Aerobic catalytic oxidative coupling of 2-naphthols and phenols by $VO(acac)_2$

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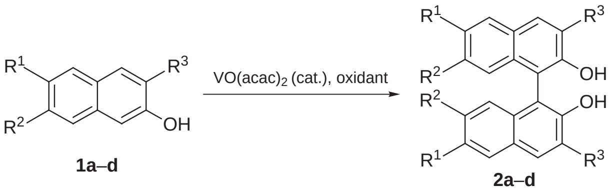
In the presence of a catalytic amount of $VO(acac)_2$, oxidative coupling of 2-naphthol or phenol derivatives with molecular oxygen occurred at room temperature and selectively gave the corresponding *ortho–ortho* coupling products in moderate to high yields.

Optically active 1,1′-bi-2-naphthol and its derivatives have been widely used in enantioselective synthesis as a source of chirality.[1] There are some known methods for the oxidative coupling of 2-naphthols to give 1,1′-bi-2-naphthols using stoichiometric amounts of oxidant,[2–4] and some methods employing catalytic oxidative coupling. These methods either use an expensive oxidant (such as AgCl) with low yield,[4c] require the preparation of a complex catalyst [such as CuCl(OH)·TMEDA, $CuSO_4(Al_2O_3)$] before the coupling reaction,[5,6] or perform the reaction at higher temperature [$CuSO_4(Al_2O_3)$, $FeCl_3$].[2a] Oxovanadium complexes were found to have specific catalytic activity towards organic syntheses especially in oxidation reactions.[7] A vast number of synthetic reactions which utilize oxovanadium(V), *i.e.* $VOCl_3$ and VOF_3, as oxidants have been documented, as exemplified by the oxidative coupling of phenols in natural product synthesis.[8] Due to the fact that $VOCl_3$ and VOF_3 are moisture sensitive, hazardous materials,[9] they are not easy to use in practice. Thus it is important to find a more convenient method for the oxidative coupling of phenols. Here we report a convenient oxidative coupling method for 2-naphthols and phenols with molecular oxygen as the oxidant in the presence of a catalytic amount (10 mol%) of $VO(acac)_2$, an inexpensive and stable catalyst (Scheme 1).[10]



Scheme 1

To achieve a catalytic cycle in the vanadium mediated coupling of phenols, one has to find an oxidant which will oxidize V^{IV} to V^{V} and will not interfere with the coupling reaction during the catalytic cycle. At the outset, a system consisting of 2-naphthol **1a**, 10 mol% $VO(acac)_2$ and oxidants such as H_2O_2, Bu^tOOH and Oxone was studied. Although 2-naphthol was consumed completely in these cases, only trace amounts of the coupling product **2a** were detected. The remaining materials were intractable. Then, $NaIO_4$ and NH_4IO_4 were used as oxidants. After reaction for 24 h under similar reaction conditions, most of the starting material was recovered and there was no coupling product. Finally, when molecular oxygen was used as oxidant and the reaction was conducted in CH_2Cl_2 at room temperature for 24 h, **1a** was consumed and **2a** was obtained in 92% yield after chromatographic purification.† The coupling product was present only in trace amounts when the reaction was conducted in MeOH.

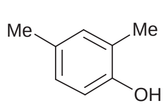
In the case of 6-bromo-2-naphthol **1b**, the coupling reaction was completed in 24 h to give **2b** in 90% yield. The reactivity of electron-donating and electron-withdrawing group substituted 2-naphthols was apparently different. Coupling of **1c** was finished within 9 h, but gave a lower yield due to the formation of some intractable materials. The coupling reaction of 3-(methoxycarbonyl)-2-naphthol **1d** was very sluggish. It gave a 35% yield of **2d** after 120 h, and 62% of **1d** was recovered (Table 1).

Table 1 Oxidative coupling of 2-naphthol and derivatives catalyzed by $VO(acac)_2$[a]

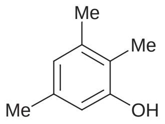
Napthol	R¹	R²	R³	*t*/h	Product[b]	Yield (%)
1a	H	H	H	24	**2a**	92
1b	Br	H	H	24	**2b**	90
1c	H	OMe	H	9	**2c**	76
1d	H	H	CO_2Me	120	**2d**	35

[a] The reactions were run with 10 mol% $VO(acac)_2$ in CH_2Cl_2 at room temperature under 1 atm O_2. [b] Compounds **2a–d** were identified according to data reported in ref. 6.

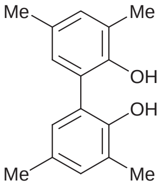
Coupling of phenol under similar reaction conditions was unsuccessful; there was no detectable amount of 1,1′-biphenol present. When 2,4-dimethylphenol **3a** and 2,3,5-trimethylphenol **3b** were subjected to the coupling reaction, the corresponding *ortho–ortho* coupling products **4a** and **4b** were obtained in moderate yields (Table 2). These two reactions are similar in terms of reaction rate. Prolonged reaction time did not give a better yield of coupling product. In the latter case, 28% of **3b**



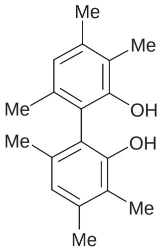
3a



3b



4a



4b

Table 2 Oxidative coupling of alkyl substituted phenols catalyzed by $VO(acac)_2$[a]

Phenol	*t*/h	Product[b]	Yield (%)
3a	120	**4a**	66
3b	48	**4b**	62

[a] Reaction conditions were similar to those for **1a**–**d**. [b] **4a**,**b** were characterized according to data reported in ref. 11.

was recovered. Reaction of **3a** for 120 h gave a similar yield of **4a** but no **3a** was recovered. Instead, some intractable material was formed.

In conclusion, a facile oxidative coupling method that selectively coupled 2-naphthol or phenol derivatives to the corresponding *ortho*–*ortho* coupling products, 1,1′-bi-2-naphthols or 1,1′-bi-2-phenols, with molecular oxygen in the presence of a catalytic amount of VO(acac)$_2$ in moderate to high yields has been demonstrated.

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Note and references

† *Typical procedure*: A stirred mixture of 2-naphthol (144 mg, 1 mmol), and VO(acac)$_2$ (26.5 mg, 0.1 mmol) in CH_2Cl_2 (10 ml) was exposed under an atmospheric pressure of molecular oxygen at room temperature for 24 h. The mixture was then filtered through a short column of silica gel and the silica gel was washed with EtOAc (40 ml). The filtrate was concentrated and purified by column chromatography (SiO_2, hexane–EtOAc = 5:1) to afford the coupling product **2a** (131 mg, 92%, mp 215–217 °C ; lit.,[4a] 216–218 °C). On a 100 mmol scale, 75–78% of the coupling product was obtained.

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