Organic Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

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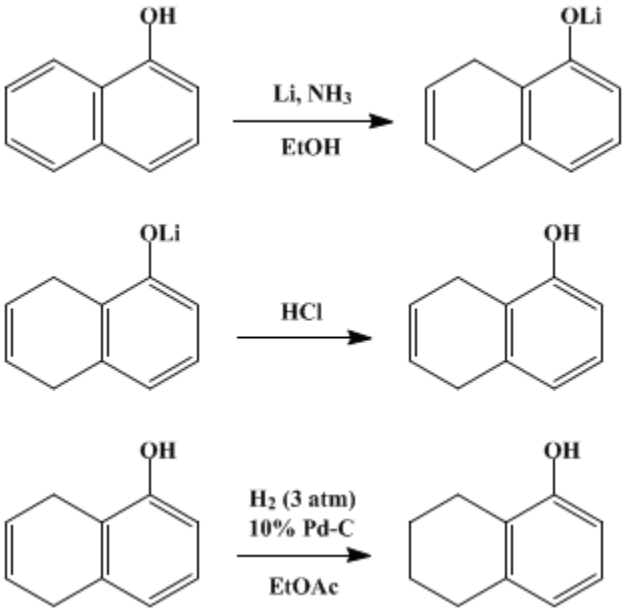
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.037.0080

Organic Syntheses, Coll. Vol. 4, p.887 (1963); Vol. 37, p.80 (1957).

ar-TETRAHYDRO-α-NAPHTHOL

[1-Naphthol, 5,6,7,8-tetrahydro-]



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1. Procedure

A 3-l. three-necked flask, equipped with a Dry Ice condenser (Note 1), a sealed Hershberg-type stirrer, and an inlet tube, is set up in a hood and charged with 108 g. (0.75 mole) of α-naphthol (Note 2). The stirrer is started, and to the rapidly stirred flask contents (Note 3) is added 1 l. of liquid ammonia as rapidly as possible (about 5 minutes). When the naphthol has gone into solution (about 10 minutes), 20.8 g. (3.0 g. atoms) of lithium metal (Note 4) is added in small pieces and at such a rate as to prevent the ammonia from refluxing too violently (Note 5). After the addition of the lithium has been completed (about 45 minutes), the solution is stirred for an additional 20 minutes and is then treated with 170 ml. (3.0 moles) of absolute ethanol which is added dropwise over a period of 30–45 minutes (Note 6). The condenser is removed, stirring is continued, and the ammonia is evaporated in a stream of air introduced through the inlet tube. The residue is dissolved in 1 l. of water, and, after the solution has been extracted with two 100-ml. portions of ether, it is carefully acidified with concentrated hydrochloric acid. The product formed is taken into ether with three 250-ml. extractions, and then the ether extract is washed with water and dried over anhydrous sodium sulfate. The ether is removed by evaporation to yield 106–108 g. (97–99%) of crude 5,8-dihydro-1-naphthol, m.p. 69–72°. This material is dissolved in 250 ml. of ethyl acetate and hydrogenated with 3.0 g. of 10% palladium on charcoal catalyst (Note 7) at 2–3. atm. pressure in a Parr apparatus until the theoretical amount of hydrogen has been absorbed (about 45 minutes). The catalyst is removed by filtration, and the solvent is removed by distillation to leave 105–107 g. of an oil which quickly solidifies, m.p. 67–69.5°. Recrystallization from 250 ml. of petroleum ether (b.p. 88–98°) gives 93–97 g. (84–88%) of almost colorless crystals, m.p. 68–68.5°.

2. Notes

1. A cold-finger type of condenser approximately 10 × 40 cm. is satisfactory.
2. Eastman's white label grade α-naphthol or equivalent is the most satisfactory starting material. Technical grade α-naphthol may be used, but it gives an inferior product that is difficult to purify.
3. Rapid stirring during the addition of the ammonia is necessary to prevent the formation of a hard cake

and resultant interference with the stirrer.
4. Lithium metal strip (Metalloy Corporation, Rand Tower, Minneapolis, Minnesota) is wiped to remove the protective grease and then placed in petroleum ether (b.p. 32–37°). Pieces are cut with scissors, air-dried to remove solvent, and added to the reaction mixture.
5. During the addition of the lithium the solution turns deep blue. After this has occurred (after about one-third of the lithium has been added), the rate of addition can be increased considerably.
6. Toward the end of the addition of the alcohol, foaming may occur but may be subdued by reducing the rate of stirring.
7. See Mozingo [*Org. Syntheses Coll. Vol.* **3**, 686 (1955)] for the preparation of this catalyst.

3. Discussion

ar-Tetrahydro-α-naphthol has been prepared by sodium and reduction of α-naphthylamine followed by diazotization and hydrolysis;[2,3] by sodium and amyl alcohol [4,5,6] or lithium and ethylamine[7] reduction of α-naphthol; by sulfonation of tetralin followed by sodium hydroxide fusion;[8] and by catalytic reduction of α-naphthol.[9] *ar*-Dihydro-α-naphthol has been prepared by reduction of α-naphthol with sodium and alcohols[10] and with sodium and ammonia.[11] The use of lithium in related systems has been investigated and provides the basis for the preparation described.[12]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 400

References and Notes

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10. Rowe and Levin, *J. Chem. Soc.*, **119**, 2021 (1921).
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12. Wilds and Nelson, *J. Am. Chem. Soc.*, **75**, 5360 (1953).

Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

petroleum ether

α-naphthylamine

ar-Tetrahydro-α-naphthol

ar-Dihydro-α-naphthol

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

ethyl acetate (141-78-6)

ether (60-29-7)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

sodium sulfate (7757-82-6)

α-naphthol,
naphthol (90-15-3)

sodium (13966-32-0)

palladium (7440-05-3)

amyl alcohol (71-41-0)

lithium (7439-93-2)

Tetralin (119-64-2)

ethylamine (75-04-7)

1-Naphthol, 5,6,7,8-tetrahydro- (529-35-1)

5,8-dihydro-1-naphthol