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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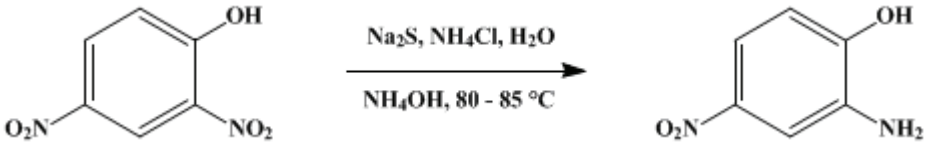
2-AMINO-4-NITROPHENOL

[Phenol, 2-amino-4-nitro-]



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1. Procedure

In a 5-l. three-necked flask, suspended over a steam bath, are placed 300 g. (1.63 moles) of technical 2,4-dinitrophenol and 2.5 l. of water. The flask is fitted with an efficient stirrer, a reflux condenser, and a thermometer which dips below the surface of the mixture. After the stirrer has been started, 600 g. (11.6 moles) of ammonium chloride and 100 ml. of concentrated aqueous ammonia (about 28%) are added, and the mixture is heated to 85°. The steam is turned off, and the mixture is allowed to cool. When the temperature reaches 70° (Note 1), 700 g. (5.4 moles) of 60% fused sodium sulfide is added in portions of about 100 g. at 5-minute intervals. After two or three such additions the temperature of the reaction mixture reaches 80–85°; it is kept in this range either by adding the remaining portions of sodium sulfide at 10-minute intervals or by wrapping the flask with a wet cloth and continuing the additions at 5-minute intervals. After all the sodium sulfide has been added, the reaction mixture is heated at 85° for 15 minutes and then filtered through a heated 6-in. Büchner funnel (Note 2).

The hot filtrate is transferred to a 5-l. round-bottomed flask and cooled overnight by a stream of cold water. The mixture is filtered, and the crystals are pressed nearly dry. The solid is dissolved in 1.5 l. of boiling water, and the solution is acidified with glacial acetic acid (about 100 ml. is required, (Note 3)). The solution is heated with 10 g. of Norit, filtered hot, and cooled to 20°. The brown crystals are collected and dried for several hours in an oven at 65° or in a vacuum desiccator (Note 4). The yield of 2-amino-4-nitrophenol melting at 140–142° is 160–167 g. (64–67%). If a purer product is desired, the crude substance is recrystallized from 1.5 l. of hot water; 147–153 g. (58–61%) of material melting at 142–143° is obtained.

2. Notes

1. If the reaction is run at temperatures below 70° it is impossible to obtain a pure product even after several recrystallizations.
2. The Büchner funnel is preheated by inverting it over a steam bath and passing a lively current of steam through it for at least 10 minutes. During the filtration, suction is applied gently and at intervals to avoid excessive cooling by evaporation in the lower part of the funnel. If the filtration is not performed rapidly and carefully, the crude product will crystallize in the funnel. The filtration can be omitted, but the presence of insoluble materials complicates the next step by making it difficult to determine when solution of the crude product is complete.
3. The amount of acid required varies with dryness of the filter cake. The acidification can be followed by observing the color of a thin layer of the solution splashed against the side of the container. The color changes from dark red to olive brown at the end point. Both colors are so deep that they are not easily distinguished except when thin layers are viewed. After the end point is observed, an additional 10 ml. of acetic acid is added.
4. Unless properly dried the substance will melt at 80–90°, owing to the presence of water of crystalliaztion.

3. Discussion

2-Amino-4-nitrophenol has been prepared by the partial reduction of 2,4-dinitrophenol chemically[1,2,3,4,5] and electrolytically,[6] and by the action of sulfuric acid on 3-nitroazidobenzene.[7]

References and Notes

1. Laurent and Gerhardt, *Ann.*, **75**, 68 (1850).
2. Post and Stuckenberg, *Ann.*, **205**, 72 (1880).
3. Auwers and Röhrig, *Ber.*, **30**, 995 (1897).
4. Pomeranz, Ger. pat. 289,454 [*Frdl.*, **12**, 117 (1914–1916)].
5. Gershzon, *J. Applied Chem. U.S.S.R.*, **9**, 879 (1936) [*C. A.*, **30**, 7554 (1936)].
6. Hofer and Jacob, *Ber.*, **41**, 3196 (1908).
7. Kehrmann and Idzkowska, *Ber.*, **32**, 1066 (1899).

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

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

ammonia (7664-41-7)

ammonium chloride (12125-02-9)

Norit (7782-42-5)

sodium sulfide (1313-82-2)

2,4-dinitrophenol (51-28-5)

2-Amino-4-nitrophenol,
Phenol, 2-amino-4-nitro- (99-57-0)

3-nitroazidobenzene