



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](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.

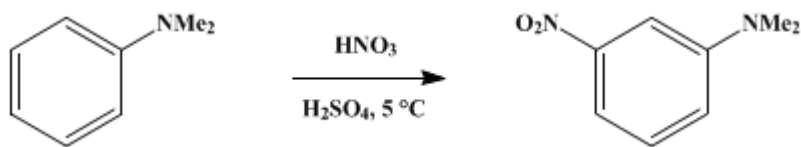
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

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## ***m*-NITRODIMETHYLANILINE**

**[Aniline, N,N-dimethyl-*m*-nitro-]**



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### 1. Procedure

In a 3-l. three-necked round-bottomed flask fitted with an effective mechanical stirrer, a dropping funnel, and a thermometer, and surrounded by an ice bath, is placed 1270 ml. (23.0 moles) of concentrated **sulfuric acid** (sp. gr. 1.84). Then 363 g. (3.0 moles) of **dimethylaniline** (Note 1) is slowly added with stirring and cooling so that the temperature remains below 25°. Stirring and cooling are continued until the temperature falls to 5°. A nitrating mixture is prepared by adding 366 g. (200 ml., 3.6 moles) of concentrated **sulfuric acid** (sp. gr. 1.84) to 286 g. (200 ml., 3.15 moles) of concentrated **nitric acid** (sp. gr. 1.42), with cooling and stirring. This is placed in the dropping funnel and added, drop by drop, the end of the dropping funnel being kept beneath the surface of the solution of **dimethylaniline sulfate**. The temperature is regulated between 5° and 10°, best by addition of small pieces of Dry Ice (Note 2); about 1.5 hours is required (Note 3). When the addition has been completed, the solution is stirred at 5–10° for 1 hour, and then poured, with stirring (Note 4), into an enameled pail containing 6 l. of ice and water (Note 5). Concentrated **ammonium hydroxide** is added slowly, with good stirring and using a dropping funnel that extends beneath the surface of the liquid, until the color of the precipitate changes to a light orange (Note 6). During this step the temperature is kept below 25°, using Dry Ice. From 1900 to 2050 ml. of **ammonium hydroxide** is required. The crude ***p*-nitrodimethylaniline** is collected on a filter and washed with 200 ml. of water (Note 7). Concentrated **ammonium hydroxide** (sp. gr. 0.90) is again added to the combined filtrate and washings, with good agitation and cooling to keep the temperature below 25°, until the liquid gives a purple color on Congo red paper (Note 8). From 1500 to 1650 ml. of **ammonium hydroxide** is required. The product is collected on a Büchner funnel and washed with 500 ml. of water. The crude ***m*-nitrodimethylaniline** (316–342 g. dry weight) is recrystallized from 400 ml. of hot 95% **ethanol** and carefully washed on the filter with 100 ml. of cold 95% **ethanol**. The yield is 280–316 g. (56–63%) of bright orange crystals that melt at 59–60°.

### 2. Notes

1. The **dimethylaniline** should be of good quality. **Dimethylaniline** (free from mono), m.p. 1°, of the Eastman Kodak Company, and **dimethylaniline**, Merck, are satisfactory.
2. A cooling bath of Dry Ice and **acetone** can be used, but addition of the solid directly to the mixture is more satisfactory and less is required.
3. The mixture may be left overnight at room temperature. It is advisable to complete the subsequent neutralization in 1 day.
4. A powerful stirrer is required to mix the large volumes.
5. If large equipment is not available, it is convenient to divide the nitration mixture into four parts (about 490 ml. each) and to pour each portion into 1.5 l. of ice and water in a 4-l. beaker. After neutralization, the precipitates from the four lots are combined on the filter.
6. It is essential that all the *para* isomer be precipitated, since it is not easily removed by recrystallization from solvents. The point at which the yellow ***p*-nitrodimethylaniline** ceases to precipitate and the orange ***m*-nitrodimethylaniline** begins to precipitate is difficult to judge without experience, since the solution itself has an orange color. If doubt exists, a small sample may be filtered so that the color of the precipitate can be clearly seen. If very much of the *para* isomer remains in

solution, a yellow precipitate or turbidity is obtained on diluting the filtrate with several volumes of water.

7. If the *para* isomer is to be recovered, the precipitate should be washed well with water to remove all acid and dried. The solid (143–155 g.) is recrystallized from 400 ml. of benzene and carefully washed on the filter with 125 ml. of cold benzene. The yield is 74–92 g. (14–18%) of bright yellow crystals that melt at 163–164°.

8. Substantially all the *m*-nitrodimethylaniline is precipitated at a pH of about 3, while any dimethylaniline present remains in solution.

### 3. Discussion

The above procedure is a modification of the method of Groll;<sup>1</sup> a more laborious method of purification has been described.<sup>2</sup> *m*-Nitrodimethylaniline can also be prepared by methylation of *m*-nitroaniline using methyl sulfate<sup>3</sup> or methyl *p*-toluenesulfonate.<sup>4</sup>

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### References and Notes

1. Groll, *Ber.*, **19**, 198 (1886).
  2. Bobranskii and Eker, *J. Applied Chem. U.S.S.R.*, **14**, 524 (1941) [*C. A.*, **36**, 3159 (1942)].
  3. Ullmann, *Ann.*, **327**, 112 (1903).
  4. Simonov, *J. Gen. Chem. U.S.S.R.*, **13**, 51 (1943) [*C. A.*, **38**, 338 (1944)].
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### Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

ethanol (64-17-5)

sulfuric acid (7664-93-9)

Benzene (71-43-2)

nitric acid (7697-37-2)

acetone (67-64-1)

ammonium hydroxide (1336-21-6)

dimethylaniline (121-69-7)

methyl sulfate (75-93-4)

dimethylaniline sulfate

*m*-nitroaniline (99-09-2)

Methyl *p*-toluenesulfonate (80-48-8)

*m*-Nitrodimethylaniline,  
Aniline, *N,N*-dimethyl-*m*-nitro- (619-31-8)

p-nitrodimethylaniline (100-23-2)

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