



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.

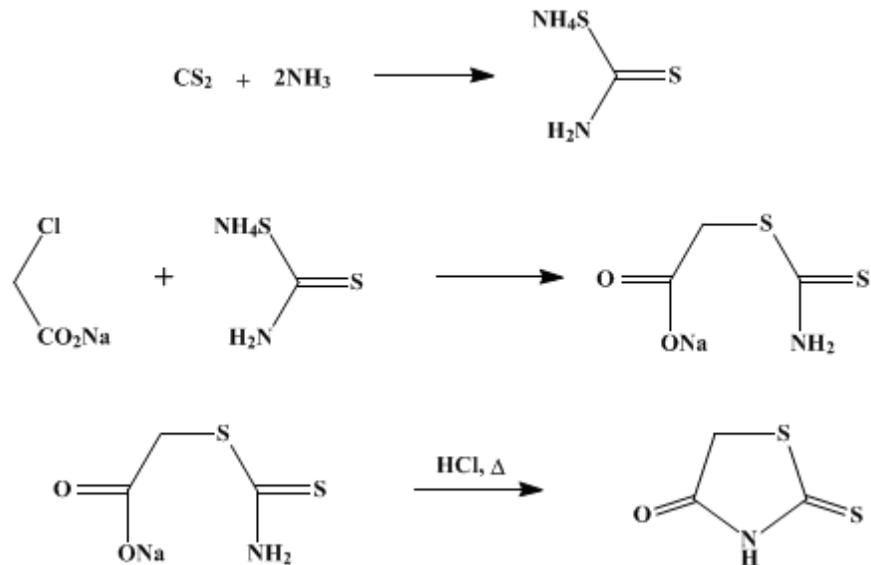
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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. 3, p.763 (1955); Vol. 27, p.73 (1947).

RHODANINE



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1. Procedure

A. *Ammonium dithiocarbamate*. Gaseous ammonia is passed into 250 ml. of 95% ethanol (Note 1) contained in a 1-l. Erlenmeyer flask immersed in an ice bath until the gain in weight is 39 g. (2.3 moles). To this solution, still cooled by the ice bath, is added a well-cooled mixture of 76 g. (60 ml., 1 mole) of carbon disulfide and 200 ml. of ether. The flask is stoppered loosely (Note 2) and allowed to remain in the ice bath for 2–3 hours and then at room temperature overnight (Note 3). The mixture is again cooled in an ice bath or refrigerator, and the crystals are collected by filtration (*hood*), sucked dry, and washed on the filter with two 50-ml. portions of ether. Air is drawn through the crystals for 5 minutes (Note 4) to effect removal of most of the ether. The product is used promptly without further treatment; the weight of the lemon-yellow solid varies between 80 and 90 g., depending principally on the completeness of the removal of the solvent.

B. *Rhodanine*. Just before the filtration of the ammonium dithiocarbamate, a solution of sodium chloroacetate is prepared by dissolving 71 g. (0.75 mole) of chloroacetic acid in 150 ml. of water contained in a 1-l. wide-mouthed round-bottomed flask and neutralizing the acid with 40 g. (0.38 mole) of anhydrous sodium carbonate (or an equivalent amount of the hydrate) while stirring the solution mechanically. This solution is cooled in an ice bath, and the ammonium dithiocarbamate from the preceding preparation is added during 5 minutes with continual stirring. As soon as the first portion of ammonium dithiocarbamate is added the solution becomes very dark in color. After all the dithiocarbamate has been added the ice bath is removed and stirring is discontinued. The solution is allowed to stand for 20–30 minutes longer, during which time the color changes to a clear yellow. In a 1-l. beaker 400 ml. of 6 *N* hydrochloric acid is heated to boiling, and the above solution (Note 5) is poured slowly with stirring into the hot acid. Heating is continued until the solution has attained a temperature of 90–95°, after which the solution is allowed to cool slowly to room temperature. The rhodanine separates as nearly colorless long blades which are collected by filtration, washed well with water, and dried. The product weighs 83–89 g. (83–89% based on the chloroacetic acid), and melts at 167–168°. Recrystallization from boiling glacial acetic acid (2 ml. per gram) raises the melting point to 168–168.5° (Note 6); the recovery, without reworking of the mother liquor, is 87%.

2. Notes

1. Absolute [ethanol](#) is satisfactory. [Methanol](#) may be used, but [ammonium dithiocarbamate](#) is much more soluble in [methanol](#) than in [ethanol](#) and the recovery will be lower.
2. The flask should be stoppered loosely to retard the escape of [ammonia](#). It is not wise to stopper it tightly, as some gas is evolved and pressure may develop. [Hydrogen sulfide](#) is present in the gases evolved.
3. The success of the preparation depends upon securing [ammonium dithiocarbamate](#) of good quality. Although much solid sometimes separates within 1–2 hours, it contains a large amount of the very unstable [ammonium trithiocarbamate](#).¹ After prolonged standing, the solid is nearly pure [ammonium dithiocarbamate](#).
4. [Ammonium dithiocarbamate](#) is relatively unstable, and no attempt should be made to dry the compound thoroughly before use.
5. If this solution is not clear and free from solid impurities it should be filtered before addition to the acid.
6. The melting points observed with the aid of a hot-stage microscope are slightly higher—170–170.5° for the unrecrystallized material, and 170.5–171° for the purified product. Although [rhodanine](#) usually is described in the literature as melting with decomposition, the checkers observed no evidence of decomposition during melting under the microscope and found the melting point unchanged when molten samples in ordinary melting-point tubes were cooled and remelted.

3. Discussion

[Rhodanine](#) has been prepared by the reaction of [chloroacetic acid](#) with [ammonium thiocyanate](#);² by the action of [ethyl chloroacetate](#) upon [ammonium dithiocarbamate](#) in the presence of alcohol and [hydrogen chloride](#);³ by saturating a solution of [thioglycolic acid](#) and [potassium thiocyanate](#) in absolute [ethanol](#) with [hydrogen chloride](#);⁴ by ring closure of [thiocarbamylthioglycolic acid](#) in various ways.^{5,6,7} The present method of preparation is adapted from that of Julian and Sturgis.⁷

References and Notes

1. Miller, *Contrib. Boyce Thompson Inst.*, **5**, 31 (1933).
2. Nencki, *J. prakt. Chem.*, (2) **16**, 2 (1877).
3. Miolati, *Ann.*, **262**, 85 (1891).
4. Fredyl, *Monatsh.*, **10**, 82 (1889).
5. Holmberg, *Ber.*, **39**, 3069 (1906); *J. prakt. Chem.*, (2) **79**, 261, 265 (1909).
6. Granacher, *Helv. Chim. Acta*, **5**, 610 (1920).
7. Julian and Sturgis, *J. Am. Chem. Soc.*, **57**, 1126 (1935).

Appendix

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

[ethanol](#) (64-17-5)

[hydrogen chloride](#),
[hydrochloric acid](#) (7647-01-0)

[acetic acid](#) (64-19-7)

[ammonia](#) (7664-41-7)

[methanol](#) (67-56-1)

ether (60-29-7)

ammonium thiocyanate (1762-95-4)

hydrogen sulfide (7783-06-4)

sodium carbonate (497-19-8)

chloroacetic acid (79-11-8)

sodium chloroacetate (3926-62-3)

carbon disulfide (75-15-0)

Ethyl chloroacetate (105-39-5)

potassium thiocyanate (333-20-0)

Rhodanine (141-84-4)

ammonium dithiocarbamate

ammonium trithiocarbamate

thioglycolic acid (68-11-1)

thiocarbonylthioglycolic acid