Organic Syntheses

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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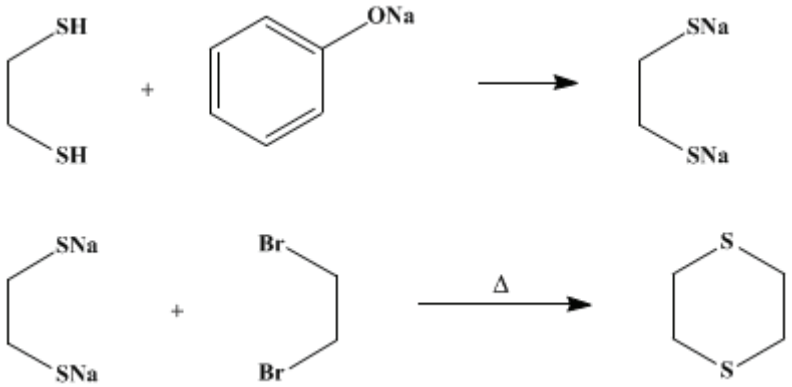
p-DITHIANE



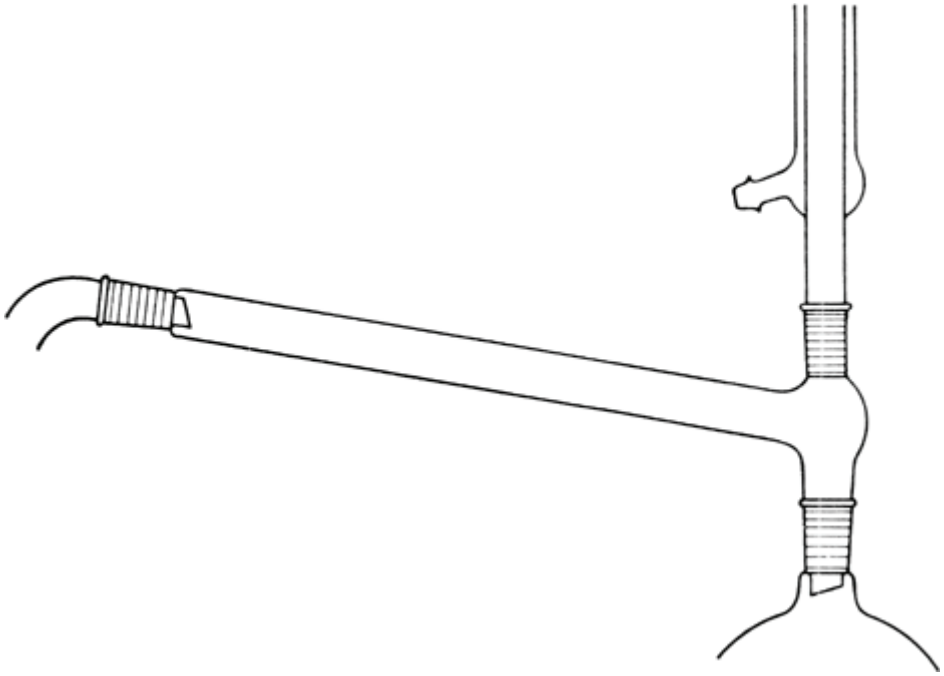
Submitted by Richard G. Gillis and A. B. Lacey[1].
Checked by B. C. McKusick and R. J. Harder.

1. Procedure

In a 3-l. round-bottomed flask fitted with a mechanical stirrer and a reflux condenser is placed 2.0 l. of anhydrous ethanol. To this is added 11.5 g. (0.5 g. atom) of sodium cut into small pieces. When the sodium is completely dissolved, 23.6 g. (21.0 ml., 0.25 mole) of 1,2-ethanedithiol (p. 401) is added, followed by 47.0 g. (21.7 ml., 0.25 mole) of ethylene dibromide. The mixture is stirred and heated under reflux for 4 hours, cooled, and filtered to remove some sodium bromide mixed with polyethylene sulfide. The solid is washed with 100 ml. of ethanol, and the combined filtrates are distilled with stirring. When bumping becomes troublesome, as it generally does when 1.3–1.5 l. of distillate has been collected, the hot reaction mixture is filtered to remove sodium bromide, and the sodium bromide is washed with 100 ml. of hot ethanol.

The combined filtrates are returned to the reaction vessel, and distillation with stirring is continued until virtually all the ethanol has been removed. The distillation is stopped when crystals of *p*-dithiane appear in the condenser or when dilution of the distillate with water causes a milky appearance or the formation of a small quantity of crystals. One liter of water is added to the residue, and the stirred mixture is distilled, using the apparatus of Fig. 8 (Note 1), until no more *p*-dithiane solidifies in the condenser.

Fig. 8. Apparatus for steam distillation of a solid.



The dithiane is filtered and dried over phosphorus pentoxide or sodium hydroxide in a desiccator at atmospheric pressure. It melts at 112–113° and weighs 16.5–18.1 g. (55–60%).

2. Notes

1. The apparatus illustrated is convenient for the steam distillation of compounds which solidify in the condenser. By having the water condenser vertical, it can easily be cleared with a glass rod. No solidification occurs in the side arm, which behaves as a short air condenser. The adapter shown need not be specially constructed but may be assembled from commercially available components; the dimensions and joint sizes are not critical.

3. Discussion

The procedure described is essentially that of Victor Meyer.[2] *p*-Dithiane has also been obtained from the pyrolysis of the polymer formed by the reaction of ethylene dibromide and potassium sulfide, either alone[3,4,5] or in phenol,[6] and by the treatment of 2-mercaptoethanol with a cation exchange resin.[7]

References and Notes

1. Australian Defence Scientific Service (Defence Standards Laboratories, Department of Supply, Melbourne, Australia).
2. Meyer, *Ber.*, **19**, 3259 (1886).
3. Crafts, *Ann.*, **124**, 110 (1862).
4. Husemann, *Ann.*, **126**, 281 (1863).
5. Masson, *J. Chem. Soc.*, **49**, 234 (1886).
6. Mansfeld, *Ber.*, **19**, 697 (1886); Fuson, Lipscomb, McKusick, and Reed, *J. Org. Chem.*, **11**, 513 (1946).
7. Swistak, *Compl. rend.*, **240**, 1544 (1955).

Appendix

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

polyethylene sulfide

ethanol (64-17-5)

sodium hydroxide (1310-73-2)

phenol (108-95-2)

sodium bromide (7647-15-6)

sodium (13966-32-0)

ethylene dibromide (106-93-4)

potassium sulfide (1312-73-8)

2-mercaptoethanol (60-24-2)

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

dithiane (505-20-4)

phosphorus pentoxide (1314-56-3)

p-Dithiane (505-29-3)