



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](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.

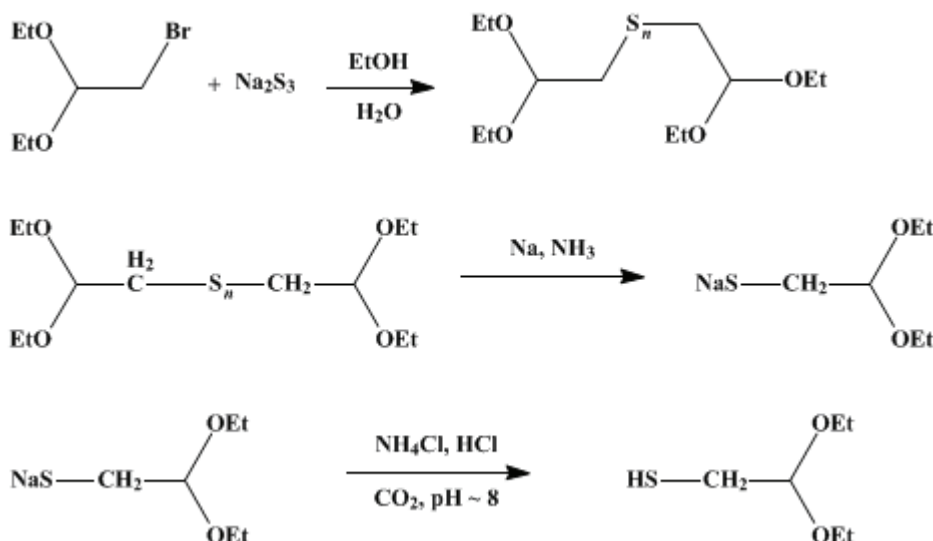
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

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## DIETHYL MERCAPTOACETAL

[Acetaldehyde, mercapto-, diethyl acetal]



Submitted by William E. Parham and Hans Wynberg<sup>1</sup>.

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### 1. Procedure

A. *1,1,1',1'-Tetraethoxyethyl polysulfide* (Note 1). In a 5-l. round-bottomed flask, equipped with a stirrer, a reflux condenser, and an addition funnel, 540 g. (2.25 moles) of sodium sulfide enneahydrate (Note 2) is dissolved in 2.7 l. of boiling 95% ethanol. Sulfur (144 g., 4.5 g. atoms) is added, and the solution is heated under reflux until it has assumed a deep-red color (10 minutes). The source of heat is removed, and 588 g. (3 moles) of diethyl bromoacetal (Note 3) is added over a period of about 30 minutes at such a rate that the solution boils gently. The mixture is heated under reflux for an additional 4 hours. During the last hour of heating, ethanol is allowed to distil from the reaction flask, and after the first 700 ml. of distillate is collected sodium bicarbonate (135 g.) (Note 4) is added to the reaction mixture. A total of 2.0–2.5 l. of ethanol is collected. Water (1.5 l.) is added, and the upper layer is separated. The aqueous layer is extracted with two 250-ml. portions of ether, and the combined organic layers are washed successively with two 100-ml. portions of 10% sodium hydroxide solution, three 100-ml. portions of water, and two 250-ml. portions of saturated sodium chloride solution, and are dried over potassium carbonate. The ether is removed by distillation, and the residue is brought to constant weight by heating for about 1 hour on the steam bath at 10–15 mm. pressure. The orange liquid obtained in this way (Note 5) weighs 450–500 g. and has  $n_D^{25}$  1.515–1.517.

B. *Diethyl mercaptoacetal*. A 12-l. three-necked flask, equipped with an efficient Hershberg stirrer, a Dry Ice condenser, and a stopper, is placed in an enameled container (Note 6). The flask is charged with 500 g. (1.38 moles, calculated as tetrasulfide) of 1,1,1',1'-tetraethoxyethyl polysulfide and 500 ml. of anhydrous ether. The condenser is filled with acetone and Dry Ice, and the contents of the flask are cooled by means of acetone and Dry Ice kept at  $-35^\circ$  to  $-45^\circ$ . Liquid ammonia (Note 7) is introduced into the stirred solution until 4.5–5.0 l. has been added (Note 8). The solution is stirred for several minutes to ensure homogeneity, and 200 g. (8.7 g. atoms) of sodium is added in 2- to 5-g. lumps to the mixture over a period of 30–45 minutes. The last 2–10 g. of sodium causes the solution to turn deep blue. The mixture is stirred for 30 additional minutes, and ammonium chloride (about 200 g.) is cautiously added with stirring until the blue color is discharged. The cooling bath is removed and replaced by a bath of hot water into which steam may be introduced. The mixture is stirred while the ammonia is removed by distillation or evaporation (the distillation should be continued until the residue

can no longer be stirred or is difficult to stir). The soft, semisolid mass containing small amounts of ammonia is cooled in ice, and 1 l. of ice-cold water is added with stirring. When most of the solid has dissolved, ice-cold hydrochloric acid is added cautiously, with frequent checks of the pH, until a pH of 8.0–8.5 is reached. The pH is then adjusted to 7.8–8.0 (preferably by a pH meter) by passing carbon dioxide into the cold solution (Note 9). The oil is separated from the aqueous layer, which is extracted with two 300-ml. portions of ether. The combined organic layers are washed successively with 100 ml. of water and two 100-ml. portions of saturated sodium chloride, and are dried over magnesium sulfate. The ether is removed by distillation, and the residue is distilled from a 500-ml. flask using a small Vigreux column or a Claisen head. The product (Note 10) weighs 320–372 g. (77–90% yield, based on polysulfide; 71–83% yield, based on bromoacetal), boils at 62–64°/12 mm., and has  $n_D^{25}$  1.4391–1.4400. The residue, 23–27 g.,  $n_D^{25}$  1.4702–1.4730, consists mainly of 1,1,1',1'-tetraethoxyethyl sulfide.

## 2. Notes

1. These directions have been used equally successfully with twice, one-third, and one-fifth the amounts specified. The reaction of chloro- or bromoacetal with sodium disulfide results in the formation of a considerable quantity of the corresponding monosulfide which is not subsequently reduced to mercaptan. Polysulfides are, however, easily reduced to mercaptans. 1,1,1',1'-Tetramethoxyethyl polysulfide has been prepared from commercially available dimethyl chloroacetal in a similar fashion. A 10-hour heating period and the addition of 5 g. of potassium iodide per 100 g. of acetal are recommended in the latter preparation.
2. The sodium sulfide ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ) should be crystalline and finely divided.
3. The procedure used for the preparation of diethyl bromoacetal (b.p. 78–79°/24 mm.,  $n_D^{20}$  1.4418) is that of Bedoukian.<sup>2</sup>
4. Di- and polysulfides are cleaved by strong alkali. The bicarbonate is added as a buffer.
5. Analysis of this material showed it to have the average composition calculated for a tetrasulfide; the yield of product, calculated as tetrasulfide, is 83–92%.
6. In order to use as little coolant as possible the flask should fit the container snugly.
7. All normal precautions should be observed during the handling of these large quantities of ammonia and sodium. A well-ventilated hood, a gas mask, and a bucket of sand were available to the submitters. The only hazard in this reaction may arise if too much ammonia escapes and the sodium does not react properly as a consequence. The addition of 0.5–1.0 l. of ammonia to the reaction mixture after the sodium has been added is a useful precaution.
8. The submitters measured the liquid ammonia in a 1-l. graduated cylinder.
9. Complete neutralization of the salt of mercaptoacetal with mineral acid may result in hydrolysis of the acetal.
10. Mercaptoacetal is sensitive to acid and oxygen. The product should be stored in a dry, alkali-washed bottle under nitrogen in a refrigerator.

## 3. Discussion

Diethyl mercaptoacetal has been prepared by treating diethyl bromoacetal with potassium hydrosulfide;<sup>3</sup> by the reduction of 1,1,1',1'-tetraethoxyethyl disulfide<sup>3</sup> with lithium aluminum hydride; by reduction of 1,1-diethoxyethyl benzyl sulfide,<sup>3,4</sup> 1,1,1',1'-tetraethoxyethyl disulfide,<sup>3</sup> and 1,1,1',1'-tetraethoxyethyl polysulfide<sup>3</sup> with sodium and liquid ammonia. The method described is adapted from the last-named preparation. Dimethyl mercaptoacetal has been prepared by the same methods.<sup>3</sup>

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## References and Notes

1. University of Minnesota, Minneapolis, Minnesota.
  2. Bedoukian, *J. Am. Chem. Soc.*, **66**, 651 (1944).
  3. Parham, Wynberg, and Ramp, *J. Am. Chem. Soc.*, **75**, 2065 (1953).
  4. Hesse and Jörder, *Ber.*, **85**, 924 (1952).
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**Appendix**  
**Chemical Abstracts Nomenclature (Collective Index Number);**  
**(Registry Number)**

1,1,1',1'-Tetraethoxyethyl polysulfide

sodium sulfide enneahydrate

diethyl bromoacetal

1,1,1',1'-Tetramethoxyethyl polysulfide

dimethyl chloroacetal

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

[potassium carbonate \(584-08-7\)](#)

[hydrochloric acid \(7647-01-0\)](#)

[ammonia \(7664-41-7\)](#)

[ether \(60-29-7\)](#)

[ammonium chloride \(12125-02-9\)](#)

[sodium hydroxide \(1310-73-2\)](#)

[sodium bicarbonate \(144-55-8\)](#)

[sodium chloride \(7647-14-5\)](#)

[oxygen \(7782-44-7\)](#)

[potassium iodide \(7681-11-0\)](#)

[nitrogen \(7727-37-9\)](#)

[sulfur \(7704-34-9\)](#)

[carbon dioxide \(124-38-9\)](#)

[acetone \(67-64-1\)](#)

[sodium \(13966-32-0\)](#)

[sodium sulfide \(1313-82-2\)](#)

[sodium disulfide](#)

[potassium hydrosulfide \(1310-61-8\)](#)

Diethyl mercaptoacetal (53608-94-9)

Acetaldehyde, mercapto-, diethyl acetal

magnesium sulfate (7487-88-9)

lithium aluminum hydride (16853-85-3)

1,1,1',1'-tetraethoxyethyl sulfide

1,1,1',1'-tetraethoxyethyl disulfide

1,1-diethoxyethyl benzyl sulfide

Dimethyl mercaptoacetal