ELSEVIER

Journal of Molecular Catalysis A: Chemical 130 (1998) 41–50

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Aerobic, enantioselective epoxidation of non-functionalized olefins catalyzed by Ni(II) chiral Schiff base complexes

R.I. Kureshy *, N.H. Khan, S.H.R. Abdi, P. Iyer, A.K. Bhatt

Central Salt and Marine Chemicals Research Institute, Bhavnagar 364 002, India

Received 19 June 1997; accepted 26 August 1997

Abstract

Some symmetrical and non symmetrical square planar Ni(II) chiral Schiff base complexes derived from 1*S*,2*S*(+)diaminocyclohexane, *S*(+)1,2-diaminopropane and 1*R*,2*R*(-)diphenyldiamino ethane with 3-acetyl-4-hydroxy-6-methyl-2-pyrone have been prepared. The characterization of the complexes was done by physico–chemical methods viz. microanalysis, conductance measurement, IR-, UV/visible-, ^{1}H-, ^{13}C{^{1}H}NMR, CD spectral studies, optical rotation and cyclic voltammetry. These complexes catalyses the epoxidation of non-functionalized olefins viz. 1-hexene, 1-octene, *trans*-4-octene and indene with molecular oxygen as terminal oxidant in presence of the sacrificial reductant. Excellent chemical yield was obtained by GC with middle and terminal long chain alkenes than indene although the enantiomeric excess is good for indene with catalyst **3** and evaluated by ^{1}H NMR using chiral shift reagent Eu(hfc)$_3$ or by chiral capillary column on GC.

Keywords: Enantioselective; Aerobic; Epoxidation; Non-functionalized olefins; Chiral Ni(II) complexes

1. Introduction

In recent years the synthesis of optically pure chiral epoxide has gained great importance, particularly in the area of pharmaceuticals, agrochemicals, flavors and fragrances [1] because of the growing awareness about the utility of the desired epoxide and the disposal of the unwanted one whose negative side effects can far outweigh the beneficial value of the right enantiomer. It is therefore becoming imperative that convenient methods be available to prepare biologically active materials in an enantiomerically pure form [2,3]. Catalytic methods represent the most efficient route for the synthesis of thousands of chiral products by utilizing just one chiral catalyst [4]. One more reason for ongoing research is to develop a better understanding about the factors controlling the enantioselectivity in the catalytic system. The Sharpless asymmetric epoxidation of allylic alcohols is the most practicable method for the preparation of epoxy alcohols [5,6]. However, the enantioselective epoxidation of non functionalized olefins remained yet a big challenge. Jacobsen [7–14] and Katsuki [15,16] have recently reported an efficient catalytic system for enantioselective epoxidation of several kinds of olefins with moderate to high enantioselectivity depending

* Corresponding author. Tel.: +91-278-567760; fax: +91-278-566970; e-mail: general@cscsmcri.ren.nic.in

1381-1169/98/$19.00
PII S1381-1169(97)00195-7

on the substitution degree of double bond using iodosyl benzene [15], NaOCl, [17] hydrogen peroxide [18], periodates [19] as terminal oxidant.

However the selective epoxidation of organic substrates with molecular oxygen [20] in presence of sacrificial reductant is a challenging goal in synthetic organic chemistry. Several reports highlighting the utility of effective reductants such as primary/secondary alcohol [21], aldehyde [22], or cyclic ketones [23] in aerobic oxidation of olefins catalyzed by transition metal complexes have appeared recently [24–26].

In continuation to our earlier communications on enantioselective epoxidation of non-functionalized olefins using Ru(II), Ru(III), Mn(III) and Co(II) chiral Schiff base complexes [27–32] and to explore a detailed mechanistic study we are reporting here the aerobic enantioselective epoxidation of non-functionalized olefins viz 1-hexene, 1-octene, *trans*-4-octene and indene with molecular oxygen in presence of isobutyraldehyde as sacrificial reductant catalyzed by Ni(II) symmetrical and non-symmetrical chiral Schiff base complexes.

2. Experimental

Nickel acetate (Sisco), 1*S*,2*S*(+)cyclohexanediamine and 1*R*,2*R*(−)diphenyldiaminoethane, 1-hexene, 1-octene, *trans*-4-octene, indene and Eu(hfc)$_3$ (Aldrich), were used as received. *S*(+)1,2-diaminopropane was resolved from racemic mixture by literature procedure [33].

2.1. Synthesis of the ligands

The ligands PROS, DPHS and CyLS were synthesized by the reported procedure [32] while for the synthesis of PROH, DPHH and CyLH a solution of appropriate chiral diamine, (0.112 mol) in chloroform was stirred with the solution of 3-acetyl-4-hydroxy-6-methyl-2-pyrone (0.112 mol) at room temperature for 6–8 h (TLC checked). The resulting solution was filtered, concentrated on rotaevaporator to yield the desired ligands. The ligands were recrystallized from CH_2Cl_2.

2.1.1. 1′S-(+)1′N{(4-hydroxy-6-methyl-2-pyrone)3-acetyledene}1′,2′ propylenediamine (PROH)

Yield 66%. ^{1}H NMR ($CDCl_3$): δ, 1.18 (d, 3H, CH_3, H'_3, $J = 6.83$), 2.02(s, 3H, CH_3, H_7), 2.29(d, 2H, CH_2, H'_2, $J = 7.08$), 2.57(s, 3H, CH_3, H_9), 3.31 (m, 1H, CH, H'_1), 5.59(s, 1H, CH, H_5), 14.10(bs, 2H, NH_2), 14.53(bs, 1H, OH keto/enol). Calcd. for C_{11} H_{16} N_2 O_3: C, 58.90; H, 7.10; N, 12.50. Found C, 58.89; H, 7.12; N, 12.45. IR (KBr) cm^{-1}: 1630 ν(H–C=N), 3320 ν(O–H).

2.1.2. 1′R,2′R-(−)1′N {(4-hydroxy-6-methyl-2-pyrone)3-acetyledene}1′,2′diphenylethylene diamine (DPHH)

Yield 60%. ^{1}H NMR ($CDCl_3$): δ, 2.10(s, 3H, CH_3, H_7), 2.72(s, 3H, CH_3, H_9), 4.42(bd, 1H, CH, H'_1), 4.92(bd, 1H, CH, H'_2), 5.75(s, 1H, CH, H_5), 7.30(bs, 10H, aromatic phenyl), 14.98–15.06(bm, 3H, NH_2 and OH ketoenol). Calcd. for C_{22} H_{22} N_2 O_3: C, 72.90; H, 6.12; N, 7.73. Found C, 72.87; H, 6.08; N,7.67. IR (KBr) cm^{-1}: 1630 ν(H–C=N), 3320 ν(O–H).

2.1.3. 1′S,2′S-(+) 1′N {(4-hydroxy-6-methyl-2-pyrone)3-acetyledene}1′,2′cyclohexane diamine (DHCH)

Yield 65%. ^{1}H NMR ($CDCl_3$): δ, 1.46–1.71(m, 8H, H'_3 to H'_6), 2.12 (s, 3H, CH_3, H_7), 2.69(s, 3H, CH_3, H_9), 3.38–3.82(m, 2H, H'_1–H'_2), 5.67(s, 1H, CH, H_5), 14.39(bs, 2H, NH_2), 14.78(bs, 1H, OH keto/enol). Calcd. for C_{14} H_{20} N_2 O_3: C, 63.60; H, 7.63; N, 10.60. Found C, 63.58; H, 7.59; N, 10.57. IR (KBr) cm^{-1}: 1630 ν(H–C=N), 3320 ν(O–H).

2.2. Preparation of symmetrical and non-symmetrical Ni(II) chiral Schiff base complexes ***1–6***

Appropriate amount of the chiral Schiff bases (0.001 mol) dissolved in ethanol was refluxed

with $Ni(CH_3COO)_2$ (0.001 mol) in presence of tri-ethylamine tetrahydrate (0.001 mol) for 10–12 h. The progress of the reaction was checked by TLC. The solutions were filtered, concentrated on rotaevaporator till dryness. The resulting complexes were washed with ethanol and dried in vacuum. The yield of all the complexes were in the range 60–65%.

2.2.1. S-(+) PROS Ni(II) ***1***

Calcd. for $C_{19}H_{20}N_2O_6$ Ni: C, 53.01; H, 4.69; N, 6.51. Found: C, 53.03; H, 4.66; N, 6.50. ^{1}H NMR ($CDCl_3$), δ, 1.55(d, 3H, CH_3, H'_3, $J = 8.67$), 2.10(s, 6H, CH_3, H_7), 2.50(s, 6H, CH_3, H_9), 3.22(d, 2H, CH_2, H'_2, $J = 7.84$), 3.69(m, 1H, CH, H'_1), 5.86(s, 2H, CH, H_5). IR (KBr) cm^{-1}: 1580 ν(H–C=N), 1265 ν(C–O). UV-Vis. (nm) (MeOH) $\lambda_{max}(\varepsilon)$312(2499), 366(1172); CD $\lambda_{max}(\Delta\varepsilon)$ (MeOH) 325(+6.2), 350(+4), 520(−2.4); $[\alpha]_D^t = +125.3$. Configuration (S); Λ_M (MeOH) 6 mho cm^{-1} mol^{-1}; ΔEpa = 0.74 V.

2.2.2. R,R-(−) DPHS Ni(II) ***2***

Calcd. for $C_{30}H_{26}N_2O_6Ni$: C, 63.37; H, 4.61; N, 4.93. Found: C, 63.39; H, 4.58; N, 4.90. ^{1}H NMR ($CDCl_3$), δ, 2.10(s, 6H, CH_3, H_7), 2.15(s, 6H, CH_3, H_9), 4.60(s, 2H, CH, H'_1 and H'_2), 5.92(s, 2H, CH, H_5), 7.48–7.55(m, 10H, aromatic phenyl). IR(KBr) cm^{-1}: 1585 ν(H–C=N), 1265 ν(C–O). UV-Vis. (nm) (MeOH) $\lambda_{max}(\varepsilon)$383(1781), 440(430), 530(107); CD $\lambda_{max}(\Delta\varepsilon)$ (MeOH) 300(+3.7), 360(+2.6), 520(−1.4) $[\alpha]_D^t = -54.47$. Configuration (R); Λ_M (MeOH) 4 mho cm^{-1} mol^{-1}; ΔEpa = 0.80 V.

2.2.3. S,S-(+) Cy LS Ni(II) ***3***

Calcd. for $C_{22}H_{24}N_2O_6Ni$: C, 56.16; H, 5.15; N, 5.96. Found: C, 56.13; H, 5.13; N, 5.93. ^{1}H NMR ($CDCl_3$), δ, 1.64–1.82(m, 8H, $(CH_2)_4$, H'_3 to H'_6), 2.29(s, 6H, CH_3, H_7), 2.84(s, 6H, CH_3, H_9), 3.83(bs, 2H, H'_1 and H'_2), 5.61(s, 2H, CH, H_5). IR (KBr) cm^{-1}: 1585 ν(H–C=N), 1260 ν(C–O). UV-Vis. (nm) (MeOH) λ_{max} (ε) 321(2499), 369(558); CD λ_{max} ($\Delta\varepsilon$) (MeOH) 305(+0.6), 350(−0.8), 530(+0.4) $[\alpha]_D^t = +27.60$. Configuration (S); Λ_M (MeOH) 3 mho cm^{-1} mol^{-1}; ΔEpa = 0.76 V.

2.2.4. S-(+) PROH Ni(II) ***4***

Calcd. for $C_{13}H_{20}N_2O_6Ni$: C, 43.57; H, 5.63; N, 7.82. Found: C, 43.53; H, 5.61; N, 7.80. ^{1}H NMR ($CDCl_3$), δ, 1.28(d, 3H, CH_3, H'_3, $J = 7.9$), 2.08(s, 3H, CH_3, H_7), 2.83(s, 3H, CH_3, H_9), 3.63(d, 2H, CH_2, H'_2, $J = 7.11$), 4.80–5.05(bs, 2H, coordinated H_2O), 5.92(m, 1H, CH, H'_1), 16.82(bs, 2H, NH_2). IR (KBr) cm^{-1}: 1590 ν(H–C=N), 1260 ν(C–O), 3300 ν(O–H), 1100, 1170 δ(O–H). UV-Vis. (nm) (MeOH) $\lambda_{max}(\varepsilon)$ 310(2499), 363(715); CD $\lambda_{max}(\Delta\varepsilon)$ (MeOH) 300(+1.5), 350(+1.6), 520(−1.1) $[\alpha]_D^t = +46.1$. Configuration (S); Λ_M (MeOH) 95 mho cm^{-1} mol^{-1}, ΔEpa = 0.72 V.

2.2.5. R,R-(−) DPHH Ni(II) ***5***

Calcd. for $C_{24}H_{26}N_2O_6$ Ni: C, 58.05; H, 5.28; N, 5.65. Found: C, 58.02; H, 5.26; N, 5.60. ^{1}H NMR ($CDCl_3$), δ, 2.13(s, 3H, CH_3, H_7), 3.52(s, 3H, CH_3, H_9), 4.59(s, 1H, CH, H_5), 4.90–5.18(bs, 2H, coordinated H_2O), 5.77 and 5.92(two bs, 2H, CH, H'_1 and H'_2), 7.34(bs, 10H, aromatic phenyl), 15.05(bs, 2H, NH_2). IR (KBr) cm^{-1}: 1585 ν(H–C=N), 1260 ν(C–O), 3300 ν(O–H), 1100, 1170 δ(O–H). UV-Vis. (nm) (MeOH) $\lambda_{max}(\varepsilon)$ 333(2499), 372(570); CD $\lambda_{max}(\Delta\varepsilon)$ (MeOH) 310(+0.3), 355(−0.6), 530(+0.4) $[\alpha]_D^t = -19.04$. Configuration (R); Λ_M (MeOH) 90 mho cm^{-1} mol^{-1}; ΔEpa = 0.77 V.

2.2.6. S,S-(+) CyLH Ni(II) ***6***

Calcd. for $C_{16}H_{24}N_2O_6Ni$: C, 48.23; H, 6.08; N, 7.03. Found: C, 48.20; H, 6.04; N, 7.02. ^{1}H NMR ($CDCl_3$), δ, 1.32(bs, 8H, H'_3 to H'_6), 2.12(s, 3H, CH_3, H_7), 3.06(s, 3H, CH_3, H_9), 4.80–5.10(bs, 2H, coordinated H_2O), 5.31(S, 1H, CH, H_5), 5.69 and 5.82(two bs, 2H, CH, H'_1 and H'_2), 16.39(bs, 2H, NH_2). IR (KBr) cm^{-1}: 1585 ν(H–C=N), 1260 ν(C–O), 3300 ν(O–H), 1100, 1170 δ(O–H). UV-Vis. (nm) (MeOH) $\lambda_{max}(\varepsilon)$ 310(2499), 372(570); CD

$\lambda_{max}(\Delta\varepsilon)$ (MeOH) 310(−1.7), 335(−2.5), 500(−0.4) $[\alpha]_D^t = +34.15$. Configuration (S); Λ_M (MeOH) 90 mho cm^{-1} mol^{-1}; ΔEpa = 0.71 V.

2.3. Aerobic enantioselective epoxidation of non-functionalized olefins by the catalyst *1*–*6*

Enantioselective epoxidation of 1-hexene, 1-octene, *trans*-4-octene and indene by the catalyst entry **1**–**6** with molecular oxygen was carried out by the following procedure: The chiral catalyst (0.006 mmol), 1-hexene, 1-octene, *trans*-4-octene and indene (2 mmol), dissolved in 10 ml dichloromethane was stirred in presence of molecular oxygen with sacrificial reductant isobutyraldehyde (6 mmol) at 4°C in dark. After each interval of 30 min an aliquot was taken from the reaction mixture and analyzed by GLC. After the reaction was completed the solvent was removed and the product epoxide was separated from the reaction mixture using short column of basic alumina in hexane:dichloromethane (9:1) as eluent. Evaluation of enantiomeric excess was done by chiraldex BPH. Besides, the product was taken in $CDCl_3$ for ^1H NMR using chiral shift reagent $Eu(hfc)_3$ for further evaluation of enantiomeric excess.

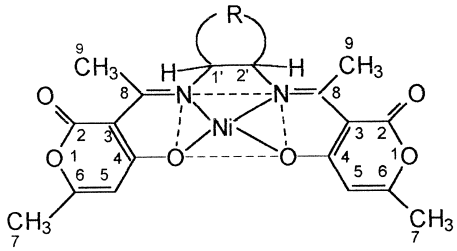
3. Methods

Microanalysis of the complexes was done on a Carlo Erba Analyzer Model 1106. Molar conductance was measured at room temperature on a Digisun electronic conductivity bridge DI-909. The IR spectra were recorded on Carl Zeiss Specord M-80 spectrophotometer in KBr/nujol mull. Electronic spectra were recorded on Shimadzu UV/Visible recording spectrophotometer Model 160. ^1H NMR 99.55 MHz were done on Jeol FX-100 NMR spectrometer in $CDCl_3$. Cyclic voltammetry, differential pulse voltammogram were recorded with a Princeton Applied Research (PAR) instrument using tetra butyl ammonium perchlorate as supporting electrolyte in dichloromethane. The optical rotation of the complexes in methanol was measured by polarimeter Atago, Japan. The CD spectra were recorded in methanol by Jasco Machine Model J-20 Japan. The purity of the solvent, substrate and analysis of the product was determined by GLC using Shimadzu GC 14B coupled with PC using 2 M long, 3 mm I.D., 4 mm O.D. stainless steel column packed with SE30, 5% mesh size 60 to 80 with FID detector. Column temperature programmed between 70 to 150°C and injection temperature 200°C with nitrogen carrier gas flow 30 ml/min. Synthetic standards of the product were used to determine yields by comparison of peak height and area. The optical yield of the product was determined by chiraldex BPH type column.

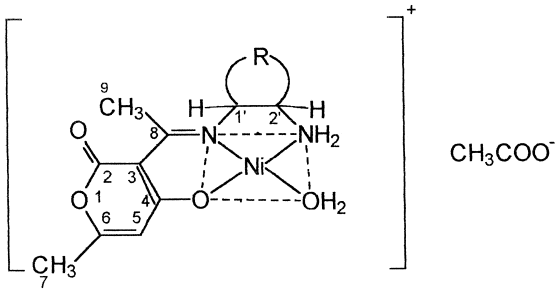
4. Results and discussion

The symmetrical and non-symmetrical Ni(II) square planar complexes **1**–**6** were isolated as solids using symmetrical and non-symmetrical chiral Schiff bases derived from 1*S*,2*S*(+)cyclohexanediamine, *S*(+)1,2-diaminopropane and 1*R*,2*R*(−)diphenyldiamino ethane with 3-acetyl-4-hydroxy-6-methyl-2-pyrone Fig. 1. Millimolar solution of the complexes **1**–**3** in methanol shows the non electrolytic nature of the complexes while the complexes **4**–**6** are 1:1 electrolyte.

A strong band near 1580–1585 cm^{-1} in all the complexes is due to coordinated azomethine nitrogen and this band lie at higher wave number in all the ligands. A strong band at 3320 cm^{-1} in all chiral Schiff bases is assigned to ν(O–H). After complexation with metal ions this band disappeared showing the replacement of hydrogen by metal atom. In such cases the ν(C–O) at 1280 cm^{-1} in all chiral Schiff bases show a red shift in the frequency of the complexes. In the case of the complexes **4**–**6** two bands at 1100–1170 cm^{-1} along with a broad band at 3300 cm^{-1} appear due to coordinated



1- 3



4- 6

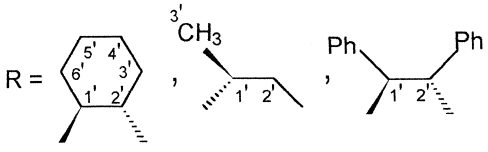


Fig. 1. Representative structures of the catalysts.

water [34] and a broad band lie at 3280 cm^{-1} is due to coordinated amino nitrogen.

The electronic spectra of the complexes in methanol show high intensity CT bands which are usually ligand centered and lie near 310 ($\varepsilon = 2499$) and 333 ($\varepsilon = 2499$) while the MLCT bands fall between 363 ($\varepsilon = 715$) and 440 ($\varepsilon = 430$) nm. In some complexes band near 530 ($\varepsilon = 170$) are assigned to d–d bands.

The CD spectra of the complexes recorded in methanol show the bands near 520(−2.4), 530 (+0.5) of opposite sign and assigned to d–d bands and spin forbidden ligand bands. The charge transfer region of the spectra shows d → π^* band between 350(+1.6) to 360(+2.6) nm and the high intensity $\pi \rightarrow \pi^*$ transition are seen near 300(+3.7) and 310(−1.7) nm. Two representative CD spectra (A) and (B) for the complexes *S*-(+) PROS Ni(II) and *S,S*-(+) CyLH Ni(II) respectively are shown in Fig. 2. Here although both the complexes have the same absolute configuration but the complex (A) is stereospecifically coordinated to nickel so that the gauche chelate ring is in λ form with a little contribution of δ form while the complex (B) is exclusively in δ form. This preferred conformational and configurational relationship is already reported earlier [27–32].

The cyclic voltammetry of the complexes **1**–**6** in dichloromethane with 0.1 M tetra butyl ammonium perchlorate as supporting electrolyte shows reversible oxidation in the range 0.71 to 0.80 V vs. SCE. These values are in consonance to those reported earlier [35,36].

4.1. Aerobic enantioselective epoxidation

The catalyst entry **1**–**6** were screened for aerobic enantioselective epoxidation of prochiral non functionalized olefins viz. 1-hexene, 1-octene, *trans*-4-octene and indene using molecular oxygen in presence of isobutyraldehyde as sacrificial reductant, by GLC to give corresponding epoxide and the carboxylic acid as coproduct. Data regarding enantioselectivity is given in Tables 1 and 2. The reductant isobutyraldehyde behaves as an effective reductant to accept one oxygen atom of molecular oxygen with concomitant co-oxidation of isobutyraldehyde to carboxylic acid in the present reaction system Scheme 1.

The catalyst **1**, **3** and **4**, **6** gave excellent conversion with 1-octene and *trans*-4-octene (75–95%) while with 1-hexene very good conversions were obtained with the catalysts **2** and **3** (85–90%). Moderate to low conversion was obtained in case of indene with these catalyst **1**–**6** (58–66%) Fig. 3.

The enantiomeric excess for the resulting epoxide separated by short column of basic

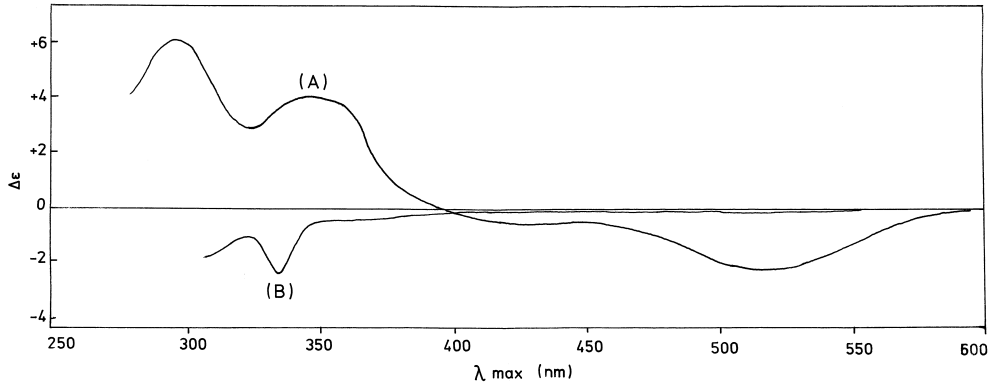


Fig. 2. CD spectra of the complexes (A) *S*-(+) PROS Ni(II) and (B) *S,S*-(+) CyLHNi(II) recorded in methanol.

alumina was evaluated by chiral capillary column (Chiraldex BPH) and also by ^{1}H NMR using chiral shift reagent Eu(hfc)$_3$.

Furthermore, it is interesting to point out that for all the three symmetric catalyst the maximum enantioinduction was in the case of indene Fig. 4, though the chemical conversions were low in comparison to the long chain olefins. The bulkiness of the substrate seems to be the main factor behind this. This factor seems to be more pronounced for catalysts **1**–**3** where ee's obtained is higher as compared with catalysts **4**–**6**. Structure simulation of intermediates involved in epoxidation step with the representative catalysts **3** and **6** Fig. 5a, a′ and b, b′ show a cavity like reaction site for catalyst **3** hence, restricted rotation, thereby, less chance for racemization, while with catalyst **6** there is a fair possibility for the free rotation at intermediate level, hence, more chances of racemization. This, in fact is reflected in our experimental results. In all the cases on employment of *S* form of the catalyst resulted in *R* form of the product as a dominant enantiomer. With similar

Table 1
Data for aerobic enantioselective epoxidation of prochiral non functionalized olefins catalyzed by Symmetrical chiral Ni(II) complexes[a]

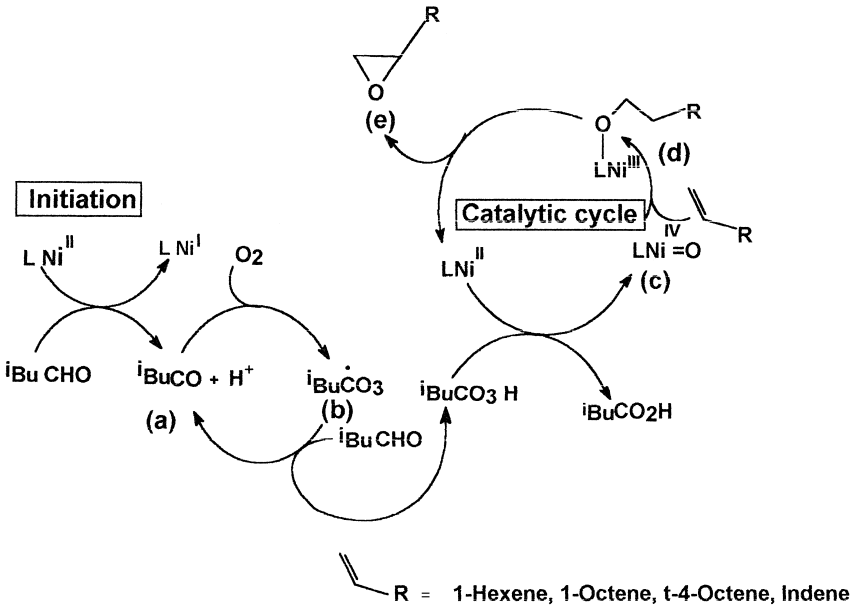
Catalyst	Substrate	Time (h)	% conversion[b]	ee[c]	Configuration
1	1-octene	12	75	17	*R*
	1-hexene	12	68	22	*R*
	t-4 octene	12	90	20	*R*
	indene	12	60	25	*R*
2	1-octene	12	55	17	*S*
	1-hexene	12	90	22	*S*
	t-4 octene	12	95	14	*S*
	indene	12	65	33	*S*
3	1-octene	12	80	30	*R*
	1-hexene	12	85	18	*R*
	t-4 octene	12	75	26	*R*
	indene	12	66	41	*R*

[a]Reaction conditions: Substrate (2 mmol), catalyst (0.006 mmol), isobutyraldehyde (6 mmol) solvent 10.0 ml dichloromethane, 1 atm. O_2 at 4°C.
[b]Determined by GC analysis.
[c]Determined by Chiraldex BPH and by ^{1}H NMR using Eu(hfc)$_3$.

Table 2
Data for aerobic enantioselective epoxidation of prochiral non functionalized olefins catalyzed by non-symmetrical chiral Ni(II) complexes[a]

Catalyst	Substrate	Time (h)	% conversion[b]	ee[c]	Configuration
4	1-octene	12	85	19	*R*
	1-hexene	12	65	20	*R*
	t-4 octene	12	90	18	*R*
	indene	12	58	18	*R*
5	1-octene	12	90	25	*S*
	1-hexene	12	70	23	*S*
	t-4 octene	12	90	20	*S*
	indene	12	60	25	*S*
6	1-octene	12	95	25	*R*
	1-hexene	12	65	20	*R*
	t-4 octene	12	80	21	*R*
	indene	12	65	20	*R*

[a]Reaction conditions: Substrate (2 mmol), catalyst (0.006 mmol), isobutyraldehyde (6 mmol) solvent 5.0 ml dichloromethane, 1 atm. O_2 at 4°C.
[b]Determined by GC analysis.
[c]Determined by Chiraldex BPH and by ^{1}H NMR using Eu(hfc)$_3$.



Scheme 1. Possible mechanism for the catalytic epoxidation reaction.

kind of ligands switching over to Ni from Ru and Mn [29–32] with molecular oxygen from iodosyl benzene resulted in better conversions, however, there was not much improvement in enantioinduction. Although enantioinduction in most of the present generation of catalysts with

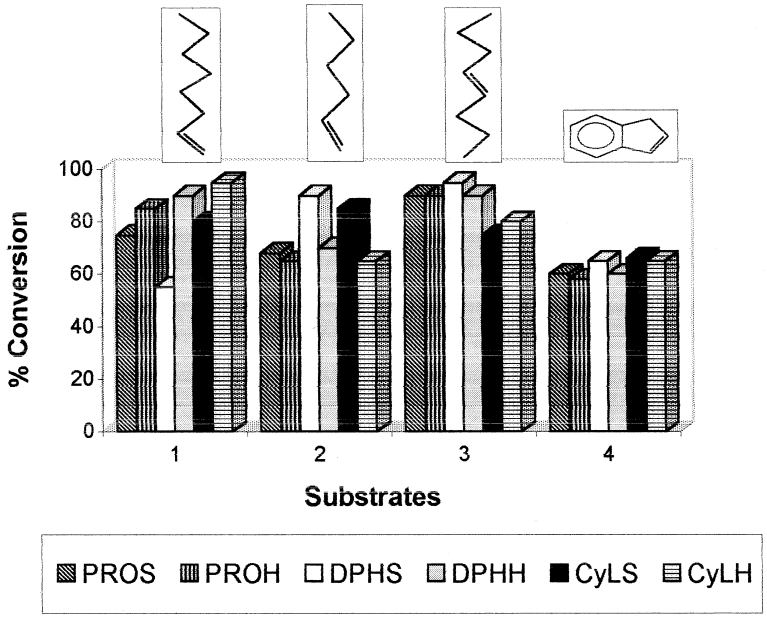


Fig. 3. Bar diagram representing the % conversion of epoxide by the catalyst **1**–**6**.

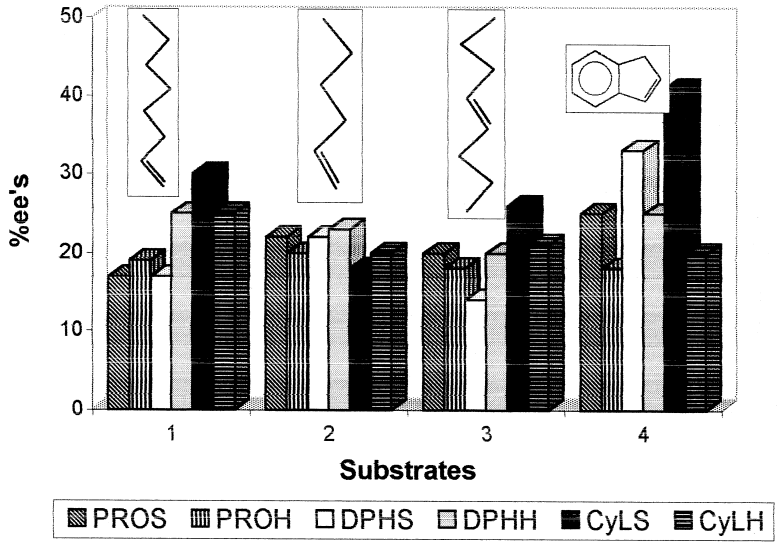


Fig. 4. Bar diagram representing the % ee's of epoxide by the catalyst **1**–**6**.

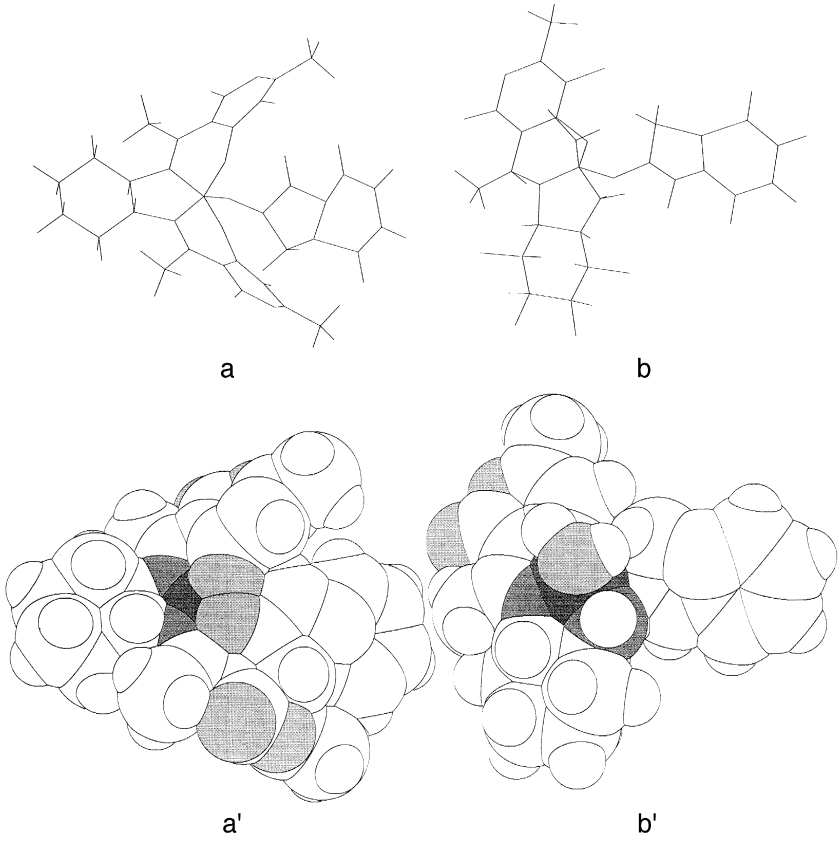


Fig. 5. (a, b) Molecular model of intermediates involved in epoxidation step with the catalysts **3** and **6** while (a′, b′) are their space filled diagrams.

cis substrates is improving by increasing bulkiness of the catalyst, while in *trans* substrates these were found to be poor.

As there is hardly any reaction in absence of catalyst under our reaction conditions the most likely mechanism operated for the metal complex catalyzed oxygenation of non functionalized olefins by molecular oxygen and isobutyraldehyde is shown in Scheme 1. Here the catalyst is assumed to play two distinctive roles. First, the catalyst reacts with isobutyraldehyde to initiate the radical chain process by generating an acyl radical (a) which then reacts with molecular oxygen to give an acylperoxy radical (b). The acyl peroxy radical acts as carrier in a chain mechanism by reacting with another isobutyraldehyde molecule to give a peroxy acid, with concomitant generation of acyl radical. The peroxyacid then react with catalyst to form high valent metal oxo intermediate (c) which on approach of the substrate gave another intermediate (d) to give respective epoxides (e) in a similar fashion analogous to that reported earlier [26].

5. Conclusion

In this paper we have presented the aerobic enantioselective epoxidation of 1-octene, 1-hexene, *trans*-4-octene and indene using Ni(II) symmetrical and non-symmetrical chiral Schiff base complexes in presence of molecular oxygen using isobutyraldehyde as sacrificial reductant. The catalyst **1**, **3** and **4**, **6** gave very good conversion with 1-octene and *trans*-4-octene while catalyst **2** and **3** favors the formation of 1-hexene oxide in good yield. The symmetric catalysts **1**–**3** gave the maximum enantioinduction with indene though the chemical conversions were low in comparison to the long chain olefins. As expected *S* form of the catalyst gave predominantly *R* form of the product. The work in the direction of moderating bulkiness of the ligand in order to achieve optimum conversions and enantioinduction in *trans* and long chain terminal alkenes is in progress.

Acknowledgements

Two of us (R.I.K. and N.H.K.) are thankful for financial assistance from CSIR Young Scientist project, DST Young Scientist project and Third World Academy of Sciences.

References

[1] A.N. Collins, G.N. Sheldrake, J. Crosby (Eds.), Chirality in Industry, The Commercial Manufacture and applications of optically Active Compounds, John Wiley, 1995.
[2] C. Brown, Chirality in Drug Design and Synthesis, Academic Press, New York, 1990.
[3] I.W. Wainer (Ed.), Drug Stereochemistry, vol. 11, Marcel Dekker, New York, 1993.
[4] I. Ojima, Catalytic Asymmetric Synthsis, VCH, New York, 1993.
[5] T. Katsuki, K.B. Sharpless, J. Am. Chem. Soc. 113 (1980) 5974.
[6] M.G. Finn, K.B. Sharpless, J. Am. Chem. Soc. 113 (1991) 106–113.
[7] S. Chang, J.M. Galvin, E.N. Jacobsen, J. Am. Chem. Soc. 59 (1994) 6937.
[8] W. Zhang, J.L. Loebach, S.R. Wilson, E.N. Jacobsen, J. Am. Chem. Soc. 112 (1990) 2801.
[9] J.F. Larrow, E.N. Jacobsen, Y. Gao, Y. Hong, X. Nie, C.M. Zepp, J. Org. Chem. 59 (1994) 1939.
[10] R. Irie, Y. Ito, T. Katsuki, Synlett 2 (1991) 265.
[11] L. Deng, E.N. Jacobsen, J. Org. Chem. 57 (1992) 4320.
[12] E.N. Jacobsen, L. Deng, Y. Furukawa, L.E. Martinez, Tetrahedron 50 (1994) 4323.
[13] W. Zhang, E.N. Jacobsen, Tetrahedron Lett. 32 (1991) 1711.
[14] E.N. Jacobsen, W. Zhang, A.R. Muci, J.R. Ecker, L. Deng, J. Am. Chem. Soc. 113 (1991) 7063.
[15] R. Irie, K. Noda, Y. Ito, N. Matsumoto, T. Katsuki, Tetrahedron Asymm. 2 (1991) 481.
[16] T. Hamada, K. Daikai, R. Irie, T. Katsuki, Tetrahedron Asymm. 6 (1995) 2441.
[17] W. Zhang, E.N. Jacobsen, J. Org. Chem. 56 (1991) 2296.
[18] R. Irie, N. Hosoya, T. Katsuki, Synlett. (1994) 255.
[19] P. Pietikainen, Tetrahedron Lett. 36 (1995) 319.
[20] K. Imigawa, T. Nagata, T. Yamada, T. Mukaiyama, Chem. Lett. (1994) 527.
[21] T. Mukiyama, T. Takai, T. Yamada, O. Rhode, Chem. Lett. (1990) 1661.
[22] T. Yamada, T. Takai, O. Rhode, T. Mukaiyama, Bull. Chem. Soc. Jpn. 64 (1991) 2109.
[23] T. Takai, E. Hata, K. Yoruzu, T. Mukaiyama, Chem Lett. (1992) 2109.
[24] T. Takai, E. Hata, K. Yoruza, T. Mukaiyama, Chem. Lett. (1992) 2077.

[25] Y. Matsuda, H. Koshima, K. Nakamaru, Y. Murakami, Chem. Lett. (1988) 625.
[26] T. Takai, T. Yamada, T. Mukaiyama, Chem. Lett. (1990) 1657.
[27] R.I. Kureshy, N.H. Khan, S.H.R. Abdi, K.N. Bhatt, Tetrahedron Asymm. 4 (1993) 1693.
[28] R.I. Kureshy, N.H. Khan, S.H.R. Abdi, J. Mol. Catal. 96 (1996) 117.
[29] R.I. Kureshy, N.H. Khan, S.H.R. Abdi, A.K. Bhatt, J. Mol. Catal. 110 (1996) 33.
[30] R.I. Kureshy, N.H. Khan, S.H.R. Abdi, P. Iyer, A.K. Bhatt, J. Mol. Catal. 120 (1997) 101.
[31] R.I. Kureshy, N.H. Khan, S.H.R. Abdi, A.K. Bhatt, P. Iyer, J. Mol. Catal. 121 (1997) 25.
[32] R.I. Kureshy, N.H. Khan, S.H.R. Abdi, P. Iyer, J. Mol. Catal. 124 (1997) 91.
[33] F.P. Dwyer, F.L. Garvan, A. Shulman, J. Am. Chem. Soc. 81 (1959) 291.
[34] M.A. Bangres, M. Gonzales, M.E. Peres, R.J. Rauno, Polyhedron 5 (1986) 1371.
[35] P.J. Chmielewski, L.L. Grazynski, Inorg. Chem. 36 (1997) 840.
[36] G.D. Santis, L. Fabbrizzi, D. Iacopino, P. Pallavicini, A. Perotti, A. Poggi, Inorg. Chem. 36 (1997) 827.