

Efficient Oxidative Coupling of 2-Naphthols Catalyzed by Alumina-Supported Copper(II) Sulfate Using Dioxygen as Oxidant

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Introduction

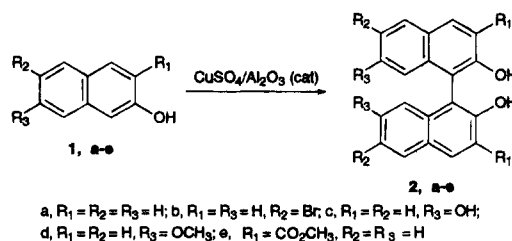
1,1'-Bi-2-naphthol and its derivatives have been of synthetic interest associated with wide applicabilities of the enantiomers in chirality induction,¹ since a convenient and economic way for obtaining the enantiomers is the resolution of the racemic binaphthols.² A well-established method for the preparation of binaphthols is the oxidative coupling of 2-naphthols using FeCl₃,^{3,4} K₃Fe(CN)₆,⁵ Mn(acac)₃,^{6,7} and Cu(II)-amine complexes^{8–10} as coupling reagents. In most cases, however, the coupling reactions are not catalytic but require more than stoichiometric amounts of the metal salts. A few exceptions are the coupling reactions that catalytically proceed upon ultrasound irradiation of aerated powder mixtures of 2-naphthols and FeCl₃ at 50 °C³ or by the use of a Cu(II)-amine complex combined with AgCl,¹¹ an expensive reagent. Therefore, it is of synthetic significance to find a conventional reaction system for the catalytic coupling reactions of 2-naphthols, in which an extraabundant oxidant (e.g., dioxygen) can be effectively used for the facile regeneration of the reagent (a metal salt) in a catalytic cycle.

In this paper, we now communicate our preliminary results on the oxidative coupling of 2-naphthols catalyzed by alumina-supported copper(II) sulfate under aerated conditions (Scheme 1).

Results and Discussion

The supported catalyst can be easily prepared from copper(II) sulfate and commercially available alumina, as shown in the Experimental Section. Of synthetic significance in the present method is the remarkable simplicity of both the reaction and the followup procedures. The oxidative coupling reactions of 2-naphthol (**1a**) and some derivatives **1b–e** can be carried out simply by a heating of slurries containing **1a–e** and 10 wt %

Scheme 1



CuSO₄/Al₂O₃ in chlorobenzene under bubbling air through the mixture. The final products can be readily isolated by filtration of the catalyst followed by evaporation of the solvent. The binaphthols **2a–d** were thus obtained in high yields and in considerably high purities with one exception (**2e**). Further purification can be conveniently achieved, if necessary, by treatment with active carbon or by simple recrystallization. Table 1 summarizes the results.

As a typical run, a slurry of 0.2 equiv of CuSO₄/Al₂O₃ and 1.0 equiv of **1a** in chlorobenzene was heated at 140 °C for 8 h under bubbling air through the mixture. Filtration of the catalyst and workup gave **2a** in 99% crude yield. Gas-liquid chromatography (GLC) showed that the crude product exclusively consists of **2a** but negligible amounts of byproducts. A simple treatment of the crude product with active carbon gave colorless **2a** in 97% overall yield (entry 1). In the case of 6-bromo-2-naphthol (**1b**), the coupling reaction was completed only for 2 h (entry 2), whereas a longer reaction time was required for the completion of reaction in the case of either 7-hydroxy- or 7-methoxy-substituted 2-naphthol (**2c** or **2d**). On the other hand, 3-(methoxycarbonyl)-2-naphthol (**1e**) was very unreactive; a reaction of **1e** in the presence of 2.0 equiv of CuSO₄/Al₂O₃ under more severe reaction conditions (at 160 °C for 8 h) gave **2e** only in 20% yield (entry 5), and the unreacted **1e** was recovered in 72% yield after preparative TLC. It should be noted that air is essential for catalysis of the coupling reaction, since **2a** was obtained only in 14% yield under a nitrogen atmosphere. It was, however, confirmed that CuSO₄/Al₂O₃ can act as an efficient stoichiometric reagent for the coupling reaction under deaerated conditions; the reaction of **1a** with 2.0 equiv of CuSO₄/Al₂O₃ at 140 °C for 8 h gave **2a** in 89% yield.

The present reaction can be effectively applied to large-scale synthesis of **2**. For example, a reaction using **1a** (14.4 g, 100 mmol), CuSO₄/Al₂O₃ (35.1 g, 20 mmol), and chlorobenzene (1 L) gave ca. 13 g of pure **2a** (89% yield) after recrystallization of the crude product (14.2 g, 99%) from toluene. The sky-blue color of the initially prepared catalyst turned dark-brown at the end of the reaction. It should be, however, noted that the recovered catalyst still reveals a comparable, but slightly lower, catalytic activity without any treatment for reactivation of the catalyst; **2a** was obtained in 72% yield by a reaction using the recovered catalyst under identical conditions. Presumably, the color change and the activity decrease would be mainly due to partial deposition of polymerized materials on the catalyst surface but not to irreversible changes of the catalyst. With a lesser amount (0.05 equiv) of the catalyst, the reaction of **1a** at 140 °C was less efficient to give **2a** in 64% yield after 17 h. However, the turnover number (2 × mol **2a** formed/mol CuSO₄ used) reaches 12.8.

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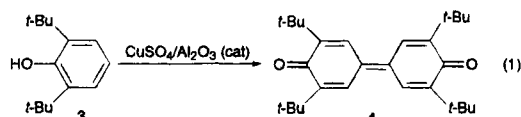
Table 1. Oxidative Coupling of 2-Naphthols Catalyzed by CuSO₄/Al₂O₃^a

entry	2-naphthols	time/h	binaphthols	isolated yield/%
1	1a	8	2a	97
2	1b	2	2b	98
3	1c	15	2c	93
4	1d	8	2d	97
5	1e	8	2e	trace (20) ^b

^a CuSO₄/2-naphthols = 0.2. Unless otherwise specified, the reactions were undertaken by heating **1a–d** and CuSO₄/Al₂O₃ under bubbling air through the mixture at 140 °C for 8 h. ^b At 160 °C; CuSO₄/1e = 2.0.

It is of interest associated with the Cu(II) salt catalysis to note that no reaction of **1a** occurred at all with solid CuSO₄ alone without support on alumina or with alumina in the absence of a Cu(II) salt or with a mixture obtained by simple admixing of CuSO₄ and alumina in powder. In order to confirm the effectiveness of other Cu(II) salts, we carried out the coupling reaction of **1a** under similar reaction conditions using Cu(OAc)₂ or CuF₂ supported on alumina; **2a** was obtained in 79% or 49% yield each. Moreover, it was confirmed that alumina is much more effective than the other catalyst supports investigated (silica gel, molecular sieve, Florisil, and Celite).

As a preliminary attempt to further application of the present Cu(II)-salt catalysis, the coupling reaction of 2,6-di-*tert*-butylphenol (**3**) was carried out. A mixture of **3** and 0.2 equiv of CuSO₄/Al₂O₃ in chlorobenzene was heated at 140 °C for 8 h under bubbling air through the mixture to yield diphenoquinone **4** in 94% yield, but no biphenol was detected (eq 1). This reaction seems to be reminiscent of enzymatic reactions of laccase.¹²



Experimental Section

General Methods. Unless stated otherwise, all reagents and chemicals were obtained commercially and used without further purification. Neutral alumina was purchased from ICN Bio-medicals (Woelm N-Super I) and used without any treatment. IR spectra were recorded on a JASCO A-202 spectrometer and NMR spectra on a JEOL JNM-GSX-400 spectrometer. GLC evaluations of product mixtures were carried out on a Shimadzu GC-8A flame ionization chromatography using a 50-mm × 0.25-mm capillary column of SE-54.

Preparation of Copper(II) Sulfate Adsorbed on Alumina (Catalyst A). To a solution of copper(II) sulfate pentahydrate (7.8 g) in distilled water (200 mL) was added neutral alumina (50 g) at room temperature, and the suspension was stirred at this temperature for 30 min. After evaporation of water by using a rotary evaporator at 80 °C under reduced pressure (2 Torr), the resulting moist solid was then dried to dryness under vacuum (1 Torr) at 150 °C for 8 h and stored in a desiccator.

1,1'-Binaphthalene-2,2'-diol (2a): General Procedure for Catalytic Oxidative Coupling of 2-Naphthols. A 30-mL three-necked round-bottom flask was charged with **A** (0.351 g, 0.2 mmol), **1a** (0.144 g, 1.0 mmol), and chlorobenzene (10 mL). A Teflon-coated stirring bar was added, and the mixture was stirred vigorously at 140 °C for 8 h under bubbling air through the mixture. Analysis by GLC indicated the complete disappearance of **1a**. The mixture was filtered, and the filtered solid was washed with dichloromethane (10 mL × 2) and then with

acetone (10 mL × 2). Evaporation of the combined filtrate under reduced pressure left crude **2a** (0.142 g, 99%) as a brownish solid, which was further purified by treatment with active carbon to give colorless **2a** (0.138 g, 97%): mp 214–216 °C (lit.⁸ mp 216–218 °C); *R_f* 0.1 (SiO₂, hexane:acetone = 4:1); ¹H NMR (400 MHz, CDCl₃) δ 7.04 (1 H, s), 7.06 (1 H, s), 7.20 (2 H, ddd, *J* = 8.14, 8.14, and 1.33 Hz), 7.27 (2 H, ddd, *J* = 8.14, 8.14, and 1.33 Hz), 7.34 (2 H, d, *J* = 8.88 Hz), 7.87 (2 H, d, *J* = 4.44 Hz), 7.88 (2 H, d, *J* = 4.44 Hz), 7.90 (2 H, d, *J* = 8.88 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 114.9, 119.5, 123.6, 125.4, 127.0, 128.9, 130.0, 130.6, 135.5, 154.5; IR (KBr) 3600 (OH), 3500, 1645, 1625, 1545, 1500, 1490, 1410, 1350, 1250 cm⁻¹.

6,6'-Dibromo-1,1'-Binaphthalene-2,2'-diol (2b): mp 208–209 °C (lit.¹⁴ mp 198–199 °C); *R_f* 0.3 (SiO₂, hexane:acetone = 7:3); ¹H NMR (400 MHz, CDCl₃) δ 2.05 (2 H, s), 6.99 (2 H, d, *J* = 4.8 Hz), 7.35 (2 H, dd, *J* = 4.8 and 2.0 Hz), 7.40 (2 H, d, *J* = 4.8 Hz), 7.92 (2 H, d, *J* = 4.8 Hz), 8.10 (2 H, d, *J* = 2.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 115.0, 116.9, 120.8, 127.4, 130.0, 130.2, 130.8, 131.1, 134.0, 155.0; IR (KBr) 3400, 1575, 1490, 1330, 1205, 1200, 1150, 1135, 1120, 925, 865, 805 cm⁻¹; EI MS *m/z* (relative intensity) 444 (M⁺, 100), 284 (M⁺ - Br × 2, 15), 256 (33), 237 (15), 226 (29), 169 (15), 142 (35), 133 (20), 113 (33), 100 (11), 69 (11), 57 (13), 41 (12).

2,2',7,7'-Tetrahydroxy-1,1'-binaphthyl (2c): mp 131–132 °C (lit.⁹ mp 111.0–113.0 °C; lit.¹³ mp 151.0–152.0 °C); *R_f* 0.2 (SiO₂, hexane:acetone = 3:2); ¹H NMR (400 MHz, CDCl₃) δ 6.36 (2 H, s), 6.90 (2 H, dd, *J* = 8.74 and 2.24 Hz), 7.10 (2 H, d, *J* = 8.74 Hz), 7.60 (2 H, s), 7.71 (2 H, d, *J* = 8.74 Hz), 7.75 (2 H, d, *J* = 8.74 Hz), 8.26 (2 H, s); ¹³C NMR (100 MHz, CDCl₃) δ 107.3, 113.5, 115.9, 116.2, 124.8, 130.2, 130.4, 137.1, 154.8, 156.7; IR (KBr) 3350, 1690, 1610, 1510, 1210, 830 cm⁻¹; FD MS *m/z* 318 (M⁺).

2,2',7,7'-Dimethoxy-1,1'-binaphthyl-2,2'-diol (2d): mp 151–152 °C (lit.¹⁴ mp 151–152 °C); *R_f* 0.38 (SiO₂, hexane:acetone = 7:3); ¹H NMR (400 MHz, CDCl₃) δ 2.78 (2 H, s), 4.09 (6 H, s), 7.08–7.17 (2 H, m), 7.34–7.47 (4 H, m), 8.05–8.15 (2 H, m), 8.77 (2 H, s); ¹³C NMR (100 MHz, CDCl₃) δ 53.5, 115.3, 124.8, 125.5, 127.0, 130.5, 131.0, 133.5, 138.3, 155.0, 171.8; IR (KBr) 3400, 3100, 1670, 1500, 1430, 1320, 1280, 1220, 795 cm⁻¹; EI MS *m/z* (relative intensity) 402 (M⁺, 73), 370 (46), 326 (21), 310 (48), 282 (15), 254 (72), 239 (15), 226 (35), 155 (28), 113 (65), 100 (12), 73 (12), 58 (22), 43 (100).

3,3'-Bismethoxycarbonyl-1,1'-binaphthyl-2,2'-diol (2e): mp 276.0–277.0 °C (lit.⁹ mp 276.0–278.0 °C); *R_f* 0.35 (SiO₂, hexane:acetone = 3:2); ¹H NMR (400 MHz, CDCl₃) δ 3.55 (6 H, s), 5.05–5.25 (2 H, s), 6.47 (2 H, d, *J* = 2.8 Hz), 7.01 (2 H, dd, *J* = 5.6 and 2.8 Hz), 7.19 (2 H, d, *J* = 5.6 Hz), 7.75 (2 H, d, *J* = 5.6 Hz), 7.84 (2 H, d, *J* = 5.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 55.1, 103.5, 110.0, 115.0, 116.0, 125.0, 130.0, 131.0, 135.0, 153.5, 158.0; IR (KBr) 3350, 1605, 1505, 1450, 1415, 1360, 1260, 1210, 1025, 825 cm⁻¹.

Stoichiometric Coupling of 1a. To a 30-mL round-bottom flask were placed **A** (3.51 g, 2.0 mmol), **1a** (0.144 g, 1.0 mmol), and chlorobenzene (10 mL). The mixture was stirred at 140 °C for 8 h under bubbling nitrogen, cooled down to room temperature, and then filtered. The filtered solid was washed with dichloromethane (10 mL × 2) and then with acetone (10 mL × 2). Evaporation of the combined filtrate under reduced pressure left crude **2a** (0.133 g, 93%) as a brownish solid, which was further purified by treatment with active carbon to give colorless **2a** (0.127 g, 89%).

Large Scale Synthesis of 2a. To a 2-L round-bottom flask were placed **A** (35.11 g, 20 mmol), **1a** (14.42 g, 100 mmol), and chlorobenzene (1 L), and the mixture was stirred mechanically at 140 °C for 8 h under bubbling air through the mixture. The reaction was cooled to room temperature and filtered. The filtered solid was washed with dichloromethane (100 mL × 2) and then with acetone (100 mL × 2). After evaporation of the combined filtrate, the brownish residue (14.17 g) was recrystallized from toluene to give colorless **2a** (12.74 g, 89%).

3,3',5,5'-Tetra-*tert*-butyl-4,4'-biphenol (3): Catalytic Oxidative Coupling of 2,6-Di-*tert*-butylphenol (3). To a 30-mL three-necked round-bottom flask were placed **A** (0.351 g, 0.2 mmol), **3** (0.206 g, 1.0 mmol), and chlorobenzene (10 mL),

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and the mixture was stirred with a Teflon-coated magnetic stirring bar at 140 °C for 8 h under bubbling air through the mixture. After filtration, the filtered solid was washed with dichloromethane (10 mL × 2) and then with acetone (10 mL × 2). Evaporation of the combined filtrate under reduced pressure left **4** (0.2 g, 98%) as a brownish solid. The crude product was further purified by treatment with active carbon to give light brownish **4** (0.19 g, 94%): mp 239–241 °C (lit.¹⁵ mp 239–242 °C); *R_f* 0.82 (SiO₂, hexane:acetone = 10:1); ¹H NMR (400 MHz, CDCl₃) δ 1.2–1.6 (36 H, m), 7.89 (4 H, s); IR (KBr) 3400, 2925,

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1590, 1450, 1350, 1270, 1085, 1035, 890 cm⁻¹; EI MS *m/z* (relative intensity) 408 (M⁺), 351 (M⁺ - *t*-Bu, 10), 191 (7), 135 (9), 107 (7), 57 (100), (35).

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Registry nos. provided by the author: **2a**, 41024-90-2; **2b**, 79082-80-7; **2c**, 66478-68-0; **2d**, 128702-28-3; **2e**, 47644-69-9.