



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.

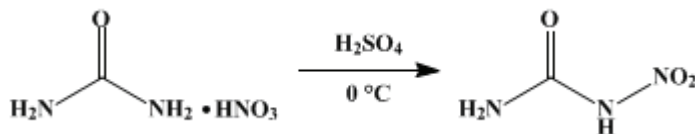
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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.417 (1941); Vol. 5, p.85 (1925).

NITROUREA

[Urea, nitro-]



Submitted by A. W. Ingersoll and B. F. Armendt.

Checked by Henry Gilman and C. C. Vernon.

1. Procedure

In a 2-l. Erlenmeyer flask provided with a mechanical stirrer and thermometer, and surrounded by an ice-salt mixture, is placed 700 cc. of concentrated [sulfuric acid](#). The stirrer is started, and when the acid is cooled to -3° or below, 200 g. (1.62 moles) of dry, powdered [urea nitrate](#) is added in small portions at such a rate that the temperature does not rise above 0° . The addition will require about one-half hour. Stirring is continued for another one-half hour, the temperature being kept below $+3^\circ$ ([Note 1](#)). Then the mixture is poured upon 1 kg. of ice.

The white, finely divided precipitate of [nitrourea](#) is filtered upon a 12-cm. Büchner funnel. A hardened filter paper ([Note 2](#)) is used in this operation, and the [nitrourea](#) is pressed as dry as possible. The product is washed in the funnel with four portions of cold water just sufficient to cover it, and pressed dry each time ([Note 3](#)). Then it is dried in the air ([Note 4](#)). By strongly cooling the filtrates, a further small amount of [nitrourea](#) may be obtained and added to the main portion. The yield of air-dried material is 120–150 g. (70–87 per cent of the theoretical amount). It melts with decomposition at $150\text{--}164^\circ$ and is sufficiently pure for use in the preparation of [semicarbazide](#) ([Note 5](#)) and ([Note 6](#)).

2. Notes

1. If bubbles of gas begin to be evolved while stirring, the mixture should be poured at once upon ice.
2. A hardened filter is necessary. Whatman's No. 50 is satisfactory.
3. Cracks appear when the [nitrourea](#) is filtered; hence, care must be taken that the water used for washing does not go through the cracks instead of through the material. If desired, the [nitrourea](#) may be removed from the funnel, made into a paste with about 800 cc. of cold water, and again filtered.
4. The product may be dried on a steam plate if the heating is not continued too long.
5. Various samples of [nitrourea](#) prepared in this way melt differently, and therefore the melting point is not a suitable indication of purity. A uniform product can also be obtained by crystallizing one-half of the crude material obtained in one run from 1 l. of water at a temperature not over 55° , and using the filtrate to crystallize the second half. Even this recrystallized material does not have a definite melting point.
6. [Nitrourea](#) may be obtained in a pure condition by recrystallization from [ether](#), [benzene](#), or [chloroform](#), in which solvents it does not rearrange, and melts sharply at $158.4\text{--}158.8^\circ$ with decomposition.¹

3. Discussion

[Nitrourea](#) can be prepared by the action of concentrated [sulfuric acid](#) on [urea nitrate](#).² The procedure described is essentially that of Thiele and Lachmann.² A modified procedure³ uses a lesser quantity of [sulfuric acid](#).

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 1, 485](#)

- [Org. Syn. Coll. Vol. 4, 361](#)

References and Notes

1. Willstätter and Pfannenstiel, *Ber.* **59**, 1870 (1926); Davis and Blanchard, *J. Am. Chem. Soc.* **51**, 1790 (1929).
 2. Thiele and Lachmann, *Ann.* **288**, 281 (1895); Backer, *Rec. trav. chim.* **31**, 21 (1912); Willstätter and Pfannenstiel, *Ber.* **59**, 1870 (1926).
 3. Davis and Blanchard, *J. Am. Chem. Soc.* **51**, 1794 (1929).
-

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

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

[Benzene \(71-43-2\)](#)

[ether \(60-29-7\)](#)

[chloroform \(67-66-3\)](#)

[Nitrourea,
Urea, nitro- \(556-89-8\)](#)

[urea nitrate](#)

[semicarbazide \(57-56-7\)](#)