



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.

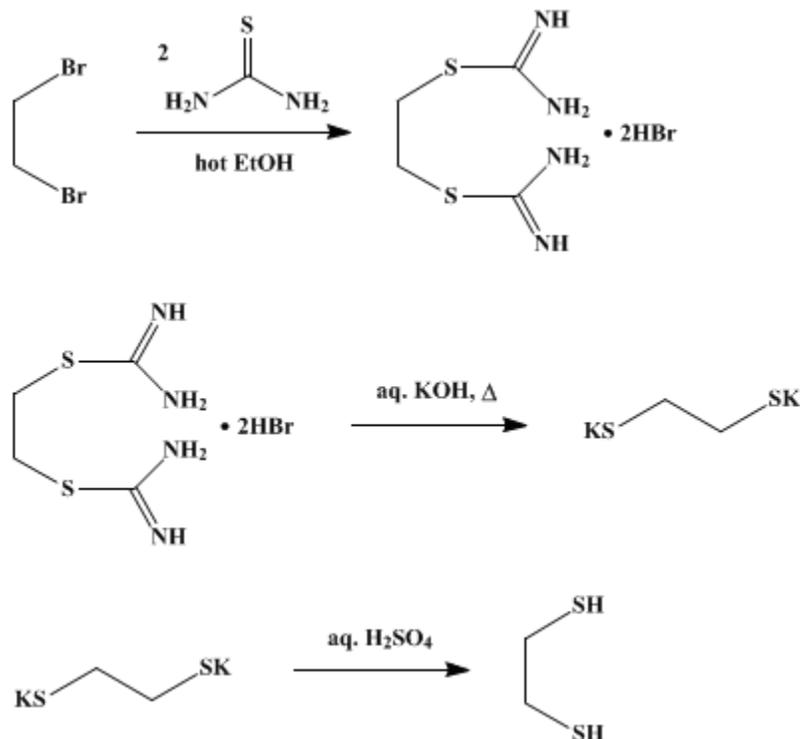
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.401 (1963); Vol. 30, p.35 (1950).

ETHANEDITHIOL

[1,2-Ethanedithiol]



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1. Procedure

Caution! This preparation requires the use of a good hood.

In a 5-l. round-bottomed flask fitted with an efficient reflux condenser are placed 2750 ml. of 95% ethanol and 609 g. (8.0 moles) of thiourea. The mixture is brought to the reflux temperature on a steam bath, and the refluxing solution is almost clear. The steam is turned off, and 751.5 g. (4.0 moles) of ethylene dibromide is added in one portion. Within 5 minutes a vigorous reaction (Note 1) ensues and ethylene diisothiuronium bromide separates from solution. The exothermic reaction is allowed to continue to completion without further application of heat. The isothiuronium salt is collected by filtration and dried. The salt melts with decomposition at 225–227° (Note 2) and weighs 1104 g. (81%).

Concentration of the filtrate to a volume of about 250 ml. and recrystallization from 95% ethanol of the crude isothiuronium salt which separates gives an additional 130 g. of material. The total yield of the salt is 1234 g. (90%).

A mixture of 255 g. (0.75 mole) of ethylene diisothiuronium bromide and 640 g. (9.7 moles) of 85% potassium hydroxide in 1360 ml. of water is placed in a 5-l. round-bottomed three-necked flask and boiled under reflux for 5 hours. Ammonia is evolved during the reflux period. The flask is then equipped with a separatory funnel, a gas-inlet tube, and a condenser set for steam distillation (Note 3). Nitrogen is admitted through the inlet tube, and a cooled solution of 415 ml. of sulfuric acid in 760 ml. of water is added dropwise (Note 4). The addition is continued until the reaction mixture becomes acid to Congo red paper, and then a 20% excess of acid is added. Approximately 725–850 ml. of the acid solution is required. The heat of neutralization is sufficient to distil part of the dithiol. At the end of the

addition of the acid, the passage of [nitrogen](#) is discontinued and steam is admitted through the inlet tube. The steam distillation is continued until about 3 l. of distillate is collected. The oil is separated from the water in the distillate, which is then extracted with two 500-ml. portions of [ether](#). The [ether](#) solution and the oil are dried separately over [calcium chloride](#). After evaporation of the solvent, the residue is added to the oil and the crude product is fractionated through a 10-in. Vigreux column under reduced pressure in an atmosphere of [nitrogen](#). The [ethanedithiol](#) boils at 63°/46 mm. (Note 5) and weighs 39–44 g. (55–62%); n_D^{20} 1.5589.

2. Notes

1. The reaction may be so vigorous that external cooling is required. A cloth wet with ice water and applied to the flask is sufficient to control the reaction.
2. The melting point seems to depend upon the rate of heating. Use of a Fisher-Johns melting-point apparatus gives a value of 240–242°.
3. At this point the reaction *must* be carried out in a good hood. The vapors of [ethanedithiol](#) may cause severe headache and nausea.
4. The alkaline solution should be at room temperature before the acidification is begun.
5. In one run the checkers observed a boiling point of 69°/46 mm.

3. Discussion

[Ethanedithiol](#) has been prepared from [ethylene dichloride](#)² or [ethylene dibromide](#)³ and alcoholic [potassium hydrosulfide](#); from [ethylene dibromide](#) and alcoholic [sodium hydrosulfide](#);⁴ from [ethylene dichloride](#)⁵ or [ethylene dibromide](#)⁶ and alcoholic [sodium hydrosulfide](#) under pressure; from [ethylene dibromide](#) and [thiourea](#);⁷ and by the catalytic hydrogenation with [cobalt trisulfide](#)⁸ or [nickel-on-kieselguhr](#)⁹ of the mixture resulting from the reaction of [ethylene](#) and [sulfur](#). The present method is a modification of one described by Mathias.⁷

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 4, 396](#)

References and Notes

1. Organic Chemicals Division, Monsanto Chemical Co., St. Louis, Missouri.
2. Löwig and Weidmann, *Ann.*, **36**, 321 (1840).
3. Fasbender, *Ber.*, **20**, 460 (1887).
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7. Mathias, *Bol. fac. filosof., ciênc. e letras, Univ. São Paulo*, **14**, Quim. No. 1, 75 (1942) [*C. A.*, **40**, 2792 (1946)].
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9. Lazier, Signaigo, and Werntz, U. S. pat. 2,402,643 [*C. A.*, **40**, 5764 (1946)].

Appendix

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

ethylene diisothiuronium bromide

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

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

ammonia (7664-41-7)

ether (60-29-7)

ethylene dichloride (107-06-2)

nitrogen (7727-37-9)

sulfur (7704-34-9)

potassium hydroxide (1310-58-3)

ethylene (9002-88-4)

ethylene dibromide (106-93-4)

potassium hydrosulfide (1310-61-8)

thiourea (62-56-6)

sodium hydrosulfide

1,2-ethanedithiol (540-63-6)

Ethanedithiol

cobalt trisulfide