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.

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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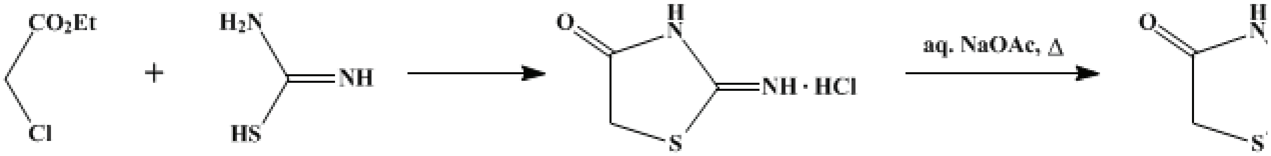
PSEUDOTHIOHYDANTOIN

[4-Thiazolidone, 2-imino-]



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1. Procedure

In a 1-l. flask surmounted by a reflux condenser, 76 g. (1 mole) of thiourea, m.p. 174–176°, is dissolved in 500 ml. of 95% ethanol by refluxing for 10–15 minutes. Then 125 g. (108 ml., 1.02 moles) of ethyl chloroacetate is added slowly (15–20 minutes) through the condenser while gentle refluxing is continued. After the mixture has been refluxed for 3 hours longer, it is allowed to cool to room temperature and the solid is filtered by suction on a 14-cm. Büchner funnel. The filtrate is used to rinse any solid adhering to the walls of the reaction flask onto the filter. The crude product is pressed down firmly and washed with 50 ml. of ethanol (Note 1).

The crude hydrochloride is dissolved in 1.2 l. of hot, freshly boiled water (Note 2) in a 2-l. beaker, a boiling solution of 121 g. of sodium acetate trihydrate in 150 ml. of water is added, and the mixture is heated to boiling (Note 3). The resulting clear solution is stored in the ice chest overnight. The crystalline pseudothiohydantoin is filtered and dried to constant weight at 60°. The product weighs 92–95 g. (79–82%). A reproducible decomposition point of 255–258° can be determined with the aid of a melting-point bar (Note 4).

2. Notes

1. The yield of the crude hydrochloride, dried to constant weight, is about 126 g.; the decomposition range is 210–255°.
2. The water is boiled before use to expel dissolved oxygen, the presence of which in the solution may cause the final product to have a yellow color.
3. Prolonged boiling should be avoided, as hydrolysis of the imino group occurs very easily. When sodium carbonate is substituted for sodium acetate the yield drops 10%.
4. The decomposition point as measured in the ordinary manner varies with the temperature of the bath at the time of the introduction of the sample. When the melting-point bath is heated so that the temperature rises by 2° per minute, a sample introduced just as the temperature reaches 200° develops an observable brown color at 206° and then darkens so rapidly that no liquid phase can be identified; if, under the same conditions, the sample is introduced when the bath temperature is 238° the decomposition begins immediately but a liquid phase can be recognized when the bath temperature is in the range 241–243°.

3. Discussion

Pseudothiohydantoin has been obtained from thiourea and ethyl chloroacetate[1] and from thiourea and chloroacetic[2,3] or dichloroacetic acids.[4]

References and Notes

1. Klason, *Ber.*, **10**, 1352 (1877).

2. Andreasch, *Monatsh.*, **8**, 424 (1887).
3. Schmidt, *Arch. Pharm.*, **258**, 229 (1920).
4. Dixon, *J. Chem. Soc.*, **63**, 816 (1893).

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

Pseudothiohydantoin

chloroacetic

dichloroacetic acids

ethanol (64-17-5)

sodium acetate (127-09-3)

sodium carbonate (497-19-8)

oxygen (7782-44-7)

Ethyl chloroacetate (105-39-5)

thiourea (62-56-6)

sodium acetate trihydrate (6131-90-4)

4-Thiazolidone, 2-imino-