



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.

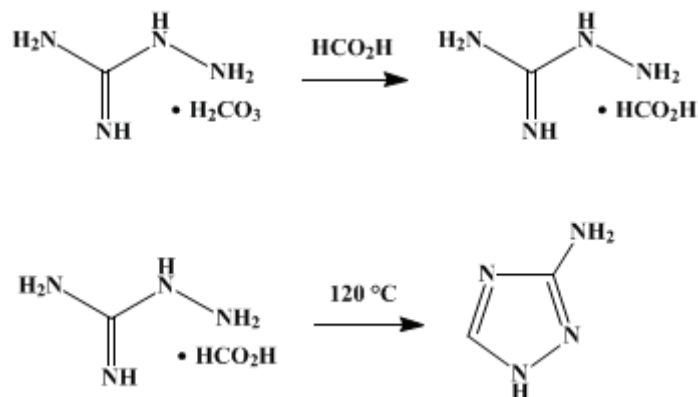
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.95 (1955); Vol. 26, p.11 (1946).

3-AMINO-1H-1,2,4-TRIAZOLE

[1H-1,2,4-Triazole, 3-amino-]



Submitted by Georg Sjostedt and Leopold Gringas.

Checked by E. C. Horning, H. Lloyd, and L. Matternas.

1. Procedure

To 136 g. (1 mole) of finely powdered [aminoguanidine bicarbonate](#) in a 500-ml. two-necked round-bottomed flask fitted with a thermometer is added 48 g. (40 ml., 1.05 moles) of 98–100% [formic acid](#) ([Note 1](#)). The foaming mixture is heated cautiously, with gentle rotation of the flask to avoid local overheating, until gas evolution ceases and the whole mass is dissolved. The solution of [aminoguanidine formate](#) is held at a temperature of 120° for 5 hours ([Note 2](#)). After the solution is cooled, 500 ml. of 95% [ethanol](#) is added, the product is dissolved by heating, and the solution is filtered while hot. The product, obtained by evaporating the [ethanol](#) solution to dryness on the steam bath, and oven-drying at 100° , is 80–81.6 g. (95–97%) of colorless crystalline [3-amino-1,2,4-triazole](#) melting at $152\text{--}156^\circ$ ([Note 3](#)). The [3-amino-1,2,4-triazole](#) can be recrystallized from [ethanol](#) ([Note 4](#)).

2. Notes

1. The submitters report that [aminoguanidine bicarbonate](#) of practical grade is satisfactory. The checkers used Eastman Kodak white label quality.
2. The submitters and checkers used an infrared heater.
3. The main part of the [ethanol](#) can be removed by distillation. From the remaining ethanolic solution yellow crystals precipitate, which are collected on a Büchner funnel. When melted and dried they lose water and give [3-amino-1,2,4-triazole](#) in its pure form.
4. The [3-amino-1,2,4-triazole](#) may be crystallized from [ethanol](#) or [ethanol-ether](#).¹ The checkers preferred [ethanol](#) (200 ml. for 40 g.). The recovery is 70–73%, m.p. $152\text{--}153^\circ$.

3. Discussion

[3-Amino-1,2,4-triazole](#) has been prepared by evaporating [formylguanidine nitrate](#) with [sodium carbonate](#),² and from 5(3)-amino-1,2,4-triazolecarboxylic acid-3(5) by heating above its melting point,^{3,4,5} or by a long digestion with [acetic acid](#).² It has been prepared from the sulfate in essentially the same yield and purity.¹

References and Notes

1. *Org. Syntheses*, **26**, 11 (1946).

2. Thiele and Manchot, *Ann.*, **303**, 45, 54 (1898).
 3. Curtius and Lang, *J. prakt. Chem.*, (2) **38**, 554 (1888).
 4. Hantzsch and Silberrad, *Ber.*, **33**, 79 (1900).
 5. Curtius, Darapsky, and Müller, *Ber.*, **40**, 818, 830 (1907).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

5(3)-amino-1,2,4-triazolecarboxylic acid-3(5)

ethanol (64-17-5)

acetic acid (64-19-7)

ether (60-29-7)

sodium carbonate (497-19-8)

formic acid (64-18-6)

Aminoguanidine bicarbonate (2582-30-1)

3-Amino-1H-1,2,4-triazole,
1H-1,2,4-Triazole, 3-amino-,
3-amino-1,2,4-triazole (61-82-5)

aminoguanidine formate

formylguanidine nitrate