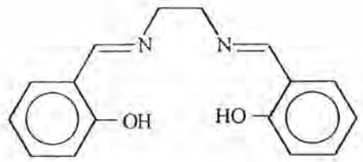
CHAPTER III
RESULTS AND DISCUSSION

Two well-known reactions were generally conducted for the epoxidation of alkenes. One is the epoxidation with peroxy acid and the other is epoxidation by utilizing metal complexes as catalysts.

This research was focused on the epoxidation of alkenes employing metal Schiff's base complexes as catalysts. These systems are composed of a metal ion or a metal complex as a catalyst, an organic ligand and an oxidant in a reaction medium. In this study, cyclohexene was mainly used as a substrate for reaction conditions optimization. Other cyclic alkenes, acyclic alkenes and natural products bearing a double bond were sometimes used for some specific purposes. Among metal Schiff's base complexes studied, Cr(III) Schiff's base complexes, were thorough examined as catalyst. The oxidants used were mainly a combination of oxygen and aldehydes. Acetonitrile was used as a major solvent in this reaction.

3.1 Characterization of Schiff's Base Ligands

Thirteen Schiff's base ligands were synthesized and confirmed their identities by comparison both physical properties and spectroscopic data including IR, ^{1}H- and ^{13}C-NMR with those reported in literature. The comparative results of physical properties and % yield of prepared Schiff's base ligands are presented in Table 3.1 and the spectroscopic data of these ligands are tabulated in Table 3.2.



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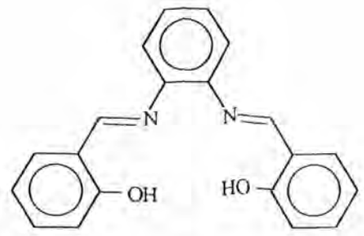

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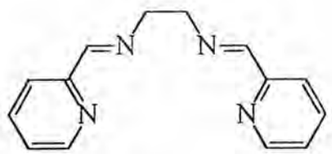

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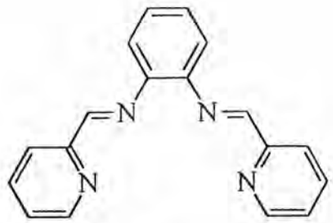

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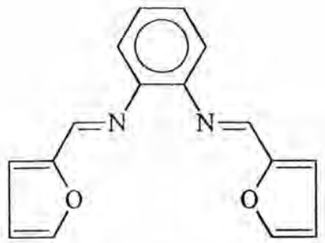

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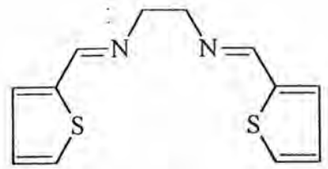

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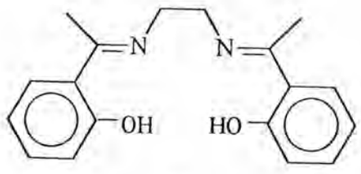

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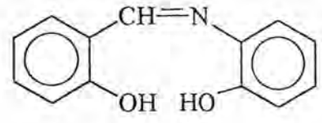

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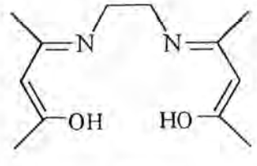

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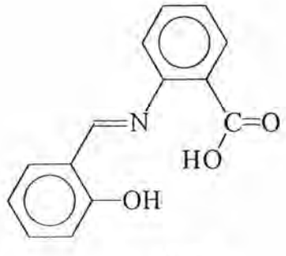

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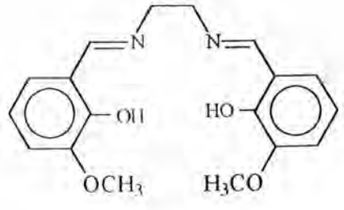

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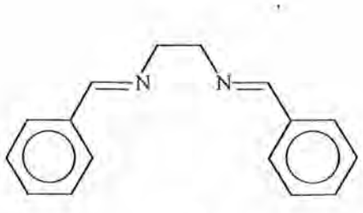

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Table 3.1 Physical properties of synthesized Schiff's base ligands

ligands	Physical properties		% yield	Reference
	Appearance	m. p.		
(1)	Bright yellow crystals	124-125	97	58
(2)	Orange needle crystals	164-165	82	59
(3)	Light yellow crystals	67-68	21	60
(4)	Yellow crystals	98-100	10	61
(5)	Pale yellow crystals	96-98	5	62
(6)	White crystals	90-91	57	63
(7)	Yellow needles crystals	148-149	62	64
(8)	Yellow needle crystals	200-201	81	-
(9)	Red needle crystals	189-190	79	65
(10)	Clear wthite crystals	111-113	57	66
(11)	Red crystals	203-205	51	65
(12)	Yellow needle crystals	163-165	97	67
(13)	Yellow crystals	48-50	84	68

Table 3.2 Spectroscopic data of synthesized Schiff's base ligands

Schiff's base ligand	IR (cm^{-1})	^{1}H NMR (ppm)	^{13}C NMR (ppm)
(1)	3500(w): O-Hν; 3050-3010(w): C-Hν aromatic; 2870-2950 (w): C-Hν alkyl group; 2000-1750(w):*ortho*-substitution; 1640(s): C=Nν; 1600-1450(S): C=Cν aromatic; 1280 (s): C-Nν; 1170 (s): C-Oν	3.84 (s, 4H, CH_2-N=), 6.83 (dt, J = 7.48, 1.2 Hz, 2H, aromatic), 6.93 (d, J = 8.24 Hz, 2H, aromatic), 7.18 (dd, J = 7.63, 1.83 Hz, 2H, aromatic), 7.26 (dt, J= 7.78, 1.53 Hz, 2H, aromatic), 8.29 (s, 2H, -CH=N-), 13.2 (s, 2H, -OH)	59.5 (CH_2-N=), 116.8, 118.5, 131.4, 132.2 (-CH= aromatic), 118.5 (-C= aromatic), 160.9 (=C-OH), 166.3 (-CH=N-)
(2)	3500(w): O-Hν; 3050(w): C-Hν aromatic; 2870-2950 (w): C-Hν alkyl group; 1630(s): C=Nν; 1485 -1560(s): C=Cν; 1275(s): C-Nν; 1190(s): C-Oν	6.85 (t, J = 7.32 Hz, 2H, aromatic), 7.02 (d, J = 13.2 Hz, 2H, aromatic), 7.20 (m, 4H, aromatic), 7.31 (m, 2H, aromatic), 7.35 (m, 2H, aromatic), 8.60 (s, 2H, -N=CH-), 13.0 (s, 2H, -OH)	117.5, 118.9, 119.6, 127.7, 132.3, 133.3 (-CH= aromatic), 119.1 (-C= aromatic), 142.4 (=C-N= aromatic), 161.3 (=C-OH aromatic), 163.6 (-CH=N-)

Table 3.2 (cont)

Schiff's base ligand	IR (cm^{-1})	^{1}H NMR (ppm)	^{13}C NMR (ppm)
(3)	3010-3050(w): C-Hν aromatic; 2870-2950 (w): C-Hν alkyl group; 1645(s): C=Nν aliphatic; 1595(s): C=Nν aromatic; 1420-1580(s): C=Cν aromatic; 1330(s): C-Nν	4.07 (s, 4H, CH_2-N=), 7.29 (ddd, J = 7.48, 4.88, 1.22 Hz, 2H, aromatic), 7.72 (dt, J = 7.63, 1.53 Hz, 2H, aromatic), 7.98 (d, J = 2.06 Hz, 2H, aromatic), 8.43 (s, 2H, -N=CH-), 8.62 (d, J = 4.58 Hz, 2H, aromatic)	66.2 (CH_2-N=), 121.3, 124.7, 136.4, 149.3 (-CH= aromatic), 154.3 (-C= aromatic), 163.3 (-CH=N-)
(4)	3006-3060(w): C-Hν aromatic; 2900-2950 (w): C-Hν alkyl group; 1630(s): C=Nν aliphatic; 1590(s): C=Nν aromatic; 1400-1560(s): C=Cν; 1170(s): C-Nν	6.29 (s, 2H, -N=CH-), 6.90 (d, J = 7.93 Hz, aromatic), 7.13 (dd, J= 7.33, 4.88 Hz, aromatic), 7.29 (m, 3H, aromatic), 7.37 (d, J = 7.94 Hz, aromatic), 7.48 (dt, J = 7.63, 1.83 Hz, aromatic), 7.83 (dt, J = 7.63, 1.83 Hz, aromatic) 7.86 (d, J = 7.93 Hz, =N-CH= aromatic), 8.48 (d, J = 8.24 Hz, -N=CH- aromatic), 8.57 (t, J = 5.94 Hz, 2H, aromatic)	51.1, 51.1 (-N=CH-), 110.8, 120.1, 120.9, 122.2, 122.9, 123.7, 123.8, 124.5, 136.8, 136.8 (-CH= aromatic), 148.6, 149.1 (=N-CH= aromatic), 142.6, 149.8, 150.3, 157.4 (=N-C= aromatic)

Table 3.2 (cont)

Schiff's base ligand	IR (cm^{-1})	^{1}H NMR (ppm)	^{13}C NMR (ppm)
(5)	3090-3140(w): C-Hν aromatic; 2950(w): C-Hν alkyl group; 1605(s): C=Nν aliphatic; 1430-1515(s): C=Cν; 1170(s): C-Nν; 1150(s): C-Oν	5.63 (s, 2H, -N-CH=), 6.23 (dd, J = 2.69, 0.62 Hz, 2H, aromatic), 6.27 (dd, J = 3.36, 1.83 Hz, aromatic), 6.60 (dd, J = 3.66, 1.83 Hz, aromatic), 7.22 (dd, J = 3.52, 0.61 Hz, -O=CH-), 7.29 (m, 2H aromatic), 7.32 (dd, J = 1.83, 0.92 Hz aromatic), 7.49 (m, aromatic), 7.64 (dd, J = 1.68, 0.61 Hz, aromatic), 7.78 (m, aromatic)	41.6, 41.6 (-N=CH-), 108.3, 109.9, 110.5, 112.0, 112.9, 119.8, 122.9, 123.2 (-CH= aromatic), 145.4, 149.6 (-O-C=), 135.5, 143.0 (=N-C= aromatic), 142.6, 143.9 (-O-CH=)
(6)	3050-3090(w): C-Hν aromatic; 2850-2920 (w): C-Hν alkyl group; 1640(s): C=Nν; 1460, 1430(S): C=Cν; 1220(s): C-Nν	3.90 (s, 4H, $-CH_2-N=$), 7.03 (t, J = 4.42 Hz, 2H, aromatic), 7.24 (d, J = 3.66 Hz, 2H, aromatic), 7.36 (d, J = 5.19 Hz, 2H, =CH-S-), 8.34 (s, 2H, -CH=N)	60.9 ($-CH_2-N=$), 120.7, 127.3, 130.5 (=CH- aromatic), 128.7 (=CH-S- aromatic), 142.3 (=C- aromatic), 156.0 (-CH=N- aromatic)

Table 3.2 (cont)

Schiff's base ligand	IR (cm^{-1})	^{1}H NMR (ppm)	^{13}C NMR (ppm)
(7)	3050-3090(w): C-Hν aromatic; 1630(w): C=Nν; 1450-1600(s): C=Cν aromatic; 1225(s): C-Nν	5.70 (s, 2H, -CH=N-), 6.86 (dd, J = 3.36, 1.22 Hz, aromatic), 6.94 (t, J = 4.43 Hz, aromatic), 7.13 (t, J = 4.27 Hz, aromatic), 7.23 (dd, J = 4.89, 1.23 Hz, aromatic), 7.29 (m, 2H, aromatic), 7.37 (dd, J = 7.32, 1.22 Hz, -S =CH-), 7.47 (dd, J = 3.82, 1.22 Hz, aromatic), 7.51 (dd, J = 5.03, 1.22 Hz, aromatic), 7.83 (dd, J = 6.87, 1.83 Hz, -S-CH=)	44.0, 138.8 (-N=CH-), 109.9, 123.3, 125.2, 128.9 (-CH= thiophene), 119.9, 123.0, 125.4, 127.2 (-CH= aromatic), 127.9, 128.0 (-S-CH=), 131.8, 135.8 (-S-C=), 143.0, 147.6 (=N-C=)
(8)	3500(w): O-Hν; 3080(w): C-Hν aromatic; 2870-2950 (w): C-Hν alkyl group; 1800-2000(w):*ortho*-substitution; 1620(s): C=Nν; 1450-1600(S): C=Cν aromatic; 1220(s): C-Nν; 1180(s): C-Oν phenol	2.37 (s, 6H, CH_3), 3.97 (s, 4H, $-CH_2$-N=), 6.78 (dt, J = 7.70, 1.28 Hz, 2H, aromatic), 6.91 (dd, J = 8.55, 1.28 Hz, 2H, aromatic), 7.27 (dt, J = 7.91, 1.28 Hz, 2H, aromatic), 7.52 (dd, J = 7.91, 1.50 Hz, 2H, aromatic), 15.80 (s, 2H, -OH)	14.7 ($-CH_3$), 50.2 ($-CH_2$-N=), 117.4, 118.5, 128.1, 132.4 (=CH- aromatic), 119.4 (=C- aromatic), 163.1 (=C-OH aromatic), 172.7 (-N=C-)

Table 3.2 (cont)

Schiff's base ligand	IR (cm^{-1})	^{1}H NMR (ppm)	^{13}C NMR (ppm)
(9)	3500(w): -OHν; 3050(w): C-Hν aromatic; 1640(s): C=Nν; 1460-1600(s): C=Cν aromatic; 1280(s): C-Nν; 1150(s): C-Oν	5.79 (s, -OH), 6.95-7.09 (m, 4H, aromatic), 7.15 (dd, J = 7.79, 1.53 Hz, aromatic), 7.22 (dt, J = 7.94, 1.53 Hz, aromatic), 7.40-7.45 (m, 2H, aromatic), 8.69 (s, -CH=N-),12.25 (s, -OH)	115.9, 117.3, 118.3, 119.6, 121.0, 128.8, 132.7, 133.7 (-CH= aromatic), 119.3 (-C= aromatic), 135.8, 149.9 (=C-OH), 160.6 (=C-N=), 164.0 (-CH=N-)
(10)	3500(w): O-Hν; 3100-3200(w): C-Hν aromatic; 2900- 3000 (w): C-Hν alkyl group; 1600-1650(br): C=Nν; 1280-1300(br): C-Nν; 1100(s): C-Oν	1.91 (s, 6H, $-CH_3$), 2.00 (s, 6H, $-CH_3$), 3.42 (d, J = 6.40 Hz, 4H, $-CH_2$-N=), 5.00 (s, 2H, aromatic), 10.90(s, 2H, -OH)	18.6, 28.8 ($-CH_3$), 43.5 ($-CH_2$-N=), 96.1 (=CH-aromatic), 162.7 (-C=N-), 195.5 (=C-OH aromatic)

Table 3.2 (cont)

Schiff's base ligand	IR (cm^{-1})	^{1}H NMR (ppm)	^{13}C NMR (ppm)
(11)	3500(w): -OHν; 3050 -3100(w): C-Hν aromatic; 1620(s): C=Nν; 1460-1580(s): C=Cν; 1240(s): C-Oν	1.50 (s, -OH), 6.66 (dd, J = 8.54, 0.91 Hz, aromatic), 6.67 (dd, J = 8.53, 1.22 Hz, aromatic), 6.99 (d, J = 8.85 Hz, aromatic), 7.03 (dd, J = 7.33, 0.92 Hz, aromatic), 7.30 (dt, J = 7.78,1.52 Hz, aromatic), 7.52 (dt, J = 7.64, 1.83 Hz, aromatic), 7.56 (dd, J = 7.78, 1.53 Hz, aromatic), 7.90 (dd, J = 8.39, 1.83 Hz, aromatic), 9.90 (s, -CH=N-), 11.00 (s, -COOH)	114.5, 116.3, 117.2, 119.0, 119.0, 119.4, 131.1, 133.6, 136.4 (-CH= aromatic), 130.4 (-C= aromatic), 151.5 (=C-OH), 160.7 (=CH-N=), 169.6 (=C-CO-), 191.8 (-CO-)
(12)	3500(w): O-Hν; 3050(w): C-Hν aromatic; 2840-2990 (w): C-Hν alkyl group; 1630(s): C=Nν; 1465(S): C=Cν aromatic; 1255(s): C-Nν; 1080(s): C-Oν	3.88 (s, 6H, O-CH_3), 3.94 (s, 4H, -CH_2-N=), 6.77 (t, J = 7.63 Hz, 2H, aromatic) 6.84 (dd, J = 7.94, 1.53 Hz, 2H, aromatic), 6.90 (dd, J = 7.94, 1.52 Hz, 2H, aromatic), 8.32 (s, 2H, -CH=N-), 13.55 (s,2H, -OH)	56.0 (O-CH_3), 59.4 (-CH_2-N=), 114.1, 118.0, 123.1 (=CH-aromatic), 118.4 (=C- aromatic), 148.3 (=C-OCH_3 aromatic), 151.4 (=C-OH aromatic), 166.6 (-CH=N-)

Table 3.2 (cont)

Schiff's base ligand	IR (cm^{-1})	^{1}H NMR (ppm)	^{13}C NMR (ppm)
(13)	3020-3090(w): C-Hν aromatic; 2850-2950 (w): C-Hν alkyl group; 1640(s): C=Nν; 1450-1580(s): C=Cν; 1280(s): C-Nν	3.97 (s, 4H, CH_2-N=), 3.35-7.40 (m, 6H, -CH= aromatic), 7.67-7.71 (m, 4H, -CH= aromatic), 8.28 (s, 2H, -CH=N-)	61.6 (CH_2-N=), 128.0, 128.5, 130.6 (-CH= aromatic), 136.1 (-C= aromatic), 162.6 (-CH=N-)

3.2 Study on the Optimum Conditions for the Epoxidation of Cyclohexene

There are various factors that need to be evaluated to optimize the epoxidation reaction explored. Cyclohexene was the first chosen substrate as a chemical model. Variable parameters studied are effects of metal salen, effects of the amount of isobutyraldehyde, effects of the reaction atmosphere, effects of type of aldehydes, effects of solvent and effect of the amount of catalyst used.

3.2.1 Effects of Metal Salen

In order to search for an appropriate metal complex that could catalyze the reaction to convert cyclohexene to cyclohexene oxide selectively, various metal salen complexes were examined. The results of utilization of various metal salen complexes are presented in Table 3.3.

Table 3.3 The results of the epoxidation of cyclohexene catalyzed by various metal salen[a]

Entry	Metal salen[b]	Products (%)		Selectivity
		Cyclohexene oxide	Cyclohexenone	epoxide/enone
1	VO(IV) salen	0	0	-
2	Ni(II) salen	0	0	-
3	Cr(III) salen.NO_3	54.34	6.31	8.61
4	Cu(II) salen	0.92	0	-
5	Fe(II) salen	12.84	0	-
6	Co(II) salen	43.44	21.16	2.05
7	Mn(II) salen	43.73	19.84	2.20

a. reaction conditions: cyclohexene (5 mmol), metal salen (0.2 mmol), acetonitrile (30 mL), O_2 and isobutyraldehyde (10 mmol), reaction time (24 hr)

b. some metal salen complexes : VO(IV) salen, Ni(II) salen, Cr(III) salen.NO_3, Cu(II) salen, Fe(II) salen, Co(II) salen and Mn(II) salen were kindly provided by Ms Duangkamol Nuntasri

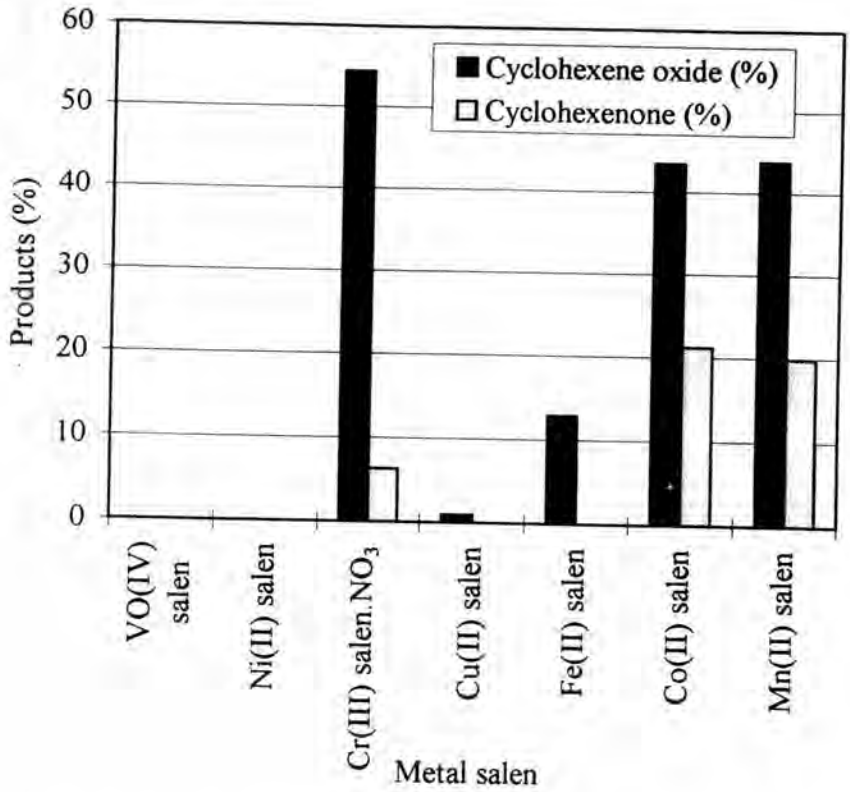


Figure 3.1 The results of the epoxidation of cyclohexene catalyzed by various metal salen

From Table 3.3, seven transition metal-salen complexes in the first row of the periodic table were screened for potentially catalytic epoxidation ability. It was found that the epoxidation of cyclohexene greatly depends on a type of transition metal complexes. The transition metal salen such as Cr(III) salen.NO_3, Co(II) salen and Mn(II) salen exhibited promising ability as catalyst for alkene epoxidation. Among them, Cr(III) salen.NO_3 complex provided the highest yield of cyclohexene oxide and gave the best selectivity for the production of cyclohexene oxide over cyclohexenone (entry 3). Thus, in this research the use of Cr(III) salen.NO_3 and its Schiff's base complexes as a catalyst for alkene epoxidation will be focused. The comparative kinetic study in the epoxidation of cyclohexene employing Cr(III) salen.NO_3 and Co(II) salen complexes will be discussed in the following topic.

3.2.2 Effects of the Amount of Isobutyraldehyde

As it is clearly seen from Table 3.3 that an excess of O_2 and 10 mmol isobutyraldehyde were used as oxidant in this epoxidation reaction. Total yield only about 60 % was obtained. Thus, the amount of isobutyraldehyde, one of crucial parameters, should be optimized. The results are tabulated in Table 3.4.

Table 3.4 The effects of the amount of isobutyraldehyde on the epoxidation reaction[a]

Entry	Isobutyraldehyde (mmol)	Products (%)		selectivity epoxide/enone
		Cyclohexene oxide	Cyclohexenone	
1	0	trace	-	-
2	10	54.34	6.31	8.61
3	15	81.80	10.92	7.50
4	20	98.71	6.16	16.02

a. reaction conditions: cyclohexene (5 mmol), Cr(III) salen.NO_3 (0.2 mmol), acetonitrile (30 mL), O_2 and isobutyraldehyde, reaction time (24 hr)

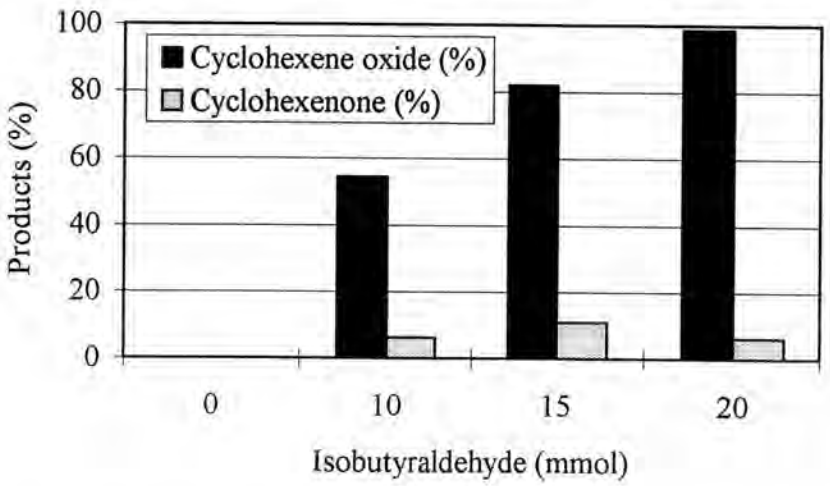


Figure 3.2 The effects of the amount of isobutyraldehyde on the epoxidation reaction of cyclohexene

From Table 3.4, a blank experiment (entry 1) clearly showed that in the absence of isobutyraldehyde, the epoxidation did not occur. Isobutyraldehyde 20 mmol was the most appropriate amount of aldehyde for the epoxidation of cyclohexene. To illustrate this, under these particular conditions, cyclohexene could be smoothly transformed to the desired product, cyclohexene oxide almost quantitative yield together with a small amount of cyclohexenone.

3.2.3 Effects of the Reaction Atmosphere

From the standard conditions employed, the epoxidation system required the use of O_2 and aldehyde. Another question was then arose whether O_2 was important in the reaction or other atmosphere could be used to replace O_2. N_2 and air were therefore selected for this verification. The results are presented in Table 3.5.

Table 3.5 The effects of the reaction atmosphere in the epoxidation reaction[a]

Entry	Atmosphere	Products (%)	
		Cyclohexene oxide	Cyclohexenone
1	O_2	98.71	6.16
2	N_2	trace	-
3	Air	6.22	trace

a. reaction conditions: cyclohexene (5 mmol), Cr(III) salen.NO_3 (0.2 mmol), acetonitrile (30 mL), isobutyraldehyde (20 mmol), reaction time (24 hr)

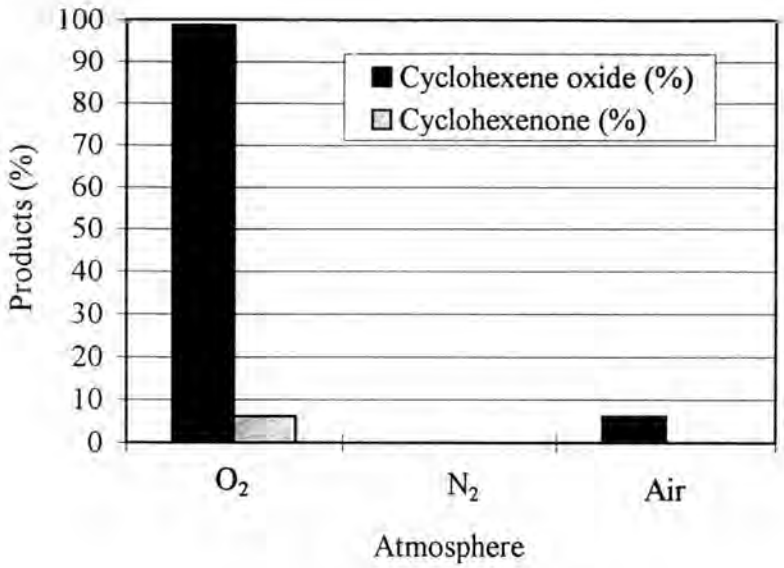


Figure 3.3 The effects of the reaction atmosphere in the epoxidation reaction

It was clearly observed from Table 3.5 that when N_2 and air were used in the reaction instead of O_2, only a little amount of products occurred. This result implied that O_2 and aldehyde are essential combination to permit the reaction to take place. The proposed mechanism of this reaction will be discussed in the following topic.

3.2.4 Effects of type of Aldehydes

The effects of type of aldehydes were the next parameter that needed to be evaluated. The results are shown in Table 3.6.

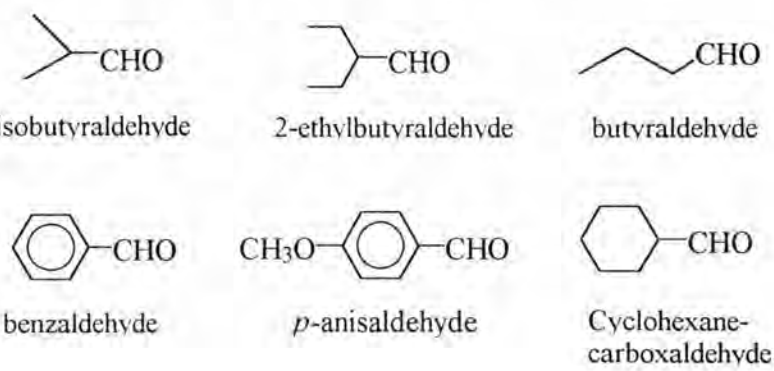


Table 3.6 The effects of type of aldehydes on the epoxidation reaction[a]

Entry	Aldehyde	Products (%)	
		Cyclohexene oxide	Cyclohexenone
1	Isobutyraldehyde	54.34	6.31
2	2-Ethylbutyraldehyde	92.55	5.44
3	Butyraldehyde	trace	-
4	Benzaldehyde	trace	-
5	*p*-Anisaldehyde	trace	-
6	Cyclohexane-carboxaldehyde	49.37	5.49

a. reaction conditions: cyclohexene (5 mmol), Cr(III) salen.NO_3 (0.2 mmol), acetonitrile (30 mL), O_2 and aldehyde (10 mmol), reaction time (24 hr)

Six aldehydes employed in this experiment could be divided into three groups, *i. e.*, an aldehyde that connects to a primary carbon such as butyraldehyde, an aldehyde functional group bearing with a secondary carbon such as isobutyraldehyde, 2-ethylbutyraldehyde and cyclohexanecarboxaldehyde, and an aromatic aldehyde such as benzaldehyde and *p*-anisaldehyde. From the results as shown in Table 3.6 and Figure 3.4, it was found that an aldehyde that connects to a secondary carbon provided impressive results (entries 1, 2 and 6), especially 2-ethylbutyraldehyde. An aldehyde that connects to a primary carbon and an aromatic aldehyde gave only trace amount of desired product. Therefore, both aldehydes: 20 mmol of isobutyraldehyde (from Table 3.4) and 10 mmol of 2-ethylbutyraldehyde were considered as appropriate aldehydes for further investigation.

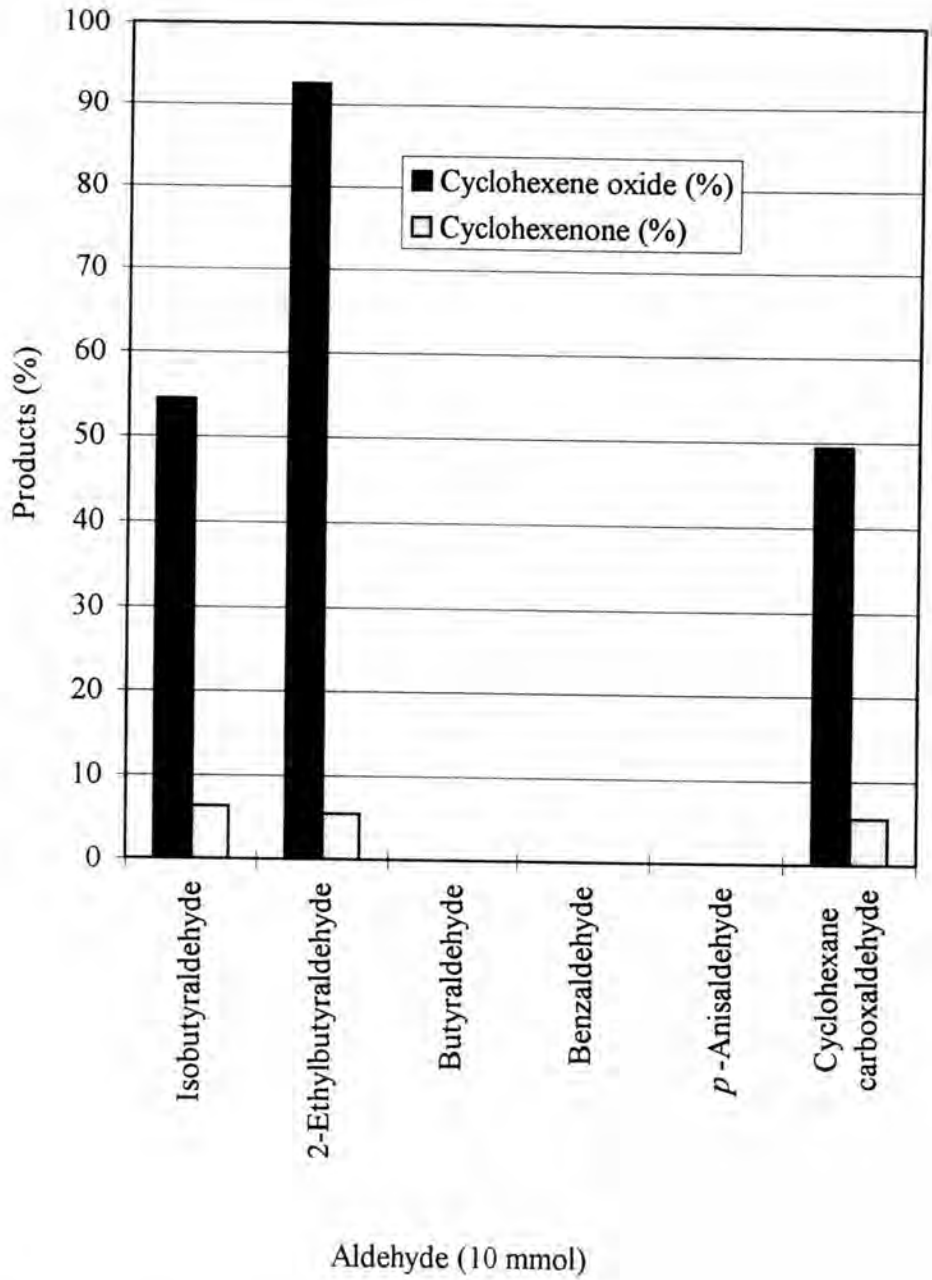


Figure 3.4 The effects of type of aldehydes on the epoxidation reaction

3.2.5 Effects of Solvent

From the experiments described above, acetonitrile was used as a reaction medium because it can dissolve both metal complexes employed and organic substrates. Other solvents were chosen to examine whether they can replace acetonitrile in this epoxidation reaction. The results are shown in Table 3.7

Table 3.7 The effects of solvent on the epoxidation reaction[a]

Entry	Solvents (30 mL)	Products (%)	
		Cyclohexene oxide	Cyclohexenone
1	Acetonitrile	92.55	5.44
2	Chloroform	3.08	0.00
3	1, 2-Dichloroethane	2.01	0.00

a. reaction conditions: cyclohexene (5 mmol), Cr(III) salen.NO_3 (0.2 mmol), O_2 and 2-ethylbutyraldehyde (10 mmol), reaction time (24 hr)

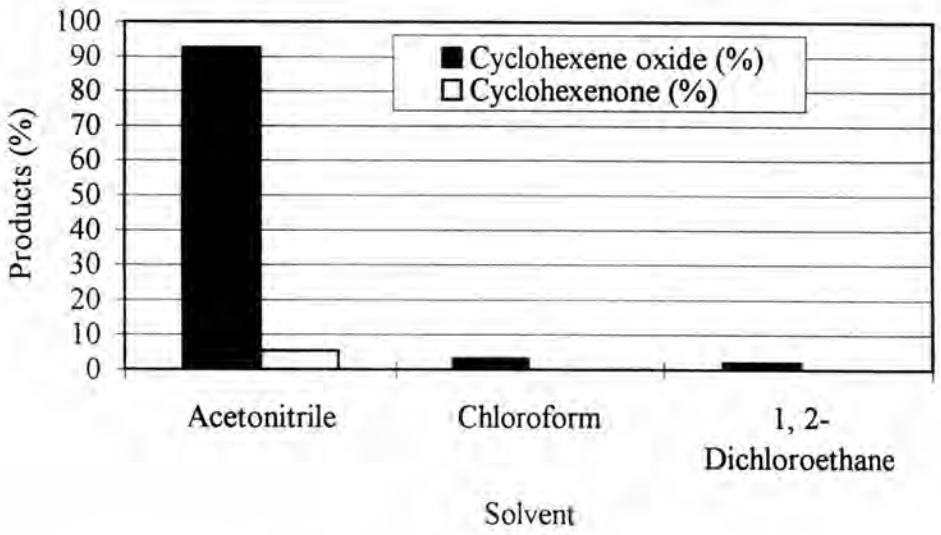


Figure 3.5 The effects of solvent on the epoxidation reaction

When chloroform and 1, 2-dichloroethane were used to replace acetonitrile in the epoxidation reaction, only a little amount of desired product occurred. Therefore, an appropriate solvent for this reaction is acetonitrile.

3.2.6 Effects of the Amount of Catalyst

Another important feature that needs to be studied was the effects of the amount of catalyst employed. Cr(III) salen.NO_3 was selected as a catalyst to examine. The results are presented in Table 3.8.

Table 3.8 The effects of the amount of catalyst (Cr (III)salen.NO_3) on the epoxidation reaction[a]

Entry	Cr(III) salen.NO_3 (mmol)	Products (%)		selectivity epoxide/enone
		Cyclohexene oxide	Cyclohexenone	
1	0.00	2.65	0.00	-
2	0.05	79.65	5.78	13.78
3	0.10	90.91	9.58	9.49
4	0.20	92.55	5.44	16.02

a. reaction conditions: cyclohexene (5 mmol), acetonitrile (30 mL), O_2 and 2-ethylbutyraldehyde (10 mmol), reaction time (24 hr)

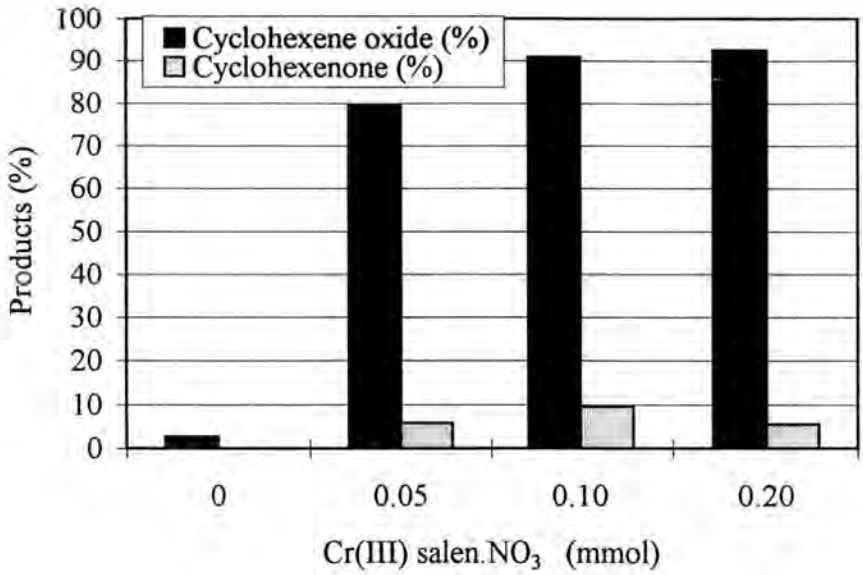


Figure 3.6 The effects of the amount of Cr(III) salen.NO_3 on the epoxidation reaction

When 0.10 mmol of Cr(III) salen.NO_3 was utilized, the reaction gave almost quantitative yield of desired products (entry 3). Nonetheless, employing Cr(III) salen.NO_3 0.20 mmol (entry 4) produced a little bit higher yield than the former, but provided much better result in terms of product distribution selectivity. Thus, 0.20 mmol of catalyst was found to be the most appropriate amount for further investigation.

From the outcome of variable factors studied as described above, it can be concluded that the optimum conditions for the epoxidation of alkenes are as follows: alkene 5 mmol as a substrate, acetonitrile 30 mL as a solvent, metal complex 0.20 mmol as a catalyst and molecular oxygen with 2-ethylbutyraldehyde 10 mmol or isobutyraldehyde 20 mmol as an oxidant. Thus, these conditions were kept as standard conditions for further investigation.

3.3 Epoxidation Reaction Catalyzed by Chromium Salts, Chromium(III) Complexes and Chromium(III) Schiff's Base Complexes

From the outcome of the effects of metal-salen explored, Cr(III) salen.NO_3 and chromium Schiff's base complexes turned out to be attractive catalysts for the epoxidation of cyclohexene in terms of providing both high yield and good selectivity. Therefore, chromium salts, chromium complexes and other chromium Schiff's base complexes were thoroughly investigated and the results are presented in Table 3.9.

Table 3.9 Epoxidation reactions catalyzed by chromium salts, chromium(III) complexes and chromium(III) Schiff's base complexes[a]

Entry	Catalyst (0.2 mmol)	Products (%)		selectivity epoxide/enone
		cyclohexene oxide	cyclohexenone	
1	Cr(III)$Cl_3.6H_2O$	35.02	7.60	4.61
2	Cr(III)$(NO_3)_3.9H_2O$	36.70	21.86	1.68
3	Cr(VI)O_3	46.60	14.54	3.20
4	Cr(III)$(acac)_3$	0.00	0.00	-
5	Cr(III)$(sal)_3$	40.78	5.93	6.88
6	Cr(III)salen.NO_3	92.55	5.44	17.01
7	[Cr(III)salen]$NO_3.2H_2O$	72.14	17.15	4.21
8	[Cr(III)salen$(H_2O)_2$]Cl	66.79	10.95	6.10
9	Cr(III)(sal-*p*-tolylen)$_3$	45.96	8.86	5.19
10	Cr(III)$(salen)_2$I	0.00	0.00	-
11	Cr(III)**(2)**	24.91	0.00	-
12	Cr(III)**(8)**	92.16	8.63	10.68
13	Cr(III)**(10)**	91.44	6.81	13.43
14	Cr(III)**(12)**	71.10	11.18	6.36

a. reaction conditions: cyclohexene (5 mmol), acetonitrile (30 mL), O_2 and 2-ethylbutyraldehyde (10 mmol), reaction time (24 hr)

From the results in table shown above, some chromium complexes displayed interesting catalytic ability. Whereas $Cr(acac)_3$ did not show any catalytic property for this particular reaction, $Cr(sal)_3$ could catalyze the transformation of cyclohexene to cyclohexene oxide and cyclohexenone in moderate yield (entries 4 and 5). This result obviously supported the concept of the importance of ligating agents around metal which will have an influence on the catalytic activity of metal complexes.[75]

However, some chromium Schiff's base complexes revealed their potential ability to oxidize cyclohexene to cyclohexene oxide in moderate to high yield (entries 6-8, 12-14). Other chromium Schiff's base complexes chosen gave lower yields of desired products probably owing to greater steric hindrance of the ligands. Hence, it will allow the formation of an oxochromium complex intermediate to take place more difficult. Among those chromium salts, complexes and Schiff's base complexes, Cr(III) salen.NO_3 was found to be the best catalyst in this epoxidation reaction studied.

3.4 Epoxidation Reaction Catalyzed by Chromium(III) Catalyst Formed *in situ*

Stemmed from the results attained from the previous section, some chromium complexes emerged to be promising catalysts for this explored reaction. The *in situ* forming chromium catalysts derived from $CrCl_3.6H_2O$ and various Schiff's base ligands were thus tested for the specific purpose to examine whether the efficiency of *in situ* catalysts can be compared with those synthesized chromium Schiff's base complexes. The results of this examination are tabulated in Table 3.10.

Table 3.10 Epoxidation of cyclohexene catalyzed by chromium(III) salen complexes formed *in situ*[a]

Entry	Catalyst (0.2 mmol)	Products (%)		selectivity epoxide/enone
		cyclohexene oxide	cyclohexenone	
1	$CrCl_3.6H_2O$	35.02	7.60	4.16
2	$CrCl_3.6H_2O$: salen (1:1)	57.51	27.97	2.06
3	$CrCl_3.6H_2O$: salen (1:2)	64.12	16.51	3.88
4	$CrCl_3.6H_2O$: salen (1:3)	57.78	12.75	4.53
5	$Cr(NO_3)_3.9H_2O$: salen (1:2)	58.85	7.19	8.18

a. reaction conditions: cyclohexene (5 mmol), acetonitrile (30 mL), O_2 and 2-ethylbutyraldehyde (10 mmol), reaction time (24 hr)

The results attained from Table 3.10 clearly pointed out that chromium salt, $CrCl_3.6H_2O$, could catalyze the transformation of cyclohexene to cyclohexene oxide and cyclohexenone in low yield compared with Cr salen complexes formed *in situ*. The ratio 1 to 2 of chromium salt, $CrCl_3.6H_2O$, and salen ligand was the most appropriate ratio for *in situ* catalyst formed (entry 3). However, when the comparative study between the utilization of $CrCl_3.6H_2O$ and salen (1: 2 ratio), and $Cr(NO_3)_3.9H_2O$ and salen (1 : 2 ratio) as catalysts was made (entries 3 and 5), it was found that the use of $CrCl_3.6H_2O$ provided higher yield of the desired products, but lower selectivity than that of $Cr(NO_3)_3.9H_2O$. Thus, $Cr(NO_3)_3.9H_2O$ was chosen to study for other *in situ* catalysts formed.

Various Schiff's base ligands were synthesized as described in Chapter II. Those ligands were then tested by replacing salen **(1)** ligand. The results are presented as shown in Table 3.11.

Table 3.11 Epoxidation of cyclohexene catalyzed by Chromium(III) Schiff's base complexes formed *in situ*[a]

Entry	Catalyst[b]	Products (%)		selectivity
		cyclohexene oxide	cyclohexenone	epoxide/enone
1	salen **(1)**	58.85	7.19	8.18
2	salophen **(2)**	36.18	7.90	4.58
3	pyren **(3)**	0.00	0.00	0.00
4	pyrophen **(4)**	75.00	14.38	5.22
5	fufuren-*o*-phen **(5)**	40.40	17.41	2.32
6	thiophen **(6)**	72.72	11.55	6.30
7	thiophen-*o*-phen **(7)**	42.34	7.40	5.72
8	Me salen **(8)**	65.46	15.26	4.29
9	salop **(9)**	27.55	17.57	1.57
10	acen **(10)**	23.24	14.13	1.64
11	saloa **(11)**	26.70	19.83	1.35
12	salen OMe **(12)**	36.89	6.13	6.02
13	bzen **(13)**	69.00	11.30	6.11

a. reaction conditions: cyclohexene (5 mmol), acetonitrile (30 mL), O_2 and 2-ethylbutyraldehyde (10 mmol), reaction time (24 hr)

b. catalyst : $Cr(NO_3)_3.9H_2O$: Schiff's base ligand (1:2)

From Table 3.11, it was found that the catalysts formed *in situ* which were derived from $Cr(NO_3)_3.9H_2O$ and Schiff's base ligands [**(4)** and **(6)**] could catalyze the epoxidation of cyclohexene to cyclohexene oxide and cyclohexenone in good yield (entries 4 and 6). These results denoted that $Cr(NO_3)_3.9H_2O$ could form complexes with Schiff's base ligands **(4)**, **(6)** *in situ* better than the others. This was probably because they are neutral ligands and have suitable holes to form complex that provides more positive charge of metal and easier to plus molecular oxygen. However, the yield of the desired products and selectivity were still lower than those obtained when Cr(III) salen.NO_3 was used as catalyst in all cases. Moreover, when chromium complexes were utilized as

catalyst as shown in Table 3.9 (entries 6 and 12-14) compared with chromium complexes formed *in situ* as shown in Table 3.11 (entries 1, 8, 10 and 12), it could manifestly be seen that the synthesized chromium complexes provided better yield of products and better product formation selectivity than the chromium complexes formed *in situ*.

3.5 Epoxidation Reaction Catalyzed by Cobalt(II) and Manganese(II) Schiff's Base Complexes

The utilization of Co(II) salen and Mn(II) salen as catalysts as shown in Table 3.3 provided higher yields than other metal salen complexes used except for Cr(III) salen.NO_3 which provided the highest yield. Table 3.12 summarized the utilization of various Co and Mn Schiff's base complexes in the epoxidation reaction of cyclohexene.

Table 3.12 Epoxidation of cyclohexene catalyzed by cobalt(II) and manganese(II) Schiff's base complexes[a]

Entry	catalyst (0.20 mmol)	Products (%)		selectivity oxide/enone
		cyclohexene oxide	cyclohexenone	
1	Co **(1)**	65.02	13.69	4.75
2	Co **(2)**	46.30	6.60	7.02
3	Co **(8)**	65.33	14.53	4.50
4	Co **(9)**	52.38	9.45	5.54
5	Co **(12)**	40.31	0.00	-
6	Mn **(1)**	37.96	9.86	3.85
7	Mn **(2)**	22.27	0.00	-
8	Mn **(8)**	52.81	15.68	1.01
9	Mn **(9)**	61.98	9.05	6.85
10	Mn **(12)**	30.06	4.60	6.53

a. reaction conditions: cyclohexene (5 mmol), acetonitrile (30 mL), O_2 and 2-ethylbutyraldehyde (10 mmol), reaction time (24 hr)

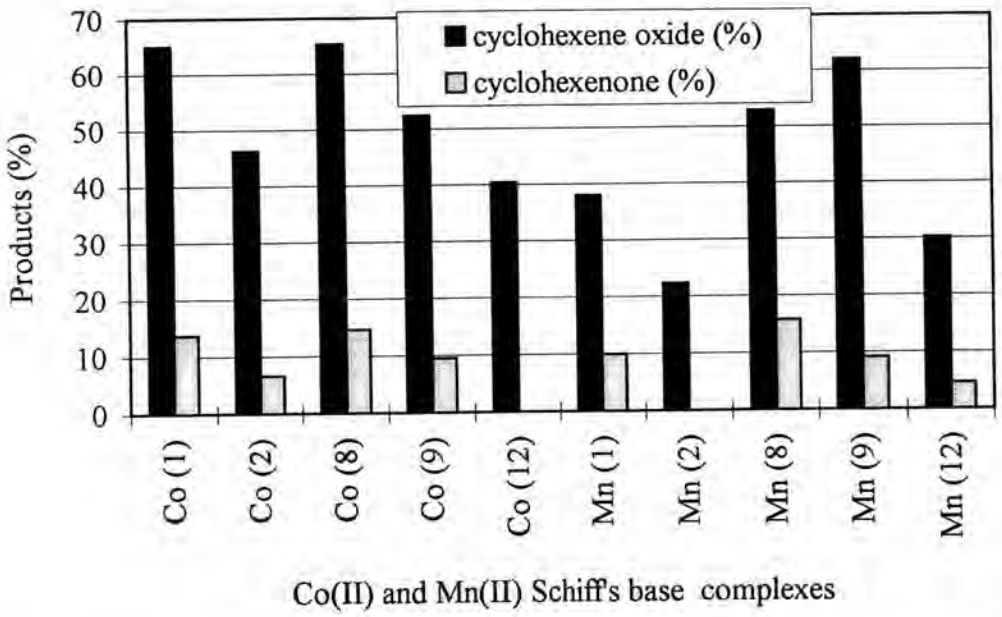


Figure 3.7 Epoxidation of cyclohexene catalyzed by cobalt(II) and manganese(II) Schiff's base complexes

In the case of cobalt(II) Schiff's base complexes, Co **(1)** and Co **(8)** gave higher yield of the desired products than other cobalt complexes (entries 1 and 3). On the other hand, the use of manganese(II) Schiff's base complexes Mn **(9)** provided higher yield than other manganese complexes. Both cobalt and manganese Schiff's base complexes still gave lower yield with poor selectivity of the distribution of products compared with Cr(III) salen.NO_3 catalyst. Among metal Schiff's base complexes investigated, it was eventually found that Cr(III) salen.NO_3 was the most appropriate catalyst for alkene epoxidation under these examined conditions. Therefore, this catalyst was employed for further investigation.

3.6 Comparative Kinetic Study on the Reaction Rate of the Epoxidation of Cyclohexene

Various catalytic systems that mimic enzymatic systems could catalyze reactions to proceed at room temperature. However, the rates of these reactions are generally slow and need to spend more time to complete the reaction. The rate of the epoxidation of cyclohexene catalyzed by Cr(III) salen.NO_3 and Co(II) salen were compared. The results are shown in Tables 3.13 and 3.14, respectively. From Figure 3.8, it was found that the rate of the reaction catalyzed by Co(II) salen was faster than that of Cr(III) salen.NO_3. However, the final yield of products catalyzed by Cr(III) salen.NO_3 was far better than that of Co(II) salen. The half-life of the reaction catalyzed by Cr(III) salen.NO_3 was approximately 6 hours.

Table 3.13 Kinetic study on cyclohexene epoxidation catalyzed by Cr(III) salen.NO_3[a]

Entry	time (hrs)	Products (%)	
		cyclohexene oxide	cyclohexenone
1	0.0	0.00	0.00
2	1.0	0.51	0.00
3	2.0	1.96	0.00
4	4.0	14.11	1.34
5	6.0	45.89	5.36
6	8.0	66.03	7.50
7	9.5	72.30	7.61

a. reaction conditions: cyclohexene (5 mmol), acetonitrile (30 mL), O_2 and 2-ethylbutyraldehyde (10 mmol), Cr(III) salen. NO_3 (0.2 mmol)

Table 3.14 Kinetic study on cyclohexene epoxidation catalyzed by Co(II) salen[a]

Entry	time (hrs)	Products (%)	
		cyclohexene oxide	cyclohexenone
1	0.0	0	0
2	1.0	35.39	5.83
3	2.0	49.11	6.20
4	4.0	49.75	9.42
5	6.0	51.64	9.93
6	8.0	52.62	9.62
7	9.5	55.97	11.16

a. reaction conditions: cyclohexene (5 mmol), acetonitrile (30 mL), O_2 and 2-ethylbutyraldehyde (10 mmol), Co(II) salen (0.2 mmol)

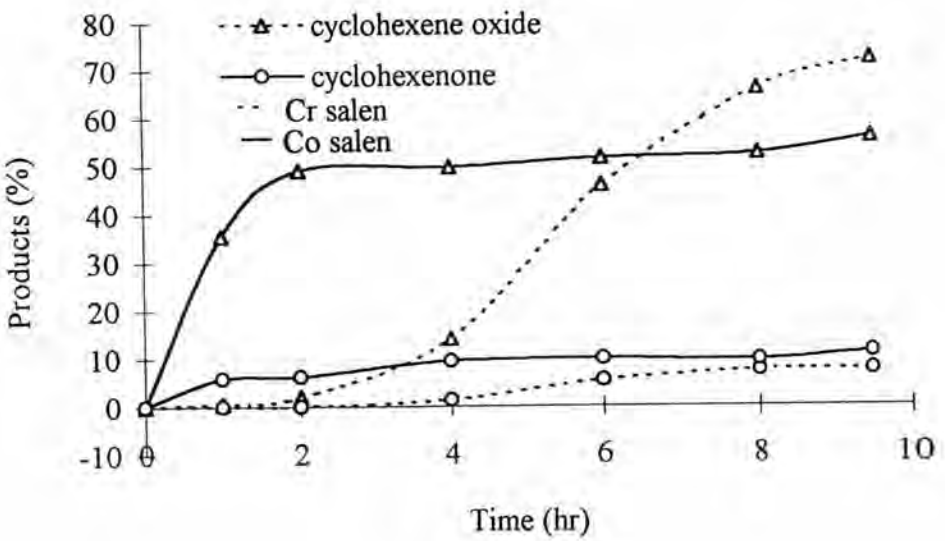


Figure 3.8 Kinetic study on cyclohexene epoxidation catalyzed by Cr(III) salen.NO_3 and Co(II) salen

3.7 Effect of Temperature on the Epoxidation of Cyclohexene

Cyclohexene epoxidation described above was carried out at room temperature. From Figure 3.7, the half-life of the reaction catalyzed by Cr(III) salen.NO_3 was approximately 6 hours at 28 °C (room temperature). The reaction performed at 0 °C and 60 °C were studied to compare the effects of temperature on the epoxidation reaction during time interval of 6 hours. The results are presented in Table 3.15. From the results attained, it could be concluded that the reaction did not occur at low temperature (0 °C). At high temperature (60 °C), the reaction gave higher yield of products and higher selectivity than that performed at room temperature (entry 3). Nevertheless, for further investigation, it is convenient to carry out the reaction at room temperature.

Table 3.15 The effects of temperature on cyclohexene epoxidation[a]

Entry	Temperature (°C)	Products (%)		selectivity epoxide/enone
		cyclohexene oxide	cyclohexenone	
1	0	0.00	0.00	-
2	28	45.89	5.36	8.56
3	60	64.49	3.82	16.88

a. reaction conditions: cyclohexene (5 mmol), acetonitrile (30 mL), O_2 and 2-ethylbutyraldehyde (10 mmol), Cr(III) salen. NO_3 (0.2 mmol), reaction time (6 hr)

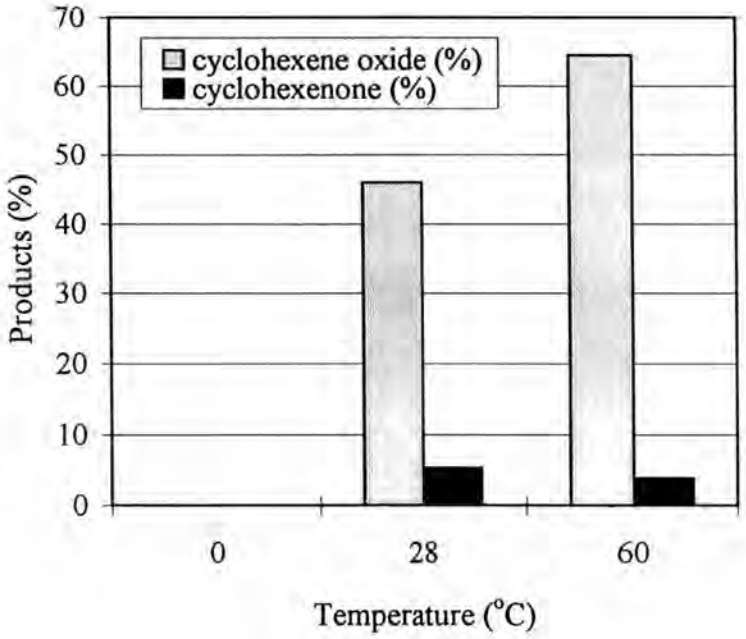
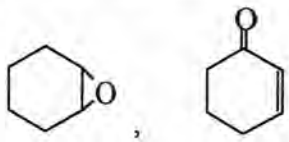
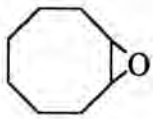
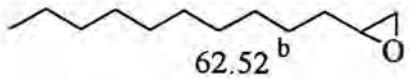
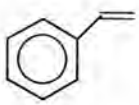
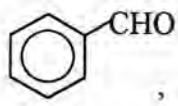
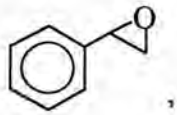
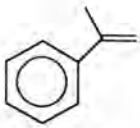
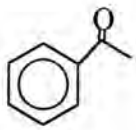
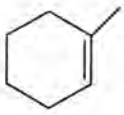
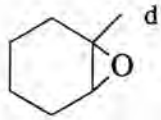


Figure 3.9 The effects of temperature on cyclohexene epoxidation

3.8 Chromium(III)-Catalyzed Epoxidation Reactions of Various Alkenes

The optimum conditions for the epoxidation of alkenes using cyclohexene as a chemical model can be concluded as follows: 5 mmol of alkene as a substrate, 30 mL acetonitrile as solvent, 0.2 mmol Cr(III) salen.NO_3 as catalyst, O_2 and 10 mmol 2-ethylbutyraldehyde or 20 mmol of isobutyraldehyde as an oxidant and reaction time 24 hr or more. Under these conditions, cyclohexene was converted to cyclohexene oxide in high yield with high selectivity. Other alkenes such as cyclooctene, 1-dodecene, styrene, α-methylstyrene and 1-methylcyclohexene were selected for regioselectivity study. The results are presented in Table 3.16.

Table 3.16 Chromium(III)-catalyzed epoxidation reactions of various alkenes[a]

Entry	Substrate (5 mmol)	reaction time (hr)	Product (s) (%)
1		24	 92.55 , 5.44
2		24	 93.12
3		24	 62.52 [b]
4		48	 ,  , c 21.91 11.87
5		48	 103.00
6		24	 d , c

a. reaction conditions: substrates (5 mmol), acetonitrile (30 mL), O_2 and 2-ethylbutyraldehyde (10 mmol), Cr(III) salen. NO_3 (0.2 mmol)
b. starting material recovered 30.22%
c. other products are not determined
d. identify by GC/MS

From the results obtained, it was clearly shown that cyclohexene and cyclooctene, endocyclic alkenes, could be converted to their analogous epoxides as predominant products in high yield, only small amount of the allylic oxidation product occurred. 1-Dodecene, aliphatic terminal alkene, was transformed to 1-dodecene oxide in moderate yield (entry 3), together with some recovered substrate. Surprising results are obtained in the case of styrene, terminal double bond substrate, it was found that terminal double bond was cleaved and benzaldehyde was obtained as a major product, while styrene oxide was attained as a minor product (entry 4).

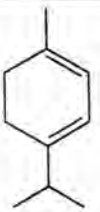
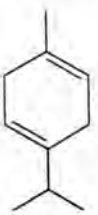
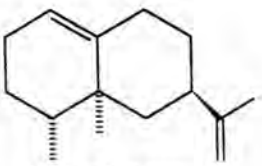
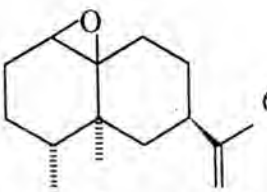
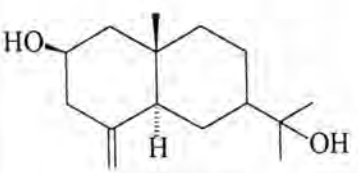
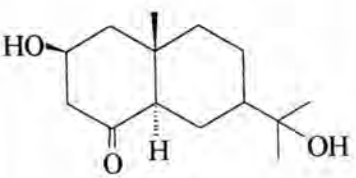
α-Methylstyrene was thus investigated to confirm this observation and it was found that acetophenone was also obtained as an excluded product instead of the analogous epoxide (entry 5). This ketone product was identified by GC/MS analysis and the molecular ion peaks at m/e 121 and 105 appeared on the mass spectrum. In addition some acetophenone was isolated by column chromatography of the crude reaction. Its identify was well-confirmed by ^{1}H and ^{13}C NMR spectra. It could therefore clearly be concluded at this stage that a terminal double bond connecting to an aromatic ring have a preference to cleave and oxidize to aldehyde or ketone similar to an ozonization reaction more than epoxidation reaction.

1-Methylcyclohexene was converted to the corresponding epoxide which was identified by GC/MS analysis and the molecular ion peaks at m/e 113, 112 and 95 appeared on the mass spectrum. Other products were also observed, but could not identify.

3.9 Application of Developed Epoxidation Reaction to Natural Products

Some alkenes originated as natural products were the next targets to examine under the epoxidation conditions studied. The results are tabulated in Table 3.17.

Table 3.17 Epoxidation reaction of alkenes from natural products[a]

Entry	Substrate	Reaction time (hr)	Product (%)
1	 α-terpinene	24	 38.84 *p*-cymene
2	 γ-terpinene	24	 41.43 *p*-cymene
3	 (+)-valencene	72	 67.51 1,10-valencene oxide
4	 pterocarpol	72	 17.00

a. reaction conditions: substrates (5 mmol), acetonitrile (30 mL), O_2 and 2-ethylbutyraldehyde (10 mmol), Cr(III) salen. NO_3 (0.2 mmol)

From Table 3.17, it was found that in the case of certain endocyclic dienes, α-terpinene and γ-terpinene, preferably aromatized to *p*-cymene which an aromatic compound in stead of the epoxidation to their corresponding epoxides. It does not surprising because an aromatic compound is easier to occur and more stable than epoxy compound since certainly gained resonance stabilization energy.

In the case of (+)-valencene, after the reaction was over within 72 hr (monitoring by TLC), the whole reaction mixture was extracted by ether and followed the general worked up as described earlier with aqueous $NaHCO_3$ and brine, respectively. The combined extract was concentrated and isolated by column chromatography. Diastereomers of valencene oxide were obtained as predominant products, eluting the column with 100 % ethyl acetate and were well-confirmed their identities by ^1H NMR. Starting material (+)-valencene, showed signals of an endocyclic alkene C1-H at δ 5.30 ppm and terminal alkene $=CH_2$ at δ 4.65 ppm. Observing in the ^1H-NMR spectrum, the epoxidation product, 1,10-valencene oxide could be detected the disappearance of proton in endocyclic alkene of valencene and showed C1 epoxide proton at δ 2.90 and 3.00 ppm. The proton integration found 1:1 ratio of diastereomers of valencene oxide. From this investigation showed that endocyclic double bond could be oxidized faster than terminal double bond.

Pterocarpol, a sesquiterpene alcohol or 2, 11-dihydroxy, $\Delta^{4(15)}$-eudesmene isolated from *Ptercarpus macrocarpus* and *P. santalinus*, was the other alkene selected. In this reaction, pterocarpol 0.25 mmol was used as a substrate in 10 mL acetonitrile. The amount of 2-ethylbutyraldehyde and Cr(III) salen.NO_3 was employed following those described in the optimum conditions. Within 72 hr, the reaction was finished and worked up by aqueous $NaHCO_3$ and brine. The product was isolated by column chromatography using 10 % MeOH-$CHCl_3$ as an eluent and identified by ^1H and ^{13}C NMR. Exocyclic double bond of pterocarpol was cleaved and oxidized to cyclic ketone. This observation was clearly confirmed by the ^{13}C NMR spectrum. To illustrated this, the double bond of C-4 and C-15 which could be detected at δ 147.8 and 108.0 ppm,

respectively disappeared and the signal belonging to C=O of product appeared at δ 200.5 ppm was detected. From this result indicated that exocyclic double bond was cleaved and oxidized to the ketone in the same fashion as that observed in the case of terminal alkene.

3.10 Competitive Studies on the Oxidation of Cyclohexene, γ-Terpinene and Cyclohexanol

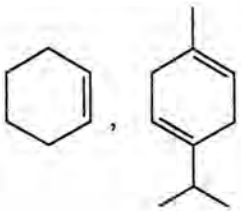
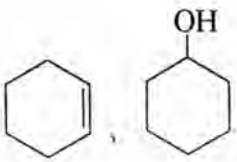
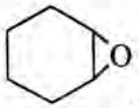
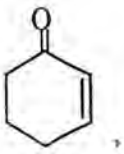
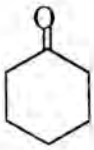
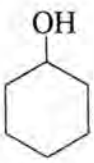
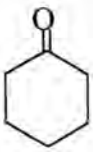
In order to examine the characteristic of this developed catalytic system, the competitive studies on the oxidation between cyclohexene and γ-terpinene, and cyclohexene and cyclohexanol were investigated. The results are shown in Table 3.18. It was found that aromatization of γ-terpinene took place much faster than the epoxidation reaction of cyclohexene (entry 1). The reason for this was probably due to the stabilization energy attained when γ-terpinene was transformed to an aromatic compound, *p*-cymene.

Epoxidation of cyclohexene to cyclohexene oxide was observed to take place faster than the oxidation of cyclohexanol to cyclohexanone (entry 3). In entry 4, cyclohexanol was oxidized to cyclohexanone in moderate yield. From these two entries it could be seen that alkene funtional group was more sensitive than alcohol under this condition.

The utilization of metalloporphyrins as catalyst and dioxygen with isobutyraldehyde or cyclohexane carboxaldehyde as an oxidant was recently disclosed by W. Nam *et al.*[76] That reaction gave cyclohexene oxide only 33 % when Cr(TPP)Cl, Mn(TPP)Cl, Fe(TPP)Cl and Co(TPP) were used as catalyst and provided similar epoxide 40 % when Ni(TPP) was used as catalyst (TPP = tetraphenylporphyrin). In other systems reported, for instance, the epoxidation of cyclohexene using Mn^{III}(Schiff base)NCS complexes[47], Fe^{III}(Schiff base) chelates[46] as catalyst and PhIO as an oxidant provided cyclohexene oxide, cyclohexenol and cyclohexenone in low yield and low selectivity compared with the system discovered in this research. Under Mukaiyama's conditions,[52, 57] variety of metal complexs were used as catalyst in the epoxidation of alkene and found that the

corresponding epoxides were obtained in good yield but in some case, absentee of epoxide and allylic oxidation took place. However, in this research the new system for the epoxidation of endocyclic alkenes to the corresponding epoxide and the oxidation of terminal alkenes or exocyclic alkenes to aldehyde or ketone were added as another feature for this type of reaction.

Table 3.18 Competitive studies of the oxidation between cyclohexene and γ-terpinene, and cyclohexene and cyclohexanol[a]

Entry	Substrates (5 mmol each)	Product(s) (mmol)
1		 1.756
2		 2.052
3		 2.864  0.233  0.337
4		 2.339

a. reaction conditions: substrate (5 mmol each), acetonitrile (30 mL), O_2 and 2-ethylbutyraldehyde (10 mmol), Cr(III) salen. NO_3 (0.2 mmol), reaction time (24 hr)

3.11 Chemoselectivity

Another important feature of the system that needs to be carefully evaluated is the chemoselectivity. From Table 3.18 (entry 3), the addition of an additive to the system would provide some clues for the chemoselectivity of the system studied. Ethanol which is a small alcohol and easily oxidized was used as an additive in the epoxidation reaction of cyclohexene. The outcome of the reaction is tabulated in Table 3.19.

Table 3.19 The effects of ethanol concentration on the epoxidation of cyclohexene[a]

Entry	EtOH (mmol)	Products (%)	
		cyclohexene oxide	cyclohexenone
1	0	92.55	5.44
2	5	90.22	14.20
3	10	88.37	12.02
4	20	75.31	7.16

a. reaction conditions: cyclohexene (5 mmol), acetonitrile (30 mL), O_2 and 2-ethylbutyraldehyde (10 mmol), Cr(III) salen. NO_3 (0.2 mmol), reaction time (24 hr)

It could clearly be seen from this table that cyclohexene epoxidation process was little suppressed by the effect of increasing the amount of ethanol. Although twice or four times of the amount of an additive were used in the reaction, the activation process of cyclohexene was still occurred to produce the corresponding epoxide and enone. Therefore, the utilization of Cr(III) salen.NO_3 as a catalyst under this particular condition produced an active species responsible to epoxidize alkenes to epoxide.

3.12 Effect of the Radical Inhibitor Added in the Epoxidation of Alkene for the Aldehyde, O_2 Catalyzed by Metal Complexes System

Mechanistic studies of the oxidation of olefins by dioxygen in the presence of aldehyde and metal complexes have been carried out. It could be concluded from this study that the principal role of the metal complex is to aid in the initiation step for the free radical autoxidation of the aldehyde and that acylperoxy radicals generated in the autoxidation reaction (or metal complexes formed by complexation of the acylperoxy radicals) are the active epoxidizing agents.[76]

$$(L_n)M^{n+} + RCHO \longrightarrow (L_n)M^{(n-1)+} + RCO^{\bullet} + H^{+}$$

$$RCO^{\bullet} + O_2 \longrightarrow RCO_3^{\bullet}$$

$$RCO_3^{\bullet} + RCHO \longrightarrow RCO_3H + RCO^{\bullet}$$

$$(L_n)M^{n+} + RCO_3H \longrightarrow (L_n)M^{(n+2)+}{=}O + RCO_2H$$

$$(L_n)M^{(n+2)+}{=}O + \text{substrate} \longrightarrow (L_n)M^{n+} + \text{Product (O)}$$

Figure 3.10 Mechanism of the epoxidation of olefins by dioxygen in the presence of aldehyde and metal complex

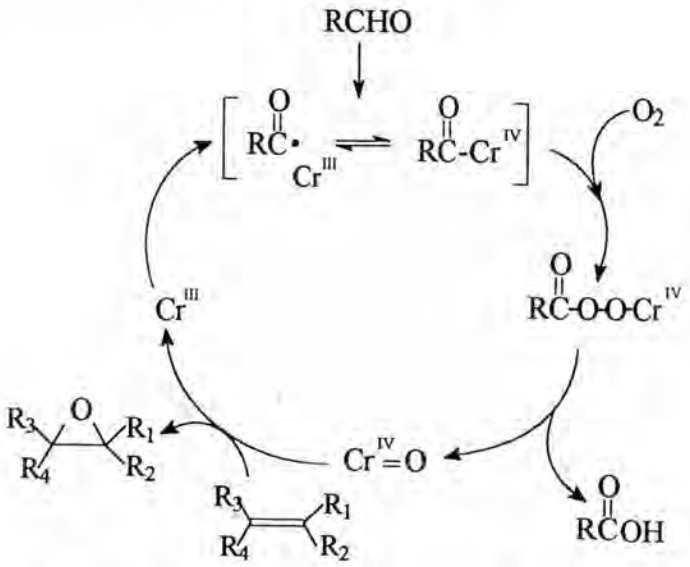
From this figure, the mechanism was thought to occur *via* free radical intermediate. Thus, the free radical inhibitor 3-picoline was added under the same reaction conditions. 1-Dodecene was used as a substrate. The results as shown in Table 3.20 confirmed that this mechanism occurred *via* free radical. That was because when the free radical inhibitor was added, the epoxidation reaction could not proceed and the substrate was almost recovered.

Table 3.20 Effects of 3-picoline on the epoxidation of 1-dodecene

Entry	aldehyde (mmol)	3-picoline (mL)	%	
			1-dodecene oxide	recovered 1-dodecene
1	0	-	0.00	99.71
2	10	-	66.52	33.23
3	15	-	61.55	17.99
4	10	1	0.00	99.52
5	10	3	0.00	99.72

3.13 Proposed Mechanism for Chromium-catalyzed Epoxidation of Alkenes

From the results described above, it was suggested that the mechanism of the chromium-catalyzed epoxidation of alkenes using molecular oxygen and aldehyde as oxidant should occur *via* free radical pathway. This mechanism was proposed as shown in Scheme 3.1.



Scheme 3.1 The proposed mechanism for the chromium-catalyzed epoxidation of alkenes using dioxygen and aldehyde as oxidant

In this mechanism, the chromium(III) complex was assumed to react with an aldehyde to generate an acyl radical ($RC(O)^{\bullet}$) which was in the equilibrium with chromium(IV)-acyl species. The chromium(IV)-acyl species was then reacted with dioxygen to form an chromium(IV)-peroxy complex. The chromium(IV)-peroxy complex formed high-valent oxo-chromium(V) complex by the oxygen-oxygen bond cleavage of the peroxy group and provided the corresponding acid as by-product. After that, the oxo-chromium(V) complex was believed to transfer an oxygen atom directly to alkenes and chromium(III) complex was driven back to the catalytic cycle.