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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

*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.*
DI-\(\text{o}\)-NITROPHENYL DISULFIDE

[Disulfide, bis \((\text{o}\)-nitrophenyl)]

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1. Procedure

In a 3-l. round-bottomed flask fitted with a reflux condenser are placed 360 g. (1.5 moles) of crystalline sodium sulfide (Note 1) and 1.5 l. of 95 per cent alcohol. The flask is heated on a steam bath until the sulfide dissolves. Then 48 g. (1.5 atoms) of finely ground sulfur is added, and the heating is continued until the sulfur has dissolved, forming a brownish-red solution of sodium disulfide (Note 2). A solution of 315 g. (2 moles) of \(\text{o}\)-chloronitrobenzene (Note 3) in 500 cc. of 95 per cent alcohol is prepared in a 5-l. round-bottomed flask fitted with a reflux condenser. The sodium disulfide solution is added slowly to this solution through a funnel placed in the top of the reflux condenser. The addition should be slow until the violence of the reaction abates somewhat.

The mixture is then heated on a steam bath, gently at first (Note 4), and then at full heat for two hours. After cooling, it is filtered by suction. The mixture of the organic disulfide and the sodium chloride is transferred to a 1-l. beaker and stirred thoroughly with 500 cc. of water to remove the sodium chloride. It is then filtered by suction and the crystalline residue is washed on the filter with 100 cc. of alcohol to remove any \(\text{o}\)-chloronitrobenzene. The product melting at 192–195° weighs 180–210 g. (58–66 per cent of the theoretical amount).

2. Notes

1. Crystals as dry as possible should be selected. If desired, an equivalent amount of analyzed fused sodium sulfide may be used. In this case, solution takes a longer time. Since an excess of sodium sulfide is added, slight inaccuracies in the amount used are not important.
2. In case a small amount of sodium disulfide separates in a layer at the bottom, it should be taken up with a little more alcohol and added to the chloronitrobenzene solution.
3. Commercial \(\text{o}\)-chloronitrobenzene containing 95–98 per cent of the ortho compound was used.
4. If too much heat is applied at first, the reaction becomes very violent.

3. Discussion

Di-\(\text{o}\)-nitrophenyl disulfide can be prepared by heating \(\text{o}\)-chloronitrobenzene in alcohol with sodium sulfide and sulfur\(^1\) and from \(\text{o}\)-nitrophenylsulfur chloride and potassium hydrosulfide.\(^2\) The procedure described is that of Blanksma\(^3\) as elaborated by Wohlfahrt.\(^4\)

This preparation is referenced from:


References and Notes

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1. Elgersma, Rec. trav. chim. 48, 752 (1929).

Appendix

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

alcohol (64-17-5)
sodium chloride (7647-14-5)
sulfur (7704-34-9)
chloronitrobenzene, o-chloronitrobenzene, ochloronitrobenzene (88-73-3)
sodium sulfide (1313-82-2)
sodium disulfide
potassium hydrosulfide (1310-61-8)
Di-o-nitrophenyl disulfide, Disulfide, bis (o-nitrophenyl) (1155-00-6)
o-Nitrophenylsulfur chloride (7669-54-7)