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.

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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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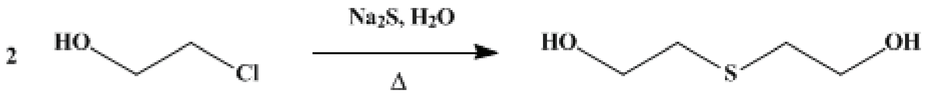
β-THIODIGLYCOL

[Ethanol, 2,2'-thiodi-]



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1. Procedure

In a 3-l. round-bottomed flask equipped with a mechanical stirrer are placed 1.5 kg. (3.7 moles) of 20 per cent ethylene chlorohydrin solution (Note 1) and 750 g. of water. The flask is set in an empty pan of suitable size to serve as a bath in case cooling becomes necessary. With the stirrer in operation, 493 g. (2.05 moles) of crystalline sodium sulfide containing nine molecules of water of crystallization is added to the chlorohydrin solution at a rate which will maintain the temperature at 30–35°. This will require from forty to sixty minutes. After all the sodium sulfide has been added the solution is stirred for thirty minutes.

The stirrer is removed, and the flask is fitted with a reflux condenser and a thermometer which dips into the liquid. The flask is then heated on a steam bath until the temperature of the liquid is 90°, and for a period of forty-five minutes the temperature is held at 90–95°. The solution is then cooled to 25° and neutralized to turmeric paper by adding concentrated hydrochloric acid drop by drop (Note 2). After filtering, the solution is returned to the flask for concentration at reduced pressure.

The flask is equipped with a short column attached to a condenser set for distillation. A capillary is provided to prevent bumping. The water is then distilled at a pressure of 30–40 mm. by heating the flask in a water bath which is raised to the boiling point as rapidly as is consistent with smooth distillation. The residue in the flask, which consists of sodium chloride and thiodiglycol, is extracted twice with 500-cc. portions of hot absolute alcohol in order to dissolve the sulfide. After the second extraction, the salt is transferred to a Büchner funnel and is washed with a little hot alcohol (Note 3).

The extract and washings are returned to the distilling flask, and the alcohol is removed under reduced pressure. When practically all the alcohol has distilled, the temperature of the bath is raised to 100° and the residue is heated for three hours under 30-mm. pressure (Note 4).

The crude product, which is colorless or very pale yellow, weighs 200–215 g. It boils at 164–166°/20 mm. and may be purified by vacuum distillation (Note 5). The yield of pure material is 180–195 g. (79–86 per cent of the theoretical amount).

2. Notes

1. Aqueous solutions of ethylene chlorohydrin of 18–40 per cent are suitable for the preparation of thiodiglycol; a 20 per cent solution is convenient because the reaction proceeds very smoothly and is easy to control.
If the chlorohydrin is available in the form of a solution weaker than 20 per cent, it may be concentrated by distillation. Chlorohydrin and water form a constant-boiling-point mixture of 42.5 per cent chlorohydrin which boils at 95.8°/735 mm.
2. At the end of the reaction the liquid is alkaline and must be neutralized; otherwise considerable decomposition occurs during distillation. Care must be taken not to pass the neutral point, as a small amount of mustard gas may be formed. Furthermore, if much acid is present, the heat necessary for vacuum distillation causes resinification and the yield of distilled material falls to about 50 per cent. The use of litmus paper for the neutralization is not satisfactory.
3. If 95 per cent alcohol is used for this extraction, some salt is dissolved with the thiodiglycol. This salt

may be filtered easily after the alcohol has been removed from the product.
4. The time of drying is dependent upon the pressure used. At 20 mm. the water and alcohol are removed in one hour. If the water has not been completely removed before the alcohol extraction, there may be a small amount of salt left in the material after the alcohol is removed. This may be removed by decanting the product or by pouring it through a glass-wool filter.
5. If chemicals of good quality are used in the preparation the crude product is practically water-white and is sufficiently pure for many purposes. A completely pure product can be obtained by vacuum distillation.

3. Discussion

The method described in the procedure is a modification of the one originally described by Meyer.[1] Irvine[2] showed that this general method could be adapted to works-scale production. β-Thiodiglycol can also be prepared from ethylene oxide and hydrogen sulfide, a process that works well only if some of the product is used as a solvent for the reactants.[3]

References and Notes

1. Meyer, Ber. **19**, 3260 (1886); Clarke, J. Chem. Soc. **101**, 1583 (1912); Gomberg, J. Am. Chem. Soc. **41**, 1414 (1919).
2. Irvine, British War Report.
3. Chichibabin, Fr. pat. 769,216 [C. A. **29**, 481 (1935)]; Chichibabin and Bestuzhev, Compt. rend. **200**, 242 (1935); Nenitzescu and Scarlatescu, Ber. **68**, 587 (1935); Othmer and Kern, Ind. Eng. Chem. **32**, 160 (1940).

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

β-Thiodiglycol

alcohol (64-17-5)

hydrochloric acid (7647-01-0)

sodium chloride (7647-14-5)

hydrogen sulfide (7783-06-4)

Ethylene oxide (75-21-8)

sodium sulfide (1313-82-2)

ethylene chlorohydrin (107-07-3)

thiodiglycol

Ethanol, 2,2'-thiodi- (111-48-8)