# Epoxidation of Alkenes Catalysed by $Mn^{III}$ (Schiff base) Complexes

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The epoxidation of cyclohexene using various $Mn^{III}$ (Schiff base) NCS complexes as catalyst and PhIO as oxidant give cyclohexeneoxide, cyclohexenol and cyclohexenone as the products. The effect of catalyst concentration shows that, on increasing the concentration of catalyst the yield of the epoxide decreases. The relative rate of reaction of cyclic alkenes follows the order; norbornene > cyclo-octene > cycloheptene > cyclohexene > cyclopentene. This shows that rigid co-ordination of alkene to oxomanganese(v) catalyst does not take place in the rate-determining step. The effect of various additives *viz.*, pyridine, imidazole, $NaHCO_3$, $NaH_2PO_4$, sodium lauryl sulphate, cetyl trimethyl ammonium bromide, and Triton X-100 shows that axial ligation due to pyridine, imidazole *etc.* increases the yield of epoxide. The surfactants Triton X-100 and sodium lauryl sulphate show that micellar catalysis plays a positive role.

The ability of cytochrome *P*-450 to activate oxygen with resultant oxygen transfer to otherwise relatively unreactive organic substrates has attracted much attention.[1-3] Although the detailed mechanism of the oxygen transfer is not yet fully understood, the generation of high valent oxidizing species in model system by the use of a wide variety of 'oxene' transfer agents including iodosobenzene, peroxy acid, hydrogen peroxide, and activated *N*-oxides is established.[4-12] From various model systems the manganese(III) complex catalysed systems[13-26] have been studied in detail. Recently Groves *et al.*[8] has shown that using *m*-chloroperbenzoic acid the manganese(III) porphyrin produces two oxomanganese(IV) and oxomanganese(V) species responsible for the oxidation reaction. The epoxidation of alkene using Mn(TPP)OAC/PhIO system[14] and $Mn^{III}(SALEN)PF_6^-/C_6H_5IO$[27] has been reported in detail but no significant conclusion regarding the mechanism could be drawn. In the present paper we study the epoxidation of alkenes using various $Mn^{III}$ (Schiff base) NCS complexes as catalyst and PhIO as oxidant. The results are interpreted in the light of effects obtained using various additives and a suitable mechanism proposed.

## Experimental

All the starting alkenes *viz.* cyclohexene, cyclopentene, cycloheptene, cyclo-octene, and norbornene were checked by gas chromatography to ensure that no oxidation product was present in the substrate. If necessary the alkenes were purified by the literature method.[28] Pyridine, imidazole, $NaH_2PO_4$, $NaHCO_3$, sodium lauryl sulphate, cetyltrimethylammonium bromide, and Triton X-100 were of reagent grade quality. Acetonitrile used as solvent was purified.[28] Iodosylbenzene was synthesized as reported in the literature.[29] The manganese(III) complexes using ligands bis(salicylaldehyde)ethylenediamine (SALEN), bis(anthranilic acid)acetylacetone (ANAC), bis(acetoacetanilide)ethylenediamine (AACEN), bis(anthranilic acid)acetoacetanilide(ANAAN), bis(acetylacetone)diaminopropane (ACDAP), bis(salicylaldehyde)propylene diamine (SALPA), bis(acetylacetone)ethylenediamine (ACEN) and $Mn(acac)_2NCS$[30] were synthesised and extracted into acetonitrile.[31] Analytical gas chromatography was carried out using a NUCON-AMIL-5700 series gas chromatograph fitted with a Shimadzu CR-3A data processor. XE-60 and carbowax-20M GC Columns were used.

*Epoxidation of Cyclohexene.*—Epoxidation of cyclohexene using various manganese catalysts was carried out in a triple-necked round-bottomed flask under nitrogen by mixing cyclohexene (5.0 mmol), catalyst (0.1 mmol) and iodosylbenzene (0.5 mmol) in acetonitrile (10 $cm^3$). The contents were stirred at room temperature (25 °C) using a teflon coated magnetic needle for 1 h. After the reaction was complete the contents were filtered and the product was analysed by GC using an XE-60 column at 120 °C.

*Competitive Epoxidation of Cyclic Alkenes.*—The competitive epoxidation of cyclic alkenes *viz.*, cyclopentene, cyclohexene, cycloheptene, cyclo-octene, and norbornene was studied by taking cyclohexene (5.0 mmol), the other cyclic alkene (5.0 mmol), manganese catalyst (0.2 mmol), and iodosylbenzene (1 mmol) in acetonitrile (10 $cm^3$) in a triple-necked round-bottomed flask under nitrogen. The contents were stirred at room temperature for 1 h. After this the contents were filtered and the product analysed by GC using an XE-60 and carbowax-20M at 120 and 90 °C respectively.

Effect of imidazole, pyridine, sodium dihydrogen phosphate, sodium bicarbonate, sodium lauryl sulphate, cetyltrimethylammonium bromide, and Triton X-100:

The effect of the previously mentioned additives on the epoxidation of cyclohexene was studied by taking cyclohexene (5 mmol), catalyst (0.1 mmol), additive (100 mg), iodosylbenzene (0.5 mmol) in acetonitrile (10 $cm^3$) in a triple-necked round-bottomed flask. The contents were stirred at room temperature under nitrogen for 1 h. The contents were filtered and analysed by GC using an XE-60 column at 120 °C.

*The effect of catalyst concentration.*—The effect of catalyst concentration on cyclohexene epoxidation was studied by taking Mn(SALEN) NCS catalyst of concentrations 0.01, 0.1, 0.2 mmol, cyclohexene (5 mmol) and iodosylbenzene (0.5 mmol) in acetonitrile (10 $cm^3$) under nitrogen. The contents were stirred for 1 h and analysed.

## Results and Discussion

Epoxidation of cyclohexene using various $Mn^{III}$ Schiff base complexes with PhIO as oxidant has been studied (Table 1). The results indicate that cyclohexene was oxidized to cyclohexene oxide, cyclohexenol, and cyclohexenone. The products cyclohexenol and cyclohexenone are produced as a

**Table 1.** Epoxidation of cyclohexene using $Mn^{III}$ Schiff base complexes /PhIO system. Time of reaction 1 h.

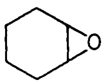
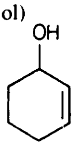
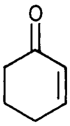
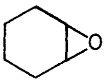
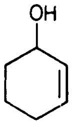
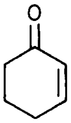
| | | Product (mmol) | | |
|---|---|---|---|---|
| S. no. | Catalyst |  (*a*) |  (*b*) |  (*c*) |
| 1 | Mn(SALEN)NCS | 0.039 | 0.028 | 0.074 |
| 2 | Mn(ANAC)NCS | 0.076 | 0.050 | 0.059 |
| 3 | Mn(AACEN)NCS | 0.033 | 0.165 | 0.110 |
| 4 | Mn(ANAAN)NCS | 0.024 | 0.156 | 0.115 |
| 5 | Mn(ACDAP)NCS | 0.018 | 0.133 | 0.171 |
| 6 | Mn(SALPA)NCS | 0.020 | 0 | 0 |
| 7 | Mn(ACEN)NCS | 0.002 | 0 | 0 |
| 8 | $Mn(acac)_2NCS$ | 0.027 | 0 | 0 |

**Table 2.** Effect of catalyst concentration on the epoxidation of cyclohexene using Mn(SALEN)NCS/PhIO system. Time of reaction 1 h.

| | | Product (mmol) | | |
|---|---|---|---|---|
| S. no. | Catalyst concentration /mmol $dm^{-3}$ |  (*a*) |  (*b*) |  (*c*) |
| 1 | 0.01 | 0.107 | 0.040 | 0.052 |
| 2 | 0.1 | 0.039 | 0.028 | 0.074 |
| 3 | 0.2 | 0.025 | 0.020 | 0 |
| 4 | 0.5 | 0.010 | Trace | 0 |

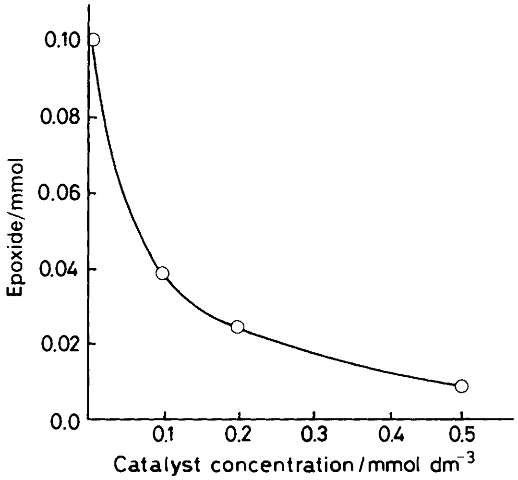


**Figure.** Effect of catalyst concentration on the epoxidation of cyclohexene using the Mn(SALEN)NCS/PhIO system.

**Table 3.** Epoxidation of cycloalkenes using Mn(SALEN)NCS/PhIO system.

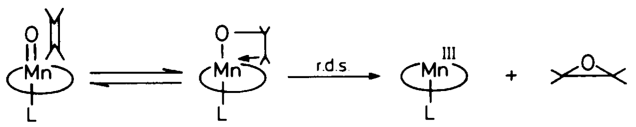
| S. no. | Substrate | Relative ratio of epoxide |
|---|---|---|
| 1 | Cyclopentene | 0.54 |
| 2 | Cyclohexene | 1.00 |
| 3 | Cycloheptene | 1.24 |
| 4 | Cyclo-octene | 1.96 |
| 5 | Norbornene | 3.00 |

result of allylic oxidation.[32] It was observed that when the reaction was carried out in air the yield of allylic oxidation product increased while the yield of epoxide decreased. A similar effect of air has been observed by Groves *et al.*[5] In the case of Mn(ANAC)NCS, the yield of cyclohexene oxide formed was more than that obtained from the Mn(SALEN)NCS catalysed reaction, but the yield of cyclohexenol and cyclohexenone was also higher. Cyclohexene with Mn(AACEN)NCS, Mn(ANAAN)NCS, and Mn(ACDAP)NCS was found to form cyclohexenone and cyclohexenol in greater yield than cyclohexene epoxide. When Mn(SALPA)NCS, Mn(ACEN)NCS, and $Mn(acac)_2NCS$ were used a high selectivity of epoxide was obtained though the yield was less than that obtained with previously studied catalysts. In the catalyst system under investigation the stability of the catalyst is also an important factor as demetalation of the catalyst reduces the yield of the epoxide. The lower catalytic activity using Mn(ACEN)NCS, Mn(SALPA)NCS or the bidentate ligand-containing catalyst, $Mn(acac)_2NCS$, shows that the stability of these catalysts in oxidation systems is much lower.

The effect of concentration of catalyst Mn(SALEN)NCS in the epoxidation of cyclohexene using PhIO was also studied (Table 2, Figure). It was observed that at lower concentration a better yield of epoxide was obtained but as the concentration of the catalyst increases the yield of epoxide decreases. But one important observation is that at lower concentration allylic oxidation products cyclohexenol and cyclohexenone were observed, at 0.1 mmol $dm^{-3}$ concentration cyclohexenol and cyclohexenone were also observed but in lesser amount than that observed with 0.01 mmol $dm^{-3}$ concentration. At 0.2 mmol $dm^{-3}$ only cyclohexenol was observed; at higher concentration (0.5 mmol $dm^{-3}$) only cyclohexene oxide was obtained but the yield was very low. It can be safely inferred from the above experiment that 0.1 mmol $dm^{-3}$ concentration, is the most appropriate.

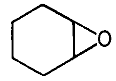
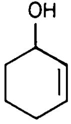
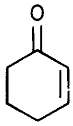
The relative rate of the epoxidation of cyclic alkenes *viz.*, cyclopentene, cyclohexene, cycloheptene, cyclo-octane, and norbornene was studied using Mn(SALEN)NCS as catalyst (Table 3). The order of reactivity was norbornene > cyclo-octene > cycloheptene > cyclohexene > cyclopentene. The higher rate of epoxidation observed for norbornene, cyclo-octene and cycloheptene relative to cyclohexene shows that the alkene is not rigidly co-ordinated to the metal centre in the rate-determining step. Had the alkene been rigidly co-ordinated to the metal centre the rate for alkenes having carbon atom number higher than cyclohexene would have been lower, contrary to the observation. $RhCl(Ph_3P)_3$ shows[33] that the rate of hydrogenation decreases with increasing alkene ring size $C_5 > C_6 > C_7 > C_8 > C_9$, as co-ordination of alkene to metal centre takes place in the transition state. A higher rate of epoxidation for cyclo-octene, norbornene, and cycloheptene has been observed with O = Mo(TPP)OMe/cumylhydroperoxide[34] and $MoO_2$(SALEN)/TBHP[35] system catalysed epoxidation. It shows that conformation, bond angle strain, and torsional strain play an important role in the anticipation of the relative rate for cyclic alkenes. Collman *et al.*[36] have found that an oxo-alkene complex is reversibly formed and the alkenes which are electron rich interact more efficiently with the oxo complex. The results of our study with various alkenes suggest that it involves a Lewis base–Lewis acid metal–alkene bond and not a rigid co-ordination as proposed by Collman *et al.*[36] It is consistent with our finding that the reactivity of alkenes increases with their nucleophilic nature and with the strong inhibition by pyridine and dimethylformamide which compete with the alkene for the vacant site on the metal, Scheme 1.

The effect of addition of pyridine, imidazole, $NaHCO_3$, $NaH_2PO_4$, sodium lauryl sulphate, cetyltrimethyl ammonium

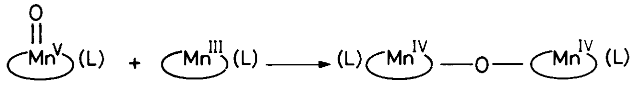


Scheme 1.

**Table 4.** Effect of various compounds on the epoxidation of cyclohexene using Mn(SALEN)NCS/PhIO system. Time of reaction 1 h.

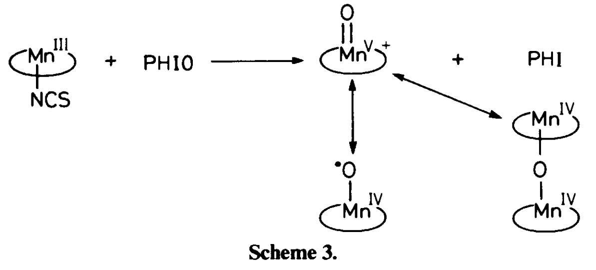
| | | Product (mmol) | | |
|---|---|---|---|---|
| | |  |  |  |
| S. no. | Reagent | (*a*) | (*b*) | (*c*) |
| 1 | No addition | 0.039 | 0.028 | 0.074 |
| 2 | Imidazole | 0.166 | 0 | 0 |
| 3 | Pyridine | 0.542 | 0 | 0 |
| 4 | $NaHCO_3$ | 0.125 | 0 | 0 |
| 5 | $NaH_2PO_4$ | 0.228 | 0.062 | 0 |
| 6 | Sodium lauryl sulphate | 0.082 | 0 | 0 |
| 7 | Triton X-100 | 0.064 | 0 | 0 |
| 8 | Cetyltrimethyl-ammonium bromide | 0 | 0 | 0 |

bromide, and Triton X-100 on the epoxidation of cyclohexene has been studied (Table 4). The addition of imidazole accelerates the reaction rate and a higher yield of epoxide is obtained. The higher yield of epoxide so obtained is in conformity with that observed for the Mn(TPP)OAC/NaOCl system.[37] The higher yield of epoxide obtained in the presence of pyridine can be explained on the basis that pyridine aids the stabilization of $Mn^V$ species[37] and inhibits the conversion of $Mn^V$ to $Mn^{IV}$, Scheme 2.



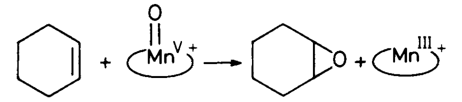
Scheme 2.

The μ-oxo dimer complex so formed also has low catalytic activity. The addition of pyridine prevents the μ-oxo dimer formation.[38] The absence of allylic oxidation products in the presence of pyridine also supports the fact that $O = Mn^V$ species is stabilized. Meunier *et al.*[24] have found that pyridine addition increases the selectivity of cyclohexene oxide using Mn(TPP)OAC/NaOCl system from 37–85%. Recently Groves *et al.*[8] have reported that in the epoxidation of alkenes by oxomanganese species generated by peracids, two complexes are able to perform oxygen transfer; one oxomanganese(IV) complex with a low stereoselectivity and an oxomanganese(V) complex with high stereoselectivity. The conversion of the latter to the $O = Mn^{IV}$ complex is prevented by the presence of pyridine. A possible mechanism for our system can be written as in Scheme 3.

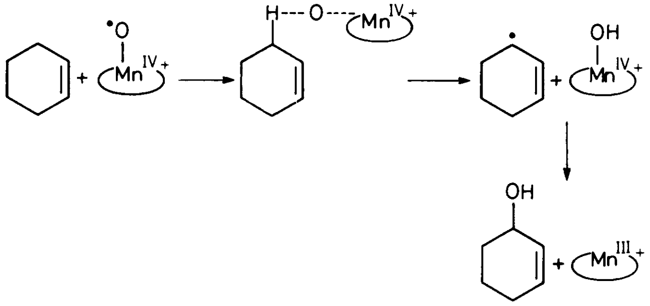


Scheme 3.

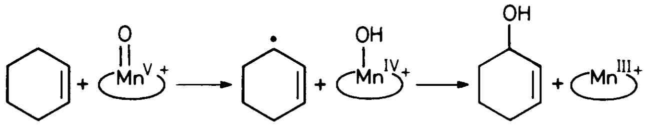
From Scheme 3 Scheme 4 can be established. Of Schemes 5 and 6 it appears that Scheme 5 is more probable, since the addition of pyridine stabilizes the $Mn^V$ species and prevents its conversion to $Mn^{IV}$, if oxomanganese(V) is considered responsible for the formation of the allylic oxidation product. The addition of pyridine must not alter the yield of allylic oxidation product. The conversion of cyclohexane to cyclohexanol was completely inhibited when pyridine was added. The other axial ligand (imidazole) addition also eliminates the yield of allylic oxidation products. Meunier and co-workers[39] have shown that high valent manganese porphyrin Mn(TPP)OCl is a monomer possessing a cation radical and this species is reported as being able to epoxidize styrene. This finding also supports our view that this species is formed and must be responsible for the allylic oxidation. Kochi and co-workers[27] have also observed that the attack of oxomanganese species on an alkenic centre becomes less selective, so much so that there is little discrimination between the electron-rich styrene, strained norbornene, and a normal α-alkene. Indeed only a rate factor of ten separates *p*-methyl styrene from oct-1-ene. The polar effect is shown by the trend in the reactivities of *para*-substituted styrenes which follow a Hammett correlation with a ρ value of only −0.3. All these observations including alkene oxidation point to a radical-like character of the oxomanganese functionality. Thus, we may say that Schemes 4 and 5 are probable for $Mn^{III}$ (SALEN)NCS catalysed epoxidation.



Scheme 4.



Scheme 5.



Scheme 6.

The addition of $NaHCO_3$ and $NaH_2PO_4$ increased the yield of the epoxide. It shows that the acidic or basic nature of the compound does not affect the yield of the epoxide as there is an increase in the yield of epoxide in both cases. It is more likely that $HCO_3^-$ and $H_2PO_4^-$ ions help in stabilizing the oxomanganese(V) cation. The cationic nature of the oxomanganese(V) species was established by its reaction with surfactant. With anionic surfactant sodium lauryl sulphate the yield of epoxide increased while the formation of epoxide was completely suppressed when cationic surfactant cetyltrimethyl ammonium bromide was used. The non-ionic surfactant Triton X-100 also promoted the yield of the epoxide but this increase was much less compared to that observed with sodium lauryl sulphate. The results observed with surfactants can be explained on the basis that in the transition state the positive charge of oxomanganese(V) catalyst is dispersed and interacts strongly with the anionic head groups of sodium lauryl sulphate thereby stabilizing the oxomanganese(V) species. While the decrease in rate using cetyltrimethyl ammonium bromide may be due to the destabilization of oxomanganese(V) species by electrostatic charge repulsion. The increased rate of epoxidation and selectivity of epoxide using Triton X-100 shows that micellar catalysis is in operation. This reaction is the first report of micellar catalysis using metal complex catalysed epoxidation of alkenes and work is in progress to study in detail the mechanism of micellar catalysis.

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