



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.

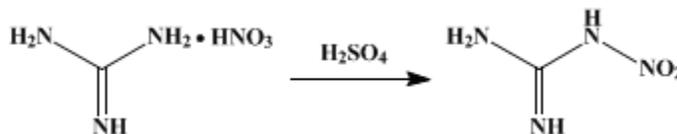
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

*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. 1, p.399 (1941); Vol. 7, p.68 (1927).*

## NITROGUANIDINE

[Guanidine, nitro-]



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Checked by H. T. Clarke and Ross Phillips.

### 1. Procedure

To 500 cc. (Note 1) of concentrated sulfuric acid (sp. gr. 1.84), previously cooled in a freezing mixture, is added, in small portions and with hand stirring, 560 g. of crude (Note 2) guanidine nitrate (obtained from 210 g. of dicyanodiamide as described on p. 302). The temperature is not allowed to rise above 20° during the addition. When all has been added, the milky mixture is allowed to stand at room temperature with occasional stirring until it is homogeneous and free from crystals (Note 3). It is then poured with stirring into 6 l. of a mixture of cracked ice and water. The precipitated nitroguanidine is filtered, washed free from acid, and recrystallized from the least possible amount (4–5 l.) of boiling water (Note 4). The yield (Note 5) is 380–390 g. (73–75 per cent of the theoretical amount, based on the dicyanodiamide used). The product melts with decomposition at about 232° (Note 6).

### 2. Notes

1. It has been found in checking that the use of 800 cc. of acid, though not necessary, gives a much less viscous solution, which becomes homogeneous more rapidly.
2. This contains ammonium nitrate, which, however, does not interfere with the reaction.
3. The mixture has to stand fifteen to twenty hours before solution is complete.
4. The solution should be allowed to cool slowly, preferably overnight, when the nitroguanidine separates in long needles which resemble sublimed phthalic anhydride. The mother liquor contains only 3–4 g. per liter, and may be discarded.
5. In checking, yields amounting to 85–90 per cent of the theoretical quantity were obtained from pure guanidine nitrate.
6. Melting points varying between 220° and 250° have been obtained on the same sample, according to the rate of heating.

### 3. Discussion

Nitroguanidine can be prepared by the nitration of guanidine salts by means of nitric acid,<sup>1</sup> or by the action of concentrated sulfuric acid, or fuming nitric acid upon guanidine nitrate.<sup>2</sup> The nitration of guanidine thiocyanate yields a product which retains a small proportion of sulfur compounds, and the nitration of the sulfate requires vigorous treatment and gives poor yields. The procedure described, which yields the *alpha* form,<sup>3</sup> is simple and economical, and furnishes a good yield. A detailed study of the preparation from guanidine nitrate and sulfuric acid has been published.<sup>4</sup>

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 302
- Org. Syn. Coll. Vol. 3, 73

1. Thiele, Ann. **270**, 16 (1892).
  2. Jouselin, Compt. rend. **88**, 1087 (1879); Pellizzari, Gazz. chim. ital. **21** (II), 406 (1891); Ewan and Young, J. Soc. Chem. Ind. **40**, 109 T (1921); Kato, Sugino, and Koidzumi, J. Electrochem. Assoc. (Japan) **2**, 187 (1934) [C. A. **28**, 7250 (1934)].
  3. Davis, Ashdown, and Couch, J. Am. Chem. Soc. **47**, 1063 (1925).
  4. Smith, Sabetta, and Steinbach, Ind. Eng. Chem. **23**, 1124 (1931).
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**Appendix**  
**Chemical Abstracts Nomenclature (Collective Index Number);**  
**(Registry Number)**

dicyanodiamide

sulfuric acid (7664-93-9)

nitric acid (7697-37-2)

phthalic anhydride (85-44-9)

ammonium nitrate

Guanidine nitrate (506-93-4)

Nitroguanidine,  
Guanidine, nitro- (556-88-7)

guanidine thiocyanate