



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.

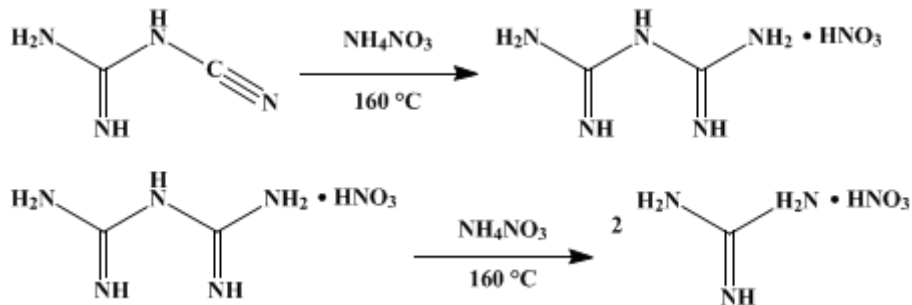
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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.

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.302 (1941); Vol. 7, p.46 (1927).

GUANIDINE NITRATE



Submitted by Tenney L. Davis
Checked by H. T. Clarke and Ross Phillips.

1. Procedure

It is strongly recommended that this procedure not be used to prepare guanidine nitrate. Mixtures of ammonium nitrate and organic materials not much different from the mixture in the procedure are now used extensively as commercial explosives. The aqueous mixture of (Note 10) is similar to some aqueous mixtures used in sizable quantities for rock blasting; a confined mixture of this sort is especially hazardous. Only a few laboratories devoted to explosives research have the barricades and remote control devices needed to run this preparation of guanidine nitrate without risk.

Guanidine nitrate can be bought from Eastman Organic Chemicals and other suppliers.

In a 1-l. round-bottomed flask is placed an intimate mixture of 210 g. of dicyandiamide (2.5 moles) and 440 g. of ammonium nitrate (5.5 moles) (Note 1) and (Note 10). The flask is introduced into an oil bath at 110–120°, and the temperature of the oil is raised during about one-half hour to 160°. The bath is then held at this temperature (Note 2) and (Note 10) for three hours. During the first hour the mass melts to a clear liquid which begins to deposit crystals and finally sets to a solid cake (Note 3). At the end of three hours the flask is removed from the bath; the product is allowed to cool and is extracted on the steam bath with successive quantities of water (about 2 l. is necessary to bring all soluble material into solution) (Note 4). The solution is filtered to remove white amorphous insoluble material (ammelene and ammelide) (Note 5).

The filtrate contains guanidine nitrate along with a small amount of ammonium nitrate and very small amounts of dicyandiamide and biguanide nitrate (Note 6). The solution is concentrated to about 1 l., and the guanidine nitrate which crystallizes on cooling is filtered off. A second crop is obtained by concentrating to 250 cc. (Note 7). The combined yield of crude guanidine nitrate is 520–560 g. (85–92 per cent of the theoretical amount). The product may be purified by recrystallization from 1 l. of water (Note 8), a second crop being taken after the mother liquor has been concentrated to 250 cc. The yield of recrystallized guanidine nitrate melting at 213–214° amounts to 500–520 g. (Note 9).

2. Notes

1. A 10 per cent excess of ammonium nitrate is used because the biguanide mononitrate which is formed as an intermediate is strongly basic and tends to attack the unreacted ammonium nitrate, as is evidenced by the liberation of ammonia during the heating. The excess of ammonium nitrate can be easily separated from the guanidine nitrate by the crystallization from water, and it does not interfere with the conversion of guanidine nitrate into nitroguanidine by the action of strong sulfuric acid.
2. When the molten mass reaches 160° its temperature begins to rise above that of the bath, generally

reaching 200° during the course of five or six minutes. The mass should not be stirred at any time, especially before the mixture has completely melted; otherwise, the temperature may run somewhat higher.

3. The [guanidine nitrate](#) begins to crystallize soon after the temperature of the mixture begins to fall.

4. The hard cake goes into solution slowly, and sufficient time must be given for each portion of water to become saturated before it is decanted.

5. When the hot filtrate cools, it will deposit flocks of [ammelide](#) along with the crystals of [guanidine nitrate](#). water may conveniently be added until the crystals dissolve, and the cold solution again filtered for the removal of [ammelide](#).

6. This filtrate on evaporation to dryness and baking at 100° leaves a residue of 650 g., which is suitable for the preparation of [nitroguanidine](#) (p. 399).

7. At this point the mother liquor (about 200 cc.) may be discarded as it contains mainly [ammonium nitrate](#).

8. [Alcohol](#) is a satisfactory solvent for [guanidine nitrate](#) but appears to have no advantage over water. A saturated solution of [guanidine nitrate](#) in water contains about 10 per cent at 15°.

9. The second mother liquor may advantageously be worked up with a subsequent run.

10. The submitter has prepared [guanidine nitrate](#) in batches of about 1 kg. by heating dicyanodiamide and [ammonium nitrate](#) in 2-l. flasks in oil baths heated to 160°. If the oil bath is kept at 160° the temperature of the reacting materials rises at times considerably above that point, but apparently the temperature does not mount dangerously high with such sized runs.

It is suggested that the best way to carry out the preparation, particularly on a large scale, is to heat the reagents in an autoclave, with a convenient amount of water, at 160° for two to three hours. The autoclave is emptied while still warm. The liquid is filtered hot for the removal of white insoluble material, and the [guanidine nitrate](#) crystallizes out as the liquid cools. (T. L. Davis, private communication.)

3. Discussion

Guanidine salts can be prepared by heating [ammonium thiocyanate](#);¹ by hydrolysis of dicyanodiamide by acids² (whereby one molecule of the guanidine salt is produced); and by the action of ammonium salts on dicyanodiamide,³ from which two molecules of guanidine salt result. The [nitrate](#) can be prepared from the [thiocyanate](#) by the action of [nitric acid](#)⁴ or by conversion to the [sulfate](#) and treatment with [calcium nitrate](#).⁵ The [nitrate](#) is also obtained by heating [ammonium nitrate](#) and calcium cyanamide.⁶ A detailed study has been made of the preparation of [guanidine nitrate](#) in improved yields from dicyanodiamide and [ammonium nitrate](#).⁷

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 1, 399](#)
- [Org. Syn. Coll. Vol. 5, 589](#)

References and Notes

1. Delitsch, J. prakt. Chem. (2) **8**, 240 (1873); (2) **9**, 2 (1874); Volhard, *ibid.* (2) **9**, 15 (1874).
 2. Baumann, Ber. **7**, 1766 (1874); Davis, J. Am. Chem. Soc. **43**, 669 (1921); *Inorganic Syntheses* **1**, 96 (1939).
 3. Rathke, Ber. **18**, 3107 (1885); Davis, J. Am. Chem. Soc. **43**, 2234 (1921).
 4. Jouselin, Bull. soc. chim. (2) **34**, 497 (1880).
 5. Glund, Keller, and Schultze, Ber. ges. Kohlentech. **4**, 21 (1931) [*C. A.* **26**, 2017 (1932)].
 6. Hercules Powder Co., U. S. pat. 2,109,934 [*C. A.* **32**, 3423 (1938)].
 7. Smith, Sabetta, and Steinbach, Ind. Eng. Chem. **23**, 1124 (1931).
-

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

calcium cyanamide

dicyanodiamide

Guanidine salts

acids

guanidine salt

ammonium salts

alcohol (64-17-5)

sulfuric acid (7664-93-9)

ammonia (7664-41-7)

ammonium thiocyanate (1762-95-4)

nitric acid (7697-37-2)

sulfate (14808-79-8)

ammonium nitrate

Guanidine nitrate (506-93-4)

ammelide (645-93-2)

biguanide nitrate,
biguanide mononitrate

Nitroguanidine (556-88-7)

nitrate

thiocyanate

calcium nitrate (10124-37-5)