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.

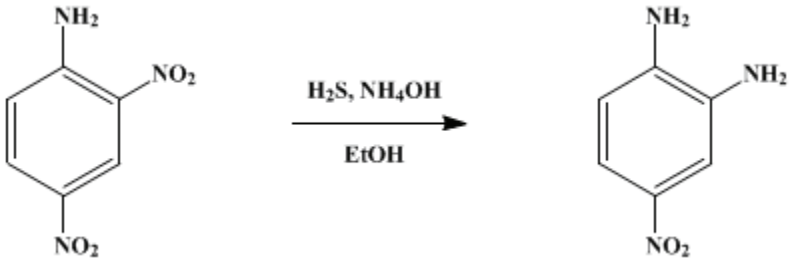
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.021.0020

Organic Syntheses, Coll. Vol. 3, p.242 (1955); Vol. 21, p.20 (1941).

1,2-DIAMINO-4-NITROBENZENE

[*o*-Phenylenediamine, 4-nitro-]



Submitted by K. P. Griffin and W. D. Peterson.
Checked by Nathan L. Drake, Ralph Mozingo, and Jonathan Williams.

1. Procedure

A 5-l. three-necked flask is fitted with a mechanical stirrer, a reflux condenser, a thermometer, and an inlet tube extending to the bottom of the flask (Note 1). In the flask is placed a mixture of 238 g. (1.3 moles) of 2,4-dinitroaniline, 2.4 l. of 95% ethanol, and 1.2 l. of concentrated ammonium hydroxide (sp. gr. 0.90).

The mixture is heated to 45°, and with good stirring hydrogen sulfide is passed into the reaction mixture while its temperature is maintained between 45° and 55° (Note 2) and (Note 3). The yellow suspended particles of 2,4-dinitroaniline dissolve slowly to form an intensely red-colored solution. The reaction is complete when all the *yellow* particles have disappeared; reduction should be complete in 30–60 minutes (Note 4).

The reaction mixture is allowed to stand in an icebox for 16–18 hours to complete the separation of the product, which forms small, well-defined, deeply red-colored crystals. The 1,2-diamino-4-nitrobenzene is filtered by suction, washed with 150–250 ml. of cold water, and sucked dry on the funnel (Note 5).

The crude product is purified by dissolving it in a boiling mixture of 900 ml. of water and 110 ml. of concentrated hydrochloric acid (sp. gr. 1.19), and filtering the hot solution through a Norit bed using suction. The filter bed is washed with a boiling mixture of 90 ml. of water and 10 ml. of concentrated hydrochloric acid, and the washings are added to the main body of the solution. The filtered solution, while still hot, is treated with 100 ml. of concentrated ammonia (sp. gr. 0.90). The precipitated 1,2-diamino-4-nitrobenzene is filtered hot on a Büchner funnel, washed on the funnel with 150 ml. of water, and dried in an oven at 40–50°.

The purified material melts at 197–198° and weighs 105–115 g. (52–58%).

2. Notes

1. The inlet tube should have a diameter of about 15 mm.
2. Enough heat is generated so that it is necessary to play a stream of cold water on the flask from time to time to maintain this temperature.
3. The rate of the gas stream should be as rapid as is consistent with complete absorption.
4. The product may begin to separate during the last few minutes.
5. Concentration of the mother liquor yields only a few grams of material (8–10 g.), a mixture of 1,4-diamino-2-nitrobenzene and 1,2-diamino-4-nitrobenzene.

3. Discussion

1,2-Diamino-4-nitrobenzene can be prepared by the partial reduction of 2,4-dinitroaniline in alcohol solution using sodium hydrosulfide[1] or ammonium sulfide.[2,3] The method described here is a modification of that given by Kehrmann.[3] 2-N,N-Dialkyl derivatives of 1,2-diamino-4-nitrobenzene have been prepared by acylation, nitration, and hydrolysis of substituted phenylenediamines.[4]

References and Notes

1. Brand, *J. prakt. Chem.*, (2) **74**, 471 (1907).
2. Heim, *Ber.*, **21**, 2305 (1888).
3. Kehrmann, *Ber.*, **28**, 1707 (1895).
4. Ger. pat. 653,259 [*C. A.*, **32**, 1946 (1938)].

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

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

hydrogen sulfide (7783-06-4)

ammonium hydroxide (1336-21-6)

ammonium sulfide

2,4-Dinitroaniline (97-02-9)

sodium hydrosulfide

1,2-Diamino-4-nitrobenzene,
o-Phenylenediamine, 4-nitro- (99-56-9)

1,4-diamino-2-nitrobenzene (5307-14-2)