



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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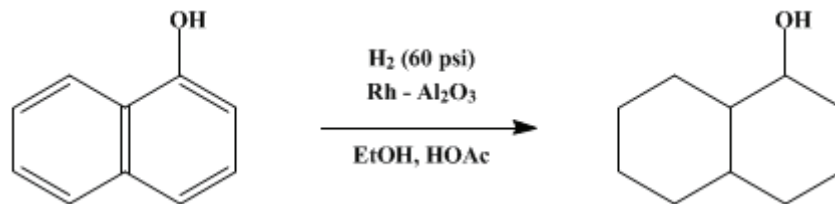
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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HYDROGENATION OF AROMATIC NUCLEI: 1-DECALOL



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1. Procedure

Caution! Benzene has been identified as a carcinogen; OSHA has issued emergency standards on its use. All procedures involving benzene should be carried out in a well-ventilated hood, and glove protection is required.

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

- The catalyst is available from Engelhard Industries.
- 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.
- 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.
- 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).
- 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^{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.

TABLE I
HYDROGENATION OF AROMATIC NUCLEI^a

Compound	g. Catalyst		Product	Yield, %
	g. Reactant			
2-Naphthol	0.50		2-Decalol ^b	88
2-Methylbenzofuran	0.33		<i>cis</i> -2-Methylhexahydrobenzofuran ^c	94
2,2-Dimethyl-2,3-dihydrobenzofuran	0.33		<i>cis</i> -2,2-Dimethylhexahydrobenzofuran ^c	91
3-Hydroxybenzoic acid	0.33		3-Hydroxycyclohexanecarboxylic acid ^b	81
4-Methoxyphenol	0.33		4-Methoxycyclohexanol ^b	88
Hydroquinone	0.33		1,4-Cyclohexanediol ^b	90
Resorcinol	0.33		1,3-Cyclohexanediol ^b	85

^a From ref. ^{3,7}

^b Obtained as mixtures of geometric isomers.

^c No detectable quantity of the *trans* isomer is obtained.

References and Notes

1. Department of Chemistry, Louisiana State University in New Orleans, New Orleans, Louisiana 70122. [Present address: Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523].
2. Present address: Wayne State University, Detroit, Michigan 48202.
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°.
4. W. G. Dauben, R. C. Tweit, and C. Mannerskantz, *J. Am. Chem. Soc.*, **76**, 4424 (1954); C. D. Gutsche and H. H. Peter, *J. Am. Chem. Soc.*, **77**, 5974 (1955); H. E. Zimmerman and A. Mais, *J. Am. Chem. Soc.*, **81**, 3648 (1959).
5. D. M. Musser and H. Adkins, *J. Am. Chem. Soc.*, **60**, 665 (1938).
6. J. Jadot and R. Braine, *Bull. Soc. Roy. Sci. Liege*, **25**, 62 (1956) [*Chem. Abstr.*, **50**, 16651h (1956)].
7. Other examples may be found in: J. H. Stocker, *J. Org. Chem.*, **27**, 2288 (1962); M. Freifelder, R. M. Robinson, and G. R. Stone, *J. Org. Chem.*, **27**, 284 (1962); J. C. Sircar and A. I. Meyers, *J. Org. Chem.*, **30**, 3206 (1965); R. A. Finnegan and P. L. Bachman, *J. Org. Chem.*, **30**, 4145 (1965).

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