



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.

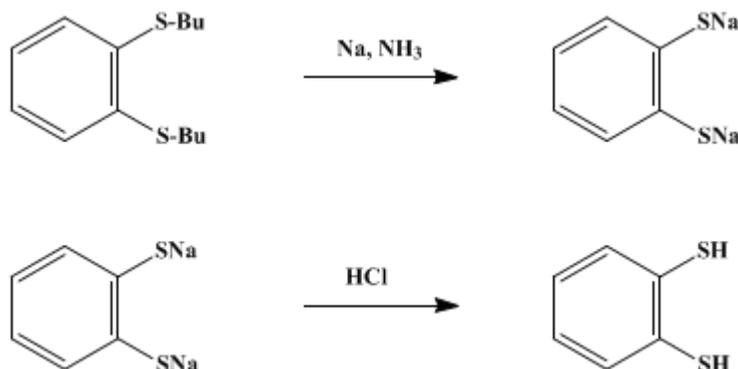
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.419 (1973); Vol. 42, p.54 (1962).

1,2-DIMERCAPTOBENZENE

[*o*-Benzenedithiol]



Submitted by Aldo Ferretti¹

Checked by William E. Parham, Wayland E. Noland, and James R. Throckmorton.

1. Procedure

A 200-ml. two-necked flask is fitted with an efficient Dry Ice-isopropyl alcohol condenser connected to a soda-lime tube, a magnetic stirrer, and a gas inlet tube. Isopropyl alcohol and Dry Ice are added to the condenser while the flask and condenser are flushed with dry nitrogen. The flask is immersed in a Dry Ice-isopropyl alcohol bath, and a vigorous stream of dry ammonia is introduced into the system. When about 80 ml. of liquid ammonia is condensed, the gas inlet tube is replaced with a ground-glass stopper. The cooling bath is removed, stirring is started, and 5.1 g. (0.020 mole) of 1,2-bis(*n*-butylthio) benzene (Note 1) is quickly introduced (Note 2).

Sodium is now added in small pieces; the solution is allowed to decolorize before each successive piece is added. A water bath is placed occasionally under the flask to ensure continuous ebullition of ammonia. The blue color will persist for at least 15 minutes after 1.6 g. (0.070 g. atom) of sodium has been added. The excess sodium is then destroyed by cautious addition of 6 g. (0.11 mole) of ammonium chloride, with stirring. Cooling and stirring are stopped, and a slow stream of argon is passed in for a period of about 12–15 hours. The white solid residue is transferred to a beaker, and 300 g. of ice water is added, together with sufficient pellets of sodium hydroxide to make the solution alkaline. The alkaline solution is then extracted twice with ether and the ether extracts discarded. The solution is then acidified to Congo red with cold 1:1 (by volume) hydrochloric acid and extracted three times with ether. The ether extracts are combined, washed with water, and dried over anhydrous sodium sulfate. The ether is evaporated and the 1,2-dimercaptobenzene is distilled under reduced pressure under an atmosphere of nitrogen, giving a product which boils at 95°/5 mm. and usually solidifies after distillation (Note 3). The yield is 1.6–2.4 g. (56–85%) (Note 4).

2. Notes

1. The preparation of 1,2-bis(*n*-butylthio) benzene is described elsewhere in this volume.²
2. 1,2-Bis(*n*-butylthio)benzene is only slightly soluble in liquid ammonia. Stirring must be very efficient during the addition and subsequently during the reaction to prevent the drops of 1,2-bis(*n*-butylthio) benzene from collecting as a solid mass. If this happens, the time necessary for completion of the reaction, and the quantity of sodium necessary for dealkylation, must be increased. The checkers found that the 1,2-bis(*n*-butylthio)benzene invariably collected as several solid masses and that it was always necessary to add additional sodium, about 0.9 g.
3. The reported melting point is 27–28°.³
4. The reported yield is 2.0 g. (70%) of an oil, b.p. 102°/6.5 mm.³ A similar procedure has been used by

the submitter to prepare 1,4-dimercaptobenzene, 2,5-dimercaptotoluene, 1,3,5-trimercaptobenzene, 2,4,6-trimercaptomesitylene, and 4,4'-dimercaptobiphenyl.³

3. Discussion

The present procedure is that of Adams and Ferretti.³ Another method is the reduction of 1,2-benzenedisulfonyl chloride with zinc powder.⁴ In a third method⁵ a 2-aminomercaptobenzene is diazotized and converted to an intermediate xanthate and then to the corresponding mercaptosulfonic acid. The latter can be converted to the dimercaptan either by: (1) oxidation to a disulfonic acid, conversion to the disulfonyl chloride, and reduction to the dimercaptan, or (2) mild oxidation to the corresponding disulfide, conversion to the sulfonyl chloride disulfide, and reduction to the dimercaptan.

4. Merits of the Preparation

The present procedure, when combined with the accompanying preparation of aryl sulfides (p. 107), provides a convenient and general method for preparing aryl mercaptans from aromatic halides.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 107](#)

References and Notes

1. Via Martiri Triestini, 12, Milan, Italy.
2. [R. Adams, W. Reifschneider, and A. Ferretti, this volume, p. 107.](#)
3. R. Adams and A. Ferretti, *J. Am. Chem. Soc.*, **81**, 4939 (1959).
4. W. R. H. Hurlley and S. Smies, *J. Chem. Soc.*, 1821 (1926).
5. P. C. Guha and M. N. Chakladar, *J. Indian Chem. Soc.*, **2**, 318 (1925).

Appendix

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

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

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

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

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

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

[sodium sulfate](#) (7757-82-6)

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

[zinc powder](#) (7440-66-6)

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

isopropyl alcohol (67-63-0)

argon (7440-37-1)

1,4-dimercaptobenzene (25212-74-2)

2,5-dimercaptotoluene

1,3,5-trimercaptobenzene

2,4,6-trimercaptomesitylene

1,2-benzenedisulfonyl chloride (6461-76-3)

2-aminomercaptobenzene

1,2-Dimercaptobenzene,
o-Benzenedithiol (17534-15-5)

1,2-BIS(n-BUTYLTHIO)BENZENE,
1,2-bis(n-butylthio) benzene (53663-38-0)

4,4'-dimercaptobiphenyl