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Halogenated tetraphenyl porphyrin; iodosylbenzene an efficient catalytic system for olefin epoxidation

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ABSTRACT: Olefin epoxidation using o-phenyl and β-pyrrole substituted tetraphenyl porphyrin complexes of Fe(III) and Mn(III) as catalysts and ^{y}Iodosylbenzene as oxidant was studied. Excellent yields of epoxide and secondary oxidation products were observed. Effect of pyridine, imadizole, sodium lauryl sulphate, and solvent variation was also studied. Effect of substituents on catalytic activity of the porphyrin complex is also explained. o-phenyl substituted complexes gave better yield of epoxide as compared to β-pyrrole substituted complexes.

KEYWORDS: epoxidation, porphyrin catalysis, olefins.

INTRODUCTION

Epoxidation of olefins continues to be an important reaction in organic synthesis, due to the feasibility of conversion of the epoxide into number of useful products [1–3]. The controlled oxygenation of alkanes alkenes, and aromatic hydrocarbons is one of the most important technologies to convert petroleum products into useful commodities [4–8]. The heme protein, cytochrome P-450 can very efficiently catalyze these complex reactions using aerial oxygen [7–8], but isolation and synthesis of cyto-chrome P-450 is very difficult and expensive. Hence development of efficient catalytic systems that mimic action of cytochrome P-450 and other such natural oxidation catalysts has always been and continues to attract much attention [9–12]. Transition metal complexes like Schiff bases, metalloporphyrins show remarkable catalytic activity towards epoxidation, due to their ability to bring the substrate and oxidant within the coordination sphere. The oxygen transfer rate is enhanced many fold as a result of face-to face proximity of the substrate and oxidant in presence of these catalysts [13–15]. Synthetic metalloporphyrin/oxidant systems have been found to be very effective catalysts for hydrocarbon epoxidation, hydroxylation and other controlled oxidation reactions [16, 17] besides being excellent biomimetic models, Iron, mangenes, ruthenium metalloporphyrins have been used efficiently for synthesis of a range of organic molecules and continue to amuse researchers all over the world [18–20]. Keeping in mind, the importance of metalloporphyrins, commercial applications of epoxidation and our continued interest in metal complex catalysts [21], we studied epoxidation of cycloolefins using metalloporphyrins as catalysts. This research paper presents the investigation of catalytic behavior of some sterically hindered metallo porphyrins having substituents at β-pyrrole and o-phenyl positions. The possible effect on calatytic activity viz-a-viz substituents is also explained.

RESULTS AND DISCUSSION

Epoxidation of cyclohexene gave cyclohexene oxide, cyclohexenol and cyclohexenone as the products (Table 1, Scheme 1) In the case of Mn(OBP)Cl acetonitrile was found to give better yield while in the case of Mn(2,6-Cl PP)Cl and Mn(OCOBP)Cl dichloromethane solvent gave better results. The yield of cyclohexene epoxide followed the order M(OCOBP)Cl > M(2,6-Cl TPP)Cl > M(OBP)Cl (where M = Mn and Fe). This shows that substitution at

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[◊] SPP full member in good standing

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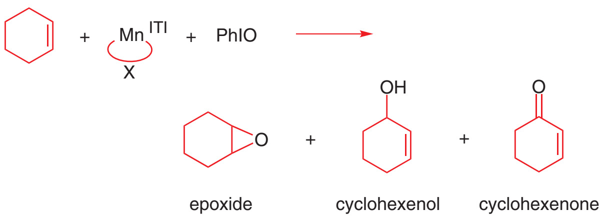


Scheme 1. Epoxidation of cyclohexene

orthoposition in mesophenyl ring makes the porphyrin catalyst more stable compared to that obtained after brominating the β-pyrrole positions.

The effect of change in catalyst concentration using Mn(III) derivatives was studied. It was observed that Mn(2,6-Cl TPP)Cl and Mn(OCOBP)Cl exhibited no significant effect on the yield of epoxide when quantity of catalyst was increased from 0.00025 to 0.00075 g. The yield of epoxide increased in case of Mn(OBP)Cl with increase in quantity of catalyst from 0.00025 to 0.00075 g. but further increase in concentration, decreased the yield of epoxide (Table 2).

Nolte *et al.* [22] while studying some Mn(III) complexes, have suggested the formation of an oxo-manganese(V) species as the rate-determining step in epoxidation. Formation of high valent oxo-iron(IV) porphyrin cation radical (Fe IV=O$^{+\cdot}$) as reactive intermediate for enzymatic oxidation reaction for iron porphyrin models has been proposed by previous workers [16, 18]. Formation of similar type of species can explain the results observed with the system, under investigation. It can be suggested that the oxo-manganese(V) species responsible for epoxidation, reacts with the Mn,(III) complex, resulting in the formation of a µ-oxo-dimer, as the concentration of Mn(OBP)Cl increases. This µ-oxo-dimer is catalytically inactive. Thus at higher concentration of Mn(OBP)Cl, the oxo-manganese(V) species is wasted in the unproductive side reaction. Since the increase in concentration of Mn(OCOBP)Cl and Mn(2,6-Cl TPP)Cl had no significant effect on epoxidation, it suggests that substitution at o-phenyl position can reduce the µ-oxo-dimer formation considerably, so that the catalyst is not wasted in side reaction even on increasing the concentration. On the other hand, substitution at β-pyrrole position decreased the electron density of metal centre and increases the rate of reaction as compared to Mn(TPP)Cl but it could not be effective in reducing the formation of µ-oxo-dimer. Similar behavior was observed with Fe(III) complexes. Here also the decrease in epoxide yield at higher concentration may be attributed to formation of catalytically inactive, µ-oxo-dimer species.

Table 2. Effect of catalyst concentration on epoxidation of cyclohexene using Mn(III) porphyrin complxes as catalyst

S. No	Catalyst	Yield of epoxide, mmol	
		Mn OCOBP	Mn(OBP)Cl
1	0.00025 g	0.646	0.272
2	0.0005 g	0.676	0.317
3	0.00075 g	0.731	0.348
4	0.001 g	0.521	0.266
5	0.002 gm	0.571	0.255

*Yields are based on amount of PhI generated.

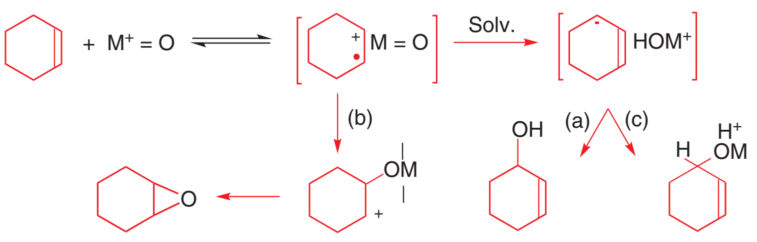
EPOXIDATION *VS.* HYDROXYLATION

Cyclohexene on epoxidation also gave cyclohexenol and cyclohexenone as allylic oxidation products (Table 1) along with cyclohexene oxide. Comparison with Fe(TPP) X and Mn(TPP)X, studied by T.G. Taylor *et al.* [23] shows that substitution at o-phenyl position of TPP brings greater selectivity towards epoxidation, suggesting the involvement of cyclohexenyl redical [a] or direct electron transfer [b] while substitution of bromine at β-pyrrole position did not improve selectivity towards epoxidation suggesting that radical abstraction [c] is responsible for allylic oxidation products; (Scheme 2). This shows

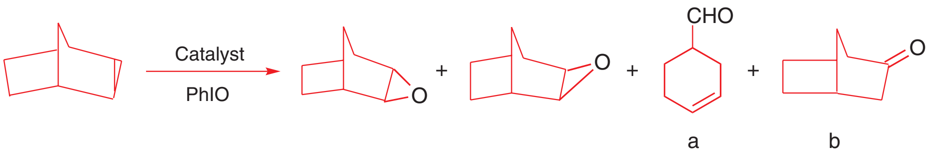
Table 1. Epoxidation of cyclohexene catalyzed by Fe(III) and Mn(III) porphyrin complexes

S. No	Catalyst	Product, mmol*		Cyclohexenone
		Epoxide	Cyclohexenol	
1	Mn(OBP)Cl	0.23	0.29	0.13
2	Mn(OCOBP)Cl	0.57	0.12	0.14
3	Mn(2,6-ClTPP)Cl	0.59	0.14	0.17
4	Fe(OBP)Cl	0.18	0.22	0.07
5	Fe(OCOBP)Cl	0.42	0.19	0.17
6	Fe(2,6-ClTPP)Cl	0.37	0.19	0.21

*Yields are based on amount of PhI generated.



Scheme 2.



Scheme 3. Epoxidation of norbornene

Table 3. Epoxidation of norbornene using Fe(III) and Mn(III) porphyrin as catalyst

S. No	Catalyst	Epoxide yield, mmol*		Relative Exo/endo ratio
		Exo epoxide	Endo epoxide	
1	Mn(OBP)Cl	0.11	0.70	1:6.6
2	Mn(OCOBP)Cl	0.12	0.94	1:7.9
3	Mn(2,6-ClTPP)Cl	0.02	0.95	1:50.1
4	Fe(OBP)Cl	0.14	0.32	1:2.3
5	Fe(OCOBP)Cl	0.10	0.54	1:5.5
6	Fe(2,6-ClTPP)Cl	0.14	0.68	1:4.9

*Yields are based on amount of PhI generated.

that location of substituent plays an important role in product formation.

The epoxidation of norbornene using Mn(III) and Fe(III) porphyrin complexes gave exo and endo epoxide along with traces of rearrangement products cyclohexene-4 carboxaldehyde (a) and norcamphor (b) (Table 3, Scheme 3). Formation of exo and endo-epoxide shows that rotation of bond is taking place leading to endo and exo epoxide. This finding suggest that either carbocation or carbon radical intermediate is involved in the reaction, as metalloxetane, ion pair and concerted insertion of oxygen will lead to exo epoxide formation only. Rearrangement of exo-epoxide can be suggested for formation of endo expoxide. It is known that M-O-C-C$^+$ can explain the formation of small amount of cyclohexene-4-carboxaldehyde and norcamphor [24]. These results suggest a nucleophilic attack of the olefin on the oxo metal and development of positive charge on unbound cabon atom. Thus the most probable intermediate being involved is the carbocation intermediate.

Comparison of data for exo/endo ratio for norbornene among the porphyrin catalysts (Table 3) shows that the exo/endo ratio of epoxide, using the β-pyrrole substituted porphyrins is lesser than M (TTP)X type of complexes. The exo/endo ratio is 7.0 for Mn(OBP)Cl) 50.0 for [Mn[2.6 ClPP]Cl and 8.0. for Mn(OCOBP)Cl, which is much less than 450 reported for Mn(TPP)X [23]. This shows that exo/endo epoxide ratio decreases as the electron density in the porphyrin decreases. The addition of bromine at β-pyrrole positions has marked effect on exo/endo ratio compared to the effect by addition of chlorine at 2,6-positions of phenyl ring. This suggests that substitution of electronegative atom near the metal center has pronounced effect compared to that in phenyl ring. The same behavior was observed using F(III) catalysts. The exo/endo ratio increased markedly from Fe(III) complexes to Mn(III) porphyrin complexes.

The effect of pyridine on the epoxidation of norbornene was studied (Table 4). Addition of pyridine increased the yield of epoxide with Mn(OBP)Cl. It can be suggested that pyridine helps in rapid transfer of oxygen to the olefin. pyridine gets co-ordinated to the oxo-manganese complex and thus (i) makes the oxygen of oxo-manganese complex less negatively charged, (ii) the oxygen atom

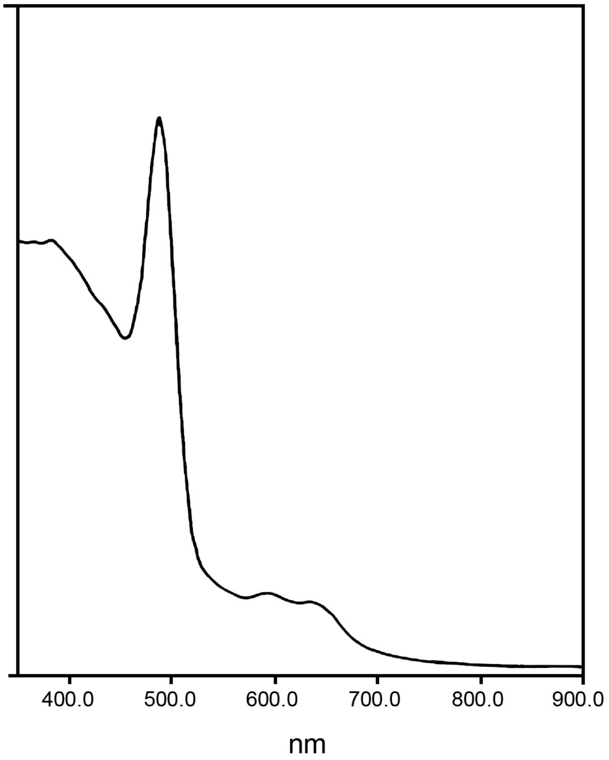


Fig. 1. Visible spectrum of cyclohexene epoxidation using Mn(OBP)Cl, PhIO, pyridine

becomes a better acceptor of π electron density and (iii). The oxo-manganese bond is weakened [25]. The λ-max of Mn(OBP)Cl (Fig. 1) catalysed epoxidation did not show any remarkable change after completion of reaction. This shows that pyridine reduces destruction of catalyst by reducing formation of μ-oxo dimer, All these factors help in promoting the yield of epoxide. In case of Mn(OCOBP)Cl and Mn(2,6-ClTPP)Cl, addition of pyridine did not effect the overall yield of epoxidation showing that substitution by chlorine or bromine makes the metal centre fairly electron deficient, which inturn results in faster rate of epoxidation. Addition of pyridine also increased the exo/endo ratio in Mn(OBP)Cl and Mn(OCOBP)Cl catalyzed reactions. This increase can be explained by the fact that in these complexes the addition of pyridine pulls the metal atom down towards the plane of the ring. This increases the steric hindrance for olefin as a result, the rotation of C–C bond is reduced and consequently the ratio of exo/endo epoxide is increased. Addition of bromine atoms at β-pyrrole positions makes the ring puckered and the metal has to go out of plane to stabilize itself, this gives freedom to C–C bond rotation and hence a low value of exo/endo ratio. Mn(2,6-Cl TPP)Cl did not exhibit significant change in exo/endo ratio on addition of pyridine.

In case of Fe(III) porphyrin complexes (Table 5) the pyridine addition was found to increase the over all yield of epoxide. This behavior is in contrast to that observed using Fe(TPP)Cl/NaOCl system [26] where pyridine inhibits catalytic activity as coordination of pyridine at distal position is faster than that at proximal position. This shows that addition of the electron withdrawing group favours the pyridine addition at the axial position thus promoting the yield of epoxide. The addition of pyridine decreased exo/endo ratio. This observation is in contrast to that observed with Mn(III) complexes, indicating that in oxo iron porphyrin, axial ligation of pyridine leads to some geometrical changes. The most conspicuous is the M-O bond length and shifting of metal atom to the other side of the porphyrin plane. This can explain the high yields of epoxide. It also suggests that Fe(III) porphyrins are more sensitive to electronic effects whereas Mn(III) porphyrins are more sensitive to steric effect.

Addition of imidazole, increased the yield of epoxide in Fe(OBP)Cl (Table 4) manyfold, but decreased exo/endo ratio. The increase can be attributed to direct co-ordination of imidazole to active metal centre (proximal effect) as well as its action as a base (distal effect). The decrease in exo/endo ratio shows that coordination of imidazole to metal-oxo species makes

Table 4. Effect of additives on the epoxidation of norbornene using Mn(III) porphyrin complexes as catalysts

S.No	Additive	Product, mmol								
		Mn(OBP)Cl			Mn(OCOBP)Cl			Mn(2,6-ClTPP)Cl		
		Endo	Exo	Exo/endo ratio	Endo	Exo	Exo/endo ratio	Endo	Exo	Exo/endo ratio
1	No addition	0.106	0.694	1:6.6	0.120	0.942	1:7.85	0.019	0.952	1:50.11
2	pyridine	0.036	0.896	1:24.9	0.032	0.946	1:29.5	0.034	0.93	1:27.35
3	Imidazole	Nil	0.231	1:0.23	0.012	0.317	1:26.4	0.033	0.678	1:20.55
4	Triton x-100	Nil	0.364	1:0.36	0.063	0.866	1:13.75	0.059	0.897	1:15.20
5	CTABr	Nil	0.283	1:0.28	Nil	0.707	1:0.70	Nil	0.897	1:0.89
6	SLS	0.119	0.694	1:5.83	0.113	0.585	1:5.18	0.095	0.580	1:6.11

Table 5. Effect of additives on epoxidation of norbornene using Fe(OBP)Cl as catalysts

S. No	Additive	Endo epoxide, mmol	Exo epoxide, Mmol
1	No addition	0.140	0.316
2	pyridine	0.428	0.480
3	Imidazole	0.828	0.458
4	Triton x-100	0.147	0.207
5	CTABr	Nil	0.039
6	SLS	0.193	0.270

it stable, enough to undergo rotation which results in formation of endo epoxide. In case of Mn(III) complexes, a general decrease in yield of epoxide was observed with all catalysts (Table 4). Although imidazole is known to increase efficiency of Metal porphyrin catalysts towards olefin oxidation [27, 28]. The possible rationale for this decrease can be oxidative destruction of imidazole in given reaction conditions resulting in unproductive side engagement of the oxidant.

Addition of methanol increased the yield of norbornene epoxide when Mn(OBP)Cl and Mn(2,6-ClTPP)Cl catalyst were used. Decrease in exo/endo ratio was observed in case of Mn(OCOBP)Cl catalyzed reaction. This shows that addition of methanol increased the polarity of the medium leading to charge separation with the formation of carbocation type intermediate which rotates to give endo epoxide. The exo/endo ratio decresed in Fe(III) catalyzed reactions as well, but over all yield remained unaltered.

In order to distinguish between carbon radical and carbocation intermediate the effect of other surfactants (Table 4) on the epoxidation of norbornene was studied. Addition of sodiumlaurylsulphate, an anionic surfactant, promoted the endo epoxide formation. This suggests that being an anionic surfactant SLS stabilize the carbocation intermediate giving it enough time to undergo C–C bond rotation, resulting in the increase of yield of endo epoxide. The addition of non-ionic surfactant triton x-100 decreased the yield of epoxide showing that micelles retard epoxidation. The addition of cetyl trimethyl-ammonium bromide (CTABr), a cationic surfactant substantially reduced the endo and exo epoxide yield. This shows that positively charged micelles of CTABr retard epoxidation in general but endo epoxide in particular. These results suggest the presence of a carbocation intermediate in this system. Fe(III) porphyrin complexes too present a similar behavior.

The results of individual and competitive epoxidation (Table 6) of cycloolefins follow the order norbornene > cyclo-heptene > cyclohexene, suggesting that coordination of olefin to metal center is not the rate determining step because coordination constant of norbornene is less than cyclohexene, yield of epoxide should be less in norbornene. This observation too discards the oxometallacycle intermediate formation. This shows that only relief in bond angle strain play an important role in anticipating the relative rate for cyclic olefins. All these studies suggest the involvement of carbocation type intermediate in the reaction.

Mechanism

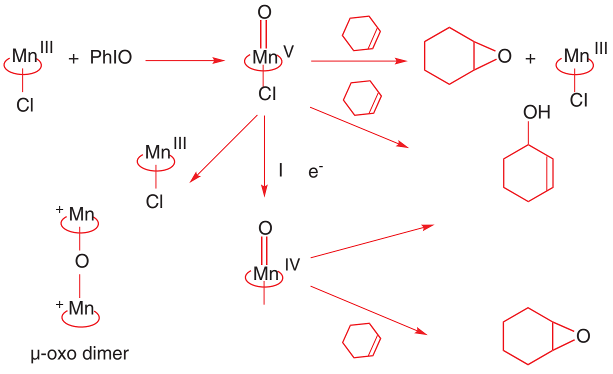
On the basis of aforementioned studies a general mechanism shown in (Scheme 4) can be proposed. It is known that Mn(TPP) X/PhIO [23] system gives oxo-manganese [V] species which, in turn aids formation of epoxide and allylic oxidation products. The epoxidation of norbornene gave exo-and endo epoxy norbornene showing that in norbornene the two O–C bonds are formed simultaneously but at different rates. Under the experimental conditions. the internediate so formed finds sufficient time to undergo rotation which explains the formation of observed products in present system.

EXPERIMENTAL

IodosyIbenzene was synthesized by Iiterature [29] procedure and stored at -20 °C. The olefins, (cyclohexene, cycloheptene, norbornene) and dichoromethane were purified before use [30]. Standard samples of the various epoxides were prepared by literature procedures [31]. Sodium lauryl sulphate [SLS], cetyl trimethyl ammonium bromide [CTABr], Triton x-100 imidazole and pyridine used were of high purity. The epoxidation

Table 6. Competitive epoxidation of cycloolefins

S. No	Catalyst	Cyclohexene	Cycloheptene	Norbornene
1	Mn(OBP)Cl	1.0	4.63	3.73
2	Mn(OCOBP)Cl	1.0	2.11	2.39
3	Mn(2,6-ClTPP)Cl	1.0	1.45	1.96
4	Fe(OBP)Cl	1.0	5.39	7.20
5	Fe(OCOBP)Cl	1.0	1.76	1.90
6	Fe(2,6-ClTPP)Cl	1.0	1.28	1.96



Scheme 4. Proposed mechanism

reactions were monitored using a NUCON-AMIL-5700 series gas chromatograph fitted with a Shimadzu CR-3A data processor. The catalyst complexes *i.e.* Fe(III) and Mn(III) Porphyrin complexes having substituents at O-phenyl and β-Pyrrole positions of tetraphenyl ring *viz* 2,6-dichlorotetraphenyl porphyrin [M.(2,6-Cl, TPP) Cl], octachloro octabromo porphyrin [M(OCOBP)Cl] and octa-bromo-tetra phenyl porphrin [M-(OBP)Cl] (where M = Fe/Mn) were synthesized by modification of literature procedure [32].

Epoxidation of olefins

It was carried out by taking 5 mmol of olefin [cyclohexene, norbornene] 0.002 g catalyst, 0.5 mmol iodosylbenzene in 10 mL dichloromethane. The contents were stirred for one hour under nitrogen at room temperature.

Effect of additives on the epoxidation of olefins

Effect of various compounds viz., pyridine, imidazole cetyltrimethylammonium bromide (CTABr), sodium lauryl sulphate (SLS) triton x-100 and methanol on the epoxidation of cycloolefins *viz*., cyclohexene and norbornene was studied by adding 100 mg of the compound to the epoxidation reaction.

Competitive epoxidation of cyclic olefins

The competitive epoxidation of cyclohexene, cycloheptene and norbornene was studied by taking 5 mmol each of any two olefins with 0.004 gm catalyst and 1.0 mmol lodosyl benzene in 10 mL dichloromethane and stirred for 1 h at room temperature. Effect of solvent on reaction, was studied by replacing dichloromethane with acetonitrile in a typical epoxidation reaction, using, cydohexene as substrate keeping rest of experimental conditions same.

It can be concluded that these substituted metalloporphyrin complexes are very efficient catalysts towards epoxidation using Ph IO as oxidant. The presence of electronegative atoms at β-pyrrole and O-phenyl position has a remarkable effect on their catalytic activity as well as selectivity in product formation.

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