



The One-Pot Three Components of Iodone, Schiff Base and Epoxide for Synthesis of Iodohydrins

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ABSTRACT

In study we report synthesis Iodohydrines in absence of the complexes Schiff-base Salen Cu, Ni and Co. The experimental results showed both that the catalysts had higher catalytic activity and better epoxide selectivity than the homogeneous catalyst.

Keywords: Schiff base, Iodohydrin, Ligand, Iodine, Homogeneous.

INTRODUCTION

With the increasing application of rare earth metals in a variety of fields, rare earth ions continually intrude into general environment and further into the bodies of plants, animals and human beings. It is therefore of significance to investigate the physiological action and long-term effect of rare earth ion on biological bodies. Various studies have shown that Schiff bases derived from Salicylaldehyde and its derivatives have considerable biological importance partly because such ligands have many donor atoms (N, O) and are analogous to biological environment to some extent. They have been widely used in the fields of

biology, pharmacology, catalysis, organic synthesis, chemical, analysis, and so on¹⁻⁴. Much attentions have been paid to these Schiff bases because of the stability of the ligands and various properties of their metal complexes⁵⁻¹⁰.

As an important strategy for the formation of 1,2-bifunctionalized chiral building blocks, the enantioselective ringopening of epoxides with different nucleophiles has attracted much attention from the organic chemists. A wide variety of nucleophiles, such as alcohols, phenols, carboxylic acids, amines, azide ions, thiols, cyanide ions and halide ions are utilized in the aforementioned reaction¹³.

In continuation of our work on enantioselective epoxidation¹⁴⁻¹⁹ of non-functionalized olefins by chiral Co(II), Ni(II) and Cu(II) Schiff base complexes and in pursuit of better selectivity through electronic tuning in the catalyst, we are reporting here the applying catalyst in ring opening epoxides.

EXPERIMENTAL

All of the reagents were supplied by Merck and Fluka, and were employed without further purification. IR spectra were recorded on a Unicam Matson 1000 FT-IR paragon 1000 spectrophotometer. ¹H NMR spectra of the ligand and the complex were recorded on a Bruker FT-NMR 500 MHz spectrometer using CDCl₃ and (CD₃)₂SO as solvents. The electronic spectra were recorded on a CARY 100 Bio UV-Vis spectrophotometer.

General Procedure for Synthesis of 2,2'-[1,2-Ethandiyl bis(nitrilopropelidene)]bis(1-naphthol)

To the stirred solution of 1-(2-hydroxynaphthalen-3-yl)propan-1-one (4 mmol) in 5ml MeOH Ethylenediamine (2 mmol) was added at room temperature. The reaction was continued for 3.4 h. The progress of the reaction was monitored by TLC. After the reaction was completed, the brown oil was collected and dissolved in hot petroleum ether. After cooling pail yellow solid product was obtained. The precipitate was filtered off and washed with cold MeOH. The crude product was purified by recrystallization in ethanol and the pure Schiff base, 2,2'-[1,2-Ethandiyl bis(nitrilopropelidene)]bis(1-naphthol) was obtained in 92% yield, m.p.=196-198°C. The structure of the Schiff base was confirmed by physical and spectroscopic methods

2,2'-[1,2-Ethandiyl bis(nitrilopropelidene)]bis(1-naphthol) (3a)

Pail yellow, m.p.=196-198 °C , IR(KBr)/ ν (cm⁻¹): 3550-3300 (OH), 1600 (C=N), 1540 (C=C, Ar), ¹H NMR/CDCl₃ δ p.p.m; 1.2-1.6(6H, t, J=7.2), 3(4H, dd, J=7.2), 4.2 (4H, s), 7-8.4 (10H, m), 8.6 (2H, d), 16.8(2H, s), λ_{max} : 322 nm.

2,2'-[1,3-propandiyl bis(nitrilopropelidene)]bis(1-naphthol) (3b)

Pail yellow, m.p.=196-198 °C , IR(KBr)/ ν (cm⁻¹): 3250-3550(OH), 1600 (C=N), 1540 (C=C, Ar), ¹H NMR/CDCl₃ δ p.p.m; 1.2-1.6(10H, m), 3 (4H, m), 4.2 (4H, s), 7-8.4 (10H, m), 8.6 (2H, m), 16.8 (2H, s), λ_{max} : 330 nm.

Preparation of the Complexes

Ethanolic solutions of metal acetate (0.025mol) and schiff base (0.05mol) were mixed and the resulting mixture under conditions N₂, until the metal Salen separated, which were then suction filtered, washed with ethanol and ether before dried in vacuum dessicator. The crystals were recrystallized from rectified spirit and dried (Mahaptra *et al.*, 1977) (Scheme1).

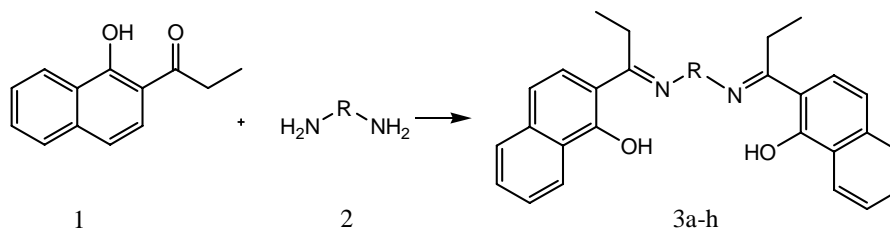
2,2'-[1,2-Ethandiyl bis(nitrilopropelidene)]bis(1-naphtholate) Copper(II) (4a)

Solid brown, m.p.=335-337°C , IR (KBr)/ ν (cm⁻¹): 1630 (C=N), 1550 (C=C, Ar), λ_{max} : 318 nm

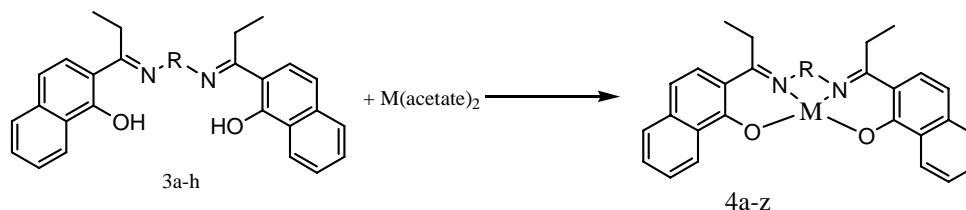
2,2'-[1,2-Ethandiyl bis(nitrilopropelidene)]bis(1-naphtholate) Cobalt(II) (4b)

Solid brown, m.p.=337-3339°C , IR (KBr)/ ν (cm⁻¹): 1635 (C=N), 1560 (C=C, Ar), λ_{max} : 320 nm.

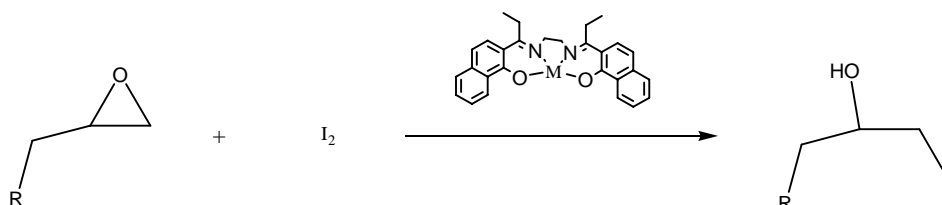
Synthesis bromohydrin by catalyst 2,2'-[1,2-Ethandiylbis (nitrilopropelidene)]bis(1-naphth-



Scheme1: Synthesis of Schiff base under condition room temperature



Scheme 2: Synthesis of Schiff base complex with Co, Cu and Ni



Scheme 3: Synthesis of iodohydrin with catalyst Schiff base

olate) Cobalt(II)

Epoxide (1 mmol) in CH_2Cl_2 (5 mL) was added to a stirred 2,2'-[1,2-Ethandiyl bis(nitrilo propelidene)]bis(1-naphtholate) Cobalt(II) catalyst (0.05 mmol) in at room temperature. Next, a solution of elemental iodine (1 mmol) in CH_2Cl_2 (5 mL) was added portion-wise (15 min) to the above mixture. The progress of the reaction was monitored by TLC. After complete disappearance of the starting material, the reaction mixture was washed with 10% aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (2x10 mL) and water (2x10 mL). The aqueous layer was extracted with CH_2Cl_2 (2x10 mL). The combined organic layer was dried over anhydrous MgSO_4 and evaporated to give crude alcohol-catalyst (Scheme 3).

1-Iodo-2-boutanol (99%)

^1H NMR (CDCl_3 , 300MHz) δ 0.95 (t, 3H, $J=7.2\text{Hz}$), 1.55-1.7 (m, 2H), 3.05-3.25(m, 1H), 3.3-3.5 (m, 1H), 3.75-3.8(m, 1H).; MS(EI) M/Z 200 (M^+).

2-Iodo Cyclohexanol (97%)

^1H NMR (CDCl_3 , 300MHz) δ 1.2-1.6(m, 4H), 1.8-1.9 (m, 1H), 2.0-2.2(m, 2H), 2.4-2.5(m, 1H), 3.5-3.65(m, 1H), 3.95-4.05(m,1H);MS(EI) M/Z 226 (M^+); IR(KBr) 3425, 2960 cm^{-1} .

2-Iodo-1-(4-Chlorophenyl)ethanol (96%)

^1H NMR (CDCl_3 , 300MHz) δ 2.45(br, 1H), 3.45-3.5 (m, 2H), 4.80-4.88(m, 1H), 7.2-7.4(m, 4H);MS(EI) M/Z 282 (M^+); IR(KBr) 3460, 2960 cm^{-1}

2-Iodo-1-phenyl ethanol (100%)

^1H NMR (CDCl_3 , 300MHz) δ 2.50(br, 1H), 3.39-3.5 (m, 2H), 4.75(m, 1H), 7.25-7.4(m, 5H);MS(EI) M/Z 248 (M^+); IR(KBr) 3398, 2960 cm^{-1}

1-Iodo-3-(4-methoxyphenyl)2-propanol (99%)

pale yellow liquid, ^1H NMR (CDCl_3 , 300MHz) δ 2.05(br, 1H), 2.85(d, 2H, $J=6.2, 9.2\text{Hz}$), 3.25 (dd, 1H, $J=4.8, 9.2\text{Hz}$), 3.35 (dd, 1H, $J=3.8, 9.2\text{Hz}$), 3.6-3.75(m, 1H), 3.80(S, 3H), 6.85(d, 2H, $J=8.2\text{Hz}$), 7.15(d, 2H, $J=8.2\text{Hz}$); ^{13}C NMR (CDCl_3 , 50Hz) δ 14.67, 41.66, 55.10, 71.62, 113.92, 128.98, 130.12, 158.25;MS (EI) M/Z 292 (M^+); IR(KBr) 3560, 3050, 2960 cm^{-1} .

1-Iodo-3-(4-acetylphenoxy)2-propanol (99%)

yellow Solid, m.p. 68-70 $^\circ\text{C}$, ^1H NMR (CDCl_3 , 300MHz) δ 2.55(S, 3H), 3.30-350 (m,2H), 3.90-4.05 (m, 3H), 6.90(d, 2H, $J=7.8\text{Hz}$), 7.9(d, 2H, $J=7.8\text{Hz}$); ^{13}C NMR (CDCl_3 , 50Hz) δ 8.84, 26.21, 69.12, 70.15, 114.66, 130.64, 162.75, 196.96; MS (EI) M/Z 320 (M^+); IR(KBr) 3460, 3020, 2970, 1710 cm^{-1} .

1-Iodo-3-(4-Chlorophenoxy)2-propanol (98%)

^1H NMR (CDCl_3 , 300MHz) δ 2.40 (br, 1H), 3.35-3.40 (m,2H), 3.45-3.50 (m, 1H), 3.95-4.0 (m, 1H), 4.05-4.10(m, 2H), 6.85(d, 2H, $J=8.2\text{Hz}$), 7.15(d, 2H, $J=8.2\text{Hz}$); MS (EI) M/Z 312 (M^+); IR(KBr) 3515 cm^{-1}

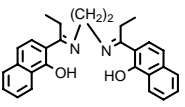
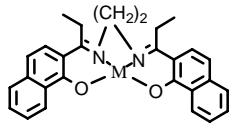
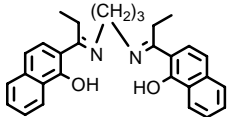
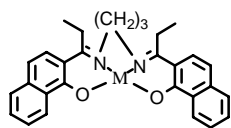
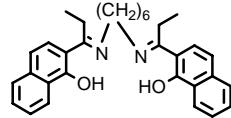
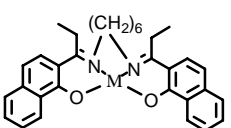
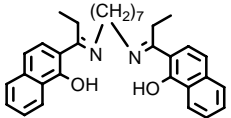
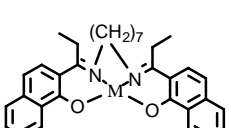
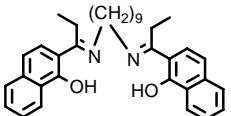
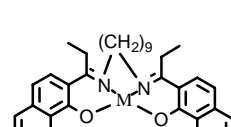
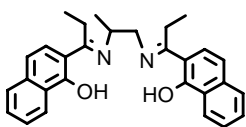
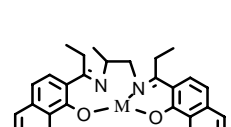
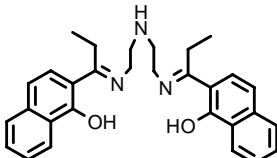
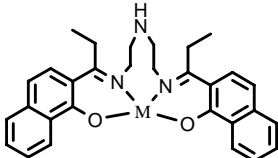
1-Iodo-3-phenoxy-2-propanol(97%)

$^1\text{H NMR}$ (CDCl_3 , 300MHz) δ 2.40(br, 1H), 3.30-3.55 (m, 2H), 3.8-4.1(m, 3H), 6.75-7.0(m, 3H) 7.15-7.35(m,2H);MS(EI) M/Z 278(M⁺); IR (KBr) 3500, 2985 cm^{-1} .

RESULTS AND DISCUSSION

As shown in Scheme 1, when 2 mols heterocyclic ketone were treated with 1 mol diamine at room temperature, a pail yellow substance obtained with high yield. In this reaction, heterocyclic

Table .1: Preparation of Schiff base containing heterocyclic rings through two component reaction

Entry	Schiff base	Complex	Time(min) [(a= Schiff base) complex(b= Cu c= Co d=Ni)]	Yield ^a (%)
1			a=10 b=20 c=20 d=20	a=93 b=95 c=95 d=95
2			a=20 b=30 c=30 d=30	a=95 b=90 c=90 d=85
3			a=20 b=35 c=35 d=35	a=90 b=80 c=87 d=85
4			a=20 b=35 c=35 d=35	a=85 b=87 c=88 d=88
5			a=20 b=40 c=40 d=40	a=85 b=75 c=75 d=75
6			a=30 b=20 c=20 d=20	a=85 b=80 c=87 d=85
7			a=30 b=60 c=60 d=60	a=85 b=80 c=75 d=78

^aIsolated product yields

ketones have been applied and corresponding products were obtained. The results and conditions of the reactions are presented in Table 1.

As can be seen in our previously reported works on synthesis of Schiff bases from ortho-hydroxy aldehyde¹⁴⁻¹⁶ and ortho-hydroxyl ketene,¹⁶⁻¹⁷ (%) the presence of hydroxyl group in ortho situation is accelerated condensation reaction. While, in used heterocyclic aldehydes, with respect to absence of o-hydroxy group, the corresponding Schiff bases were obtained in high yields and appropriate reaction times (Table 1, Entries 1, 2).

All the new, potentially hexadentate Schiff base ligands were cleanly synthesized in 1-1.5 minutes and >80% yield according to elemental analyses and ¹H and ¹³C NMR analyses of the bulk products after recrystallization from ethanol (Table 1). Their structures are supported by the absence from their IR spectra of the carbonyl and primary amine bands of the reagents, and the presence of a Schiff base $\nu(\text{C}=\text{N})$ band in the 1631-

1652 cm^{-1} region; the alkyl C–H stretching vibrations appear in the 2800–2900 cm^{-1} region. In the ¹H NMR spectra, the azomethine protons appear at $\delta = 8.22\text{--}8.73$ ppm and the aromatic ring protons at $\delta = 6.5\text{--}8.4$ ppm.

In conjunction with ongoing work in our laboratory on the synthesis and formation of complex heterocyclic compounds containing donor nitrogen atoms, with neutral molecules such as bromine, we found out that 2,2'-[1,2-Ethandiy]bis(nitrilopropelidene)]bis(1-naphtholate) Cobalt(II) with frame nano efficiently catalyzed the addition of elemental bromine to epoxides under mild reaction conditions with high regioselectivity (Scheme 3).

In this study, we wish to report the results of the reactions of some styrene oxide with elemental bromine in the presence of a substoichiometric 0.01 mmol amount of catalyst Schiff base (Scheme 3, Table 2).

Table 2: Amount of catalyst in ring opening epoxide.

Entry	Complex Schiff base	Yield ^a (%)	Entry	Complex Schiff base	Yield ^a (%)	Entry	Complex Schiff base	Yield ^a (%)
1	4a	40	8	4h	15	15	4q	10
2	4b	70	9	4k	10	16	4r	5
3	4c	25	10	4l	10	17	4s	5
4	4d	30	11	4m	20	18	4t	10
5	4e	15	12	4n	10	19	4w	5
6	4f	20	13	4o	10	20	4x	5
7	4g	10	14	4p	10	21	4y	5

^aIsolated product yields

Table 4: Cleavage styrene oxide with amount difference of catalyst 4b

Entry	Complex 4b (% mol)	Yield ^a (%)	Entry	Complex 4b (% mol)	Yield ^a (%)	Entry	Complex 4b (mol)	Yield ^a (%)
1	1	70	4	4	90	7	7	100
2	2	75	5	5	98	8	10	100
3	3	80	6	6	98	9	15	100

^aIsolated product yields

The crude products were purified on a column of silica gel. The solvent was evaporated and pure iodohydrin was obtained. The iodohydrins obtained throughout this procedure were identified by comparison, where possible, with authentic samples prepared in accordance with literature procedures.

CONCLUSION

In conclusion, this new method appears to be highly competitive with the other methods reported in the literature. The reaction occurs in

neutral and mild conditions on the acid-sensitive substrates and vicinal iodohydrins were obtained in high yields and regioselectivity. In addition, in comparison with our previous methods, 2,2'-[1,2-Ethandiylbis(nitrilopropelidene)] bis(1-naphtholate) Cobalt(II) is cheaper, less step need for preparation, and overall yield is higher

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