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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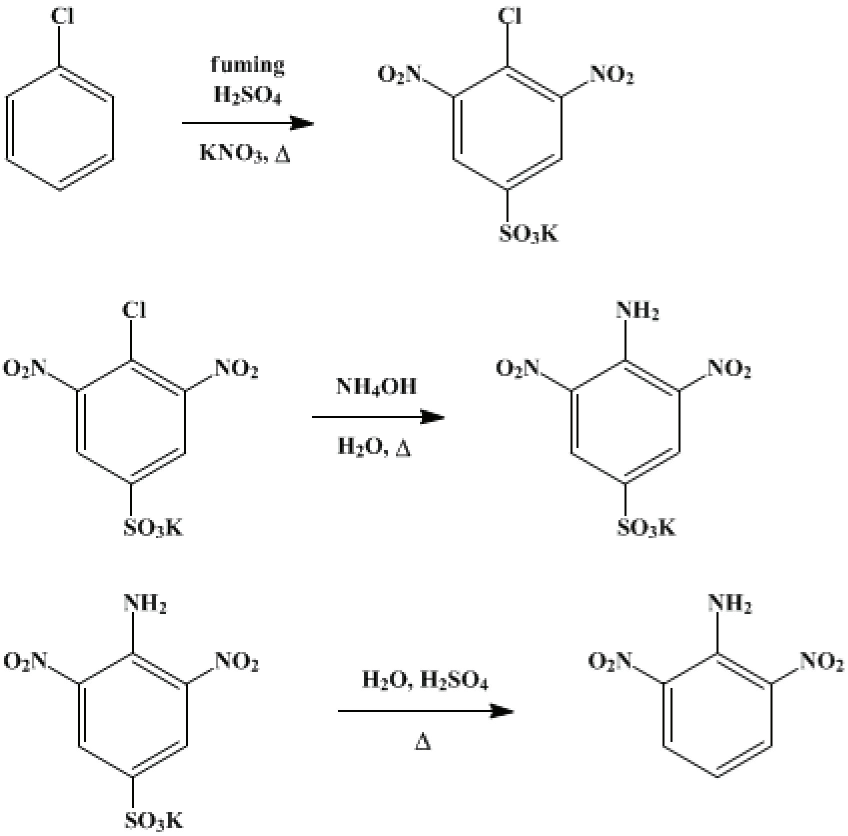
2,6-DINITROANILINE

[Aniline, 2,6-dinitro-]



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1. Procedure

In a 1-l. round-bottomed flask fitted with a mechanical stirrer are placed 50 ml. (55.4 g., 0.49 mole) of chlorobenzene (Note 1), 300 ml. of concentrated sulfuric acid (sp. gr. 1.84), and 50 ml. (92 g.) of fuming sulfuric acid (containing approximately 25% free sulfur trioxide). The mixture is stirred and heated on a steam bath for 2 hours and then cooled to room temperature. The stirrer is removed from the reaction flask and replaced with a thermometer. To the clear solution is added 170 g. (1.68 moles) of potassium nitrate in 4 portions. The temperature of the mixture during this time is held at 40–60° by cooling the flask and its contents in ice water. After the mixture has been swirled briefly in the reaction flask to dissolve most of the potassium nitrate, it is heated to 110–115° (Note 2) and held at that temperature for 20 hours. The hot contents of the flask are poured onto 2 kg. of cracked ice. After the ice has melted, the yellow precipitate is filtered with suction and pressed as dry as possible.

Without further drying, the potassium 4-chloro-3,5-dinitrobenzenesulfonate is recrystallized from 600 ml. of boiling water (Note 3). Insoluble material is removed by decantation and filtration of the hot solution. The solution is cooled to 5–10° for 12 hours, and the crystalline potassium salt is collected on a suction filter, pressed as dry as possible, and placed at once in a solution of 400 ml. of concentrated ammonium hydroxide (sp. gr. 0.90) in 400 ml. of water. The solution is boiled for 1 hour under a reflux condenser which has been connected to a gas absorption trap,[2] and then is cooled at 5–10° for 12 hours. The orange, crystalline potassium 4-amino-3,5-dinitrobenzenesulfonate is filtered with suction and pressed as dry as possible on a 10-cm. Büchner funnel.

The damp salt is placed in a solution of 200 ml. of concentrated sulfuric acid (sp. gr. 1.84) and 200 ml. of water in a 1-l. round-bottomed flask, and the mixture is boiled vigorously under reflux for 6 hours (Note 4). The hot acid solution is poured onto 1 kg. of cracked ice, filtered on a 7.5-cm. Büchner funnel, slurried twice with 100-ml. portions of water, and pressed as dry as possible on the funnel. The damp, impure 2,6-dinitroaniline is dissolved in 500 ml. of hot 95% ethanol, and the solution is boiled under reflux for 10 minutes with 3 g. of Norit and 3 g. of filter aid. The hot ethanol solution is filtered through a heated funnel (Note 5) and cooled slowly to room temperature. Light-orange needles of 2,6-dinitroaniline separate and are collected on a suction filter and air-dried. The yield is 27.4–32.3 g. (30–36%) (Note 6), m.p. 139–140°.

2. Notes

1. The best grade of Eastman Kodak Company chlorobenzene was used.
2. Since the reaction is moderately exothermic during the first 4 hours, the temperature of the reaction mixture must be controlled carefully. A gas trap[2] may be used to absorb the small amount of nitrogen dioxide evolved, or the reaction may be carried out in a hood. Excessive fuming is avoided if the temperature is kept in the range 110–115°.
3. If the potassium 4-chloro-3,5-dinitrobenzenesulfonate is not recrystallized before ammonolysis very impure 2,6-dinitroaniline is obtained.
4. The condenser should be cleared occasionally with a small glass rod to remove the 2,6-dinitroaniline that may collect there.
5. The funnel must be heated to avoid crystallization during filtration.
6. The solubility of pure 2,6-dinitroaniline in 95% ethanol at room temperature is about 0.4 g. per 100 ml.

3. Discussion

2,6-Dinitroaniline has been prepared by the ammonolysis of 2,6-dinitroanisole,[3] 2,6-dinitroiodobenzene,[4] 2,6-dinitrophenyl 4-nitrobenzyl ether,[5] and 2,6-dinitrochlorobenzene;[6] by the rearrangement of *o*-nitrophenylnitramine;[7] and by the desulfonation of potassium 4-amino-3,5-dinitrobenzenesulfonate.[8,9,10] The method described above is based on the procedures of Ullmann[8] and Welsh.[9]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 160

References and Notes

1. University of Miami, Coral Gables, Florida.
2. *Org. Syntheses Coll. Vol.* **2**, 4 (1943).
3. Salkowski, *Ann.*, **174**, 273 (1874).
4. Koerner, *Gazz. chim. ital.*, **4**, 324 (1874).
5. Kumpf, *Ann.*, **224**, 118 (1884).
6. Borsche and Rantscheff, *Ann.*, **379**, 162 (1911).
7. Hoff, *Ann.*, **311**, 108 (1900).
8. Ullmann, Engi, et al., *Ann.*, **366**, 102 (1909).
9. Welsh, *J. Am. Chem. Soc.*, **63**, 3276 (1941).
10. Fisher and Joullie, *J. Org. Chem.*, **23**, 1944 (1958).

Appendix
Chemical Abstracts Nomenclature (Collective Index Number);

(Registry Number)

ethanol (64-17-5)

sulfuric acid (7664-93-9)

sulfur trioxide (7446-11-9)

Norit (7782-42-5)

chlorobenzene (108-90-7)

nitrogen dioxide (10102-44-0)

ammonium hydroxide (1336-21-6)

potassium (7440-09-7)

potassium nitrate (7757-79-1)

2,6-dinitrochlorobenzene (606-21-3)

2,6-Dinitroaniline,
Aniline, 2,6-dinitro- (606-22-4)

potassium 4-chloro-3,5-dinitrobenzenesulfonate

potassium 4-amino-3,5-dinitrobenzenesulfonate

2,6-dinitroanisole

2,6-dinitroiodobenzene

2,6-dinitrophenyl 4-nitrobenzyl ether

o-nitrophenylnitramine