SHORT PAPER

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Efficient solvent-free oxidative coupling of 2-naphthols by copper(II) oxymetasilicate under microwave irradiation

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Abstract: Solvent-free oxidative coupling of 2-naphthols by copper(II) oxymetasilicate without solvent under microwave irradiation gives the corresponding 1,1′-binaphthalene–2,2′-diols in 75-97% yields.

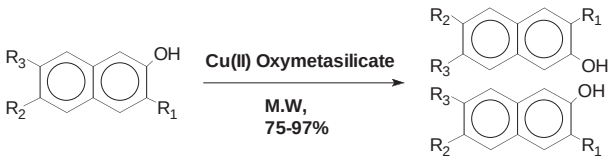
Keywords: Oxidative coupling, Cu(II) Oxymetasilicate, 2-naphthols, binaphthols, solvent-free

Chiral 1,1′-binaphthalene-2, 2′-diol derivatives such as BINOL and BINAP have been widely used in asymmetric synthesis as chiral auxiliaries. The most employed method for construction of the binaphthyl structure is oxidative coupling of 2-naphthol derivatives. Several procedure have been reported in the literature for this chemical bond formation, such as use of $FeCl_3$,[1] $K_3Fe(CN)_6$,[2] $Mn(acac)_3$,[3] Cu(II)-amine complexes,[4] $CuSO_4$-support,[5] $VO(acac)_2$[6] and $FeCl_3.6H_2O$.[7] Most of these methods require long reaction times and some of them produce low yields of the product. The other disadvantage of some of these methodologies is using chlorobenzene as a solvent for high temperature refluxing which makes the separation and isolation of the products a rather tedious process.

Toda and his coworkers have described the possibility of phenol coupling by oxidative reactions under solvent-free conditions by $FeCl_3.6H_2O$.[7] Ultrasound irradiation has been also tried for this purpose but the results are not encouraging.

A large number of dry reactions initiated by microwave irradiation are reported in the literature.[8] Solvent-free conditions coupled with the high yields and short reaction times often associated with microwave irradiation reactions make these procedures very attractive for synthesis. Coupling of 2-naphthols by $FeCl_3.6H_2O$ irradiated by microwave irradiation is a low yielding process and gives the corresponding binaphthols in 3–76% yields.[9] The disadvantages of this method are the low yields of the process and also the fact that an ordinary commercial microwave oven cannot be used for this process. Recently, binaphthols have been synthesised over copper-supported mesoporous molecular sieves in chlorobenzene at high temperature.[10]

We now introduce a new and simple method for the synthesis of 1,1'-binaphthalene-2, 2′-diols from the corresponding 2-naphthols using Cu(II) oxymetasilicate as a reagent under microwave irradiation (M.W.) in an ordinary appliance microwave oven under solvent-free conditions in 75–97% yields (Scheme 1,Table 1).



Scheme 1

Cu(II) oxymetasilicate is readily prepared by reaction of copper sulfate and commercially available sodium silicate solution[11]. The oxidative coupling reactions of 2-naphthol and some of its derivatives can be carried out simply by irradiation of the mixture of finely powdered **1a**–**1f** and copper(II) oxymetasilicate in a commercial kitchen microwave oven in the absence of solvent. Under these conditions, 2-naphthol derivatives coupled very quickly and the termination of the reaction could be detected by the change of the colour of the reaction mixture. The blue colour of the initially prepared reagent turned into dark green at the end of the reaction. The reagent could be regenerated and reused several times after removal of the product completely with ether and heating for 3 h in air at 250 °C.

As it is evident from Table 1, when an OH group is present in the molecules the yields of the products are not as good as when this group is replaced by the OCH_3 group. We believe that this effect is probably due to the stronger interaction of OH with the reagent, which deactivates the oxymetasilicate. The more electron-donating effect of the OCH_3 group facilitates the coupling reaction of the aromatic rings and as a result higher yields of the products are obtained.

Table 1 Oxidative coupling of naphthols (1) to give the corresponding binaphthols (**2**) by copper(II) oxymetasilicate under microwave irradiation

Naphthol	R1	R2	R3	Time/min	Product	Yield/%[a]	M.p./°C	Lit.m.p./°C
1a	H	H	H	3	**2a**	95	215–217	214–216[5a]
1b	H	H	OH	3	**2b**	80	127–129	131–132[5a]
1c	H	H	OCH_3	2	**2c**	90	147–149	151–152[5a]
1d	OH	H	H	3	**2d**	75	267–269	275[12]
1e	OCH_3	H	H	3	**2e**	85	251–253	255.5–256.5[13]
1f	H	Br	H	3	**2f**	97	203–205	208–209[5a]

[a] Isolated yields.

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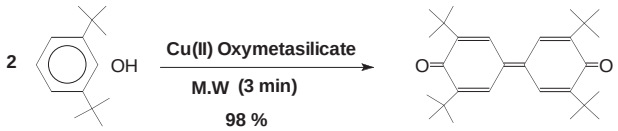
Coupling of phenol under similar reaction conditions was not successful but when 2,6-*di*-*tert*-butylphenol (**3**) was subjected to the coupling reaction the corresponding dibenzoquinone (**4**) was obtained in 98 % yield in only 3 min (Scheme 2) {m.p. 237–239°C, Lit. m.p. 239–241°C[5a]}. The same reaction in chlorobenzene under reflux conditions gave the corresponding quinone in 91% yield after 2h.



Scheme 2

In conclusion, Cu(II) oxymetasilicate, an easily prepared reagent from cheap and commercially available compounds, is an efficient reagent for oxidative coupling of 2-naphthols to form binaphthols under microwave irradiation under solvent-free conditions. This methodology is associated with reusability of the reagent, short reaction times, easy work-up, excellent yields, and the stability of the reagent which lasts for months.

Experimental

General: Yields refer to isolated products. The reactions proceeded under solvent free conditions and under microwave irradiation. The microwave oven used was a commercially available model (Butan M 245 Kitchen oven) at maximum power level of 1000 W. Products were characterised by comparison with authentic samples (IR, ^{1}H NMR, TLC).

Preparation of copper(II) oxymetasilicate: To a solution of copper(II) sulfate pentahydrate (25 g) in distilled water (200 ml) was added sodium silicate solution (water glass 50 ml 196.6 gdm^{-3} pH12 at room temperature and copper(II) oxymetasilicate was precipitated immediately. The resulting blue suspension was stirred at room temperature for 1 h. The mixture was filtered through Buckner filter and 75g of a wet precipitate was formed. After 3 hr in an oven (130°C) it became dried and finally 30g reagent was obtained. This reagent is stable for months without losing its reactivity. The reagent contains 10.13% Cu.

*Oxidative coupling of 2-naphthol (**1a**) to form 1,1'-binaphthalene-2, 2'-diol (**2a**):* In a typical run a mixture of copper(II) oxymetasilicate (1.3g) and 2-naphthol (0.16g, 1.1 mmol) was powdered and mixed. The mixture was irradiated in an open Pyrex tube 8mm diameter in a commerical microwave oven for 3 minutes. Then the reaction mixture was extracted with 10 ml ether. The crude product was passed through a short column packed with silica gel (hexane: acetone 50:50), to form the product on removal of the solvent 1,1'-binaphthalene-2, 2'-diol (**2a**) (0.15g) in 95% yield, m.p. 215–217°C (lit[4a], m.p. 216–218°C) was obtained.

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