



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.

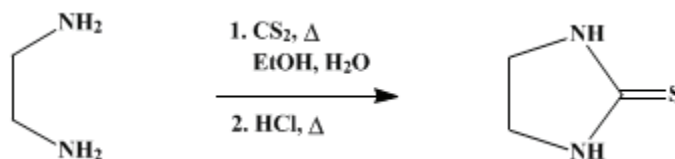
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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ETHYLENE THIOUREA

[2-Imidazolidinethione]



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Checked by R. L. Shriner and Curtis D. Snow.

1. Procedure

In a 2-l. round-bottomed flask are placed 120 g. (1.83 moles) of 92% ethylenediamine (Note 1), 300 ml. of 95% ethanol, and 300 ml. of water. The flask is attached to an efficient reflux condenser, and 121 ml. of carbon disulfide is placed in a separatory funnel attached to the top of the condenser by means of a notched cork. About 15 to 20 ml. of the carbon disulfide is added, and the flask is shaken to mix the contents. A vigorous reaction takes place (Note 2), and it may be necessary to cool the flask. After the reaction has started, a water bath at 60° is placed under the flask and the balance of the carbon disulfide is added at such a rate that the vapors reflux about one-third the way up the condenser. About 2 hours is required for the addition of the carbon disulfide. At this time the bath temperature is raised to about 100°, and the mixture is allowed to reflux for 1 hour. Then 15 ml. of concentrated hydrochloric acid is added, and the mixture is refluxed under a good hood (bath at 100°) for 9–10 hours. The mixture is cooled in an ice bath, and the product is filtered by suction on a Büchner funnel and washed with 200–300 ml. of cold acetone (Note 3). A yield of 156–167 g. (83–89%) of white crystals is obtained melting at 197–198° (Note 4) and (Note 5).

2. Notes

1. If commercial ethylenediamine is used, it should be redistilled. The concentration of the ethylenediamine may be determined by titration with standard acid and the proper amount taken.
2. Care should be exercised to make certain that the reaction starts, before an additional quantity of carbon disulfide is added. In one experiment in which the carbon disulfide was added all at once, a very violent reaction occurred.
3. Since all the likely contaminants are readily volatile, extensive washing is unnecessary.
4. This product is pure enough for most purposes. It gives no precipitate with copper sulfate solution, indicating the absence of the open-chain acid.¹
5. It has been reported (J. VanAllan) that this procedure may also be used for the preparation of 2-thio-3,4,5,6-tetrahydropyrimidine; in this case 130 g. (150 ml., 1.76 moles) of propylenediamine is used in place of ethylenediamine. The yield is 160 g. (80%) of colorless product, m.p. 207–208°, after recrystallization from water.

3. Discussion

The only practical method for preparing alkylene thioureas is by the action of the diamines upon carbon disulfide in aqueous alcohol.^{1,2,3,4,5} The final heating is essential to convert the thiocarbamic acid into the cyclic compound, the addition of hydrochloric acid being beneficial. Alkylene thioureas have also been prepared by heating N-formylalkylenediamines with sulfur.⁶

References and Notes

1. Ruiz and Libenson, *Anales asoc. quim. argentina*, **18**, 37 (1930) [*C. A.*, **24**, 5726 (1930)].

2. Hofmann, *Ber.*, **5**, 242 (1872).
 3. Johnson and Edens, *J. Am. Chem. Soc.*, **64**, 2707 (1942).
 4. Schackt, *Arch. Pharm.*, **235**, 442 (1897).
 5. Klut, *Arch. Pharm.*, **240**, 675 (1902).
 6. Zienty, *J. Am. Chem. Soc.*, **68**, 1388 (1946).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

copper sulfate (7758-98-7)

sulfur (7704-34-9)

acetone (67-64-1)

carbon disulfide (75-15-0)

Ethylene thiourea,
2-Imidazolidinethione (96-45-7)

ethylenediamine (107-15-3)

2-thio-3,4,5,6-tetrahydropyrimidine (2055-46-1)

propylenediamine (78-90-0)

thiocarbamic acid