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.

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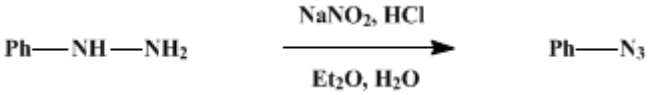
PHENYL AZIDE

[Benzene, azido-]



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1. Procedure

In a 1-l. three-necked flask fitted with a stirrer, a thermometer, and a dropping funnel are placed 300 ml. of water and 55.5 ml. of concentrated hydrochloric acid. The flask is surrounded by an ice-salt bath, the stirrer is started, and 33.5 g. (0.31 mole) of phenylhydrazine (Note 1) is added dropwise (5–10 minutes is required). Phenylhydrazine hydrochloride separates as fine white plates. Stirring is continued, and, after the temperature has fallen to 0°, 100 ml. of ether is added, after which a previously prepared solution of 25 g. of technical sodium nitrite in 30 ml. of water is added from the dropping funnel at such a rate that the temperature *never* rises above 5°. This requires 25–30 minutes.

The reaction mixture is subjected to steam distillation until about 400 ml. of distillate is obtained. The ether layer is removed from the distillate, and the aqueous layer is extracted once with 25 ml. of ether. The combined ethereal solutions are dried over 10 g. of anhydrous calcium chloride. The dried solution is placed in a 200-ml. ordinary Claisen flask arranged for vacuum distillation. *The flask must be surrounded by a cylindrical wire screen, and a laminated glass screen must be interposed between the operator and the apparatus* (Note 2). The flask is immersed in a water bath at 25–30°, and the ether is removed under reduced pressure. Then the temperature of the water bath is raised to 60–65°, and the product is distilled under reduced pressure. Phenyl azide boils at 49–50° at 5 mm. (Note 3). A yield of 24–25 g. (65–68%) of the pungent, pale yellow, oily azide is obtained (Note 4).

2. Notes

1. The phenylhydrazine used was the best grade supplied by the Eastman Kodak Company. With technical material, or a preparation that was appreciably discolored, the yield was much less (45–50%), and a considerable amount of tar was formed.
2. Care must be exercised during the distillation. Phenyl azide explodes when heated at ordinary pressure, and occasionally at lower pressures. The water-bath temperature should never be permitted to rise above 80° at any time.
3. Phenyl azide boils at 66–68°/21 mm. with a bath temperature of 70–75°. It is advisable to use as low a bath temperature as possible and a pressure of 5 mm. or less. The checkers have used these directions repeatedly without any explosions.
4. The product should be stored in a brown glass bottle. It will keep for a month in a cool, dark place.

3. Discussion

Phenyl azide has been prepared by the action of nitrous acid upon phenylhydrazine hydrochloride;[1] of ammonia upon diazobenzene perbromide;[2] and by the reaction between a diazo salt and sodium azide,[3] hydroxylamine,[4] or *p*-toluenesulfonamide.[5]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 74
- Org. Syn. Coll. Vol. 4, 380

References and Notes

1. Dimroth, *Ber.*, **35**, 1032 (1902).
2. Griess, *Ann.*, **137**, 68 (1866).
3. Nölting, *Ber.*, **26**, 86 (1893).
4. Fischer, *Ann.*, **190**, 96 (1877); Mai, *Ber.*, **25**, 372 (1892); **26**, 1271 (1893); Forster and Fierz, *J. Chem. Soc.*, **91**, 855, 1350 (1907).
5. Bretschneider and Rager, *Monatsh.*, **81**, 970 (1950).

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

diazobenzene perbromide

calcium chloride (10043-52-4)

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

ether (60-29-7)

sodium nitrite (7632-00-0)

nitrous acid (7782-77-6)

Phenylhydrazine (100-63-0)

hydroxylamine (7803-49-8)

sodium azide (26628-22-8)

phenylhydrazine hydrochloride (59-88-1)

PHENYL AZIDE,
Benzene, azido- (622-37-7)

p-toluenesulfonamide (70-55-3)