



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.

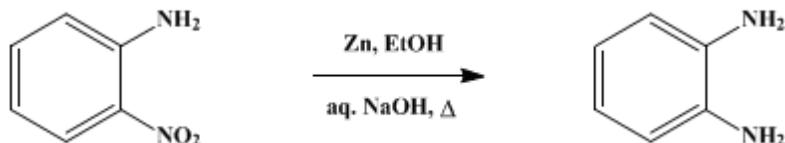
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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. 2, p.501 (1943); Vol. 19, p.70 (1939).

***o*-PHENYLENEDIAMINE**



Submitted by E. L. Martin

Checked by W. W. Hartman and S. S. Fierke.

1. Procedure

In a 1-l. three-necked, round-bottomed flask, fitted with a liquid-sealed mechanical stirrer and reflux condenser, are placed 69 g. (0.5 mole) of *o*-nitroaniline (*Org. Syn. Coll. Vol. I, 1941, 388*), 40 cc. of a 20 per cent solution of sodium hydroxide, and 200 cc. of 95 per cent ethanol. The mixture is stirred vigorously and heated on a steam bath until the solution boils gently. The steam is turned off, and 10-g. portions of 130 g. (2 gram atoms) of zinc dust (*Note 1*) are added frequently enough to keep the solution boiling (*Note 2*) and (*Note 3*). After the addition of zinc dust has been completed the mixture is refluxed with continued stirring for one hour; the color of the solution changes from a deep red to nearly colorless. The hot mixture is filtered by suction, and the zinc residue is returned to the flask and extracted with two 150-cc. portions of hot alcohol. To the combined filtrates is added 2–3 g. of sodium hydrosulfite, and the solution is concentrated under reduced pressure (using a water pump), on a steam bath, to a volume of 125–150 cc. After cooling thoroughly in an ice-salt bath, the faintly yellow crystals are collected, washed once with a small amount of ice water, and dried in a vacuum desiccator. The yield of crude *o*-phenylenediamine melting at 97–100° is 46–50 g. (85–93 per cent of the theoretical amount). If a purer product is desired, the material is dissolved in 150–175 cc. of hot water containing 1–2 g. of sodium hydrosulfite and treated with decolorizing charcoal. After cooling thoroughly in an ice-salt mixture, the colorless crystals are filtered by suction and washed with 10–15 cc. of ice water. The purified *o*-phenylenediamine weighs 40–46 g. (74–85 per cent of the theoretical amount) and melts at 99–101° (*Note 4*) and (*Note 5*).

2. Notes

1. The zinc dust should be at least 80 per cent pure, and the amount used should be equivalent to 130 g. of 100 per cent material. A large excess of zinc dust has been used without changing the yield.
2. Great care must be taken not to add too much zinc dust at first as the reaction becomes very vigorous. It is well to have a bath of ice and wet towels at hand in order to control the reaction if it should become too violent.
3. Occasionally the reaction suddenly stops and it is necessary to add an additional 10 cc. of 20 per cent sodium hydroxide solution, which causes the reaction to proceed.
4. The product can also be purified by distillation under reduced pressure in an inert atmosphere, but, unless the material is very nearly pure, considerable decomposition occurs and the distilled product darkens rapidly in contact with air.
5. The free diamine may also be converted into the dihydrochloride, and the salt purified as follows: The crude *o*-phenylenediamine is dissolved in a mixture of 90–100 cc. of concentrated hydrochloric acid (sp. gr. 1.19) and 50–60 cc. of water containing 2–3 g. of stannous chloride, and the hot solution is treated with decolorizing charcoal. To the hot, colorless filtrate is added 150 cc. of concentrated hydrochloric acid, and the mixture is cooled thoroughly in an ice-salt bath. The colorless crystals are filtered by suction, washed with a small amount of cold concentrated hydrochloric acid, and dried in vacuum over solid sodium hydroxide. The yield of *o*-phenylenediamine dihydrochloride is 77–81 g. (85–90 per cent of the theoretical amount based on the weight of *o*-nitroaniline used).

3. Discussion

o-Phenylenediamine has been prepared by the reduction of *o*-nitroaniline by means of tin and hydrochloric acid,¹ stannous chloride and hydrochloric acid,² sodium stannite,³ zinc dust and water,⁴ sodium hydrosulfite and sodium hydroxide,⁵ and zinc dust and alcoholic alkali;⁶ by electrolytic reduction in aqueous alcohol in the presence of sodium acetate;⁷ and from *o*-dichlorobenzene or *o*-chloroaniline by treatment with aqueous ammonia at 150° under pressure in the presence of copper.⁸ The procedure described above is a modification of the method of Hinsberg and König.⁶

o-Phenylenediamine has been proposed as a reagent for the identification of aliphatic acids, by conversion to crystalline 2-alkylbenzimidazoles (p. 65).

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 65
- Org. Syn. Coll. Vol. 4, 569
- Org. Syn. Coll. Vol. 4, 824

References and Notes

1. Zincke and Sintenis, Ber. **6**, 123 (1873); Koerner, Gazz. chim. ital. **4**, 320 (1874); Hübner, Ann. **209**, 361 (1881).
2. Goldschmidt and Ingebrochtsen, Z. physik. Chem. **48**, 448 (1904); Goldschmidt and Sunde, ibid. **56**, 23 (1906).
3. Goldschmidt and Eckardt, ibid. **56**, 400 (1906).
4. Bamberger, Ber. **28**, 250 (1895).
5. Borsche, Chem. Zentr. **1909**, II, 1550.
6. Hinsberg and König, Ber. **28**, 2947 (1895).
7. Rohde, Z. Elektrochem. **7**, 339 (1900).
8. Soc. pour l'ind. chim. à Bâle, Fr. pat. 788,348 [C. A. **30**, 1395 (1936)].

Appendix

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

alcohol,
ethanol (64-17-5)

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

sodium acetate (127-09-3)

sodium hydroxide (1310-73-2)

sodium hydrosulfite (7775-14-6)

tin (7440-31-5)

stannous chloride

copper (7440-50-8)

zinc (7440-66-6)

sodium stannite

o-Phenylenediamine (95-54-5)

o-NITROANILINE (88-74-4)

o-chloroaniline (95-51-2)

o-dichlorobenzene (95-50-1)

o-phenylenediamine dihydrochloride (615-28-1)