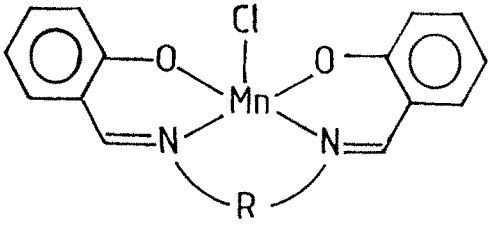
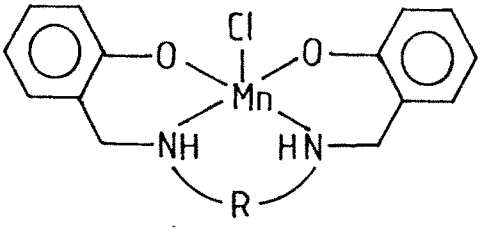
CHAPTER 2
Manganese(III) mannich-base complexes

There has been intense research in the study of metal complexes with ligands derived from the condensation of salicylaldehyde with diamines [1-4]. The use of monomeric metal complexes of 'salen' type of schiff-base ligands as catalysts for the epoxidation and other oxidations of alkenes and alkanes has attracted considerable attention. Interest in such systems is derived from the fact that they are planar, like porphyrins, simpler to be synthesized and structurally modified, and hence providing suitable models for cyt P-450. Several studies have been carried out to observe the effect of substitutions in the schiff-base ligand on epoxidation activity of its metal complexes [5-10]. Correlation between ligand nature, electrochemical behaviour and epoxidation activity for such systems has been reported, as detailed in the previous chapter.

With an aim to study further the effect of ligand nature on catalytic activity, and to see the effect of reduction of the >C=N- link in the schiff-base complex on the catalytic activity, we prepared and characterized the Mannich-base complexes **3** and **4**. Their catalytic activity towards epoxidation of alkenes, using iodosylbenzene as oxidant, has been studied and compared with the corresponding Schiff-base complexes **1** and **2**.





1. R = $(CH_2)_2$
2. R = $(CH_2)_3$

3. R = $(CH_2)_2$
4. R = $(CH_2)_3$

Experimental

Materials

Synthesis : Manganous chloride tetrahydrate ($MnCl_2.4H_2O$), 1,2-diaminoethane, 1,3-diaminopropane and salicylaldehyde were of AR grade and were used as received. The solvents were purified by standard literature methods [11]

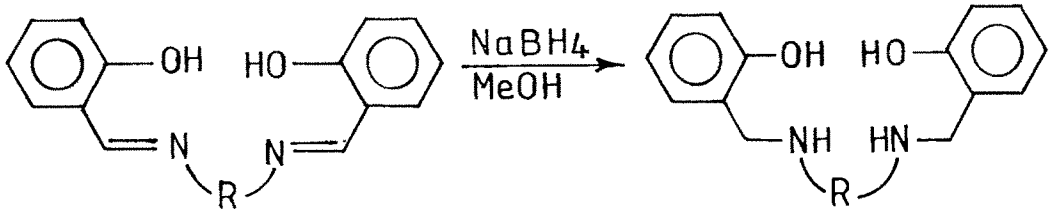
Oxidation : The substrates for epoxidation studies - norbornene, cyclohexene, styrene, *cis*-cyclooctene and the oxidation products - cyclohexene oxide, cyclohex-2-en-1-ol, cyclohex-2-en-1-one and styrene oxide were obtained from Aldrich Company and were used as received. The purity of solvents used and the internal standards were ascertained by Gas Chromatography. High purity nitrogen was used for blanketing the reactions. Norbornene oxide, cyclooctene oxide and iodosylbenzene were synthesized by literature methods [12,13].

Physical Measurements :

Elemental analyses were carried out on a Carlo-Erba 1106 C, H, N elemental analyzer. UV-Vis spectra were recorded on a Shimadzu UV-160A spectrophotometer. IR spectra were recorded on Shimadzu IR-408 spectrophotometer. Measurements were made on samples as KBr pellets. Thermal analyses were performed on a Shimadzu DT-30 thermal analyzer. Solution electrical conductivities were measured at room temperature using Toshniwal conductivity bridge. Magnetic susceptibility measurements were carried out at room temperature by Guoy method, using $Hg[Co(CNS)_4]$ as a standard. Gas chromatographic analyses were performed on a Shimadzu GC-7A equipped with Shimadzu C-R1B or C-R4A chromatopac, using FID, carbowax 20M 15% on chromosorb W column (3M) and N_2 as carrier gas

Synthesis of the complexes

The Schiff-base complexes **1** and **2** were prepared following the literature procedure [14]. The Mannich-base ligands were prepared by reduction of the corresponding Schiff-base ligands with $NaBH_4$ in MeOH and recrystalized from EtOH [15].



The complexes **3** and **4** were prepared as follows To a stirred, warm solution of $MnCl_2.4H_2O$ (0.594 gm, 3 x 10^{-3}M) in EtOH (15 ml) was added dropwise a solution of the ligand ($3x10^{-3}$M) in EtOH (10 ml) The colour of the solution immediately darkened and a dark-green precipitate was formed. No attempt was made to exclude air from the reaction mixture. The mixture was stirred for 30 min in the presence of air and filtered under suction The precipitates were washed thoroughly with EtOH and dried under vacuum at 78 °C for 2h

Procedure for oxidation studies

Epoxidation of alkenes was carried out using the complexes **1-4** as catalysts and PhIO as oxidant, as detailed below. The alkenes used were norbornene, *cis*-cyclooctene,

cyclohexene and styrene All the oxidation studies were carried out under N_2 atmosphere in a Schlenk tube. To a solution of catalyst (0.01 mmol) in CH_3CN (3 ml) was added a solution of alkene (2.5 mmol) in CH_3CN (2 ml) and the mixture deaerated by bubbling N_2 for 10 min PhIO (0.5 mmol) was added and the mixture stirred under N_2 at 25 °C for 6h. A suitable internal standard was added to the reaction mixture and the products were analyzed by gas chromatography. The amount of internal standard added was close to the amount of the epoxide formed.

An advantage in the internal standard method is that it eliminates the error in volume of the reaction mixture injected in the gas chromatograph. Anisole or chlorobenzene was used as internal standard due to following reasons

1 They are inert under the reaction conditions They do not react with the components of the system.

2 They elute from the GC column, adequately separated from all the reaction components, under the analysis conditions.

The response factors for the various epoxides with reference to the internal standard used were determined. This is necessary since the peak areas of two different compounds having the same concentration, will be different in a gas chromatogram. The response factor was determined as follows

Three synthetic mixtures having same quantity of the internal standard and varying amount of the epoxide (which is close to the weight of internal standard taken) were prepared

and injected in gas chromatograph under the standard analysis conditions set for the epoxide From the known weight and peak areas of the internal standard and the epoxide, the corresponding response factor was calculated using the equation

$$\text{Response factor} = \frac{\text{weight of the epoxide x area of internal standard}}{\text{area of epoxide x weight of internal standard}}$$

With known response factor for an epoxide, amount of that epoxide formed in a reaction mixture after a catalytic run can be calculated using the same equation, since weight of internal standard added is known and the peak areas are obtained from chromatogram Blank runs established that the alkene used did not undergo epoxidation in the absence of either a catalyst or an oxidant

The temperature programming used for analysis of reaction mixture by gas chromatograph for different alkenes is given below

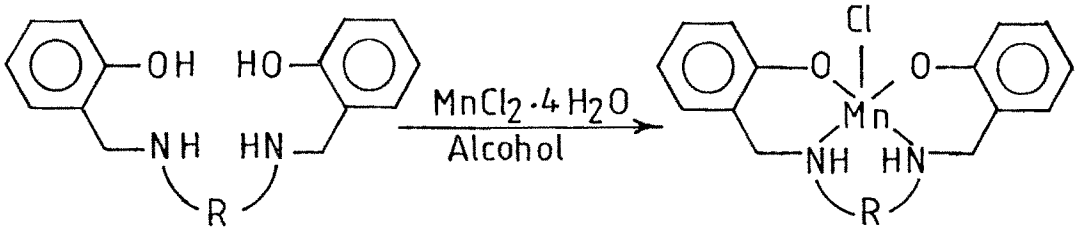
GC Column Temperature Programme

Substrate	Initial Time (min)	Initial Temperature °C	Heating Rate °C / min	Final Temperature °C	Final Time (min)
Norbornene	0	70	2	150	10
Cyclohexene	0	70	2	150	10
cis-cyclooctene	0	140	-	140	30
Styrene	0	100	2	150	10

GC injection port temperature of 240 °C and carrier gas (dinitrogen) flow rate of 30 ml/min were maintained. A 1μl aliquot was used for all the analyses.

Results and Discussion

The elemental analysis (Table 1) of the complexes correspond to the proposed formulae. The reaction leading to the formation of the complex can be shown as below.



Literature reports [16] show that **1** and **2** are nonconducting in CH_3CN, whereas, the conductance in MeOH shows 1:1 electrolyte behaviour. This shows that the complexes have chloride in the coordination sphere of the metal complex. We observed that **3** and **4** also exhibit similar behaviour In CH_3CN and DMF the molar conductances of **3** and **4** are in the range of 3-10 $ohm^{-1}cm^2mole^{-1}$ whereas in CH_3CN and H_2O mixture (1:1, v/v) the conductance is 66 $ohm^{-1}cm^2mole^{-1}$, corresponding to one chloride. This shows that the chloride in these complexes is coordinated to the metal centre.

Magnetic moment values (Table 1) for **3** and **4** are slightly less than the value for **1** [16] All the three values correspond to four unpaired spins, confirming that the oxidation state of manganese in these complexes is III.

Thermal analysis of **3** and **4** does not show any weight loss upto 200 °C indicating absence of solvent molecules in the complexes.

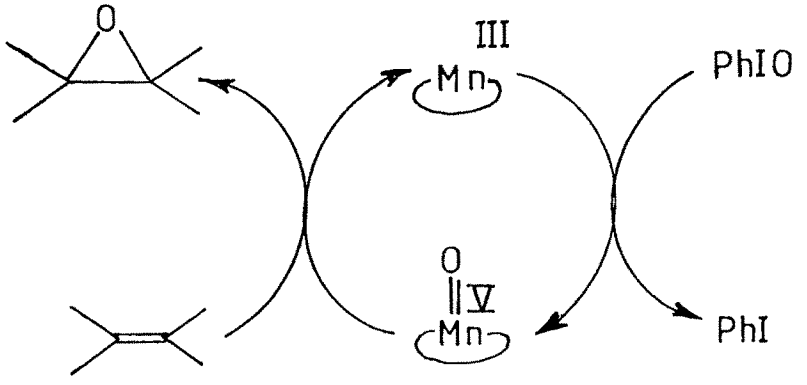
IR spectra of **3** and **4** show disappearance of characteristic $\nu_{C=N}$, present in the corresponding Schiff-base complexes, and a new band corresponding to ν_{N-H} is observed at 3045 cm^{-1} No band is observed in the ν_{O-H} range 3500-3400 cm^{-1} showing that the phenolic O-H deprotonates on coordination to metal.

Oxidation Studies

In control experiments, in which either PhIO or catalyst was excluded, no epoxide was obtained from *cis*-cyclooctene Thus, both, oxidant and catalyst are essential for the reaction.

Results of the oxidation studies of four alkenes, using the metal complexes **1-4** as catalysts, is shown in Table 2. Norbornene and *cis*-cyclooctene gave corresponding epoxides, selectively. Oxidation of cyclohexene gave cyclohexene oxide together with substantial amounts of cyclohex-2-en-1-one and cyclohex-2-en-1-ol arising from allylic oxidation. Styrene gave corresponding epoxide and phenylacetaldehyde. Styrene oxide is known to undergo thermal isomerization during GC analysis [7] Phenylacetaldehyde is also reported to have been formed in such reactions using manganese porphyrin catalysts [8]. Comparison of the catalytic activity of Schiff-base complexes **1** and **2** with that of corresponding Mannich-base complexes **3** and **4** indicates that the latter show relatively lower catalytic activity for alkene epoxidation

In the oxidations catalyzed by the Mn(salen)-PhIO system the proposed mechanism [9] involves formation of Mn^{V}=O as a reactive intermediate which transfers oxygen to the substrate (Scheme 1).



Scheme-I

The Mannich-base complexes also can be considered to follow the same pathway. This is evident from the product distribution pattern in case of **3** and **4** which is similar to that of **1** and **2**. This is also supported by the observation that addition of PhIO to the mixture of alkene and catalyst in CH_3CN is accompanied by a visible colour change from light brown to dark brown. After completion of the reaction, original colour of the solution is restored. This is attributed to the intermediate formation of the Mn^{V}=O species However, UV-Vis studies do not show a distinct band at about 530 nm, characteristic of Mn^{V}=O [6], although some increase in the intensity is observed in the range of 400 to 700 nm, on addition of PhIO to **3** in CH_3CN. New band due to Mn^{V}=O could not be seen, probably due to the tailing of the charge transfer band in this region.

In the oxidation of *cis*-cyclooctene using catalyst **3** (Table 2) it was observed that the reaction ceases after 6h. To this mixture, extra amount of PhIO (0.05 mmol) was added and

stirred for 2h. It was found that there was very little increase in the yield of epoxide indicating that most of the complex had become catalytically inactive

Termination

The activity of metal complex as an epoxidation catalyst depends on its ease to form M^{V}=O and ability of this M^{V}=O to transfer "O" to the substrate

Termination of the catalytic activity occurs by oxidative degradation of the metal chelate catalyst or formation of dimeric species of Mn^{IV}-O-Mn^{IV} type, which is inactive or a poor catalyst [19] IR spectrum of the recovered complex at the end of the catalytic run (Table 2, complex **3)** with *cis*-cyclooctene does not show all the characteristic ligand bands present in the spectrum of the original complex. A new band is observed at 1655 cm^{-1} corresponding to quinone $\nu_{C=O}$. This indicates oxidation of phenol to quinone and break-down of the Mn-O bond in the complex. Formation of species of M-O-M type could not be confirmed by IR spectrum as there are several bands in the region 800 cm,$^{-1}$ where $\nu_{Mn\text{-}O\text{-}Mn}$ is expected.

It is thus observed that the mannich base complexes **3** and **4** are less active as catalyst in epoxidation reactions, compared to the corresponding schiff-base complexes **1** and **2**, due to easy oxidative degradation of the complexes **3** and **4**

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Table 1 Analytical and magnetic data of the complexes

	Analysis Found (Calcd.) %				
Complex	Mn	C	H	N	$\mu_{eff}\mu_{\beta}$
1	15 23(15.40)	53 92(53.88)	4.17(3 96)	7.61(7.85)	4.85
2	15.59(14.82)	55.41(55.08)	4.46(4.35)	7.28(7.56)	-
3	14.94(15.23)	53 41(53.27)	5.34(5 03)	7 46(7.77)	4.68
4	14.68(14.66)	54.62(54 48)	5 40(5.38)	7.29(7.48)	4.74

Table 2 Oxidation of alkenes with PhIO catalyzed by the complexes **1-4**[a]

Catalyst	Norbornene		cis-Cyclooctene		Cyclohexene		Styrene	
	Epoxide (%)	TN[b]	Epoxide (%)	TN[b]	Epoxide (%)	TN[b]	Epoxide (%)	TN[b]
1	55	28	40	20	55(33)[c]	44	25(46)[d]	36
2	35	18	27	14	29(52)[c]	41	14(29)[d]	22
3	42	21	19	10	26(21)[c]	24	17(21)[d]	19
4	30	15	25	12	26(32)[c]	29	14(30)[d]	22

a Catalyst.PhIO:alkene mole ratio = 1 50:250, Catalyst = 0 01 mmol.
Yields are based on PhIO charged.
b Turnover Number, moles of oxidation product per mole of catalyst taken.
c Combined yield of cyclohex-2-en-1-one and cyclohex-2-en-1-ol.
d Phenylacetaldehyde.