Organic Syntheses

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.

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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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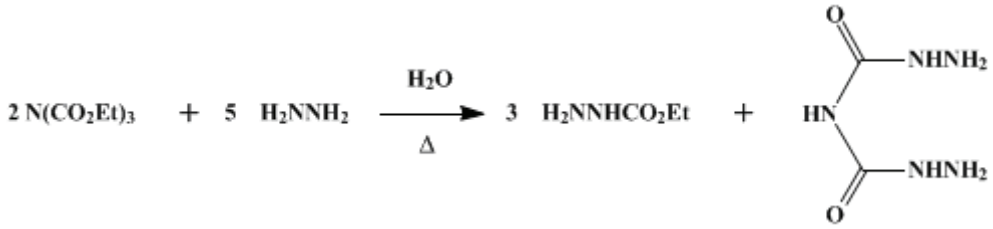
ETHYL HYDRAZINECARBOXYLATE AND DIAMINOBIURET

[Carbazic acid, ethyl ester]

[Imidodicarboxylic acid dihydrazide]



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1. Procedure

In a 3-l. round-bottomed flask equipped with a reflux condenser are placed 582 g. (2.5 moles) of N-tricarboxylic ester (p. 415) and 800 g. (6.7 moles) of 42% hydrazine hydrate (Note 1). The flask is shaken by hand to mix the two layers. After a short time, reaction begins with considerable evolution of heat, and all the N-tricarboxylic ester goes into solution (Note 2). After the reaction subsides, the solution is heated for 1 hour on a steam bath and then evaporated under reduced pressure until the mixture becomes a thick slurry of diaminobiuret crystals (Note 3). The mixture is cooled, 2 l. of 95% ethanol is added, and the diaminobiuret which has crystallized is filtered, washed with 250 ml. of ethanol, and dried. The substance melts at 205° with decomposition. The yield is 115–125 g. (69–75%).

The filtrate is now evaporated at atmospheric pressure to remove the ethanol, and the residual oil is distilled using a Vigreux column. Ethyl hydrazinecarboxylate boils at 92–95° /13 mm. The yield is 350–370 g. (90–95%). After distillation in vacuum, the ester may crystallize; the crystals melt at 51–52°.

2. Notes

1. This reaction can be carried out successfully with these amounts, but, if larger quantities of starting materials were to be used, it would be advisable to dilute the ester with ethanol and run in the hydrazine slowly. Several hours of refluxing on a steam bath would serve to complete the reaction. In smaller runs no difficulty is encountered.
2. It is advisable to keep an ice bath at hand in case the reaction becomes too violent and it is necessary to cool the mixture rapidly.
3. If insufficient water is removed by evaporation, too much diaminobiuret will remain in solution and will interfere during the distillation of the ethyl hydrazinecarboxylate.

3. Discussion

Diaminobiuret has been prepared only from N-tricarboxylic ester and hydrazine hydrate.[1] Ethyl hydrazinecarboxylate has been prepared by reduction of nitrourethan electrolytically[2] or with zinc dust and acetic acid,[3] and by the action of hydrazine hydrate on diethyl carbonate,[4,5] ethyl chlorocarbonate,[6] and N-tricarboxylic ester.[1]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 6, 936

References and Notes

1. Diels, *Ber.*, **36**, 736 (1903).
2. Backer, *Rec. trav. chim.*, **31**, 20 (1912).
3. Thiele and Lachmann, *Ann.*, **288**, 293 (1895).
4. Diels, *Ber.*, **47**, 2186 (1914).
5. Merck, Ger. pat. 285,800 [*Frdl.*, **12**, 94 (1914–1916)].
6. Stollé and Benrath, *J. prakt. Chem.*, (2) **70**, 276 (1904).

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

Imidodicarboxylic acid dihydrazide

N-tricarboxylic ester

ethanol (64-17-5)

acetic acid (64-19-7)

zinc (7440-66-6)

hydrazine hydrate (7803-57-8)

hydrazine (302-01-2)

ethyl chlorocarbonate (541-41-3)

diethyl carbonate (105-58-8)

Ethyl hydrazinecarboxylate,
Carbazic acid, ethyl ester (4114-31-2)

diaminobiuret (4375-11-5)

nitrourethan