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 enantiomeric synthesis as a source of chirality. There are some known methods for the oxidative coupling of 2-naphthols to give 1,1′-bi-2-naphthols using stoichiometric amounts of oxidant, and some methods employing catalytic oxidative coupling. These methods either use an expensive oxidant (such as AgCl) with low yield, or employing catalytic oxidative coupling. These methods either use an expensive oxidant (such as AgCl) with low yield, or employing catalytic oxidative coupling. These methods either use an expensive oxidant (such as AgCl) with low yield, or employing catalytic oxidative coupling. These methods either use an expensive oxidant (such as AgCl) with low yield, or employing catalytic oxidative coupling. These methods either use an expensive oxidant (such as AgCl) with low yield, or employing catalytic oxidative coupling. 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To achieve a catalytic cycle in the vanadium mediated coupling of phenols, one has to find an oxidant which will oxidize VO$_{2}^{+}$ to VO$_{5}^{+}$ 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$_2$O$_2$, BuOOH and Ozone 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$_3$ and NH$_4$IO$_4$ 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$_2$Cl$_2$ 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>
<thead>
<tr>
<th>Naphthol</th>
<th>$t/h$</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>24</td>
<td>2a</td>
<td>92</td>
</tr>
<tr>
<td>1b</td>
<td>24</td>
<td>2b</td>
<td>90</td>
</tr>
<tr>
<td>1c</td>
<td>9</td>
<td>2c</td>
<td>76</td>
</tr>
<tr>
<td>1d</td>
<td>120</td>
<td>2d</td>
<td>35</td>
</tr>
</tbody>
</table>

$^a$ The reactions were run with 10 mol% VO(acac)$_2$ in CH$_2$Cl$_2$ 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 correspond-
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.

We are grateful to the National Science Council, Republic of China, for support of this work.

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$_2$Cl$_2$ (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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