



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.

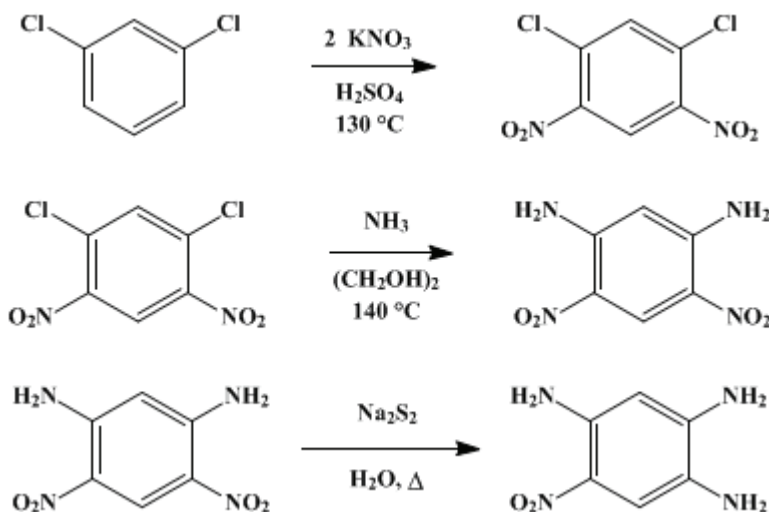
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.1067 (1973); Vol. 40, p.96 (1960).

2,4,5-TRIAMINONITROBENZENE

[1,2,4-Benzenetriamine, 5-nitro-]



Submitted by J. H. Boyer and R. S. Buriks¹.

Checked by James Cason and Taysir M. Jaouni.

1. Procedure

A. *1,5-Dichloro-2,4-dinitrobenzene* **Caution!** (Note 1). To a well-stirred solution of 140 g. (1.386 moles) of **potassium nitrate** in 500 ml. of concentrated **sulfuric acid** is added 100.0 g. (0.680 mole) of *m*-**dichlorobenzene** in one portion. The temperature of the reaction mixture rises during a few minutes to $135\text{--}140^\circ$, then drops slowly to 125° . The stirred mixture is kept at $120\text{--}135^\circ$ for an additional hour. After the reaction mixture has been cooled to about 90° it is poured over 1.5 kg. of crushed ice. The precipitated product is collected by suction filtration, drained well on the funnel, and dissolved in about 1 l. of boiling 95% **ethanol**. A small amount of insoluble impurity is removed by filtration of the hot solution by gravity through a fluted filter paper, and the product is allowed to crystallize in the refrigerator at about 0° (Note 2). The yield of yellow needles is 112–115 g. (70–71.5%), m.p. $103\text{--}104^\circ$.

B. *1,5-Diamino-2,4-dinitrobenzene* **Ammonia** gas from a tank is bubbled into a well-stirred, clear yellow solution of 60.0 g. (0.253 mole) of *1,5-dichloro-2,4-dinitrobenzene* in 400 ml. of technical grade **ethylene glycol** (heated to 140°), at such a rate that the gas is just absorbed. Within 30 minutes the color of the solution changes through orange to deep red. About 1 hour after the start of the reaction an orange, crystalline precipitate begins to separate. Heating is continued for an additional 2 hours as a slow stream of **ammonia** gas is bubbled through the reaction mixture. Finally, the reaction mixture is cooled to room temperature, the product is collected by suction filtration, and the finely divided orange-brown crystals are washed with boiling water and boiling **ethanol**. The yield of dried product, m.p. 300° (subl.), is 44–48 g. (88–95.5%) (Note 3).

C. *2,4,5-Triaminonitrobenzene*. A well-stirred slurry (Note 4) of 22.5 g. (0.114 mole) of *1,5-diamino-2,4-dinitrobenzene* in 150 ml. of water is heated (Note 4) to the boiling point under reflux in a 500-ml. three-necked flask. To this vigorously stirred mixture, a clear orange-red solution of sodium polysulfide (prepared by heating a mixture of 30.0 g. of **sodium sulfide nonahydrate**, 7.25 g. of **sulfur**, and 125 g. of water) is added dropwise during a period of 1.5 hours. After completion of the addition, reflux of the well-stirred reaction mixture is maintained for an additional 1.5 hours. The resultant deep red mixture is cooled to 0° and the total insoluble material is collected by suction filtration. This residue of product, **sulfur**, and some starting material is thoroughly extracted with five 200-ml. portions of boiling water. The combined hot extracts are filtered by gravity and cooled to room temperature to yield

9.5–10.0 g. (49.5–52%) of red needles, m.p. 200–207°, of [2,4,5-triaminonitrobenzene](#).

2. Notes

1. Unnecessary contact with [dichlorodinitrobenzene](#) should be avoided. It is a skin irritant and may cause severe blisters.
2. When a first crop of crystals was collected at room temperature and a second at 0°, the two lots exhibited the same melting point. When the filtrate from crystallization at 0° was concentrated to about 500 ml., the small crop of additional crystals had a much lower melting point.
3. The product is very slightly soluble in most solvents. It was used satisfactorily in the next step without further purification. Melting with sublimation occurs between 285° and 300°, depending on the rate of heating.
4. The submitters report that the best yield in this heterogeneous reaction depends upon particle size of the [diaminodinitrobenzene](#) and efficient stirring, and that the diamine should be thoroughly ground in a mortar before use. The checkers found that grinding had no effect on the yield if heating was in an oil bath. Heating with a flame or heating mantle caused some caking and charring on the bottom of the flask, even with rather efficient stirring, and in one run the bottom of the flask dropped out during the reaction.

3. Discussion

[1,5-Dichloro-2,4-dinitrobenzene](#) has been prepared from *m*-dichlorobenzene and [nitric acid](#)² or [potassium nitrate](#)³ in the presence of [sulfuric acid](#). [1,5-Diamino-2,4-dinitrobenzene](#) has been prepared by the nitration of *m*-bis-acetamidobenzene followed by hydrolysis;⁴ or from [1,5-dichloro-2,4-dinitrobenzene](#) and alcoholic ammonia in a pressure bottle at 150° for 8 hours.^{2,5} The preparation and characterization of previously unknown [2,4,5-triaminonitrobenzene](#) will be published elsewhere.

The present procedures represent simplified methods for obtaining the subject compounds and for accomplishing the illustrated conversions.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 7, 27](#)

References and Notes

1. Department of Chemistry, Tulane University, New Orleans, Louisiana.
 2. R. Nietzki and A. Schedler, *Ber.*, **30**, 1666 (1897).
 3. Footnote No. 7 in Th. Zincke, *Ann.*, **370**, 302 (1909) refers to this method used by Fries.
 4. R. Nietzki and E. Hagenbach, *Ber.*, **20**, 328, 2114 (1887).
 5. P. Ruggli and R. Fischer, *Helv. Chim. Acta*, **28**, 1270 (1945).
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Appendix

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

sodium polysulfide

[ethanol](#) (64-17-5)

[sulfuric acid](#) (7664-93-9)

[ammonia \(7664-41-7\)](#)

[nitric acid \(7697-37-2\)](#)

[sulfur \(7704-34-9\)](#)

[ethylene glycol \(107-21-1\)](#)

[potassium nitrate \(7757-79-1\)](#)

[sodium sulfide nonahydrate \(1313-84-4\)](#)

[2,4,5-Triaminonitrobenzene,
1,2,4-Benzenetriamine, 5-nitro- \(6635-35-4\)](#)

[1,5-Dichloro-2,4-dinitrobenzene \(3698-83-7\)](#)

[1,5-Diamino-2,4-dinitrobenzene \(4987-96-6\)](#)

[dichlorodinitrobenzene](#)

[diaminodinitrobenzene](#)

[m-dichlorobenzene \(541-73-1\)](#)

[m-bis-acetamidobenzene \(10268-78-7\)](#)