Supplementary Material

Reduction of phenylacetylenes using Raney Ni–Al alloy, Al powder in the presence of noble metal catalysts in water

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1. Experimental Section

1.1 General remarks

All melting points are uncorrected. $^1$H NMR spectra were recorded at 300 MHz on a Nippon Denshi JEOL FT-300 NMR spectrometer in CDCl$_3$ with Me$_4$Si as an internal reference. IR spectra were measured as KBr pellets on a Nippon Denshi JIR-AQ20M spectrometer. Mass spectra were obtained on Shimadzu GCMS-QP5050A Ultrahigh Performance Mass Spectrometer AOC-20I, 100V using a direct-inlet system. GLC analyses were performed by Shimadzu gas chromatographer, GC-2010.

1.2 Reagent list

Raney Ni–Al alloy (500 wt%), Al powder (500 wt%) (53–150 µm, 99.5%) (Wako), Pt/C, Pd/C, Ru/C and Rh/C (5 wt%) (Wako), Distilled water (Wako).

1.3 Typical procedure

The mixture of a substrate (20 mg, 0.20 mmol) (Wako), Raney Ni–Al alloy (500 wt%), Al powder (500 wt%) (53–150 µm, 99.5%) (Wako) and Pt/C, Pd/C, Ru/C or Rh/C (20 mg) (4.5 mole % metal) was added to water (0.5 mL) (Wako distilled water). After heating the mixture at 60–120 °C for 6–12 h, it was cooled to room temperature. The solution was then diluted with 1 mL water and stirred overnight at room temperature in a sealed tube. After 24 h, the solution was extracted with diethyl ether (3 × 2 mL) as per the reported procedure. The combined organic layers were dried over anhydrous MgSO$_4$ and filtered through a porous cotton plug followed by concentrating in vacuum to afford the corresponding hydrogenated product. The yields were determined by GLC analysis using the standard compound (1,2,3,4-tetrahydronaphthalene), and the products were identified by GC–MS.

Reduction of phenylacetylenes (1)

\[
\begin{align*}
R \quad & \xrightarrow{\text{Ni-Al alloy/Al powder/Catalyst}} \quad R = H, \quad R = CH_3, \quad R = OCH_3, \quad R = C(CH_3)_3 \\
+ H_2O, \Delta \quad & \text{in a sealed tube (oil bath)} \quad + R_{\text{phenylacetylene}}, + R_{\text{phenylacetylene}}, + R_{\text{phenylacetylene}} \\
\end{align*}
\]

Scheme S1. Reduction of phenylacetylene by using Al powder in the presence of catalyst in water.

**GC Conditions:**

<table>
<thead>
<tr>
<th>Rate (°C/min)</th>
<th>Temperature (°C)</th>
<th>Hold (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>35</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>100</td>
</tr>
</tbody>
</table>

**GC Spectra**
Table 2 Entry 3

Reduction of phenylacetylene using Ni-Al and Al powder in H₂O at 120 °C for 6 h

Table 5 Entry 1

Reduction of phenylacetylene using Ni-Al, Al powder and Pt/C in H₂O at 60 °C for 12
Table for figure 1
Reduction of phenylacetylene (1a) using Raney Ni–Al, Al powder and noble metal catalysts in H\textsubscript{2}O\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temp. (°C)</th>
<th>Pt/C</th>
<th>Pd/C</th>
<th>Ru/C</th>
<th>Rh/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>120</td>
<td>30.9</td>
<td>4.5</td>
<td>0</td>
<td>37</td>
</tr>
<tr>
<td>2</td>
<td>90</td>
<td>31.3</td>
<td>7.5</td>
<td>16</td>
<td>27.5</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>33.7</td>
<td>3.4</td>
<td>25.9</td>
<td>26.3</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Substrate: 20 mg (0.20 mmol), Raney Ni–Al: 100 mg (500 wt%), Al powder: 100 mg (500 wt%), catalyst: 4.5 mol\% (metal), H\textsubscript{2}O: 0.5 mL.

\textsuperscript{b}Conditions: time: 6 h.

\textsuperscript{c}The yields were determined by GLC.

Table for figure 2
Reduction of phenylacetylene (1a) using Raney Ni–Al, Al powder and Pt/C in H\textsubscript{2}O\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temp. (°C)</th>
<th>Yield (%)\textsuperscript{c}</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60</td>
<td>13.1</td>
<td>86.9</td>
</tr>
<tr>
<td>2</td>
<td>80</td>
<td>28.7</td>
<td>71.3</td>
</tr>
<tr>
<td>3</td>
<td>120</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Substrate: 20 mg (0.20 mmol), Raney Ni–Al: 100 mg (500 wt%), Al powder: 100 mg (500 wt%), catalyst: 4.5 mol\% (metal), H\textsubscript{2}O: 0.5 mL.

\textsuperscript{b}Conditions: time: 12 h.

\textsuperscript{c}The yields were determined by GLC.