



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.

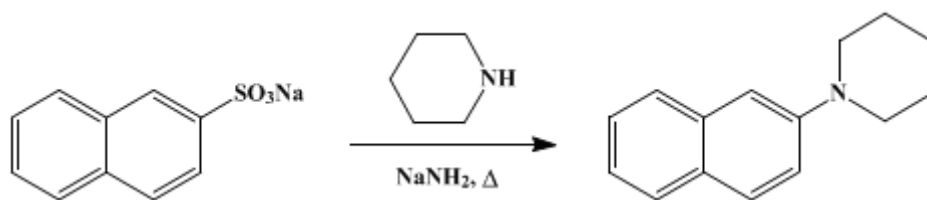
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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.

Organic Syntheses, Coll. Vol. 5, p.816 (1973); Vol. 40, p.74 (1960).

N-β-NAPHTHYLPIPERIDINE

[Piperidine, 1-(2-naphthyl)-]



Submitted by J. F. Bunnett, T. K. Brotherton, and S. M. Williamson¹.
Checked by Virgil Boekelheide and F. Lind.

1. Procedure

A dry 1-l. three-necked round-bottomed flask is fitted in the center neck with a sweep-blade stirrer whose shaft passes through an airtight bearing (Note 1). One side neck is fitted with a condenser topped by a soda-lime drying tube, and the other is fitted with a solid stopper. In the flask are placed 75 ml. of piperidine (Note 2) and 15.6 g. (0.4 mole) of sodium amide (Note 3), and the mixture is heated at reflux (Note 4) for 15 minutes with good stirring. The mixture is cooled just below reflux temperature, and 46 g. (0.2 mole) of sodium β-naphthalenesulfonate (Note 5) is added, followed by an additional 75 ml. of piperidine. The mixture is then heated at reflux for 12 hours with stirring.

To the cooled reaction mixture, 200 ml. of water is added carefully with stirring. Potassium carbonate is added with continued stirring until the water layer is saturated; the mixture is now transferred to a separatory funnel and extracted three times with 60-ml. portions of ether. The combined ether extracts are dried over solid sodium hydroxide and are then transferred to a simple distillation apparatus. Distillation is commenced with a steam bath as source of heat; when most of the ether has been removed, the steam bath is replaced by a flame. Distillation is continued until most of the piperidine (b.p. 106°) has been removed. The cooled residue in the distillation flask is recrystallized from petroleum ether (boiling range 30–60°) with the use of charcoal. There is obtained 30.0 g. (71%) of N-β-naphthylpiperidine as tan crystals, m.p. 52–56°. An additional recrystallization from the same solvent gives crystals, m.p. 56–58°, with about 10% loss in weight (Note 6).

2. Notes

1. The submitters used a ball-joint bearing. A mercury seal or a Trubore bearing should also suffice.
2. Commercial piperidine was purified by 6 hours' refluxing with sodium metal followed by distillation from sodium.
3. Sodium amide from Farchan Research Laboratories, Cleveland, Ohio, was used.
4. The submitters used an electric heating mantle as a source of heat.
5. Sodium β-naphthalenesulfonate, technical grade, from Matheson, Coleman and Bell was dried in an oven and then used directly.
6. The melting point of pure β-naphthylpiperidine is 58–58.5°. ^{2,3} By the same procedure the submitters have obtained N-phenylpiperidine (94%) from sodium benzenesulfonate and N-α-naphthylpiperidine (23%) from sodium α-naphthalenesulfonate.

3. Discussion

N-β-Naphthylpiperidine has been prepared by the condensation of β-bromonaphthalene^{2,3} or of β-naphthol⁴ with piperidine at elevated temperatures; from the action of 1,5-dibromopentane on β-naphthylamine;⁵ and from the action of the sodium amidepiperidine reagent on each of the eight monohalonnaphthalenes^{3,6} or on methyl β-naphthyl sulfone.⁶ The present procedure is adapted from that of Brotherton and Bunnett.⁷

References and Notes

1. Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina.
 2. E. Lellman and M. Büttner, *Ber.*, **23**, 1383 (1890).
 3. J. F. Bunnett and T. K. Brotherton, *J. Am. Chem. Soc.*, **78**, 155 (1956).
 4. W. Roth, *Ber.*, **29**, 1175 (1896).
 5. M. Scholtz and E. Wassermann, *Ber.*, **40**, 856 (1907).
 6. J. F. Bunnett and T. K. Brotherton, *J. Am. Chem. Soc.*, **78**, 6265 (1956).
 7. T. K. Brotherton and J. F. Bunnett, *Chem. & Ind. (London)*, **60**, (1957).
-

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

petroleum ether

β -naphthylpiperidine

sodium amidepiperidine

potassium carbonate (584-08-7)

ether (60-29-7)

sodium hydroxide (1310-73-2)

β -naphthol (135-19-3)

Sodium Benzenesulfonate (515-42-4)

sodium (13966-32-0)

piperidine (110-89-4)

1,5-dibromopentane (111-24-0)

β -bromonaphthalene (580-13-2)

sodium α -naphthalenesulfonate (130-14-3)

sodium β -naphthalenesulfonate (532-02-5)

sodium amide (7782-92-5)

N-phenylpiperidine (4096-20-2)

β -naphthylamine (91-59-8)

N- β -Naphthylpiperidine,
Piperidine, 1-(2-naphthyl)- (5465-85-0)

N- α -naphthylpiperidine

methyl β -naphthyl sulfone

Copyright © 1921-2005, Organic Syntheses, Inc. All Rights Reserved