



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.

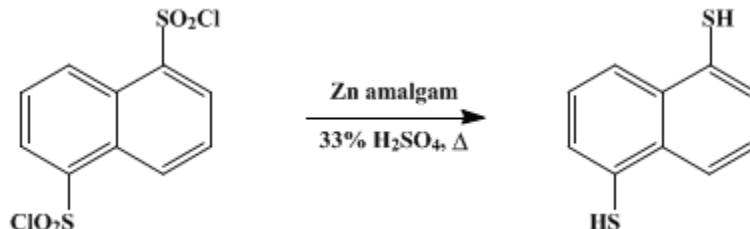
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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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1,5-NAPHTHALENEDITHIOL



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1. Procedure

A 2-l. round-bottomed flask having standard-taper, ground-glass fittings is equipped with a bulb condenser (Note 1) and an efficient Hershberg stirrer. To this are added with stirring 600 g. (2.0 moles) of 33% sulfuric acid, 20 g. (0.06 mole) of finely divided 1,5-naphthalenedisulfonyl chloride (p. 693), and 100 g. (1.5 g. atoms) of zinc dust amalgam (Note 2) at room temperature (Note 3). The zinc dust amalgam is added directly after the disulfonyl chloride in the course of 2–5 minutes. The mixture is heated to reflux, held there for about 6 hours, and allowed to cool overnight without agitation (Note 4).

The product is filtered, and the precipitate is extracted with a total of 1 l. of warm ether (Note 5). The combined ether extracts are evaporated to a volume of 50 ml., cooled, and filtered. The filtrate is further evaporated to a volume of about 10 ml., cooled, and again filtered. The precipitates melt at 119–121° and total 7.1–9.1 g. This represents a yield of 60–77%.

The 1,5-naphthalenedithiol can be further purified to a melting point of 120–121° by sublimation under high vacuum in a molecular still, followed by reprecipitation of the water-soluble disodium salt of the sublimate from excess hydrochloric acid. The pure compound obtained from 9.1 g. of product weighs 8.6 g. (73%).

2. Notes

1. The product collects in the condenser, and it may be necessary to clear the condenser with a glass rod.
2. A good grade of zinc and mercury(II) chloride should be used. The zinc dust amalgam is prepared by dissolving 20 g. of mercury(II) chloride in a solution of 10 ml. of concentrated hydrochloric acid in 300 ml. of distilled water, and adding quickly, with stirring, 100 g. of zinc dust (Schaar chemicals, 95% purity). After 10–15 minutes of stirring and crushing lumps, the mixture is filtered through a Büchner funnel, and the zinc dust amalgam is carefully washed with a total of 500 ml. of distilled water containing a trace of hydrochloric acid. The water is then removed by ethanol, the ethanol by ether, and most of the ether by air. It is advisable to remove the zinc dust amalgam from the Büchner funnel and add it to the reduction mixture before all the ether is removed to assure minimum contact with the air. An occasional batch of zinc dust failed to effect the desired reduction, possibly because of excessive oxide deposition on the surface of the zinc. It is suggested, therefore, that the surface of the zinc dust be cleaned with dilute hydrochloric acid just before amalgamation.
3. This technique eliminates the long induction period at 0° and the violent foaming described in the preparation of thiophenol.² However, in a larger-scale operation it would be advisable to check the rate of addition of the zinc dust somewhat, lest an exception arise.
4. The overnight period was a matter of convenience and is not considered to be vital to the completeness of the reaction.
5. When unamalgamated zinc dust is used, a considerable proportion of yellow insoluble product is often noted at this point. Since the disulfide has been isolated as an intermediate in a similar reduction of *m*-chlorosulfonylbenzoic acid,³ it is probable that this material is a mixture of disulfides of varying molecular weight.

3. Discussion

This method has been applied successfully to the preparation of phenoxybenzene-4,4'-dithiol (84% of the theoretical amount), diphenylmethane-4,4'-dithiol, and *m*-sulfhydrylbenzoic acid³ (80%). It did not prove satisfactory for the preparation of higher-melting thiols of lower solubility, such as 2,7-naphthalenedithiol, 2,6-naphthalenedithiol, and 4,4'-biphenyldithiol. These were better prepared by the use of tin(II) chloride 2-hydrate in glacial acetic acid saturated with hydrogen chloride.⁴

1,5-Naphthalenedithiol can be prepared by adding 1,5-naphthalenedisulfonyl chloride to an ethanol solution of tin(II) chloride 2-hydrate saturated with hydrogen chloride.⁵ An 80% yield of the crude dithiol melting at 103° was previously reported using zinc dust and sulfuric acid.⁶

References and Notes

1. University of Illinois, Urbana, Illinois.
 2. *Org. Syntheses Coll. Vol. 1*, 504 (1941).
 3. Tennyson, Private communication.
 4. Marvel and Caesar, *J. Am. Chem. Soc.*, **73**, 1097 (1951).
 5. Corbellini and Albenga, *Gazz. chim. ital.*, **61**, 111 (1931); Tilak, *Proc. Indian Acad. Sci.*, **33**, 71 (1951).
 6. Braun and Ebert, *Ber.*, **25**, 2735 (1892).
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Appendix

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

phenoxybenzene-4,4'-dithiol

diphenylmethane-4,4'-dithiol

m-sulfhydrylbenzoic acid

tin(II) chloride 2-hydrate

ethanol (64-17-5)

sulfuric acid (7664-93-9)

hydrogen chloride,
hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

ether (60-29-7)

zinc (7440-66-6)

mercury(II) chloride (7487-94-7)

Thiophenol (108-98-5)

1,5-Naphthalenedisulfonyl chloride (1928-01-4)

1,5-Naphthalenedithiol (5325-88-2)

2,7-naphthalenedithiol

2,6-naphthalenedithiol

m-chlorosulfonylbenzoic acid (4025-64-3)

4,4'-biphenyldithiol