



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.

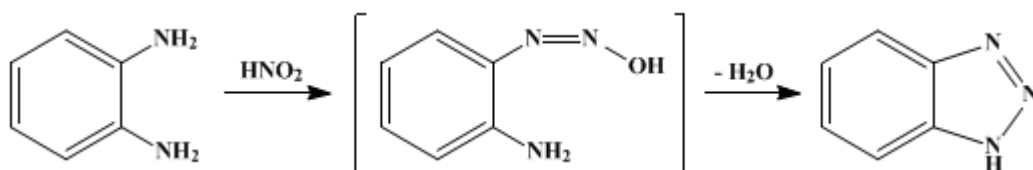
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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. 3, p.106 (1955); Vol. 20, p.16 (1940).

1,2,3-BENZOTRIAZOLE

[1H-Benzotriazole]



Submitted by R. E. Damschroder and W. D. Peterson.
Checked by W. E. Bachmann and W. S. Struve.

1. Procedure

In a 1-l. beaker are placed 108 g. (1 mole) of *o*-phenylenediamine, 120 g. (115 ml., 2 moles) of glacial acetic acid, and 300 ml. of water. By warming the mixture slightly a clear solution is obtained. The beaker is placed in ice water, and the contents are cooled to 5°. As soon as this temperature is reached, a cold solution of 75 g. (1.09 moles) of sodium nitrite in 120 ml. of water is added all at once, the mixture being stirred with a glass rod or by a slow mechanical stirrer. The reaction mixture turns dark green, and the temperature rises rapidly to 70–80° (Note 1). The color of the solution changes to a clear orange-red. The beaker is now removed from the cooling bath, and the contents are allowed to stand for 1 hour; as the solution cools, the benzotriazole separates as an oil. The beaker is then packed in ice, and the mixture is stirred until it sets to a solid mass. After being kept cold for 3 hours, the solid is collected on a Büchner funnel, washed with 200 ml. of ice water, and sucked as dry as possible under a rubber dam. The tan-colored product, after drying at 45–50° overnight, weighs 110–116 g.

The crude benzotriazole is placed in a 200-ml. modified Claisen flask and distilled under reduced pressure (Note 2). The yield of white solid (yellow cast) boiling at 201–204° at 15 mm. or 156–159° at 2 mm. is 92–99 g. The product in the receiver is melted over a luminous flame and poured into 250 ml. of benzene. The clear solution is stirred until crystallization sets in; after being chilled for 2 hours, the product is filtered on a Büchner funnel. The colorless benzotriazole weighs 90–97 g. (75–81%) (Note 3) and melts at 96–97°.

2. Notes

1. Too efficient cooling and stirring are to be avoided. It is essential that the temperature rise to 80°. Too rapid cooling after this temperature has been reached results in lower yields. With runs one-tenth this size it is advisable to remove the mixture from the cooling bath as soon as the sodium nitrite has been added in order to ensure the rise in temperature.
2. The crude product can be purified by repeated crystallizations from benzene or water. Greater losses accompany this tedious method of purification than a single distillation.
3. The submitters report that runs of double this size can be made with equally good results.

3. Discussion

1,2,3-Benzotriazole has been prepared directly by the action of nitrous acid on *o*-phenylenediamine¹ and by the hydrolysis of an acylated or aroylated benzotriazole which has been previously prepared by the action of nitrous acid on the corresponding mono acylated or aroylated *o*-phenylenediamine.^{2,3,4} The above procedure is the direct method and gives better over-all yields than the methods involving several intermediate steps. Most methods described in the literature employ mineral acid. Acetic acid is much more satisfactory.

References and Notes

1. Ladenburg, *Ber.*, **9**, 219 (1876).
 2. Bell and Kenyon, *J. Chem. Soc.*, **1926**, 954.
 3. Fieser and Martin, *J. Am. Chem. Soc.*, **57**, 1838 (1935).
 4. Charrier and Beretta, *Gazz. chim. ital.*, **51**, (Part 2), 267 (1921).
-

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

acetic acid (64-19-7)

Benzene (71-43-2)

sodium nitrite (7632-00-0)

nitrous acid (7782-77-6)

1,2,3-Benzotriazole,
1H-Benzotriazole,
benzotriazole (95-14-7)

o-Phenylenediamine (95-54-5)