



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.

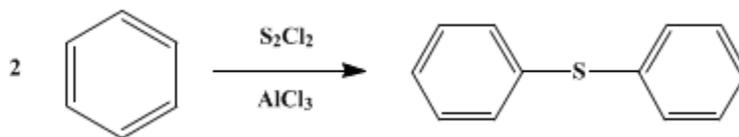
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.242 (1943); Vol. 14, p.36 (1934).

DIPHENYL SULFIDE

[Phenyl sulfide]



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1. Procedure

In a 5-l. three-necked, round-bottomed flask, fitted with a mechanical stirrer, dropping funnel, and a condenser connected to an apparatus for removing hydrogen chloride, are placed 858 g. (980 cc., 11 moles) of dry benzene (Note 1) and 464 g. (3.48 moles) of aluminum chloride. The reaction mixture is cooled in an ice bath to 10°, and then 405.1 g. (3 moles) of commercial sulfur chloride in 390 g. (450 cc., 5 moles) of benzene is added, with stirring, over a period of one hour, the temperature being kept at about 10°. The reaction begins at once as evidenced by the evolution of hydrogen chloride and the separation of a yellow viscous aluminum chloride complex. When all the sulfur chloride has been added, the reaction mixture is removed from the ice bath, stirred at room temperature for two hours, and then heated at 30° until practically no hydrogen chloride is evolved (one hour). The mixture is then poured on 1 kg. of cracked ice, and, when hydrolysis is complete, the benzene layer is separated from the water layer by means of a separatory funnel. The benzene is distilled on a steam bath, and the resulting dark-colored oil is cooled to 0° and filtered through a Büchner funnel to remove the sulfur which separates. The residue is dissolved in 500 cc. of commercial methyl alcohol, and the solution is cooled to 0°. Stirring is continued for three hours, and the precipitated sulfur is removed as before. The alcohol is removed on a steam bath, and the residue is distilled from a 1-l. modified Claisen flask with a water-cooled side-arm receiver. After a small amount of low-boiling product passes over, there is obtained 470–490 g. (Note 2) of a yellow liquid boiling at 155–170°/18 mm. The material thus obtained is heated for one hour on a steam bath, with stirring, with 70 g. of zinc dust and 200 g. of 40 per cent sodium hydroxide solution (Note 3). The diphenyl sulfide is then separated from the sodium hydroxide, washed with two 500-cc. portions of water, dried over anhydrous sodium sulfate, and distilled. The yield of colorless diphenyl sulfide boiling at 162–163°/18 mm. is 450–464 g. (81–83 per cent of the theoretical amount).

2. Notes

1. The benzene can be dried by distilling on a steam bath until the distillate is no longer milky. About 15 per cent of the benzene is distilled.
2. On distillation of the residue in the distillation flask a fraction boiling at 170–200°/18 mm. is obtained. Crystallization of this material from methyl alcohol yields 8–10 g. of thianthrene, melting at 155–156°.
3. It is necessary to treat the diphenyl sulfide as described in order to obtain a colorless product.

3. Discussion

Diphenyl sulfide can best be prepared by treating benzene and aluminum chloride with sulfur chloride,¹ sulfur dichloride,² or sulfur.³ In addition to diphenyl sulfide, traces of thiophenol and varying amounts of thianthrene are found.

References and Notes

1. Böeseken, Rec. trav. chim. **24**, 209 (1905); Böeseken and Waterman, *ibid.* **29**, 319 (1910); Böeseken and Koning, *ibid.* **30**, 116 (1911); Genvresse, Bull. soc. chim. (3) **15**, 409 (1896); Hartman, Smith, and Dickey, Ind. Eng. Chem. **24**, 1317 (1932).
 2. Böeseken, Rec. trav. chim. **24**, 217 (1905); Böeseken and Koning, *ibid.* **30**, 116 (1911).
 3. Friedel and Crafts, Ann. chim. phys. (6) **14**, 437 (1888); Böeseken, Rec. trav. chim. **24**, 17, 219 (1905); Dougherty and Hammond, J. Am. Chem. Soc. **57**, 117 (1935).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

hydrogen chloride (7647-01-0)

Benzene (71-43-2)

methyl alcohol (67-56-1)

sodium hydroxide (1310-73-2)

sodium sulfate (7757-82-6)

sulfur (7704-34-9)

aluminum chloride (3495-54-3)

zinc (7440-66-6)

sulfur chloride

Thiophenol (108-98-5)

Diphenyl sulfide,
Phenyl sulfide (139-66-2)

thianthrene (92-85-3)

sulfur dichloride (10545-99-0)