Chinese Chemical Letters Vol. 15, No. 8, pp 903-906, 2004
http://www.imm.ac.cn/journal/ccl.html

A Novel and Efficient Catalytic System for Aerobic Oxidative Coupling of 2-Naphthol Derivatives

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Abstract: The paper reported a novel and efficient aerobic oxidative coupling reaction of 2-naphthol derivatives catalyzed by CuCu (I or II)N-alkylimidazole complexes in excellent yields. The crystal structure of CuCu (II)N-methylimidazole complex to be determined by X-Ray.

Keywords: Binaphthol , oxidative coupling, Cu (I or II)-N-alkylimidazole complex.

Binaphthol is a versatile source of a variety of compounds with the binaphthyl skelecton, much attention has been paid to the effective synthesis of it[1]. Oxidative coupling of 2-naphthol derivatives represents a well established method for the preparation of binaphthol derivatives. Various oxidizing agents such as Fe(III)[2,3], Mn(III) [4], or Cu(II) [5]are now being used for oxidative coupling of 2-naphthol derivatives. But these routs suffer from disadvantages: requirement of stoichiometric quantities of oxidant, producing stoichiometric amounts of waste, which are difficult to remove from the reaction mixture and must be disposed with special care. Recently, several catalytic processes for aerobic oxidative coupling were developed. For example Nakajima has already developed the aerobic oxidative coupling of 2-naphthol derivatives catalyzed by a copper-amine complex [Cu(OH)Cl-TMEDA][6], in which water is the sole byproduct. From this point of view, aerobic oxidative coupling is an ideal method.

As a cheap and commercially available material, imidazole is important and versatile ligand and can be used in many fields. The interest of our group has been focused on the synthesis and application of imidazole, imidazolium and their derivatives, such as the condensation of benzaldehyde[7], the oxidation of benzoin[8], the hydrolysis of carboxylates[9], the enantioselective recognition[10], and the anion recognition[11]. We herein report a novel and efficient aerobic oxidative coupling of 2-naphthol derivatives by use of catalytic amount of Cu (I or II) -N-alkylimidazole complexes providing a practical synthesis of binaphthol derivatives. To our knowledge, this is the first example of employing Cu (I or II)-N-alkylimidazole complexes as catalysts for aerobic oxidative coupling of 2-naphthol derivatives.

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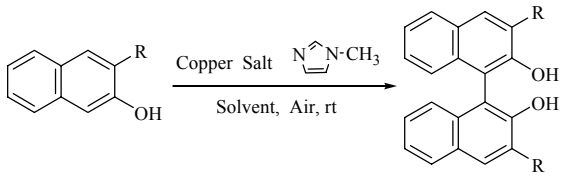


Table 1 Catalytic oxidative coupling of 2-naphthol derivatives

entry	R	Copper salt	Solvent	Time(h)	Yield [a] (%)
1	H	CuCl	MeOH	6	70
2	H	CuCl	CH_3COCH_3	6	20
3	H	CuCl	AcOEt	6	35
4	H	CuCl	CH_2Cl_2	6	88
5[b]	H	CuCl	CH_2Cl_2	6	91
6	H	CuBr	CH_2Cl_2	6	62
7	H	$CuCl_2{\cdot}2H_2O$	CH_2Cl_2	48	50
8	H	$Cu(NO_3)_2{\cdot}3H_2O$	CH_2Cl_2	48	75
9	H	$Cu(OAc)_2{\cdot}H_2O$	CH_2Cl_2	72	89
10	$COOCH_3$	CuCl	CH_2Cl_2	24	99
11	$COOCH_3$	CuCl	MeOH	24	99
12	$COOC_2H_5$	CuCl	CH_2Cl_2	24	99
13	$COOPr^i$	CuCl	CH_2Cl_2	24	99

a. isolated yield. b. reaction temperature: 0^oC.

The effect of solvents was first examined. CH_2Cl_2, MeOH, CH_3COCH_3, AcOEt were tested, and the best result was obtained with dichloromethane (**Table 1**,entries 4, 5, 10, 12, 13). When the oxidative coupling of 2-naphthol derivatives were performed in methanol (**Table 1**,entries 1, 11), binaphthol derivatives were obtained also in good yield. Other solvents were not achieved satisfactory result along with byproducts (**Table 1**, entries 2, 3).

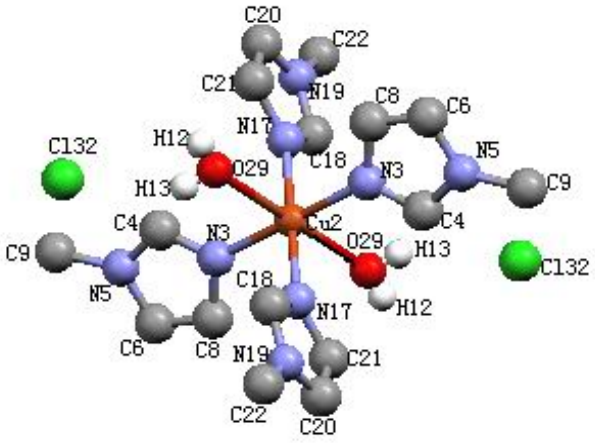
We then made a survey of the effect of different copper salts. $Cu(NO_3)_2{\cdot}3H_2O$, $CuCl_2{\cdot}2H_2O$ or $Cu(OAc)_2{\cdot}H_2O$ had often been employed stoichiometric oxidative coupling[5], but we used catalytic amount of them, binaphthol was obtained in good yield (**Table 1**, entries 8 or 9). CuCl, CuBr were also examined, it was observed that CuCl was the best copper salt, gave binaphthol in 88-91% yield (**Table 1**, entries 4, 5) and 2,2′-dihydroxy-1,1′-binaphthalene-3,3′-dicarboxylate in 99% yields (**Table 1**, entries 10-13).

Several N-alkylimidazoles such as methyl, ethyl, *n*-heptanyl, phenyl, and benzylimidazole were employed the oxidative coupling. All the ligands exhibited good catalytic activity except phenylimidazole. N-methylimidazole is cheap and commercially, so we chosed it for the reaction.

The catalytic system also proved to be high efficient for 3-hydroxy-2-naphthoic acid derivatives. The coupling of these compounds affored the corresponding binaphthols in up to 99% yields, (**Table 1**, entries 10-13). It implied that the ester moiety at the 3-position restrained the form of byproducts, so excellent yields were obtained.

A mixture of $CuCl_2{\cdot}2H_2O$ and N-methylimidazole in dichloromethane was stirred under the air atmosphere at room temperature for 1 h, we obtained the crystal of Cu(II)-

Figure 1 Crystal structure of the complex $[Cu(C_4H_6N_2)_4Cl_2{\cdot}3H_2O]$



Selected bond lengths [Å] and angle [°]: Cu2-N3 1.995(6); Cu2-N17 2.022(6); Cu2-O29 2.495(6); N17-Cu2-O29 89.7(3); N3-Cu2-O29 89.3(2); N3-Cu2-N17 89.1(2); O29-Cu2-O29 179.995; N17-Cu2-N17 179.994. (only the H atoms at the O atoms are show, one molecular of crystal water is omitted).

N-methylimidazole complex $[Cu(C_4H_6N_2)_4Cl_2{\cdot}3H_2O]$ (**Figure 1**). The crystal structure of the complex was given by X-ray. We can see that the four imidazole groups are in the same plane, two moleculars of water are up and down perpendicular to this plane, respectively. There are two groups of different Cu-N bond lengths in the crystal structure, respectively: Cu2-N3 1.995(6); Cu2-N17 2.022(6). The crystal structure was a octahedron.

Conclusion

We have developed a new and highly efficient aerobic oxidative coupling reaction of 2-naphthol derivatives catalyzed by Cu (I or II)-N-alkylimidazole complexes for the first time. One of the complexes' structure also was determined. A mechanistic study is now in progress in our lab.

Acknowlegments

This work is supported by the National Natural Science Foundation of China. (No.20172038, 20132020).

References and Notes

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13. General procedure for the aerobic coupling of 2-naphthol derivatives catalyzed by Cu (I or II)-N-alkylimidazole complexes: A mixture of CuCl (0.2 mmol) and N-methylimidazole (0.4 mmol) in dichloromethane (15 mL) was stirred in the air atmosphere at room temperature for 1 h, and then 2-naphthol derivatives (1 mmol) was added. After the reaction was completed, the mixture was concentrated and followed by silica gel column chromatography (CH_2Cl_2-petrolem) afforded the corresponding binaphthol derivatives. The spectroscopic properties of the products were coincident with those previously reported[1,6]
14. Spectral data of the compounds:
Binaphthol. MS m/z 286(M^+). 226 (M-60)$^+$. mp 217-218℃, (lit[12]: 217-219°C).
Dimethyl 2,2′-dihydroxy-1,1′-binaphthalene-3,3′-dicarboxylate. MS m/z 402(M^+), 371 (M-31)$^+$, 226(M-176)$^+$. ^{1}H NMR δ ($CDCl_3$, ppm), 4.06(s, 6H), 7.16 (ddd, 2H, J=3.1, 3.1, 1.2Hz), 7.32-7.37 (m, 4H), 7.92 (ddd, 2H, J=3.1, 3.1, 2.2Hz), 8.70(s, 2H), 10.73(s, 2H).
Diethyl 2,2′-dihydroxy-1,1′-binaphthalene-3,3′-dicarboxylate. MS m/z 430(M^+), 385(M-45)$^+$, 310 (M-120)$^+$, 226 (M-204) $^+$ 1H NMRδ ($CDCl_3$, ppm), 1.51 (t, 6H, J=7.1Hz), 4.52 (q, 4H, J=7.1Hz), 7.16(dd, 2H, J=6.3, 3.4Hz), 7.31-7.34(m, 4H), 7.93(dd, 2H, J=6.3, 3.1Hz), 8.70(s, 2H), 10.82 (s, 2H).Diisopropyl 2,2′-dihydroxy-1,1′-binaphthalene-3,3′-dicarboxylate. MS m/z 458(M^+),399 (M-59)$^+$, 356(M-102)+, 226(M-232)$^+$. 1H NMRδ (CDCl3, ppm), 1.49(d, 12H, J=6.3Hz), 5.40 (septet, 2H, J=6.3Hz), 7.17 (ddd, 2H, J=2.7, 3.6, 1Hz), 7.31-7.37(m, 4H), 7.94 (ddd, 2H, J=3.2, 3.4, 2.8Hz), 8.68(s, 2H), 10.92(s, 2H).
15. The analytical data and crystal data were submitted to editorial office of CCL.

Received 18 August, 2003