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Copper (II) Schiff base catalysed aerobic oxidative coupling of 2-naphthols: an efficient and simple synthesis of binaphthols

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Abstract

Copper (II) Schiff base complexes of 2-(1-phenylethyl imino) methylphenol (**3**), methyl-*N*-(2-hydroxyphenyl)-L-serine (**4**) and methyl-*N*-(2-hydroxyphenyl)-L-tyrosine (**5**) were found to be an efficient catalyst for the aerobic oxidative coupling of 2-naphthols to binaphthols. Among the various copper (II) Schiff base complexes, the complex **3** was found to be the most reactive for this transformation.

Keywords: Copper; Oxidation; Schiff base; Oxygen; Coupling

1. Introduction

Oxidative coupling of 2-naphthols is an important synthetic transformation as 1,1′-bi-2-naphthols are widely used chiral inducers in synthetic organic chemistry [1–7]. A wide variety of stoichiometric reagents like $FeCl_3$ [8], $K_3Fe(CN)_6$ [9], $Mn(acac)_3$ [10] and Cu(II)–amine complexes [11] have been used for this transformation. However, these methods suffer from drawbacks such as the use of an expensive oxidant (AgCl), the production of copious amounts of heavy metal wastes and the need for high temperatures. Recently several catalytic methods using chiral diamine–copper complexes [12], $CuSO_4/Al_2O_3$ [13,14], $VO(acac)_2$ [15], CuCl [16] and mesoporous molecular sieves [17] as the catalysts and molecular oxygen as the primary oxidant have also been reported in the literature. Most of these methods require longer reaction times and complex preparations of the catalysts, leaving scope for further improvement in the catalytic oxidative coupling of 2-naphthols. As part of our studies on oxidation with molecular oxygen as the primary oxidant [18–23], we report here a simple and convenient method for the aerobic oxidative coupling of 2-naphthols (**1**) to their corresponding 1,1′-bi-2-naphthols (**2**) in excellent yields by using copper (II) Schiff base complexes **3**–**5** as catalysts (Scheme 1).

2. Results and discussion

The oxidation of various substituted 2-naphthols was carried out with molecular oxygen in refluxing chlorobenzene using copper (II) Schiff base complex **3** derived from $CuCl_2$ and 2-(1-phenylethyl imino) methylphenol as catalyst. All the substrates studied were converted smoothly and selectively to their corresponding *ortho–ortho* coupled products in excellent yields. These results are presented in Table 1 and clearly indicate that 6-bromo-2-naphthol was the most reactive and gave the highest yield of coupled product while 3-(carboxy)-2-naphthol was found to be the least reactive and gave only 10% yield of the coupled product.

To evaluate the catalytic efficiency of various copper (II) Schiff base complexes, we also prepared the copper Schiff base complexes **4** and **5** from $CuCl_2$ with methyl-*N*-(2-hydroxyphenyl)-L-serine and methyl-*N*-(2-hydroxyphenyl)-L-tyrosine, respectively, and carried out the oxidation of 2-naphthol under similar reaction conditions. These results are presented in Table 2, and show that copper (II) Schiff base complex **3** was found to be the most efficient catalyst for this transformation. In blank experiment no oxidation was observed under similar conditions in the

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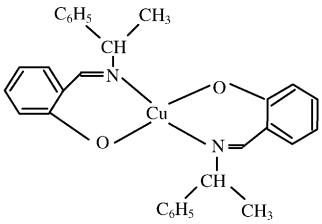

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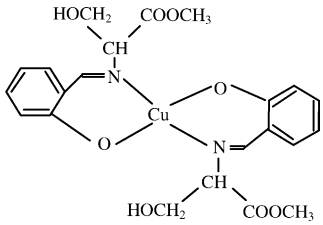

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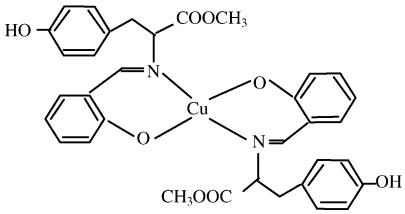
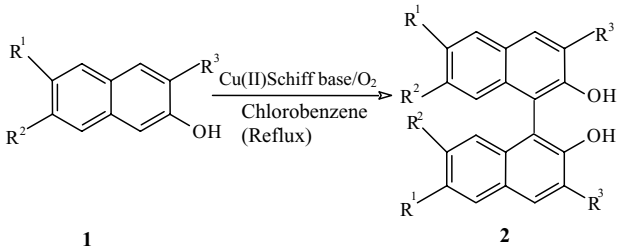


5

absence of catalyst. While oxidative coupling of phenol gave intricate mixture of the products, 2,4-dimethylphenol (**6**) was selectively oxidised to its *ortho–ortho* coupled product **7** under similar reaction conditions (Scheme 2).



1 **2**

Scheme 1.

Table 1
Copper (II) Schiff base complex **3** catalysed aerobic oxidation of 2-naphthols[a]

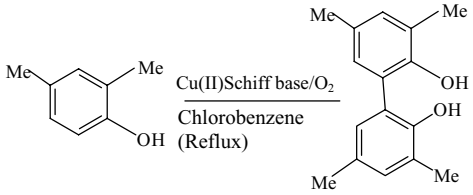
Entry	Naphthol (**1**)	Reaction time (h)	Yield (%)[b]
1a	$R^1 = R^2 = R^3 = H$	12	90
1b	$R^1 = Br$; $R^2 = R^3 = H$	8	95
1c	$R^1 = R^3 = H$; $R^2 = OCH_3$	10	92
1d	$R^1 = R^2 = H$; $R^3 = COOCH_3$	20	35
1e	$R^1 = R^2 = H$; $R^3 = COOH$	24	10

[a] 2-Naphthol (1 mmol), copper (II) Schiff base (5 mol%) in chlorobenzene (5 ml) at reflux temperature under an oxygen atmosphere.
[b] Isolated yields.

Table 2
Aerobic oxidation of 2-naphthol using different copper Schiff base complexes as catalyst[a]

Entry	Catalyst	Reaction time (h)	Conversion (%)
1	Schiff base complex **3**	12	100
2	Schiff base complex **4**	20	100
3	Schiff base complex **5**	24	100
5	–	24	0

[a] Substrate (1 mmol), catalyst (5 mol%) in chlorobenzene (5 ml) at reflux temperature under atmospheric pressure of O_2.



6 **7**

Scheme 2.

To evaluate the effect of solvents, the aerobic oxidation of 2-naphthol was carried out under similar reaction conditions by using different solvents: chlorobenzene, acetonitrile, 1,2-dichloroethane and toluene. Among the solvents studied, chlorobenzene was found to be most suitable solvent. The oxidative coupling of 2-naphthols was found to be very slow at room temperature and could be carried out more efficiently in refluxing chlorobenzene. The mechanism of this reaction is not clear at this stage and further studies in this direction are being carried out.

3. Conclusion

We report for the first time a new catalytic method for the aerobic oxidation of 2-naphthols to their corresponding 1,1′-bi-2-naphthols by using copper (II) Schiff base complexes as catalyst. The simplicity of the system, easy preparation of the catalyst and applicability make copper (II) Schiff base catalysed oxidation an attractive, environmentally acceptable synthetic tool for the oxidation of 2-naphthols to binaphthols.

4. Experimental section

4.1. Materials

All the 2-naphthols and phenols used were purchased from Aldrich and used without further purifi-

cation. Copper (II) Schiff base complexes **3**–**5** were prepared by the reaction of 2-(1-phenylethyl imino) methylphenol, methyl-*N*-(2-hydroxyphenyl)-L-serine and methyl-*N*-(2-hydroxyphenyl)-L-tyrosene, respectively, with anhydrous $CuCl_2$ following the literature procedures [24–26] and elemental analysis of these complexes were found to be satisfactory.

4.2. A typical experimental procedure for oxidative coupling 2-naphthol is as follows

To a stirred solution of 2-naphthol (144 mg, 1 mmol) in chlorobenzene (5 ml) was added copper (II) Schiff base complex **3** (0.025 g, 0.05 mmol, 5 mol%) and the reaction mixture was refluxed for 12 h under an oxygen atmosphere. The reaction progress was monitored by TLC (SiO_2). After completion of the reaction the solvent was evaporated under reduced pressure and the residue left was dissolved in dichloromethane. The dichloromethane layer was washed twice with water and dried over anhydrous sodium sulphate followed by evaporation of the solvent. The residue thus obtained was purified by column chromatography on silica gel using ethyl acetate/hexane (1:4) as eluent. Evaporation of the solvent yielded 1,1′-bi-naphthylene-2,2′-diol (129 mg, 90%).

4.3. Product identification

Melting points were determined in open capillary tubes on a Büchi apparatus and are uncorrected. The ^{1}H NMR spectra were recorded on Bruker 300 MHz spectrometers and chemical shift values are recorded in δ units (parts per million) relative to Me_4Si as internal standard. IR spectra were recorded on a Perkin Elmer 1760X FTIR spectrometer in potassium bromide disc or neat thin film.

4.3.1. 1,1′-Bi-naphthylene-2,2′-diol

mp 214–216 °C (216–218[lit]). ^{1}H NMR ($CDCl_3$) δ (ppm): 7.10–7.50 (m, 8H), 7.80–8.00 (m, 4H), 8.50–8.80 (broad s, 2H). IR (KBr, cm^{-1}): 3500, 1640, 1625, 1540, 1480, 1250 [13].

4.3.2. 6,6′-Dibromo-1,1′-binaphthyl-2,2′-diol

mp 195–196 °C (198–199[lit]). ^{1}H NMR ($CDCl_3$) δ (ppm): 6.98 (d, 2H), 7.35 (dd, 2H), 7.39 (d, 2H), 7.92 (d, 2H), 8.10 (d, 2H), 8.30 (broad s, 2H). IR (KBr, cm^{-1}): 3400, 1575, 1490, 1210, 925, 805 [13].

4.3.3. 7,7′-Dimethoxy-1,1′-naphthyl-2,2′-diol

mp 150 °C (151–152[lit]). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.50 (s, 6H), 6.50 (s, 2H), 7.08 (dd, 2H), 7.19 (d, 2H), 7.75 (d, 2H), 7.84 (d, 2H), 9.20 (broad s, 2H). IR (KBr, cm^{-1}): 3400, 1600, 1501, 1205, 925, 795 [13].

4.3.4. 3,3′-Bismethoxycarbonyl-1,1′-naphthyl-2,2′-diol

mp 275–276 °C (276–278[lit]). ^{1}H NMR ($CDCl_3$) δ (ppm):4.10 (s, 6H), 6.85–7.15 (m, 4H), 7.34–7.50 (m, 4H), 7.85–8.05 (m, 2H), 8.75 (broad s, 2H). IR (KBr, cm^{-1}): 3350, 3225, 1666, 1505, 1450, 825 [13].

4.3.5. 3,3′-Dicarboxy-1,1′-naphthyl-2,2′-diol

mp 329–330 °C (330–333[lit]). ^{1}H NMR ($CDCl_3$) δ (ppm): 6.80–7.15 (m, 4H), 7.35–7.50 (m, 4H), 7.40 (dd, 2H), 7.88–7.85 (m, 2H). IR (KBr, cm^{-1}): 3225, 1650, 1510, 1449, 824 [27].

4.3.6. 3,3′5,5′-Tetramethyl-1,1′-biphenyl-2,2′-diol

mp 195–196 °C (198–199[lit]). ^{1}H NMR ($CDCl_3$) δ (ppm): 2.35 (s, 12H), 5.90 (broad s, 2H), 6.80–7.30 (m, 4H). IR (KBr, cm^{-1}): 3333, 1525, 1470, 877 [28].

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