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.

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.

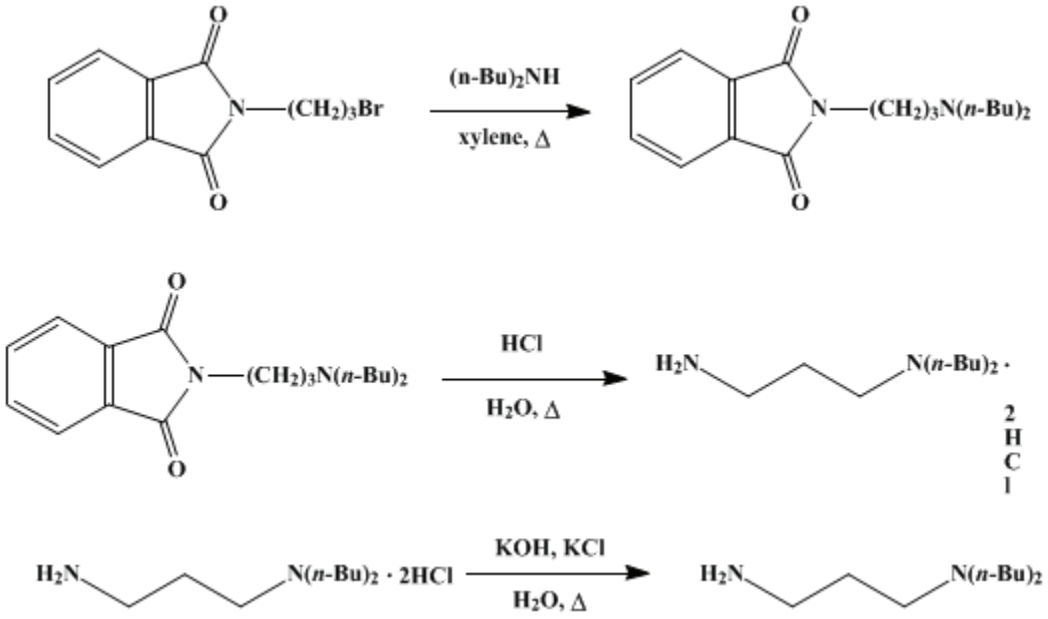
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.024.0044

Organic Syntheses, Coll. Vol. 3, p.256 (1955); Vol. 24, p.44 (1944).

γ-DI-*n*-BUTYLAMINOPROPYLAMINE

[1,3-Propanediamine, N,N-di-*n*-butyl-]



Submitted by Lawrence H. Amundsen and James J. Sanderson.
Checked by R. L. Shriner and John L. Rendall.

1. Procedure

In a 500-ml. distilling flask are placed 107 g. (0.40 mole) of γ-bromopropylphthalimide (Note 1) and 240 ml. of xylene. Solution is effected by heating, and 24 ml. of xylene is distilled to remove traces of moisture. After cooling, the solution is transferred to a 1-l. round-bottomed flask with a ground-glass joint and treated with 107 g. (140 ml., 0.83 mole) of di-*n*-butylamine. The flask is fitted with a reflux condenser and heated with occasional shaking for 10 hours in an oil bath maintained at 140–150°.

The solution is allowed to cool, and the di-*n*-butylamine hydrobromide, which separates in the course of the reaction, is removed by means of a suction filter (Note 2). The filtrate is transferred to a 500-ml. distilling flask, and the xylene is removed by distillation. The crude γ-di-*n*-butylaminopropylphthalimide, a brown oil, is transferred to a 500-ml. round-bottomed flask with a ground-glass joint and treated with 20 ml. of water and 120 ml. of 12 *N* hydrochloric acid. The flask is fitted with a reflux condenser, and the solution is heated for 6 hours in an oil bath maintained at 140–150°. After the solution has cooled to room temperature, the precipitated phthalic acid is removed by filtration and washed with four 25-ml. portions of cold water. The combined filtrates are transferred to a 600-ml. beaker and heated on a steam bath to evaporate the water and hydrochloric acid.

The residue, a thick brown oil, which is crude γ-di-*n*-butylaminopropylamine dihydrochloride, is treated with a solution of 80 g. of potassium hydroxide in 80 ml. of water. A brown oil separates above the aqueous layer, which contains a considerable amount of solid potassium chloride. The whole is extracted with one 200-ml. portion and two 50-ml. portions of benzene (Note 3). The combined extracts are then placed in a 500-ml. Erlenmeyer flask over 50 g. of potassium hydroxide and allowed to dry overnight.

The dried benzene extract is placed in a 500-ml. round-bottomed flask with a ground-glass joint. The flask is fitted with a Vigreux column, and the benzene is distilled from the solution at atmospheric pressure, an oil bath maintained at 100–110° being the source of heat. The crude γ-di-*n*-

butylaminopropylamine is fractionated under reduced pressure from a 250-ml. Claisen flask; heat is supplied by an oil bath maintained at 170–180°. The yield of product boiling at 108–110.5°/5–6 mm. or 98–100°/2 mm. amounts to 57–60 g. (77–80%) (Note 4).

2. Notes

1. The γ-bromopropylphthalimide was prepared from potassium phthalimide and trimethylene bromide in 78% yield, using the conditions and molar quantities specified for the preparation of β-bromoethylphthalimide.[1] γ-Bromopropylphthalimide can also be prepared from phthalimide, potassium carbonate, and trimethylene bromide.[2]
2. About 55–58 g. of di-*n*-butylamine hydrobromide is recovered.
3. The increase in volume of the first portion is about 75 ml. There is no noticeable increase in the volumes of the two 50-ml. portions.
4. This same procedure has been followed in the preparation of γ-diethylaminopropylamine and γ-di-*n*-propylaminopropylamine. When these substances are prepared by the method described, yields of 60% and 67% respectively are obtained.

3. Discussion

The above procedure is based on the directions of Sanderson.[3] γ-Di-*n*-butylaminopropylamine has also been prepared from β-di-*n*-butylaminopropionitrile by the action of sodium and alcohol[4] and by catalytic reduction.[5] (β-Di-*n*-butylaminopropionitrile has been prepared from di-*n*-butylamine and acrylonitrile.)

References and Notes

1. *Org. Syntheses* Coll. Vol. **1**, 119 (1941).
2. *Org. Syntheses* Coll. Vol. **2**, 84, note 5 (1943).
3. Sanderson, M.S. Thesis, University of Connecticut, 1942.
4. Singh and Singh, *J. Indian Chem. Soc.*, **23**, 224 (1946).
5. Burckhalter, Jones, Holcomb, and Sweet, *J. Am. Chem. Soc.*, **65**, 2012 (1943).

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

potassium carbonate (584-08-7)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

Trimethylene bromide (109-64-8)

potassium hydroxide (1310-58-3)

sodium (13966-32-0)

β-Bromoethylphthalimide

Potassium Phthalimide (1074-82-4)

xylene (106-42-3)

phthalic acid (88-99-3)

potassium chloride (7447-40-7)

γ-bromopropylphthalimide

acrylonitrile (107-13-1)

γ-diethylaminopropylamine (104-78-9)

di-n-butylamine (111-92-2)

γ-DI-n-BUTYLAMINOPROPYLAMINE,
1,3-Propanediamine, N,N-di-n-butyl- (102-83-0)

di-n-butylamine hydrobromide

γ-di-n-butylaminopropylphthalimide

γ-di-n-butylaminopropylamine dihydrochloride

γ-di-n-propylaminopropylamine (34155-34-5)

β-di-n-butylaminopropionitrile (25726-99-2)