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Aerobic Oxidative Coupling of 2-Naphthol Derivatives Catalyzed by a Copper–Amine Complex without Solvent

Makoto NAKAJIMA,*,[a] Shun-ichi HASHIMOTO,[a] Masahiro NOJI,[b,1] and Kenji KOGA[b,2]

Graduate School of Pharmaceutical Sciences, Hokkaido University,[a] Kita-12 Nishi-6, Kita-ku, Sapporo 060–0812, Japan and Graduate School of Pharmaceutical Sciences, University of Tokyo,[b] 7–3–1, Hongo, Bunkyo-ku, Tokyo 113–0033, Japan.

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Aerobic oxidative coupling of naphthols catalyzed by a copper–amine complex was found to proceed without solvent in high efficacy. The present reaction was applied to a practical synthesis of 1,1′-binaphthalene-2,2′-diol on multi-gram scale.

Key words binaphthol; aerobic oxidation; copper–amine complex

Homochiral 1,1′-binaphthalene derivatives have emerged as important chiral auxiliaries and ligands for a growing range of asymmetric organomatallic transformations.[3] Since 1,1′-binaphthalene-2,2′-diol (BINOL) is a versatile source of a variety of compounds with the binaphthyl skeleton, much attention has been paid to the effective synthesis of BINOL. Oxidative coupling of 2-naphthols employing a stoichiometric amount of oxidizing agent is a well-established method for the preparation of binaphthols.[4] While various oxidizing agents are now being used for oxidative coupling of 2-naphthols, they are often hazardous and expensive, precluding their use for large-scale reactions. In addition, most oxidizing agents form equimolar amounts of waste, which are difficult to remove from the reaction mixture and must be disposed with special care. From this point of view, aerobic oxidative coupling is an ideal reaction, in which water is the sole by-product. We have already developed the aerobic oxidative coupling of 2-naphthols catalyzed by a copper–amine complex, which has provided the first successful example of the catalytic oxidative coupling.[5] Despite its efficacy, the present reaction requires dichloromethane as a solvent, contamination of which in the effluent is tightly restricted under law. After considerable screening of ecologically friendly solvents, we were surprised to find that the aerobic oxidative coupling catalyzed by the copper–amine complex proceeded without solvent, even though both substrate and catalyst are solids.

Solid state reactions, *i.e.* solid to solid reaction without solvent, has recently received particular attention from an ecological point of view; however, few examples have been reported on a catalytic reaction in the solid state.[6] It seems reasonable to suppose that turn-over numbers of the catalytic reaction would be poor because the solid state reaction is a consequence of the movement of molecules in the solid state. In fact, Toda has reported catalytic oxidative coupling of naphthols in the solid state by the aid of ultrasound irradiation, wherein the turn-over number is less than 5.[7]

We investigated the aerobic oxidative coupling of 2-naphthol (**1a**) in the presence of Cu(OH)Cl–tetramethylethylenediamine (TMEDA) complex without solvent. A mixture of 2-naphthol (**1a**) (mp 122—123 °C) and 5 mol% of Cu(OH)Cl–TMEDA[5,8] (mp 137—138 °C) was finely ground into powders with a mortar and pestle and heated at 50 °C for 2 h. The mixture remained as powders without being liquidified in appearance. Washing the mixture with aqueous ammonia and water afforded practically pure BINOL **2a** in quantitative yield, which could be further purified by column chromatography or recrystallization. The results obtained for the oxidative coupling of a variety of naphthols are summarized in Table 1. Naphthols with various substituted patterns were oxidized into the corresponding binaphthols in high yields. It should be noted that **1c** having an ester moiety at the 3-position also produced **2c** in high yield, which demonstrates that the catalyst maintains its high reactivity without solvent. The present protocol has the advantages of providing a facile access to BINOL on multi-gram scale, and including practical value as well as operational safety and simplicity.

While the reaction mechanism without solvent is open to a variety of interpretations, the movement of the catalyst molecules might be assisted by water generated as a by-product. In fact, the oxidation of **1a** in the presence of the copper–amine complex in water under heterogeneous conditions did afford **2a** (50 °C, 24 h, 60%), though the reaction proceeded relatively slowly. If so, the present reaction might not be included in a category of the solid state reaction, though it is too early to make a judgement.

In conclusion, we have developed the aerobic oxidative coupling of naphthols catalyzed by a copper–amine complex without solvent, which provides an efficient means for a large-scale preparation of binaphthols. A mechanistic study is now in progress in our laboratory.

Experimental

Melting points were measured using a Büchi 535 melting point apparatus and were not corrected. ^{1}H-NMR spectra were recorded on a JEOL EX-270 (^{1}H, 270 MHz) spectrometer in deuteriochloroform. Chemical shift values are expressed in ppm relative to internal tetramethylsilane. Coupling constants (J) are reported in Hertz (Hz). Abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, br, broad. Cu(OH)Cl–TMEDA was prepared by the literature methods.[5a,8]

General Procedure for Aerobic Oxidative Coupling of Naphthols without Solvent. 1,1′-Binaphthalene-2,2′-diol (2a) A mixture of 2-naphthol (**1a**) (1.0 g, 7.0 mmol) and Cu(OH)Cl–TMEDA (80 mg, 0.35 mmol) was finely ground with a mortar and pestle and heated at 50 °C for 2 h. Washing with 10% aq. NH$_3$ and water afforded practically pure **2a** (0.95 g, 96%) as brown needles. Column chromatography (silica gel, hexane–ethyl acetate, 10 : 1) afforded **2a** (0.91 g, 92%) as colorless needles of mp 212—214 °C (lit.[4c] 214—216 °C). ^{1}H-NMR (CDCl$_3$) δ: 5.05 (s, 2H, OH), 7.14 (d, 2H, J=8.3 Hz, 8,8′-H), 7.30—7.37 (m, 4H, 6,6′,7,7′-H), 7.37 (d, 2H, J=8.9 Hz, 3,3′-H), 7.88 (d, 2H, J=7.3 Hz, 5,5′-H), 7.96 (d, 2H, J=8.9 Hz, 4,4′-H).

3,3′-Dimethyl-1,1′-binaphthalene-2,2′-diol (**2b**): mp 210—211 °C (lit.[4d] 205 °C). ^{1}H-NMR (CDCl$_3$) δ: 2.51 (s, 6H, CH$_3$), 5.10 (s, 2H, OH), 7.07 (d, 2H, J=8.2 Hz, 8,8′-H), 7.30—7.37 (m, 4H, 6,6′,7,7′-H), 7.80 (s, 2H, 4,4′-H), 7.81 (d, 2H, J=6.6 Hz, 5,5′-H).

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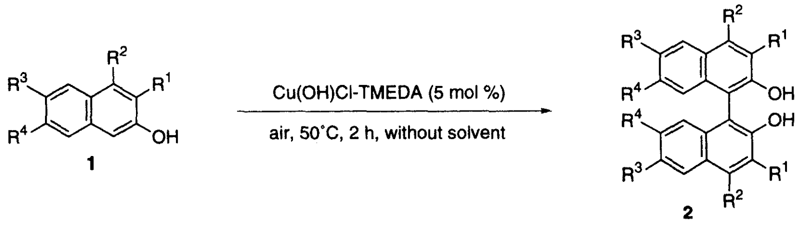
* To whom correspondence should be addressed.

Table 1. Aerobic Oxidative Coupling of Naphthols Catalyzed by Cu(OH)Cl–TMEDA without Solvent[a]



Naphthol					Binaphthol	
	R^1	R^2	R^2	R^4		Yield, %[b]
1a	H	H	H	H	**2a**	92
1b	CH_3	H	H	H	**2b**	88
1c	$COOCH_3$	H	H	H	**2c**	93
1d	H	H	Br	H	**2d**	92
1e	H	H	H	OCH_3	**2e**	92
1f	–CH=CH–CH=CH–		H	H	**2f**	89

a) All the reactions were performed on 7 mmol scale. *b*) Isolated yield after silica gel column chromatography.

Dimethyl 2,2′-Dihydroxy-1,1′-binaphthalene-3,3′-dicarboxylate (**2c**): mp 280—282 °C (lit.[4i] 276—278 °C). ^{1}H-NMR ($CDCl_3$) δ: 4.02 (s, 6H, OCH_3), 7.13—7.17 (m, 2H, 8,8′-H), 7.30—7.33 (m, 4H, 6,6′,7,7′-H), 7.88—7.91 (m, 2H, 5,5′-H), 8.67 (s, 2H, 4,4′-H), 10.71 (s, 2H, OH).

6,6′-Dibromo-1,1′-binaphthalene-2,2′-diol (**2d**): mp 209—211 °C (lit.[4b] 208—209 °C). ^{1}H-NMR ($CDCl_3$) δ: 5.16 (s, 2H, OH), 6.93 (d, 2H, J=8.9 Hz, 3,3′-H), 7.27—7.40 (m, 4H, 4,4′,8,8′-H), 7.95 (d, 2H, J=8.0 Hz, 7,7′-H), 8.01 (d, 2H, J=2.0 Hz, 5,5′-H).

7,7′-Dimethoxy-1,1′-binaphthalene-2,2′-diol (**2e**): mp 151—152 °C (lit.[4i] 151—152 °C). ^{1}H-NMR ($CDCl_3$) δ: 3.55 (s, 6H, OCH_3), 5.10 (s, 2H, OH), 6.46 (d, 2H, J=2.6 Hz, 8,8′-H), 7.01 (dd, 2H, J=2.6, 8.9 Hz, 6,6′-H), 7.18 (d, 2H, J=8.9 Hz, 3,3′-H), 7.74 (d, 2H, 8.9 Hz, 5,5′-H), 7.82 (d, 2H, J=8.9 Hz, 4,4′-H).

9,9′-Phenanthrene-10,10′-diol (**2f**): mp 239—240 °C (lit.[4e] 240—241 °C). ^{1}H-NMR ($CDCl_3$) δ: 5.54 (s, 2H, OH), 7.26 (d, 2H, J=7.9 Hz, 8,8′-H), 7.31 (t, 2H, J=7.4 Hz, 7,7′-H), 7.49 (t, 2H, J=7.4 Hz, 6,6′-H), 7.69 (t, 2H, J=7.6 Hz, 2,2′-H), 7.78 (t, 2H, J=6.9 Hz, 3,3′-H), 8.44 (d, 2H, J=7.9 Hz, 1,1′-H), 8.71 (d, 2H, J=8.3 Hz, 5,5′-H), 8.77 (d, 2H, J=8.2 Hz, 4,4′-H).

Multi-Gram Scale Synthesis of 2a without Solvent A mixture of **1a** (50 g, 0.35 mol) and Cu(OH)Cl–TMEDA (4.0 g, 0.017 mol) was finely ground with a mortar and pestle and heated at 50 °C in a beaker for 4 h. Washing with 10% aq. NH_3 and water afforded practically pure **2a** (48 g, 96%) as brown needles. Recrystallizations from methanol (300 ml)–water (600 ml) and then from toluene (300 ml) afforded **2a** (38 g, 76%) as colorless needles.

References and Notes

1) Present address: *Meiji Pharmaceutical University, 2–522, Noshio, Kiyose, 204–8588, Japan.*
2) Present address: *Nara Institute of Science and Technology, 8916–5, Takayama, Ikoma, 630–0101, Japan.*
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8) Cu(OH)Cl–TMEDA dimer (di-μ-hydroxo-bis[(*N,N,N′,N′*-tetramethylethylenedi-amine)copper(II)] chloride) is now in commercially available (Tokyo Kasei, D2542).