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.

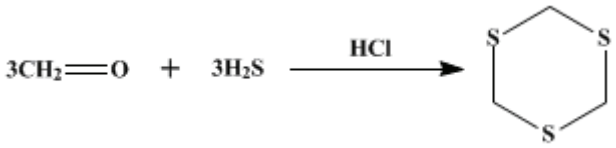
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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.

DOI:10.15227/orgsyn.016.0081

Organic Syntheses, Coll. Vol. 2, p.610 (1943); Vol. 16, p.81 (1936).

sym.-TRITHIANE



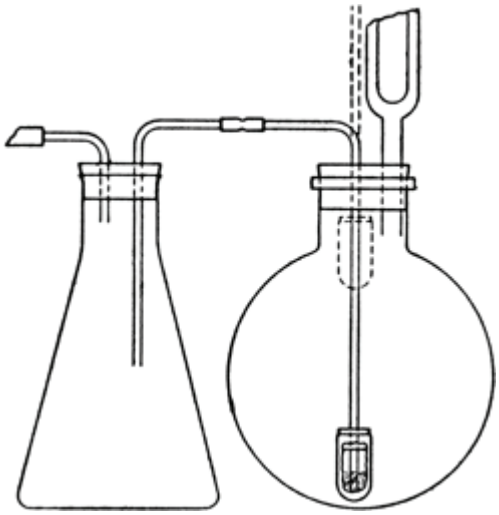
Submitted by R. W. Bost and E. W. Constable.
Checked by Reynold C. Fuson and C. F. Woodward.

1. Procedure

A mixture of 326 g. (3.9 moles) of a 36 per cent formaldehyde solution (Note 1) and 700 cc. of concentrated hydrochloric acid (sp. gr. 1.18) is placed in a tall glass cylinder (Note 2), and hydrogen sulfide is passed through the solution until no more precipitate is formed. In order to facilitate the process, the accumulated mass of crystals is removed from time to time by filtration. The time required for completion of the reaction varies from twelve to twenty-four hours. A crude yield of 176 g. (98 per cent of the theoretical amount) of fine, nearly colorless needles melting at 210–213° is obtained.

The product is purified by the inverted filtration method. The apparatus used is shown in Fig. 20. A 2-l. round-bottomed flask is equipped with a reflux condenser and a bent glass tube, 8–10 mm. in diameter (Note 3). To the lower end of this tube is attached, by means of a cork, a 25-mm. tip prepared from a paper Soxhlet thimble and packed with glass wool. A 2-l. conical flask serves as a receiver for the hot filtrate.

Fig. 20



The crude product is placed in the round-bottomed flask, 1 l. of benzene is added, and heat is applied until the solvent boils vigorously. After a few minutes the source of heat is withdrawn and the mixture is allowed to become quiet. The filtering thimble, which up to this point is kept at the top of the flask (see Fig. 20), is now lowered to its normal position and the conical flask is attached. Gentle suction is applied, and the liquid is drawn over into the conical flask. The hot solution is removed, allowed to cool, and filtered. In the meantime, the extraction process is repeated with a second 1-l. portion of benzene. The two portions of benzene are used alternately over and over in the manner described until all the crude product has been recrystallized. This requires about ten separate extractions, using each 1-l. portion of benzene five times.

The yield of pure product, melting at 214–215°, is 165–169 g. (92–94 per cent of the theoretical

amount).

2. Notes

1. The formaldehyde content of the solution is determined by analysis, for which the iodimetric method of Borgstrom and Horsch[1] is recommended. The yield is calculated upon the basis of the amount of formaldehyde actually present, as shown by analysis. Since commercial solutions of formaldehyde contain methyl alcohol, the formaldehyde present cannot be estimated accurately by reference to specific-gravity tables—compare Org. Syn. Coll. Vol. I, **1941**, 378, Note 1.
2. A tall cylindrical vessel ensures good contact between the solution and the gas bubbling through it. Hydrogen sulfide from a commercial cylinder was used.
3. Successful use of the inverted filtration method requires attention to these details: (*a*) use of a sufficiently wide transfer tube; (*b*) minimum exposure of tubing between the flasks; (*c*) rapid transfer of the hot solution; (*d*) avoidance of too strong an application of suction.
The inverted filtration device is convenient for simple recrystallizations as well as repeated extractions. It is of particular advantage for the manipulation of volatile, inflammable solvents and of lachrymatory solutions.

3. Discussion

sym.-Trithiane has been prepared by treating carbon bisulfide,[2] ethyl isothiocyanate,[3] or potassium thiocyanate[3] with zinc and hydrochloric acid; by heating methylene iodide with alcoholic sodium hydrosulfide;[4] and by treating aqueous formaldehyde with hydrogen sulfide and concentrated hydrochloric acid.[5]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 443
- Org. Syn. Coll. Vol. 2, 590
- Org. Syn. Coll. Vol. 4, 560

References and Notes

1. Borgstrom and Horsch, J. Am. Chem. Soc. **45**, 1493 (1923).
2. Girard, Compt. rend. **43**, 396 (1856); Ann. **100**, 306 (1856).
3. Hofmann, Ber. **1**, 176, 179 (1868).
4. Husemann, Ann. **126**, 293 (1863).
5. Hofmann, ibid. **145**, 360 (1868); Baumann, Ber. **23**, 67 (1890).

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

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

methyl alcohol (67-56-1)

formaldehyde (50-00-0)

hydrogen sulfide (7783-06-4)

zinc (7440-66-6)

potassium thiocyanate (333-20-0)

Methylene iodide (75-11-6)

carbon bisulfide

sodium hydrosulfide

ethyl isothiocyanate (542-85-8)

sym.-TRITHIANE (291-21-4)