Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red “Caution Notes” within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*
HYDROGENATION OF AROMATIC NUCLI: 1-DECALOL

Submitted by A. I. Meyers¹, W. N. Beverung, and R. Gault².
Checked by P. Freidenreich and R. Breslow.

1. Procedure

A 500 ml., Parr hydrogenation bottle is flushed with nitrogen, and 20.0 g. of 5% rhodium-on-
alumina (Note 1) is weighed directly into the hydrogenation bottle. The catalyst is wet by cautiously
adding 25 ml. of 95% ethanol, and a solution of 40.0 g. (0.278 mole) of 1-naphthol (Note 2) in 125 ml.
of 95% ethanol is added to the bottle, along with 3 ml. of acetic acid. The mixture is shaken in a Parr
apparatus (Note 3) at an initial pressure of 55–60 p.s.i. of hydrogen. The theoretical hydrogen
absorption is reached in about 12 hours (Note 4). The catalyst is removed by suction filtration and
washed twice with 50 -ml. portions of ethanol (Note 5). The combined ethanol solutions are
concentrated with a rotary evaporator, yielding a viscous residue (39–41 g.), which is dissolved in 150
ml. of benzene. The solution is washed with 75 ml. of 10% sodium hydroxide solution, then with 75 ml.
of water, dried over magnesium sulfate for at least 3 hours, and concentrated with a rotary evaporator,
giving 39–41 g. (94–97%) of a mixture³ consisting of the geometrical isomers of 1-decalol. cis,cis-1-
Decalol may be isolated as a crystalline solid from the mixture by the addition of 15–20 ml. of heptane,
followed by cooling. The product is isolated by filtration and recrystallized from a minimum amount of
n-heptane, yielding 13–14 g. (30–33%) of cis,cis-1-decalol, m.p. ⁴ 92–93°.

2. Notes

1. The catalyst is available from Engelhard Industries.
2. A purified grade of 1-naphthol should be used. Material available from Eastman Organic Chemicals,
Aldrich Chemical Company, Inc., and Matheson, Coleman and Bell is satisfactory. Experiments with
technical grade 1-naphthol have indicated that this material requires purification by sublimation in order
to give satisfactory results.
3. It has been found that the rhodium catalyst is not nearly as sensitive to poisoning as platinum or
palladium catalyst. The metal inlet tube to the reaction bottle was merely rinsed with acetone, followed
by ethanol, and the rubber stopper was soaked in 30–40% sodium hydroxide solution overnight.
4. A variety of experiments have shown that for bicyclic aromatic nuclei the weight ratio of reactant to
catalyst should be 2:1, whereas for monocyclic aromatic nuclei, the reactant to catalyst ratio should be
3:1. For the latter systems, hydrogen absorption is usually complete within 6–8 hours (see Discussion
section).
5. The catalyst may be reused after washing thoroughly with ethanol and drying at 125° for 12–15
hours. The activity, however, is somewhat decreased. Care should be exercised to never leave the
catalyst exposed to air in the presence of a flammable solvent.

3. Discussion
1-Naphthol has been reduced to 1-decalol using platinum,^4^ Raney nickel,^5^ and Raney copper.\(^6\) The reactions catalyzed by nickel and copper required elevated temperatures and pressure. The present procedure allows the preparation of substantial quantities of 1-decalol under much more convenient conditions and shorter reaction times. Previous methods\(^3\),\(^4\),\(^5\),\(^6\) require costly catalysts or high-pressure equipment and frequently result in a high degree of hydrogenolysis. The submitters have found that the present method is applicable to a wide variety of aromatic nuclei, some of which are listed in Table I.

### References and Notes

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3. A. I. Meyers, W. Beverung, and G. Garcia-Munoz, *J. Org. Chem.*, 29, 3427 (1964). The discrepancy between the work reported earlier and the present work regarding isomer distribution may be due to variations in catalyst activity. The present reduction mixture consists of four decalol isomers of which the *cis-cis* product represents 50–55% as determined by gas chromatography analysis on a 250-cm. column containing 10% Carbowax 20M on Chromosorb P at 150–200°.


### TABLE

**HYDROGENATION OF AROMATIC NUCLEI^a^**

<table>
<thead>
<tr>
<th>Compound</th>
<th>g. Catalyst</th>
<th>Product</th>
<th>Yield, %</th>
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</thead>
<tbody>
<tr>
<td>2-Naphthol</td>
<td>0.50</td>
<td>2-Decalol(^b)</td>
<td>88</td>
</tr>
<tr>
<td>2-Methylbenzofuran</td>
<td>0.33</td>
<td><em>cis</em>-2-Methylhexahydrobenzofuran(^c)</td>
<td>91</td>
</tr>
<tr>
<td>2,2-Dimethyl-2,3-dihydrobenzofuran</td>
<td>0.33</td>
<td><em>cis</em>-2,2-Dimethylhexahydrobenzofuran(^c)</td>
<td>94</td>
</tr>
<tr>
<td>3-Hydroxybenzoic acid</td>
<td>0.33</td>
<td>3-Hydroxycyclohexanecarboxylic acid(^b)</td>
<td>81</td>
</tr>
<tr>
<td>4-Methoxyphenol</td>
<td>0.33</td>
<td>4-Methoxycyclohexanol(^b)</td>
<td>88</td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>0.33</td>
<td>1,4-Cyclohexanediol(^b)</td>
<td>90</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>0.33</td>
<td>1,3-Cyclohexanediol(^b)</td>
<td>85</td>
</tr>
</tbody>
</table>

^a^ From ref. 3, 7

^b^ Obtained as mixtures of geometric isomers.

^c^ No detectable quantity of the *trans* isomer is obtained.
Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

rhodium-on-alumina

Raney copper

ethanol (64-17-5)

acetic acid (64-19-7)

Benzene (71-43-2)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

hydroquinone (123-31-9)

nitrogen (7727-37-9)

1-Naphthol (90-15-3)

2-naphthol (135-19-3)

platinum (7440-06-4)

copper (7440-50-8)

nickel,
Raney nickel (7440-02-0)

acetone (67-64-1)

palladium (7440-05-3)

resorcinol (108-46-3)

magnesium sulfate (7487-88-9)

heptane,
n-heptane (142-82-5)

1-Decalol (529-32-8)

2-Methylbenzofuran (4265-25-2)

2,2-Dimethyl-2,3-dihydrobenzofuran (6337-33-3)

4-Methoxyphenol (150-76-5)
2-Decalol (825-51-4)

rhodium (7440-16-6)

3-Hydroxybenzoic acid (99-06-9)

3-Hydroxycyclohexanecarboxylic acid

4-Methoxycyclohexanol

1,4-Cyclohexanediol (556-48-9)

1,3-Cyclohexanediol (504-01-8)

cis,cis-1-decalol

cis-2-Methylhexahydrobenzofuran

cis-2,2-Dimethylhexahydrobenzofuran