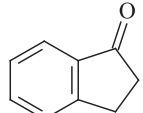
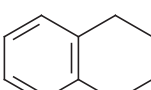
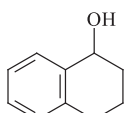
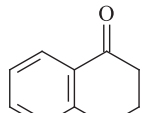
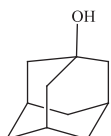
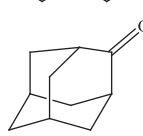
ImH/Mn(TPPBr ₃)OAc Ratio(X)	Conversion (%) ^b	Epoxide yield (%) ^b	Selectivity (%)
0	30	30	100
5	72	72	100
10	94	94	100
20	100	100	100
40	100	100	100
60	98	98	100
80	96	96	100
100	92	92	100

^aAll reactions were run at room temperature for 2 min. The molar ratio for oxidant: alkene:ImH:catalyst is 190:100:X:1.

Oxidation of secondary C-H bonds of saturated hydrocarbons in the same conditions gives alcohols and/or ketones as the products (Table 4).

The influence of the solvent nature in this catalytic system was examined and dichloromethane has been shown to be the best one.

Table 4. Hydroxylation of saturated hydrocarbons with ⁿBu₄NHSO₅ catalyzed by Mn(TPPBr₃)OAc in the presence of ImH^a.

Entry	Hydrocarbons	Conversion (%) ^b	Alcohol	Yield (%) ^b	Ketone	Yield (%) ^b
1		12		6		6
2		18		trace		18
3		64		29		35
4		72		12		60
5		58 ^c		49		trace

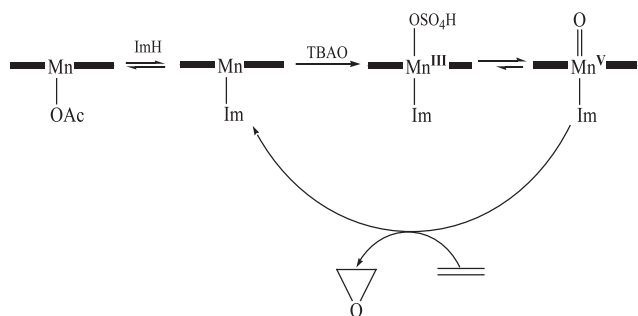
^aAll reactions were run at room temperature for 2 min. The molar ratio for oxidant: alkane:ImH:catalyst is 190:100:20:1.

^bGLC yields are based on the starting alkanes.

^cYield of 2-adamantanol is 9%.

Active Oxidant

Usually, the competitive epoxidation of *cis*- and *trans*-stilbenes with different oxygen donors in the presence of metalloporphyrins bearing non-bulky *ortho*-substituents on the phenyl groups has been carried out to investigate the nature of active oxidant.^[9,32] In this reaction, a low ratio of *cis*- to *trans*-stilbene oxide has been proposed to be a supporting evidence for the involvement of a high valent metal-oxo porphyrin species. In Mn(TPPBr₃)OAc/Im/TBAO catalytic system, the competitive oxidation of *cis*- and *trans*-stilbenes yielded *cis*- and *trans*-stilbene oxide in nearly the same ratio which suggests a high valent Mn-oxo porphyrin as the main active oxidant (Scheme 1).



Scheme 1.

Conclusions

In summary, Mn(TPPBr₃)OAc is an efficient catalyst for epoxidation of alkenes in the presence of imidazole. Under the same reaction condition, saturated hydrocarbons were oxidized to alcohol or ketones in only low to moderate yields.

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