Iridium-promoted conversion of terminal epoxides to primary alcohols under acidic conditions using hydrogen

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Contents
General considerations.....................................................................................................................2
Typical hydrogenation procedure. ...................................................................................................2
GC-FID data for Table 1..................................................................................................................3
$^1$H NMR spectra of isolated products..........................................................................................8
General considerations
(POCOP)IrCO, \(^1\) indene oxide, \(^2\) benzyloxirane, \(^3,4\) and 2-methyl-2-phenyloxirane \(^4\) were prepared as previously reported. All other chemicals and solvents were obtained from commercial vendors and used as received.

GC-MS data was collected using an Agilent 6890-5873 GC-MS equipped with an HP-5MS column (30 m x 0.25 mm x 0.25 μm). GC-FID data was collected using an Agilent 7890A GC-FID equipped with an HP-5 column (30m x 0.32 mm x 0.25 μm). NMR spectra were recorded on a Bruker AV500 spectrometer in CDCl\(_3\) solvent.

Catalytic reactions were performed in a 10 mL high pressure reactor fitted with a PTFE liner and equipped with a pressure sensor and a programmable temperature controller. A new liner and stirbar were used for each reaction. A PFTE lid with a small hole for gas equilibration was placed on top of the liner. The well holding the thermocouple probe was covered with a heat-shrinkable PFA probe cover. These covers were purchased from Tef-Cap Industries Inc.

Typical hydrogenation procedure.
In air the reactor was charged with the epoxide substrate (1.4 mmol), dioxane (0.7 mL), (POCOP)IrCO (5.0 mg, 0.0081 mmol, 0.60 mol %), triflic acid (aq, 0.681 M, 0.010 mL, 0.50 mol %), and decane (25 μL). The reactor was pressurized to 600 psi at room temperature. With magnetic stirring, the reactor was heated to 35 °C for 90 min then ramped to a temperature of 195 °C over 30 min. The reaction was held at 195 °C for 15 hours then allowed to cool to room temperature. The reactor was then vented. The reaction mixture was filtered through Celite ®. The reactor was thoroughly rinsed with THF (total volume, 5 mL). The rinses were filtered through Celite ® and combined with the reaction mixture. A sample of the filtrate (approximately 0.2 mL) was diluted using THF (final volume approximately 1.5 ml). The sample was then analyzed by GC-MS and GC-FID. Alcohol products were identified by comparison to authentic standards and quantified using calibration curves constructed using authentic samples. Isolated products were obtained after filtration through a plug of MgSO\(_4\) and column chromatography on silica gel with hexanes and ethyl acetate (1:1 mixture) as the eluant.

1-Octanol. (87 mg, 48 %). Colorless oil. The \(^1\)H NMR spectrum is consistent with previously reported data.\(^5,6\) \(^1\)H NMR (CDCl\(_3\), 500 MHz, 298 K) δ 3.65 (t, \(J = 6.7\) Hz, 2H), 1.90 (br, 1H), 1.58 (m 2H), 1.31 (m, 10H), 0.90 (t, \(J = 6.9\) Hz, 3H).

1-Dodecanol. (130 mg, 50 %). Colorless oil. The \(^1\)H NMR spectrum is consistent with previously reported data.\(^7\) \(^1\)H NMR (CDCl\(_3\), 500 MHz, 298 K) δ 3.62 (t, \(J = 6.7\) Hz, 2H), 2.05 (br, 1H), 1.56 (m 2H), 1.27 (m, 16H), 0.88 (t, \(J = 7.0\) Hz,3H).

3-Phenylpropanol. (71 mg, 38 %). Pale yellow oil. The \(^1\)H NMR spectrum is consistent with previously reported data.\(^5,8\) \(^1\)H NMR (CDCl\(_3\), 500 MHz, 298 K) δ 7.33 (m, 2H), 7.25 (m, 3H), 3.71 (t, \(J = 6.5\) Hz, 2H), (br, 1H), 2.75 (m, 2H), 1.94 (m, 2H).

2-Phenylethanol. (124 mg, 72 %). Colorless oil. The \(^1\)H NMR spectrum is consistent with previously reported data.\(^9,10\) \(^1\)H NMR (CDCl\(_3\), 500 MHz, 298 K) δ 7.35 (m, 2H), 7.27 (m, 3H), 3.86 (t, \(J = 6.7\) Hz, 2H), 2.89 (t, \(J = 6.7\) Hz, 2H), 2.18 (br, 1H).
**2-Phenylpropanol.** (106 mg, 53 %). Pale yellow oil. The $^1$H NMR spectrum is consistent with previously reported data.$^{10,11}$ $^1$H NMR (CDCl$_3$, 500 MHz, 298 K) δ 7.37 (m 2H), 7.29 (m, 3H), 3.74 (d, $J = 6.8$ Hz, 2H), 2.98 (m 1H), 2.56 (br, 1H), 1.31 (d, $J = 7.0$ Hz, 3H).

**2-Indanol.** (63 mg, 35 %). Off white solid. The $^1$H NMR spectrum is consistent with previously reported data.$^{10,12}$ $^1$H NMR (CDCl$_3$, 500 MHz, 298 K) δ 7.28 (m, 2H), 7.20 (m, 2H), 4.71 (m, 1H), 3.24 (dd, $J = 16.4$, 5.9 Hz, 2H), 2.94 (dd, $J = 16.3$, 3.2 Hz, 2H), 2.04 (br, 1H).

**Cyclopentylmethanol.** (35 mg, 26 %). Pale yellow oil. The $^1$H NMR spectrum is consistent with previously reported data.$^{13-14}$$^1$H NMR (CDCl$_3$, 500 MHz, 298 K) δ 3.52 (d, 2H), 2.10 (m, 1H), 1.73 (m, 2H), 1.56 (m, 5H), 1.23 (m, 2H).

**GC-FID data for Table 1**

**Table S1.** GC-FID retention times and response factors for products from the reaction of epoxyoctane.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention time (min.)</th>
<th>Response factor (counts/M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>2.87</td>
<td>n/a</td>
</tr>
<tr>
<td>dioxane</td>
<td>3.88</td>
<td>n/a</td>
</tr>
<tr>
<td>octane</td>
<td>6.07</td>
<td>3.07E6</td>
</tr>
<tr>
<td>octene isomers$^a$</td>
<td>5.83-6.40</td>
<td>1.75E6</td>
</tr>
<tr>
<td>decane</td>
<td>9.12</td>
<td>2.98E6</td>
</tr>
<tr>
<td>octanal</td>
<td>9.18</td>
<td>1.99E6</td>
</tr>
<tr>
<td>1-octanol</td>
<td>9.84</td>
<td>2.37E6</td>
</tr>
<tr>
<td>1,2-octane diol</td>
<td>11.22</td>
<td>2.22E6</td>
</tr>
<tr>
<td>THF impurity</td>
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</tr>
<tr>
<td>dioctyl ether</td>
<td>13.88</td>
<td>4.77E6</td>
</tr>
</tbody>
</table>

$^a$The response factor for 4-trans octene was used for all octene isomers.
Figure 1. Chromatogram for Table 1 entry 1.

Figure 2. Chromatogram for Table 1 entry 2.
Figure 3. Chromatogram for Table 1 entry 3.

Figure 4. Chromatogram for Table 1 entry 4.
**Figure 5.** Chromatogram for Table 1 entry 5.

**Figure 6.** Chromatogram for Table 1 entry 6.
Figure 7. Chromatogram for Table 1 entry 7.

Figure 8. Chromatogram of a reaction starting with 1,2-octane diol rather than epoxyoctane.
$^1$H NMR spectra of isolated products

![Figure 6. $^1$H NMR spectrum of 1-octanol (Table 2, Entry 1)](image)

![Figure 7. $^1$H NMR spectrum of 1-dodecanol (Table 2, Entry 2)](image)
Figure 8. $^1$H NMR spectrum of 3-phenylpropanol (Table 2, Entry 3)

Figure 9. $^1$H NMR spectrum of 2-phenylethanol (Table 2, Entry 4)
**Figure 10.** $^1$H NMR spectrum of 2-phenylpropanol (Table 2, Entry 5)

**Figure 11.** $^1$H NMR spectrum of 2-indanol (Table 2, Entry 6)
Figure 12. $^1$H NMR spectrum of cyclopentanemethanol (Table 2, Entry 7)

5 Spectral Database for Organic Compounds (SDBS); $^1$H NMR spectrum; SDBS No.: 1938; RN 111-87-5; http://riodb01.ibase.aist.go.jp/sdbs/ (accessed Sept. 6, 2018).
8 Spectral Database for Organic Compounds (SDBS); $^1$H NMR spectrum; SDBS No.: 2671; RN 122-97-4; http://riodb01.ibase.aist.go.jp/sdbs/ (accessed Sept. 6, 2018).
9 Spectral Database for Organic Compounds (SDBS); $^1$H NMR spectrum; SDBS No.: 2670; RN 122-97-4; http://riodb01.ibase.aist.go.jp/sdbs/ (accessed Sept. 6, 2018).
12 Spectral Database for Organic Compounds (SDBS); $^1$H NMR spectrum; SDBS No.: 6339; RN 4254-29-9; http://riodb01.ibase.aist.go.jp/sdbs/ (accessed Sept. 6, 2018).
13 Spectral Database for Organic Compounds (SDBS); $^1$H NMR spectrum; SDBS No.: 53255; RN 3637-61-4; http://riodb01.ibase.aist.go.jp/sdbs/ (accessed Sept. 6, 2018).