



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.

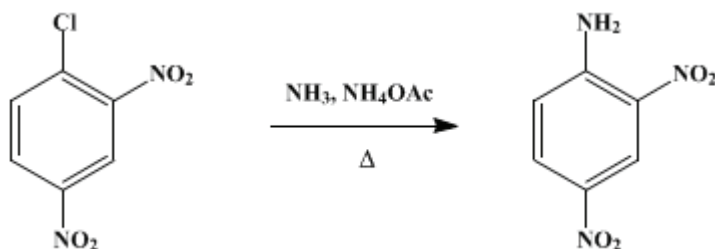
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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2,4-DINITROANILINE

[Aniline, 2,4-dinitro-]



Submitted by F. B. Wells and C. F. H. Allen.

Checked by Reynold C. Fuson and Chan Mann Lu.

1. Procedure

A wide-mouthed 250-cc. flask (Note 1) containing a mixture of 50 g. (0.25 mole) of technical 2,4-dinitrochlorobenzene (Note 2) and 18 g. (0.23 mole) of ammonium acetate is half immersed in an oil bath. The flask is fitted with a reflux condenser and an inlet tube, the lower end of which is at least 2 cm. wide (to prevent clogging) and which nearly touches the surface of the reaction mixture. During the operation ammonia gas is introduced through a bubble counter which contains a small amount of strong potassium hydroxide solution (12 g. of potassium hydroxide in 10 cc. of water).

The oil bath is heated to 170° and maintained at that temperature for six hours during which time ammonia gas is passed through at the rate of three to four bubbles per second. After the mixture has cooled, the solid is broken up by means of a glass rod and mixed with 100 cc. of water; the mixture is then heated to boiling and filtered while hot. The residue is dissolved in 500 cc. of boiling alcohol, and water is added (about 150 cc.) until the solution becomes turbid. Heat is applied until the turbidity disappears and then the solution is allowed to cool. After standing overnight, the crystals are filtered and dried. The yield is 31–35 g. (68–76 per cent of the theoretical amount) of 2,4-dinitroaniline, melting at 175–177° (Note 3) and (Note 4). For further purification the product is recrystallized in the same manner from alcohol and water, using 20 cc. of alcohol per gram of solid. Ninety per cent of the crude material is recovered as recrystallized product melting sharply at 180°.

2. Notes

1. The neck of the flask must be large enough to admit the wide inlet tube. A 250-cc. extraction flask is most convenient.
2. The technical dinitrochlorobenzene used had a freezing point of 45°. The higher yield given is obtained using a product once recrystallized from alcohol (m.p. 48°).
3. Some specimens of technical dinitrochlorobenzene used contained undetermined impurities that formed double compounds with the dinitroaniline. These remained in the filtrate. It was not worth the trouble to recover the small amount of amine thus lost.
4. The value of this method is that no autoclave is required. It was not satisfactory when applied to the nitrochlorobenzenes.

3. Discussion

2,4-Dinitroaniline has been prepared by heating dinitrochlorobenzene and ammonia under pressure;¹ by heating 1,2,4-trinitrobenzene with concentrated ammonia;² by heating dinitrochlorobenzene with urea³ or ammonium acetate;⁴ by hydrolysis of the dinitroacetanilide obtained when dinitrochlorobenzene and acetamide are heated at 200–210°;⁵ by heating 2,4-dinitroanisole or 2,4-dinitroanisic acid with aqueous or alcoholic ammonia under pressure;⁶ by heating 2,4-dinitrophenol and aqueous ammonia

under pressure;⁷ and by the rearrangement of *p*-nitrophenylnitroamine spontaneously⁸ or with concentrated sulfuric acid at 0°.⁹

References and Notes

1. Clemm, J. prakt. Chem. (2) **1**, 170 (1870); Willgerodt, Ber. **9**, 979 (1876).
 2. Hepp, Ann. **215**, 362 (1882).
 3. Rohm and Haas Company, U. S. pat. 1,752,998 [C. A. **24**, 2468 (1930)].
 4. Soc. chim. de la Grande-Paroisse, Brit. pat. 169,688 [C. A. **16**, 721 (1922)].
 5. Kym, Ber. **32**, 3539 (1899).
 6. Salkowski, Ann. **174**, 263 (1874).
 7. Barr, Ber. **21**, 1542 (1888).
 8. Bamberger and Dietrich, *ibid.* **30**, 1253 (1897).
 9. Hoff, Ann. **311**, 98 (1900).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

alcohol (64-17-5)

sulfuric acid (7664-93-9)

Acetamide (60-35-5)

ammonia (7664-41-7)

ammonium acetate (631-61-8)

potassium hydroxide (1310-58-3)

urea (57-13-6)

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

2,4-dinitrochlorobenzene (97-00-7)

dinitrochlorobenzene

dinitroaniline

1,2,4-trinitrobenzene (610-31-1)

dinitroacetanilide

2,4-dinitroanisole (119-27-7)

2,4-dinitroanistic acid

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

p-nitrophenylnitroamine

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