ELSEVIER

Journal of Molecular Catalysis A: Chemical 124 (1997) 91–97

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Chiral Ru(III) metal complex-catalyzed aerobic enantioselective epoxidation of styrene derivatives with co-oxidation of aldehyde

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

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

Received 30 December 1996; accepted 10 March 1997

Abstract

Ru(III) chiral Schiff base complexes **1–3** derived from dehydroacetic acid with 1*S*,2*S*-(+) diaminocyclohexane, 1*R*,2*R*-(−)1,2 diphenyl ethylenediamine and *S*-(+)1,2 diaminopropane have been prepared. The characterization of the complexes was done by microanalysis, magnetic moment, IR-, UV/Vis-, CD spectral studies, optical rotation, conductance measurements and cyclic voltammetry. The enantioselective epoxidation of styrene and substituted styrenes viz., 4-chloro-, 4-nitro- and 4-methyl styrene was achieved by the combined use of molecular oxygen and sacrificial reductant isobutyraldehyde catalyzed by the above synthesized Ru(III) chiral Schiff base complexes. Good yields of the desired epoxides were obtained with styrene and 4-chlorostyrene by GLC. Enantiomeric excess of the epoxide was evaluated by ^{1}H-NMR using chiral shift reagent Eu(hfc)$_3$ and by chiral capillary column. The extent of enantioselectivity is shown on Hammet plots.

Keywords: Chiral; Enantioselective epoxidation; Styrene; Ruthenium; Molecular oxygen

1. Introduction

The designing of an oxidative metal catalyst bearing stereogenic center in the ligand moiety is one of the most challenging topics for the enantioselective epoxidation of olefins [1–4] because the epoxides formed are very useful synthetic intermediates for complex chiral bioactive natural products or may be used in the production of epoxy resins. Much efforts have been made for asymmetric epoxidation of allylic alcohols by titanium(IV) alkoxide in the presence of optically active tartrate, by Sharpless and coworkers [5,6]. Recently Jacobsen and Katsuki independently reported the enantioselective epoxidation of unfunctionalized alkenes catalyzed by chiral Mn(III) salen complexes [7–15] with terminal oxidants such as iodosyl benzene and NaOCl, while several efficient methods have been investigated on the utilization of molecular oxygen which is one of the most available [16] and safe oxidants because of the abundance, cleanness and easier to handle in asymmetric epoxidation of non-functionalized alkenes [17–23] catalyzed by metal complexes such as Co(II), Ni(II), Fe(III), V(IV), Pr(III), Mn(II) and Mn(III) in coexistence of a suitable reductant such as primary/secondary alcohol [16,24], aldehyde

* Corresponding author. Fax: +91-278-426970; e-mail: general@csesmcri.ren.nic.in.

1381-1169/97/$17.00
PII S1381-1169(97)00076-9

[18] or cyclic ketones [25] which can accept one oxygen atom from molecular oxygen to perform the reaction.

In continuation of our earlier work on enantioselective epoxidation of non functionalized olefins using Co(II), Ru(II), Ru(III) and Mn(III) chiral Schiff base complexes [26–30] and to explore a mechanistic study of an efficient catalytic system we report here an aerobic enantioselective epoxidation of styrene and substituted styrenes using molecular oxygen with isobutyraldehyde as reductant catalyzed by Ru(III) chiral Schiff base complexes derived from dehydroacetic acid with 1*S*,2*S*-(+)1,2 diaminocyclohexane, 1*R*,2*R*-(−)1,2 diphenyl ethylenediamine and *S*-(+)1,2 diaminopropane with and without pyridine N-oxide as axial base.

2. Experimental

$RuCl_3 \cdot 3H_2O$ (Johnson and Mathey), dehydroacetic acid, 1*S*,2*S*-(+)1,2 cyclohexane diamine, 1*R*,2*R*-(−)1,2 diphenyl ethylenediamine, styrene, 4-chloro-, 4-nitro-, 4-methyl styrene and $Eu(hfc)_3$ (Aldrich) were used as such. The metal complex $K_2[RuCl_5(H_2O)]$ was prepared by the known method [31]. *S*-(+)1,2 diaminopropane was resolved from dl form by reported procedure [32].

2.1. Synthesis of chiral schiff bases

Methanolic solution of 1*S*,2*S*-(+)1,2 cyclohexane diamine, 1*R*,2*R*-(−)1,2 diphenyl ethylenediamine, *S*-(+)1,2 diamino propane (0.01 mol) was added to the hot methanolic solution of dehydroacetic acid (0.02 mol) and the resulting solution was refluxed for 6 to 8 h (TLC checked). After the completion of reaction the solution was concentrated on rotaevaporator and the desired ligands were precipitated by 40–60 petroleum ether.

The chiral Schiff bases were characterized by microanalysis, IR-, ^{1}H- and $^{13}C\{^1H\}$-NMR spectroscopy.

2.1.1. 1*S*,2*S*-(+) *N*,*N*′ *bis* {(4-hydroxy-6-methyl-2-pyrone)3-acetyledene} 1′,2′-cyclohexanediamine (DHCH)

Yield 60%, mp d. 220°C. ^{1}H-NMR ($CDCl_3$): d, 1.4–1.9 (m, 8H, $(CH_2)_4$ H'_3 to H'_6), 2.12 (s, 6H, CH_3, H_7), 2.63 (s, 6H, CH_3, H_9), 3.38 (m, 2H, H'_1 H'_2), 5.66 (s, 2H, H_5), 14.77 (bs, 2H, OH keto/enol). $^{13}C\{^1H\}$-NMR (CH_2Cl_2): δ, 18.43, 23.55, 33.53 (C'_3–C'_6), 58.20 (C'_1, C'_2), 73.5 (C_9), 96.82 (C_7), 161.4 (C_8), 162.06 (C_4), 176.70 (C_2), 105.2 (C_3), 101.5 (C_5), 107.5 (C_6). Calcd. for $C_{22}H_{26}N_2O_6$: C, 63.75; H, 6.3; N, 6.7. Found: C, 63.70; H, 6.0; N, 6.5. IR (KBr): ν(H–C=N) 1620 cm^{-1}.

2.1.2. 1′*S*-(+) *N*,*N*′ *bis* {(4-hydroxy-6-methyl-2-pyrone)3-acetyledene} 1′2′, diaminopropane (DHPR)

Yield 63%, mp 112°C. ^{1}H-NMR ($CDCl_3$): δ, 1.42 (3H, d, CH_3, 3′H), 2.02 (s, 6H, CH_3, H_7), 2.80 (s, 6H, CH_3, H_9), 2.24 (d, 2H, CH_2, 2′H), 2.53 (m, 1H, CH, 1′H), 5.60 (s, 2H, 5H), 14.62 (bs, 2H, OH keto/enol). $^{13}C\{^1H\}$NMR (CH_2Cl_2): δ, 13.6 (C'_3), 24.8 (C'_2), 29.02 (C'_1), 73.2 (C_9), 96.70 (C_7), 161.0 (C_8), 162.62 (C_4), 176.65 (C_2), 104.8 (C_3), 101.2 (C_5), 107.4 (C_6). Calcd. for $C_{19}H_{22}N_2O_6$: C, 60.96; H, 5.92; N, 7.48. Found: C, 60.82; H, 5.88; N, 7.42. IR (KBr): ν(H–C=N) 1630 cm^{-1}.

2.1.3. 1′*R*,2′*R*-(−) *N*,*N*′ *bis* {(4-hydroxy-6-methyl-2-pyrone)3-acetyledene} 1′2′, diamino diphenyl ethylene (DHPD)

Yield 65%, mp 205°C. ^{1}H-NMR ($CDCl_3$): δ, 2.10 (s, 6H, CH_3, H_7), 4.58 (s, 2H, H'_1), 2.84 (s, 6H, CH_3, H_9), 5.58 (s, 2H, 5H), 7.28–7.54 (m, aromatic phenyl), 15.28 (bs, 2H, OH keto/enol), $^{13}C\{^1H\}$ (CH_2Cl_2): δ, 30.42 (C'_1 and C'_2), 72.8 (C_9), 96.45 (C_7), 118–126 (phenyl, 4 lines), 160.6 (C_8), 162.20 (C_4), 175.82 (C_2), 106.4 (C_3), 101.8 (C_5), 108.1 (C_6). Calcd. for $C_{30}H_{28}N_2O_6$: C,70.30; H, 5.50; N, 5.46. Found: C, 70.26; H, 5.47; N, 5.44. IR (KBr): ν(H–C=N) 1630 cm^{-1}.

2.2. Preparation of Ru(III) chiral schiff base complexes 1–3

Ethanolic solution of the chiral Schiff bases (0.001 mol) was allowed to reflux in inert atmosphere with $K_2[RuCl_5(H_2O)]$ (0.001 mol) for 8 to 10 h. The completion of reaction was checked on TLC. The resulting solution was filtered and concentrated on rota evaporator. The residue was redissolved in dried dichloromethane to remove KCl. The filtered solution was again concentrated till dryness. Recrystallization of the complexes was done in acetonitrile. The overall yield for all the complexes lies in the range 58–65%.

The analytical data for the complexes is given below:

2.2.1. S,S-(+) DHCH Ru(III) 1

Calcd. for $C_{22}H_{26}N_2O_7ClRu$: C, 46.60; H, 4.62; N, 4.94. Found: C, 46.52; H, 4.60; N, 4.91. IR (KBr) cm^{-1} 1585 ν(H–C=N), 3400 ν(OH), 1100, 1170 δ(OH), UV/Vis nm MeOH $\lambda_{max}(\varepsilon)$, 232(30625), 308(36650), 486(1325); CD λ_{max} $(\Delta\varepsilon)$ (MeOH) 340 (+1.3), 400 (−0.8), 550(−0.4); $[\alpha]_t^D = +161.28$; Configuration (*S*); Λ_M (MeOH), 5 mho cm^{-1} mol^{-1}: μ_{eff} (BM) 1.99; $\Delta E_{pc} = -0.52$ V.

2.2.2. S-(+) DHPR Ru(III) 2

Calcd. for $C_{19}H_{22}N_2O_7ClRu$: C, 43.31; H, 4.20; N, 5.31. Found: C, 43.28; H, 4.18; N, 5.29. IR (KBr) cm^{-1} 1580ν (H–C=N), 3400 ν(OH), 1100, 1170 δ(OH), UV/Vis. nm (MeOH) $\lambda_{max}(\varepsilon)$, 224(20750), 309(21100) 420(2025); CD λ_{max} $(\Delta\varepsilon)$ (MeOH) 330(+0.8), 380(+0.7), 520(−0.3); $[\alpha]_t^D = +172.44$; Configuration (*S*); Λ_M (MeOH) 4 mho cm^{-1} mol^{-1}: μ_{eff} (BM) 2.02; $\Delta E_{pc} = -0.55$ V.

2.2.3. R,R-(−) DHDA Ru(III) 3

Calcd. for $C_{30}H_{28}N_2O_7ClRu$: C, 54.18; H, 4.24; N, 4.21. Found: C, 54.16; H, 4.20; N, 4.19; IR (KBr) cm^{-1} 1575ν (H–C=N), 3400 ν(OH), 1100, 1170 δ(OH), UV/Vis. nm (MeOH) $\lambda_{max}(\varepsilon)$, 220(15600), 306(9250), 524(2250); CD $\lambda_{max}(\Delta\varepsilon)$ (MeOH) 330 (−1.3), 390(−0.5), 510(−0.3); $[\alpha]_t^D = -138.88$ Configuration (*R*); Λ_M (MeOH) 4 mho cm^{-1} mol^{-1}: μ_{eff} (BM) 2.04; $\Delta E_{pc} = -0.50$ V.

3. Epoxidation of styrene and substituted styrenes by catalyst 1–3.

Enantioselective epoxidation of styrene, 4-chloro-, 4-nitro- and 4-methyl styrene by the catalyst **1–3** with molecular oxygen was carried out by the following procedure: The chiral catalyst (0.006 mmol), styrene, 4-chloro-, 4-nitro- and 4-methyl styrene (2 mmol), isobutyraldehyde (2.0 mmol), pyridine N-oxide (0.24 mmol) dissolved in 5 ml dichloromethane was stirred in the presence of molecular oxygen at 4°C in dark. After each interval of 30 min an aliquot was taken from the reaction mixture and analyzed by GLC. The product was isolated by a short silica gel column (60–120 mesh) in hexane:dichloromethane (9:1) as eluent. Evaluation of enantiomeric excess was done by GC on chiraldex GTA capillary column. Besides, the product was taken in $CDCl_3$ for ^{1}H-NMR using chiral shift reagent Eu(hfc)$_3$ for further confirmation of enantiomeric excess.

4. Methods

Microanalysis of the complexes was done in 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 Ziess Specord M-80 spectrophotometer in KBr/nujol mull. Electronic spectra were recorded on Shimadzu UV/Visible recording spectrophotometer Model 160. ^{1}H-NMR 99.55 MHz and $^{13}C\{^1H\}$-NMR 24.99 MHz were done on Jeol FX-100 NMR spectrophotometer in $CDCl_3$ and CH_2Cl_2, respectively. The magnetic moment measurements were done at 298°C by the Gouy method using $Hg[Co(SCN)_4]$ as callibrant and experiment susceptibilities were cor-

rected for diamagnetism. Cyclic voltammetry, a differential pulse voltammogram was recorded with a Princeton applied research (PAR) instrument using tetrabutyl ammonium fluoroborate as supporting electrolyte in acetonitrile. The optical rotation of the complexes in methanol was measured by a polarimeter Atago, Japan. The CD spectra were recorded in methanol by a Jasco Machine Model J-20 Japan. The purity of the solvent, substrate and analysis of the product was determined by GLC using a Shimadzu GC 14B coupled with PC using 2 m long, 3 mm ID, 4 mm OD stainless steel column packed with SE30, 5% mesh size 60 to 80 with FID detector. The column temperature was programmed between 70 and 170°C and the injection temperature 200°C with a nitrogen carrier gas flow of 30 ml/min, synthetic standards of the product were used to determine yields by comparison of the peak height and area. The optical yield of the product was determined by ^{1}H-NMR using Eu(hfc)$_3$ as a chiral shift reagent and by a chiral capillary column.

5. Results and discussion

Ruthenium (III) chiral Schiff base complexes **1–3** were isolated as neutral solids (Fig. 1) with the stoichiometry: RuLX(H_2O), where X = Chloride, L = chiral tetradendate Schiff bases derived from 1*S*,2*S*-(+)1,2 diamino cyclohexane, 1*R*,2*R*-(−)1,2 diphenyl ethylenediamine, *S*-(+)1,2 diamino propane with dehydroacetic acid. The magnetic moments of the complexes lie in the range of 1.99–2.04 B.M. indicating the presence of Ru(III) ions with a spin paired $4d_5$ electronic configuration.

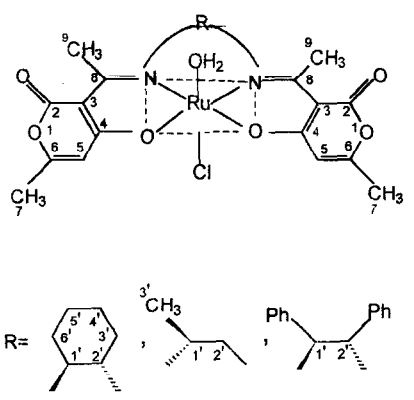


Fig. 1.

In the infrared region a strong band near 1620–1630 cm^{-1} of the chiral Schiff bases, undergoes a modest decrease to lower wave number after complexation inferring the involvement of an azomethine group in coordination to the metal ions. A broad band centered at ca. 3400 cm^{-1} assigned to ν(OH) along with two deformation bands at 1100 and 1170 cm^{-1} due to coordinated water [33].

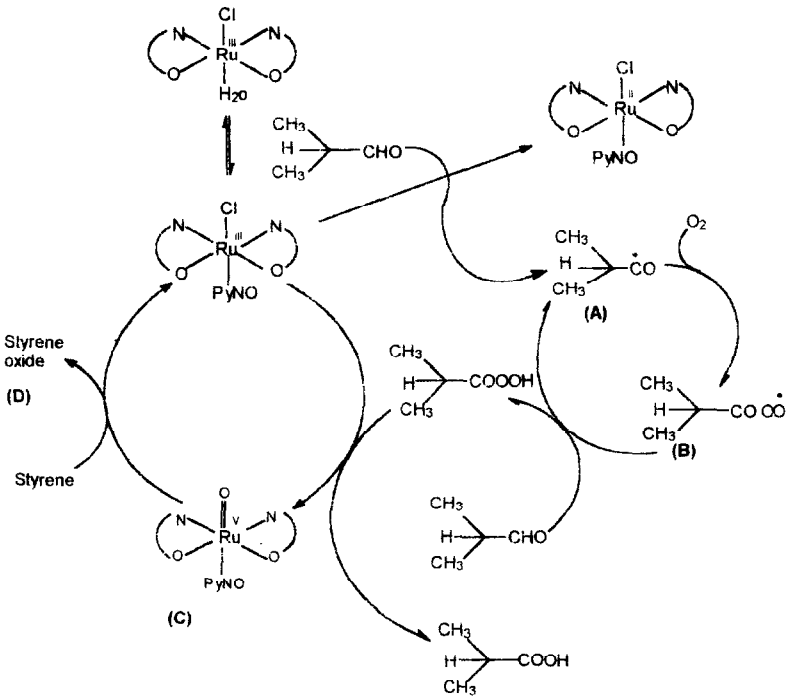
The electronic spectra in methanol show the high intensity charge transfer band in the range 220 (ε = 15 600) and 309 (ε = 21 100) nm while the MLCT bands fall between 420 (ε = 2025) and 486 (ε = 1325) nm. One more band lies near 524 (ε = 225) nm, assigned to forbidden ligand field transition of the Ru(III) metal ion.

CD spectra of these complexes were measured in methanol. Interestingly complex **3** was stereospecifically coordinated to ruthenium so that the gauch ring was almost exclusively in the d form where as the complexes **1** and **2** are located in λ form with a little contribution from the δ form. A similar trend was also reported elsewhere [32,33]. In the ligand field region the CD bands near 550(−0.3) and 510(−0.6) nm are assigned to dd bands and spin forbidden ligand bands while d—π^* bands fall between 400(−0.8) and 390(−0.5) nm. The high intensity π—π^* transition lies between 330 (−1.3) and 340 (+1.3) nm.

The cyclic voltammogram of the complexes in acetonitrile is one electron reduction process and the Ru(III)/Ru(II) couple lie near −0.50 to −0.55 V which is in consonance to those reported earlier [28,29].

6. Aerobic enantioselective epoxidation

Ru (III) chiral Schiff base complexes, entry **1–3**, have been used as catalysts for aerobic



Scheme 1.

enantioselective epoxidation of styrene, 4-chloro-, 4-nitro- and 4-methyl styrene using molecular oxygen in the presence of isobutyraldehyde as sacrificial reductant, with and without pyridine N-oxide as axial base to give their corresponding epoxides. 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.

As there is hardly any reaction in absence of catalyst under our reaction conditions the most likely mechanism operating for the metal complex-catalyzed oxygenation of styrenes by molecular oxygen and isobutyraldehyde is shown in Scheme 1. Here the catalyst is assumed to play two distinctive roles. At first the catalyst reacts with aldehyde 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 acylperoxy radical acts as a carrier in a chain mechanism by reacting with another isobutyraldehyde molecule to give the peroxyacid, thereby generating an-

Table 1
Data for aerobic enantioselective epoxidation of styrene derivatives catalyzed by chiral Ru(III) Schiff base complexes without pyridine N-oxide [a]

Catalyst	Substrate	Time (h)	% conversion [b]	ee [c]	Configuration
1	styrene	24	75	12	*R*
	4-chloro styrene	24	69	14	*R*
	4- nitro styrene	24	48	19	*R*
	4- methyl styrene	24	70	11	*R*
2	styrene	24	72	20	*R*
	4-chloro styrene	24	65	22	*R*
	4- nitro styrene	24	50	25	*R*
	4- methyl styrene	24	65	17	*R*
3	styrene	24	83	20	*S*
	4-chloro styrene	24	78	30	*S*
	4- nitro styrene	24	55	24	*S*
	4- methyl styrene	24	70	15	*S*

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

Table 2
Data for aerobic enantioselective epoxidation of styrene derivatives catalyzed by chiral Ru(III) Schiff base complexes with pyridine N oxide [a]

Catalyst	Substrate	Time (h)	% conversion [b]	ee [c]	Configuration
1	styrene	24	90	18	*R*
	4-chloro styrene	24	92	19	*R*
	4- nitro styrene	24	55	23	*R*
	4- methyl styrene	24	75	16	*R*
2	styrene	24	85	24	*R*
	4-chloro styrene	24	70	26	*R*
	4- nitro styrene	24	55	30	*R*
	4- methyl styrene	24	70	22	*R*
3	styrene	24	95	20	*S*
	4-chloro styrene	24	90	22	*S*
	4- nitro styrene	24	62	24	*S*
	4- methyl styrene	24	80	20	*S*

[a] Reaction conditions: Substrate (2 mmol), catalyst (0.006 mmol), Isobutyraldehyde (2 mmol), pyridine N-oxide (0.24 mmol), solvent 5.0 ml dichloromethane, 1 atm. O_2 at 4°C.
[b] Determined by GC analysis.
[c] Determined by Chiraldex GTA and by ^{1}H-NMR using Eu(hfc)$_3$.

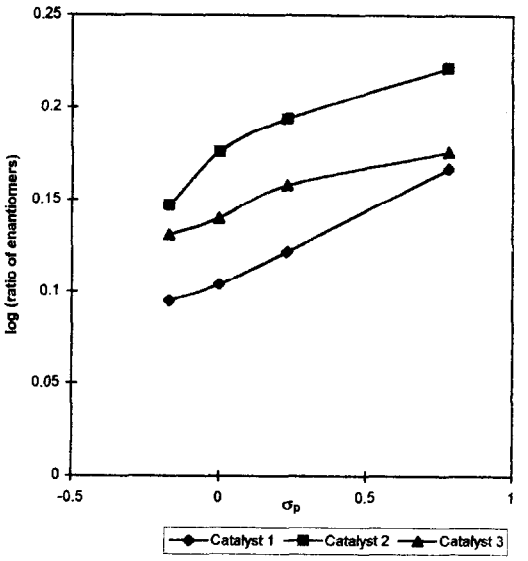


Fig. 2. Hammet Plot showing the extent of enantioselectivity with respect to the substituents at *para* position of styrene without pyridine N-oxide.

other acyl radical. The peroxyacid then reacts with the catalyst to form a high-valent metal oxo intermediate (C) which in turn reacts with styrene to give styrene oxide (D) in a similar fashion analogous to that reported earlier [34].

Evaluation of optical yields for the resulting epoxide separated by a short silica gel column (mesh 60–120) was carried out by ^{1}H-NMR using chiral shift reagent. Tris-[hepta fluoropropyl hydroxy methylene] camphorato(+) Eu(III) and also by chiral capillary column (chiraldex GTA).

In absence of pyridine N-oxide, styrene and 4-chloro styrene gave very good conversion with catalyst **1–3** (65–83%) while better conversion was obtained with 4-methyl styrene with catalyst **1** and **3** (70%) Table 1. Moderate to low conversion was obtained in case of 4-nitro styrene with these catalysts (48–55%). When the reaction was conducted in presence of pyridine N-oxide, the epoxide conversion was improved in all cases Table 2. The results obtained for enantioselectivity for each catalyst and substrate is presented as Hammet plots, Fig. 2 and Fig. 3 which show a clear trend with respect to the substituents at para position of styrene. The nitro styrene showed better selectivity with all the catalysts. Furthermore, it is interesting to point out that the presence of a catalytic amount

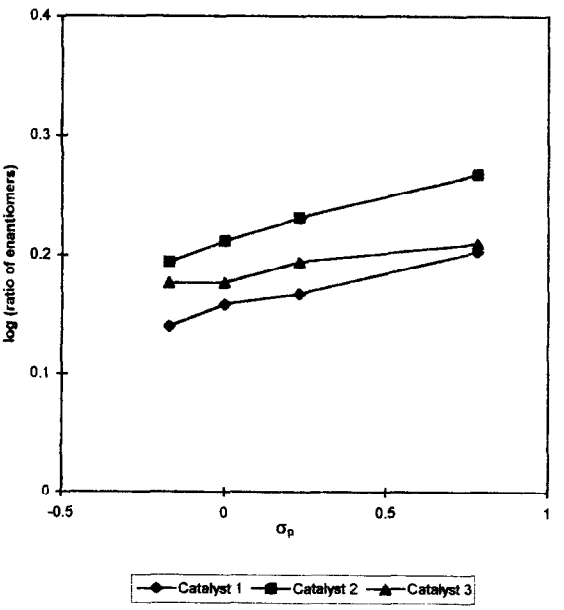


Fig. 3. Hammet Plot showing the extent of enantioselectivity with respect to the substituents at *para* position of styrene with pyridine N-oxide.

of pyridine N-oxide improves the enantioselectivity without any change in configuration. In all the cases on employment of the *S* form of the catalyst resulted in the *R* form of the product as a dominant enantiomer. This trend was already seen by Jacobsen [12–14] and Katsuki [9,10] for Mn(III) Salen complexes using iodosyl benzene as terminal oxidant and with combined use of molecular oxygen with aldehyde [35].

7. Conclusion

In this paper we have highlighted the aerobic enantioselective epoxidation of styrene, 4-chloro-, 4-nitro- and 4-methyl styrene using Ru(III) chiral schiff base complexes in the presence of molecular oxygen using isobutyraldehyde as sacrificial reductant. The catalysts **1–3** gave very good conversion with styrene and 4-chloro styrene. However, in the presence of pyridine N-oxide both conversion and enantioselectivity were improved by maintaining the absolute configuration. Further investigation regarding the improvement in enantioselectivity on the present reaction system and development of more effective ligands are under process.

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] C.W. Ho, W.C. Cheng, M.C. Cheng, S.M. Peng, K.F. Cheng, C.M. Che., J. Chem. Soc. Dalton Trans. (1996) 405.
[2] P. Besse, H. Veschambre, Tetrahedron 50 (1994) 8885.
[3] T. Takai, E. Hata, K. Yoruzu, T. Mukaiyama, Chem. Lett. (1992) 2109.
[4] T. Yamada, K. Imagawa, T. Mukiyama, Chem. Lett. (1992) 2109.
[5] T. Katsuki, K.B. Sharpless, J. Am. Chem. Soc. 102 (1980) 5974.
[6] M.G. Fin, K.B. Sharpless, Asymmetric Synthesis, in: J.D. Morrison (Ed.), Vol. 5, Academic Press, New York, NY, 1985, p. 247.
[7] M. Paulucki, P. Hanson, E.N. Jacobsen, Tetrahedron Lett. 33 (1992) 7111.
[8] K. Srinivasan, S. Perier, J.K. Kochi, J. Am. Chem. Soc. 108 (1986) 2309.
[9] R. Irie, K. Noda, Y. Ito, N. Matsumoto, T. Katsuki, Tetrahedron Asym. 2 (1991) 481.
[10] H. Sasaki, R. Irie, T. Hamada, K. Suzuki, T. Katsuki, Tetrahedron 50 (1994) 11827.
[11] B.D. Brandes, E.N. Jacobsen, J. Org. Chem. 59 (1994) 4378.
[12] E.N. Jacobsen, W. Zhang, M.L. Guler, J. Am. Chem. Soc. 113 (1991) 6703.
[13] E.N. Jacobsen, W. Zhang, A.R. Muci, J.R. Ecker, L. Deng, J. Am. Chem. Soc. 113 (1991) 1063.
[14] W. Zhang, E.N. Jacobsen, J. Org. Chem. 56 (1991) 2296.
[15] H. Sasaki, R. Irie, T. Hamada, K. Suzuki, T. Katsuki, Tetrahedron Asym. 4 (1993) 1693.
[16] T. Mukiyama, T. Takai, T. Yamada, O. Rhode, Chem. Lett. (1990) 1661.
[17] T. Yamada, O. Rhode, T. Takai, T. Mukaiyama, Chem. Lett. (1991) 5.
[18] T. Yamada, T. Takai, O. Rhode, T. Mukaiyama, Bull. Chem. Soc. Jpn. 64 (1991) 2109.
[19] T. Takai, E. Hata, T. Yamada, T. Mukaiyama, Bull. Chem. Soc. Jpn. 64 (1991) 2513.
[20] T. Yamada, K. Imagawa, T. Mukaiyama., Chem. Lett. (1992) 2231
[21] T. Takai, E. Hata, K. Yoruzu, T. Mukaiyama., Chem. Lett. (1992) 2077.
[22] S. Inoki, T. Takai, T. Yamada, T. Mukaiyama, Chem. Lett. (1991) 941.
[23] Shell International Research, JP Patent Tokkaisho 59-231077, 1984.
[24] K. Kato, T. Yamada, T. Takai, S. Inoki, S. Isayama, Bull. Chem. Soc. Jpn. 63 (1990) 179.
[25] T. Takai, E. Hata, K. Yoruzu, T. Mukaiyama, Chem. Lett. (1992) 2109.
[26] R.I. Kureshy, N.H. Khan, S.H.R. Abdi, K.N. Bhatt, Tetrahedron Asymm. 4 (1993) 1693.
[27] R.I. Kureshy, N.H. Khan, S.H.R. Abdi, J. Mol. Catal. 96 (1996) 117.
[28] R.I. Kureshy, N.H. Khan, S.H.R. Abdi, A.K. Bhatt, J. Mol. Catal. 110 (1996) 33.
[29] R.I. Kureshy, N.H. Khan, S.H.R. Abdi, A.K. Bhatt, P. Iyer, J. Mol. Catal., in press.
[30] R.I. Kureshy, N.H. Khan, S.H.R. Abdi, P. Iyer, J. Mol. Catal., in press.
[31] E.E. Mercer, R.R. Buckley, Inorg. Chem. 4 (1965) 1692.
[32] F.P. Dwyer, F.L. Garvan, A. Schulman, J. Am. Chem. Soc. 81 (1959) 291.
[33] M.A. Bangres, M. Gonzales, M.E. Peres, R.J. Ruano, Polyhedron 5 (1986) 1371.
[34] W. Nam, H.J. Kim, S.H. Kim, R.Y.N. Ho, J.S. Valentine, Inorg. Chem. 35 (1996) 1045.
[35] T. Mukaiyama, T. Yamada, T. Nagata, K. Imagawa, Chem. Lett. (1993) 327.