Microwave thermolysis: Part III—A rapid and convenient coupling of 2-naphthols in solvent-free condition

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A rapid and environmentally benign method for the coupling of 2-naphthols is described using copper (II) acetonylacetate under microwave irradiation in dry media. The procedure is very convenient and avoids the use of excess solvent for reaction.

1,1-Bis-naphthol and its derivatives have attracted attention of chemists because of their important application in asymmetric synthesis, particularly in chirality induction. There are well documented methods for the coupling of 2-naphthols using Cu(II) amine complexes, K₂Fe(CN)₆, naphthoxide-amine and alumina supported Cu(II) sulphate. But all these procedures require the large excess of solvent which is detrimental to the environment. Moreover, some of the methods need higher temperature, inert atmosphere and longer reaction time. However, the little success has been achieved with FeCl₃ using ultrasonic irradiation. Consequently, in the wake of green procedures it is desirable to develop a rapid, manipulatively easy and preferentially environmentally benign solvent-free protocol.

Recently, the metal ion catalysed reactions have fascinated the organic synthesis, in particular copper (II) (acac) catalysed coupling reactions, prompted us to explore its further applications.

Microwave heating is used for a wide variety of organic reactions and for the induction of reactions under dry conditions. Solid state microwave assisted organic transformations reactions have gained wide popularity over the usual homogeneous and heterogeneous slurry reactions as this easy and eco-friendly technique has several advantages, like many-fold reduction in reaction time, easy work-up and solvent-free condition which are an asset to an organic chemist.

In continuation of our work on solid supported and microwave assisted reactions, herein we wish to report coupling of 2-naphthols using Cu (II) (acac) under microwave irradiation in dry media. (Scheme I).

![Scheme I](image)

R = H / OH / Br / OCH₃; R¹ = H
R = H; R¹ = COOCH₃

Experimental Section

Melting points were recorded on a Buchi R535 apparatus and are uncorrected unless otherwise mentioned the chemicals were commercially available and were used without further purification. IR spectra
Table 1— Oxidative coupling of 2-naphthols using Cu (II) acetylacetonate

<table>
<thead>
<tr>
<th>Entry</th>
<th>2-Naphthols</th>
<th>Ratio of naphthol: Cu (II)(acac)</th>
<th>Reaction time (sec.)</th>
<th>Yield (%)</th>
<th>m.p. (°C)</th>
<th>Found (Reported)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td></td>
<td>1:7</td>
<td>120</td>
<td>70</td>
<td></td>
<td>214-16 (216-18)3</td>
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<tr>
<td>2.</td>
<td></td>
<td>1:6</td>
<td>130</td>
<td>72</td>
<td></td>
<td>113-15 (111-13)12</td>
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<tr>
<td>3.</td>
<td></td>
<td>1:6</td>
<td>120</td>
<td>75</td>
<td></td>
<td>199-200 (198-99)11</td>
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<tr>
<td>4.</td>
<td></td>
<td>1:7</td>
<td>110</td>
<td>71</td>
<td></td>
<td>151-52 (151-52)13</td>
</tr>
<tr>
<td>5.</td>
<td></td>
<td>1:6</td>
<td>120</td>
<td>66</td>
<td></td>
<td>275-77 (276-78)12</td>
</tr>
</tbody>
</table>

All products exhibited physical and spectral (NMR,IR & mass) properties in accordance with the assigned structures.

were recorded on a IR Nicolet 740 FT IR spectrometer; 1H NMR spectra on a FT (200 Gemini) spectrometer, and mass spectra on either Micromass 7070 or Finnigan Mat 1020 B mass spectrometer operating at 70 eV. TLC was done on precoated silica gel 60f 254 (0.5 mm) glass plates.

Typical procedure

2-Naphthol (entry-1, 1 mmole) was dissolved in minimum quantity of solvent (dichloromethane) and mixed with neutral alumina. After removal of solvent, dry powder was mixed with Cu(II) (acac) (7 mmole) thoroughly. The mixture was transferred into a test tube and subjected to microwave irradiation (2 minutes, BPL make, Hi power). After completion of the reaction (monitored by TLC), the reaction mixture was directly loaded on small pad of silica gel, eluted with hexane-EtOAc (70:30) to get pure product, 1,1-binaphthalene-2,2-diol 2a, m.p.215-15.5°C (lit.9 214-16°C); 1H NMR (CDCl3): δ 7.99 (d, J = 8.8 Hz, 2H), 7.91 (d, J = 7.5 Hz, 2H), 7.5 - 7.1 (m, 8H), 5.06 (s, 2H). All other compounds were prepared following the same procedure.

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References