



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 SULFIDE



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1. Procedure

Into a 500-ml., two-necked, round-bottomed flask equipped with a thermometer (Note 1) and leading to a condenser equipped with a distillation head and a receiver is placed 145 g. (1.5 mole) of potassium thiocyanate (Note 2). The system is evacuated to about 1 mm., and the flask is heated with a free flame until the temperature of the molten salt is in the 165–175° range (Note 3). After the flask has been heated for 15 minutes, it is cooled to room temperature and 88 g. (1.0 mole) of ethylene carbonate (Note 4) is added. The apparatus is reconnected and the receiver protected with a calcium chloride tube.

The reaction flask is slowly heated by means of a sand bath, and the receiver is cooled in a Dry Ice-acetone bath. When the temperature in the fused potassium thiocyanate layer reaches 95°, reaction occurs. Ethylene sulfide distills and is collected in the receiver. Heating is continued for about 3 hours at 95–99° (Note 6). The distillate amounts to 41–45 g. (68–75%) (Note 7) and is sufficiently pure to be used directly (Note 8).

2. Notes

1. The thermometer may be inserted through a neoprene stopper in one neck or into a suitably designed thermometer well.
2. J. T. Baker's analytical grade was used.
3. The purpose of this operation is to ensure dryness, as potassium thiocyanate is hygroscopic. The presence of even small amounts of water is detrimental to the yield. The initially colorless salt melts to a blue liquid. On cooling, this solidifies to a colorless solid. It has been reported that this procedure is more easily reproduced when the potassium thiocyanate is heated to *ca.* 100–110° at 0.1 mm. so that the salt does not melt, and a larger surface is available for reaction (Nelson N. Schwartz, private communication).
4. Ethylene carbonate obtained from the Eastman Kodak Company or the Jefferson Chemical Company was vacuum distilled and the fraction, b.p. 125°/10 mm., was used.
5. It has been reported that an oil bath may be used to provide greater uniformity of heating (Nelson N. Schwartz, private communication).
6. Differences in the rate of heating and time of heating cause small changes in the yield of ethylene sulfide obtained. If the time of heating is reduced and the rate of heating increased, the yield drops somewhat. For many purposes the saving in time offsets the higher yield obtained under optimum conditions. The submitters have obtained yields in the 81–87% range.
7. This product can be stored at room temperature for several weeks without polymerization. On distillation, pure ethylene sulfide, b.p. 54.0–54.5°, n_D^{20} 1.4960, is obtained.
8. For example, this product is suitable for reaction with amines.²

3. Discussion

Ethylene sulfide has been prepared by the reaction of ethylene oxide with aqueous potassium thiocyanate;^{2,3} by the reaction of 2-chloroethyl mercaptan with aqueous sodium bicarbonate;⁴ by the reactions of 2-chloroethylthiocyanate⁵ and 1,2-dithiocanoethane⁶ with alcoholic sodium sulfide; and by the thermal decomposition of monothiolethylene carbonate.⁷

4. Merits of Preparation

The advantage of the present procedure is the easy availability at low expense of the starting material, ethylene carbonate.⁸ Its advantages over the other methods are high yields and degree of purity of the product, combined with greater simplicity of procedure.

References and Notes

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

monothioethylene carbonate

sodium bicarbonate (144-55-8)

Ethylene oxide (75-21-8)

sodium sulfide (1313-82-2)

potassium thiocyanate (333-20-0)

Ethylene sulfide (420-12-2)

ethylene carbonate (96-49-1)

2-chloroethyl mercaptan

2-chloroethylthiocyanate (928-57-4)

1,2-dithiocyanoethane