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A New Catalytic System for Aerobic Oxidative Coupling of 2-Naphthol Derivatives by the Use of CuCl-Amine Complex: A Practical Synthesis of Binaphthol Derivatives

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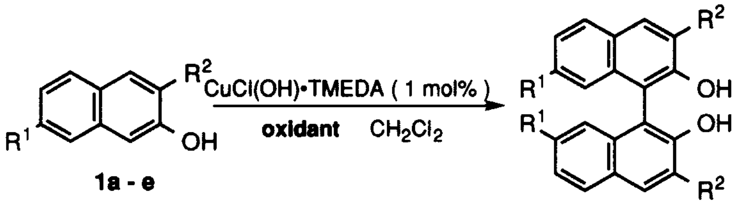
Abstract: Aerobic oxidative coupling of 2-naphthol derivatives by the use of 1 mol% of CuCl-amine complex afforded binaphthol derivatives in excellent yields.

Axially chiral binaphthalenes have been widely used in organic synthesis as chirality inducers.[2] Oxidative coupling of 2-naphthols represents a well established method for the preparation of binaphthols. The couplings are usually carried out by treatment of naphthols with more than equimolar amount of metal such as Fe(III),[3-5] Mn(III),[4,5] and Cu(II).[8-12] Very recently catalytic processes were developed by the use of $CuCl_2$-amine / AgCl system[12c] or $FeCl_3$ in solid state.[5] But both of the systems still need 20 mol% of metals and are hard to be utilized for practical method. We wish to report herein the first efficient catalytic process for the aerobic oxidative coupling of naphthol derivatives by use of a catalytic amount (***1 mol%***) of CuCl to establish a practical synthesis of binaphthol derivatives.



1a - e

2a - e

Table 1 Oxidative Coupling of Naphthols

naphthol	R_1	R_2	oxidant	time, h	temp	yield, %
1a	H	H	O_2	8.5	0°C	90
1b	H	Me	O_2	1	r.t.	92
1c	MeO	H	O_2	1.5	r.t.	96
1d	H	CO_2Me	O_2	96	reflux	99*
1e	9-Phenanthrol		O_2	0.5	r.t.	79
1a	H	H	Air	20	0°C	96
1b	H	Me	Air	1	r.t.	96
1c	MeO	H	Air	2	r.t.	95
1d	H	CO_2Me	Air	144	reflux	99*
1e	9-Phenanthrol		Air	1.5	r.t.	77

* Reaction was performed in MeOH

Cu(I)-amine complex has been known to catalyze the oxidative coupling of acetylenes and active methine compounds.[13] Phenols can be also oxidized to give mixtures of quinones and the reactions are usually not selective enough for preparative purpose. We have found 2-naphthol derivatives are oxidized with CuCl-TMEDA under molecular oxygen or even in air to give binaphthol derivatives in excellent yields. The present reaction is equally promoted by CuCl(OH)•TMEDA[14] which is easily prepared from CuCl and TMEDA under oxygen and has the advantage of its stability and manipulability over CuCl itself.

Results are summarized in Table 1. Naphthols of wide variety can be oxidized to form binaphthols in excellent yields. A typical reaction procedure is as follows. **1a** (0.50 g, 0.35 mmol) was added to a mixture of CuCl(OH)•TMEDA (8 mg, 0.035 mmol) in dichloromethane (35 ml) and the whole was stirred at 0°C for 20 h in open air. Concentration followed by column chromatography (silica gel, hexane:ether=9:1) afforded **2a** (0.48 g, 96%) of mp 216-218°C (lit.[8a] 216-218°C).

Further studies on enantioselective oxidative coupling are now in progress.

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REFERENCES AND NOTES

1. Present Address: Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060, Japan.
2. Rosini, C.; Franzini, L.; Raffaelli, A.; Salvadori, P. *Synthesis* **1991**, 503-517.
3. Pummerer, R.; Prell, E.; Rieche, A. *Ber.* **1926**, *59*, 2159-2161.
4. Feringa, B.; Wynberg, H. *J. Org. Chem.* **1981**, *46*, 2547-2557.
5. Toda, F.; Tanaka, K.; Iwata, S. *J. Org. Chem.* **1989**, *54*, 3007-3009.
6. Dewar, M.J.S.; Nakaya, T. *J. Am. Chem. Soc.* **1968**, *90*, 7134-7135.
7. Yamamoto, K.; Fukushima, H.; Okamoto, Y.; Hatada, K.; Nakazaki, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1111-1112.
8. (a) Feringa, B.; Wynberg, H. *Tetrahedron Lett.* **1977**, 4447-4450; (b) Feringa, B.; Wynberg, H. *Bioorg. Chem.* **1978**, *7*, 397-408.
9. Yamamoto, K.; Fukushima, H.; Nakazaki, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1490-1491.
10. Brussee, J.; Groenendijk, J.L.G.; teKoppele, J.M.; Jansen, A.C.A. *Tetrahedron* **1985**, *41*, 3313-3319.
11. Hovorkova, M.; Günterová, J.; Závada, J. *Tetrahedron Lett.* **1990**, *31*, 413-416.
12. (a) Smrčina, M.; Lorenc, M.; Hanuš, V.; Kočovský, P. *Synlett* **1991**, 231-232; (b) Smrčina, M.; Lorenc, M.; Hanuš, V.; Sedmera, P.; Kočovský, P. *J. Org. Chem.* **1992**, *57*, 1917-1920; (c) Smrčina, M.; Poláková, J.; Vyskočil, Š.; Kočovský, P. *J. Org. Chem.* **1993**, *58*, 4534-4538.
13. deJong, C.R.H.I. : In *Organic Syntheses by Oxidation with Metal Compounds.* Mijs, W.J.; deJong, C.R.H.I. Eds.; Plenum Press Inc., New York, **1986**; pp. 423-443.
14. The catalyst was prepared according to the procedure in lit.[13] as follows: a mixture of CuCl (8.2 g) and TMEDA (19 g) in 95 % methanol was stirred under oxygen atmosphere at rt for 1 h. The resulting precipitates were collected by filtration and washed with acetone. Drying in vacuo gave purple powder (19 g, 98 %) of mp 137-138°C(dec).

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