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Oxidative Coupling of 2-Naphthol and 2-Alkoxy Naphthalene by $CuCl_2$ and $FeCl_3$ Investigation of Stereo Selective Induction Effects of Optically Active Compounds on the Coupling Process under Solid-State Conditions and Ionic Liquid Media

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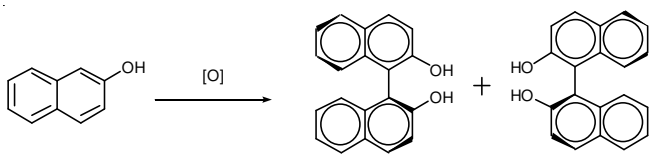
A new method for the 1,1′-binaphthalene-2,2′-diol and 1,1′-binaphthyl-2,2′-dialkylether by $CuCl_2$ and $FeCl_3$ under solid-state condition and ionic liquid is described. The stereo selectively coupling of 2-naphthol by $CuCl_2$ and $FeCl_3$ in presence of optically active amino acid is also studied. The optically purity of (S)-binaphthalene-2,2′-diol in the presence of L-2-phenylglycine by $FeCl_3{\cdot}H_2O$ in solid state and ionic liquid is 41 and 96 %, respectively.

Key Words: Oxidative coupling, Binaphthalene, Chiral amino acid, Ionic liquid.

INTRODUCTION

Because of restricted rotation of the two naphthalene ring in a 1,1′-binaphthyl[1], compounds of this class of molecules are chiral. This unusual physical property has caused the use of these compounds as an important source for inducing chirality in many chemical reaction[1]. 1,1′-Binaphthalene-2,2′-diol has been used in a variety of research filed. According to the reported papers during past two decades, chiral binaphthol has been used as reagent[2], immobilized onto stationary phase for chromatographic resolution[3], chiral shift reagent[4], enantioselective reduction of ketones[5] and synthesis of chiral macrotricyclic ligands[6]. Several methods have been reported for synthesis of binaphthol[2] in the literature. The most important methods are coupling of 2-naphthol by $FeCl_3$ in the solid state[7], coupling by Mn(III)[8] and $CuCl_2$-amine/AgCl system[9]. However, there are sporadic reports for the synthesis of optically active binaphthyls: *e.g.*, intramolecular ullman coupling[10], nucleophilic aromatic substitution[11] and oxidative dimerization of 2-naphthol with copper(II)-amine complexes as oxidants[12] (**Scheme-I**).



1 (S)-2 (R)-2

Scheme-I

In recent years, considerable attention has been focused on the application of ionic liquids to environmentally being chemical technologies because of its advantages *i.e.*, low vapour pressure, high thermal stability and ease of handing[13]. Also there are beneficial effects of ionic liquid on rates and selectivity of important organic transformations, *e.g.*, Diels-Alder reaction[14], Wittig reaction[15], Heck reaction[16], Friedel-Crafts alkylation reaction[17], 1,3-dipolar cycloaddition reaction[18] and Suzuki cross-coupling reaction[19].

EXPERIMENTAL

General procedure: All products were identified by comparison with an authentic sample (IR, NMR, m.p.). ^1H NMR spectra were recorded on a Varian EM-390 NMR spectrometer operating at 90 MHz, or a Varian Unity 250 Fourier Transform NMR spectrometer operating at 250 MHz. The spectra were measured in $CDCl_3$ unless otherwise state, relative to TMS. Mass spectra were recorded on a Shimadzu GC-MS-QP 1000PX.

Preparation in presence of $CuCl_2$: A mixture of 0.58 g (4 mmol) of **1** and 1.08 g (8 mmol) of $CuCl_2$ was finely powdered in a mortar and kept at 50-55 °C in an oil bath for 35 min. After completion of the reaction, followed by TLC, the reaction flask was cooled to room temperature. The reaction mixture was dissolved in 30 mL of methanol and quenched with 10 % HCl to pH 3. By addition of water, the precipitates of **2** and **3** were formed, filtered, washed with 20 mL of methanol, 20 mL of water and dried at room temperature to afford precipitates

(0.4 g). By sublimation of these precipitates at 50 °C under 1 atm the product **3** was removed (0.02 g) in 5 % of yield, m.p. 66-68 °C (lit.[24] 70 ºC). The compound **3** was characterized by IR and ^{1}H NMR analysis. The unsublimed product was compound **2** (0.38 g, 95 % yield), m.p. 211-215 °C (lit.[25] 216-218 °C) characterized with mass, IR, ^{1}H NMR and ^{13}C NMR spectra.

A typical procedure for preparation of 2 by $CuCl_2$ in the presence of optically active amino acid: In a mortar a mixture of finely powdered of L-proline (1.37 g, 12 mmol) and $CuCl_2$ (1.62 g, 12 mmol) was added to 1 (0.864 g, 6 mmol). The mixture was ground for 10 min and kept at 60 °C for 0.5 h. After the completion of the reaction (monitored by TLC) 40 mL of methanol and 25 mL HCl 10 % (pH 3) was added. Addition of 120 mL of water yielded a brown precipitate that after filtration and washing with 10 % HCl (30 mL) converted to a yellow precipitate (1.2 g). The column chromatography of the precipitate on silica gel using ethyl acetate:cyclohexane (10:90) as eluent gave (s)-(-)-2 (0.24) in 20 % of yield, m.p. 201-205 °C $[\alpha]_D^{25}$-3.833° (C 0.287, THF), (lit.[26] -35.5, C1.03, THF), 10 % ee and **3** (0.96 g, m.p. 64-66 °C, 60 % yield).

A typical procedure for preparation of 2 by $FeCl_3{\cdot}6H_2O$ in the presence of optically active amino acid: A mixture of finely powdered of L-proline (1.14 g, 10 mmol), $FeCl_3{\cdot}6H_2O$ (2.7 g, 10 mmol) and **1** (0.72 g, 5 mmol) was kept at 60 °C for 24 h. To the mixture of reaction 30 mL of methanol was added and quenched with 10 % HCl to pH 3. By addition of 150 mL of water, needle crystal of (s)-(-)-2 was formed, collected and washed with 10 % HCl (20 mL), m.p. 209-212 °C, 0.5 g (70 %), 8 % ee and $[\alpha]_D^{25}$-2.81° (C 0.5, THF).

Prepation of (s)-(-)-2 by $CuCl_2$ in the presence of (R)-(+)-phenylethylamine: When a mixture of powdered **1** (0.14 g, 1 mmol) and $CuCl_2{\cdot}2H_2O$ (0.314 g, 2 mmol) was added on (R)-(+)-phenylethylamine (0.97 g, 8 mmol) and the brown reaction mixture was kept at room temperature for 24 h. The TLC experiment confirmed the completion of reaction. After addition of 20 mL of methanol and quenching of reaction with 10 % HCl in pH 3, water (30 mL) was added. The yielded crystals of (s)-(-)-2 were collected, washed with 60 mL of 10 % HCl and 30 mL water. The drying of these crystals at room temperature gave (s)-(-)-2 in 60 % (0.0852 g) yield, m.p. 203-206 °C, ee 25.6 %, $[\alpha]_D^{25}$ -9.09° (C 0.82 THF).

Preparation of (s)-(-)-2 by $FeCl_3{\cdot}6H_2O$ in presence of (R)-(+)-phenylethylamine: A mixture of finely ground of **1** (0.144 g, 1 mmol) and $FeCl_3{\cdot}6H_2O$ (0.54 g, 2 mmol) was added on (R)-(+)-phenylethylamine (0.97 g, 8 mmol) and kept at room temperature for 24 h. With addition of 20 mL methanol a yellow solution was formed, quenched with 10 % HCl to pH 3. The addition of 60 mL water produced the needle crystals that after collection and washing with 30 mL of water gave (s)-(-)-2 in 72 % (0.1 g) m.p. 205-207 °C, ee 41 %, $[\alpha]_D^{25}$ -14.54° (C 0.738, THF).

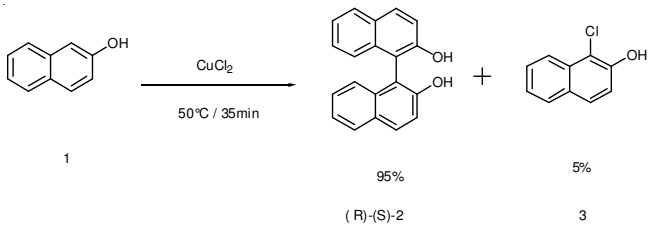
Preparation of 3 in presence of $PhCH_2Ph_3P^+Cl^-$: When a mixture of finely powdered of **1** (0.144 g, 1 mmol), $CuCl_2{\cdot}2H_2O$ (0.27 g, 2 mmol) and $PhCH_2Ph_3P^+Cl^-$ (0.777 g, 2 mmol) was kept at 40 °C for 15 h, compound **3** was formed (based on TLC) as the only product. The mixture was dissolved in methanol (20 mL) and 10 % HCl (10 mL), then 50 mL of water added and the crystals were isolated by filtration, sublimed at 1 atm and 45 °C gave **3** in 88 % (0.15 g) of yield, m.p. 64-67 °C.

Preparation of (1,1′-binaphthyl)-2,2′-dimethylether (7): A mixture of finely powered of **5** (0.156 g, 1 mmol) and $FeCl_3{\cdot}6H_2O$ (0.27 g, 2 mmol) was ground in a mortar for 10 min and kept at 60 °C in oil bath for 40 min. After completion of reaction (tested by TLC) 20 mL of chloroform was added, stirred magnetically until all mixture was dissolved, washed by 10 % HCl several times (3 × 10). The organic layer was dired gave **7** in 77 % (0.12 g) of yield, 187-190 °C (lit.[26] m.p. 190 °C).

A typical procedure for preparation of 2 by $FeCl_3{\cdot}6H_2O$ in the presence of optically active amino acid under ionic liquid media: A mixture of finely powdered of L-proline (1.14 g, 10 mmol), $FeCl_3{\cdot}6H_2O$ (5.4 g, 20 mmol), **1** (1.44 g, 10 mmol) and (EMim PF_6) (10.7 g, 20 mmol) was kept at 90 °C for 4 h. To the mixture of reaction 30 mL of methanol was added and quenched with 10 % HCl to pH 3. By addition of 150 mL of water needle crystal of (s)-(-)-2 was formed, collected and washed with 10 % HCl (20 mL), m.p. 209-212 °C, 0.5 g (70 %), 32.2 % ee and $[\alpha]_D^{25}$-11.76° (C 0.5, THF[27]).

RESULTS AND DISCUSSION

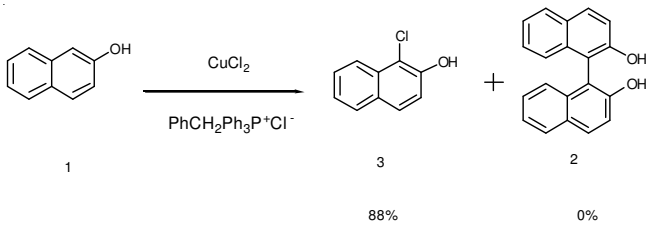
In 1989 Toda and co-workers reported the coupling of 2-naphthol using $FeCl_3{\cdot}H_2O$ as oxidant under solid state condition[20]. In continuation of our research under solid state[21,22], we wish here to report a simple and efficient method for synthesis of binaphthol under solid state condition by $CuCl_2{\cdot}2H_2O$ and $FeCl_3{\cdot}6H_2O$ in the absence and presence of optically active reagents. When a mixture of finely powdered 2-naphthol **1** and two molar ratio of $CuCl_2$ was ground in an oil bath, the binaphthol **2** was produced in 95 %. Formation of trace amounts of 1-choloro-1-naphthol in the coupling reaction by $CuCl_2$ can be assumed that the coupling process competes with chlorination reaction (**Scheme-II**).



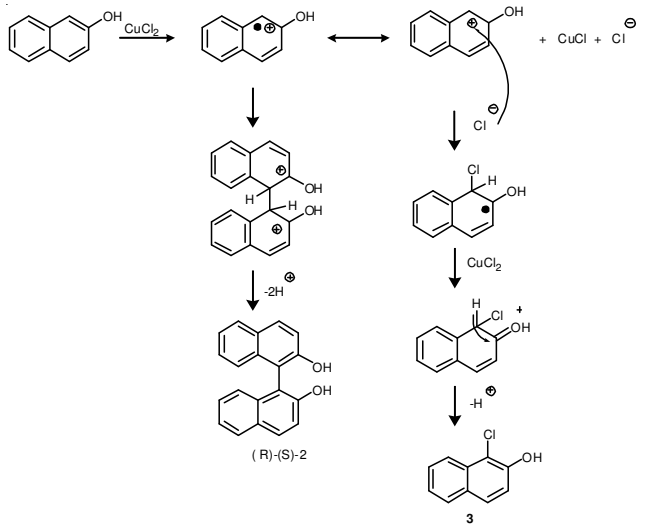
Scheme-II

There is competition between formation of compounds **2** and **3**. By increasing the concentration of chloride ion the major product will be **3**. When a mixture of finely ground **1**/$CuCl_2$ and KCl as the chloride ion source (1:2:8 ratio), in presence of a trace amount of H_2O (1 mL) was kept at 40 °C for 12 h, the compound **3** was produced as the only product in 40 % yield. In another experiment, benzyltriphenylphosphonium chloride ($PhCH_2Ph_3P^+Cl^-$) was used as the source of chloride ion in the absence of water. Interestingly, the compound **3** was obtained in 88 % yield as the only product (**Scheme-III**).

Although the transition metals have been used for coupling 2-naphthol for years, the mechanism of this oxidation is not clear[23]. The possible mechanism in the first step of this reaction could be the generation of naphthoxy radical (**Scheme-IV**).



Scheme-III



Scheme-IV

The oxidative coupling of **1** in the presence of optically reagents such as non-racemic chiral amino acid was also studied under solid state *e.g.*, when a mixture of finely powdered of L-proline/$CuCl_2$/**1** (2:2:1 mol ratio) was ground at 60-65 °C for 1.5 h the compounds **2** and **3** were formed in the 40 % and 60 % yields, respectively. The results of this experiment are summarized in Table-1.

TABLE-1
ENANTIOSELECTIVE SYNTHESIS OF (s)-(-)-2 UNDER SOLID STATE IN PRESENCE OF OPTICALLY ACTIVE AMINO ACID BY $CuCl_2$

Entry	Amino acid	Temp. (ºC)	Time (min)	Yield (%)	ee (%)
1	Alanine	60	90	50	0
2	L-Proline	60	90	40	10.0
3	L-Leucine	60	90	56	1.5
4	L-Aspartic acid	60	90	40	0

The formation of (s)-**2** with 10 % ee, stimulated our interest to producing of this compound with oxidative coupling by $FeCl_3 \cdot 6H_2O$. In the presence of non-racemic chiral amino acid (Table-1), when a mixture of **2**/$FeCl_3 \cdot 6H_2O$/ L-proline (1:2:2 mol ratio) was kept at 60 °C for 24 h in an oil bath, the (s)-**2** was obtained with 14 % optically purity and 72 % chemical yield (Table-2).

Brusee and co-workers[22] reported the oxidative coupling of 2-naphthol by $CuCl_2$ in the presence of (+)amphetamine as catalyst in methanol in this report the (s)-(-)-**2** was synthesized with optically purity up to 95 %. It is decided to repeat this method under solid state conditions with chiral amine.

When a mixture of 2-naphthol/(R)-(+) phenylethylamine/ $CuCl_2 \cdot 2H_2O$ (1:8:2 mol ratio) was kept at room temperature for 24 h, the (s)-(-) **2** was produced with 26 % ee. This result encouraged us to study this reaction by $FeCl_3 \cdot 6H_2O$ as oxidative coupling. Interestingly, when a mixture of 2-naphthol/ (R)-(+) phenylethylamine/$FeCl_3 \cdot 6H_2O$ (1:8:2 mol ratio) was kept at room temperature for 24 h, the (s)-**2** was obtained in 72 % chemical yield and 41 % optically purity. In order to study that whether oxidative coupling induces this optically purity or racemization of produced binaphthol is responsible for stereoselectivly of the reaction. A mixture of **2**/ $CuCl_2 \cdot 2H_2O$/(R)-(+) phenyl ethyl amine (1:2:8 mol ratio) kept at room temperature for 24 h, but no optical purity was observed in **2** at all. We found, that the optical purity was not stem from stereoselective coupling process, but at first the racemic binaphthol is formed then its (R)-(+)enantiomer is converted to (s)-(-)enantiomer under reaction condition. We obtain best result of non-racemic amino acid, when we examined bulk amino acid in this condition. It is noted that the optical purity and chemical yield increasing by $CuCl_2$ and $FeCl_3$ (Tables 3 and 4).

TABLE-2
ENANTIOSELECTIVE SYNTHESIS OF (s)-(-)-2 UNDER SOLID STATE IN PRESENCE OF OPTICALLY ACTIVE AMINO ACID BY $FeCl_3 \cdot 6H_2O$

Entry	Amino acid	Temp. (ºC)	Time (h)	Yield (%)	ee (%)
1	Alanine	60	24	78	0
2	L-Proline	60	24	72	14.0
3	L-Leucine	60	24	87	4.7
4	L-Aspartic acid	60	24	70	2.3

TABLE-3
ENANTIOSELECTIVE SYNTHESIS OF (s)-(-)-2 UNDER SOLID STATE IN PRESENCE OF BULK OPTICALLY ACTIVE AMINO ACID BY $CuCl_2$

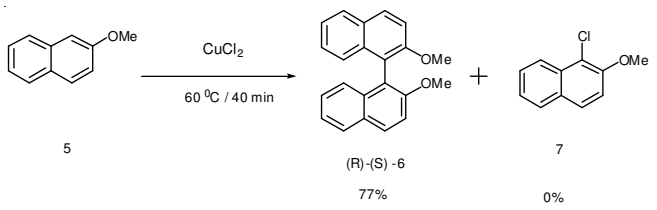
Entry	Amino acid	Temp. (ºC)	Time (min)	Yield (%)	ee (%)
1	L-Isoleucine	65	90	60	7.1
2	L-Pipecolinic acid	65	90	60	10
3	L-*tert*-Leucine	65	90	61	5
4	L-2-Phenylglycine	65	90	63	20

TABLE-4
ENANTIOSELECTIVE SYNTHESIS OF (s)-(-)-2 UNDER SOLID STATE IN PRESENCE OF BULK OPTICALLY ACTIVE AMINO ACID BY $FeCl_3 \cdot 6H_2O$

Entry	Amino acid	Temp. (ºC)	Time (h)	Yield (%)	ee (%)
1	L-Isoleucine	60	24	90	15.2
2	L-Pipecolinic acid	60	24	90	27.0
3	L-*tert*-Leucine	60	24	90	18.0
4	L-2-Phenylglycine	60	24	95	41.0

We also studied oxidative coupling of 2-methoxy naphthalene **5** by $FeCl_3$ under solid state. Surprisingly this reaction afforded only coupling product **6** and no expected substitution product **7** was observed at all but ee is 0 % (**Scheme-V**).

In continuation we tested other 2-alkoxy naphthalene in presence of non-racemic amino acid. When a mixture of 2-alkoxy naphthalene/$FeCl_3 \cdot 6H_2O$/L-amino acid (1:2:2 mol ratio) was kept at 60-65 °C for 4 h only (s)-1,1′-binaphthol-2,2′-alkyl ether was formed with high ee % (Table-5).



Scheme-V

TABLE-5
ENANTIOSELECTIVE SYNTHESIS OF (s)-(-)-2-ALKOXYNAPHTHALENE UNDER SOLID STATE IN PRESENCE OF OPTICALLY ACTIVE AMINO ACID BY $FeCl_3.6H_2O$ AT 100 ºC FOR 4 h

Entry	Amino acid	2-Alkoxynaphthalene	ee (%)
1	L- *tert*-leucine	2-Isopropylnaphthalene	96
2	L-2-Phenylglycine	2-Isopropylnaphthalene	97
3	L-*tert*-leucine	2-Butylnaphthalene	98
4	L-2-Phenylglycine	2-Butylnaphthalene	98
5	L-*tert*-leucine	2-Isobutylnaphthalene	90
6	L-2-Phenylglycine	2-Isobutylnaphthalene	90
7	L- *tert*-leucine	2-Hexylnaphthalene	98
8	L-2-Phenylglycine	2-Hexylnaphthalene	99

In order to develop the method for green chemistry, in this work we studied the oxidative coupling of **1** in presence of 1-buthyl-3-methyl imidazolium hexafluoro (EMim PF_6) as ionic liquid media. When a mixture of **1**/$FeCl_3{\cdot}6H_2O$/(EMim PF_6)/L-amino acid (1:2:2:1 ratio) was kept at 100 °C for 4 h, chemical yield and optical purity increasing (Table-6).

TABLE-6
ENANTIOSELECTIVE SYNTHESIS OF (s)-(-)-2 UNDER IONIC LIQUID MEDIA IN PRESENCE OF OPTICALLY ACTIVE AMINO ACID BY $FeCl_3{\cdot}6H_2O$

Entry	Amino acid	Temp. (ºC)	Time (h)	Yield (%)	ee (%)
1	Alanine	90	4	80	12
2	L-Proline	90	4	70	32
3	L-Leucine	90	4	85	25
4	L-Aspartic acid	95	4	75	20
5	L-Isoleucine	100	4	90	72
6	L-Pipecolinic acid	100	4	95	90
7	L-*tert*-leucine	100	4	93	88
8	L-2-Phenylglycine	100	4	95	96

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