



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.

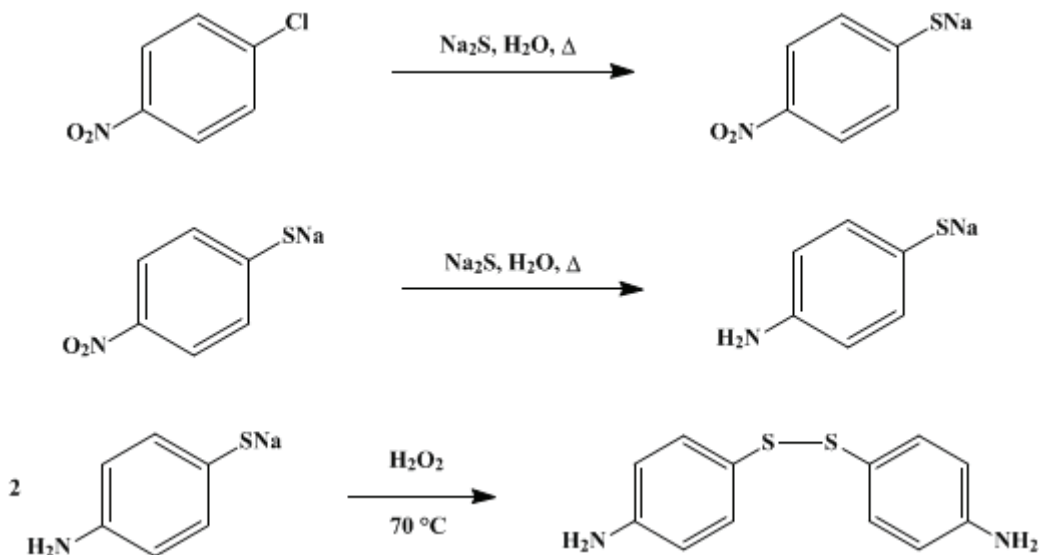
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.86 (1955); Vol. 28, p.14 (1948).

p-AMINOPHENYL DISULFIDE

[Aniline, *p,p'*-dithiodi-]



Submitted by Charles C. Price and Gardner W. Stacy.
Checked by Cliff S. Hamilton and Theo Brown.

1. Procedure

In a 5-l. round-bottomed flask equipped with a reflux condenser and a mechanical stirrer are placed 236 g. (1.5 moles) of *p*-chloronitrobenzene, 960 g. (4 moles) of sodium sulfide nonahydrate, and 2.5 l. of water. With rapid agitation, the reaction mixture is slowly heated to the reflux temperature (Note 1). Heating is continued over a period of 20 hours.

The mixture is cooled to about 15° and filtered on a large Büchner funnel to remove insoluble material, chiefly *p*-chloroaniline. The filtrate is placed in a 5-l. three-necked flask, equipped with a dropping funnel, a mechanical stirrer, and a downward condenser; it is concentrated by distillation over a flame to a volume of 1.5 l. (Note 2). The condenser is replaced by a thermometer, the stirrer is started, and the dropping funnel is charged with 230 ml. of 30% hydrogen peroxide. The temperature of the reaction mixture is maintained at 65–70° while the hydrogen peroxide is added dropwise over a period of about 2 hours (Note 3).

The reaction mixture is cooled, and the crude *p*-aminophenyl disulfide, obtained as spherical lumps amounting to 125–150 g. and melting at 73°, is collected on a Büchner funnel. It is dissolved in 1 l. of hot ethanol, and the small amount of insoluble material is removed by filtration. To the hot solution is then added 800 ml. of water containing several grams of sodium hydrosulfite to prevent discoloration of the solution by oxidation. The solution is cooled, and an additional 700 ml. of water is added with stirring to reduce the solubility of the product. The crystalline precipitate is removed by filtration and dried in a vacuum desiccator. The yield of pure product melting at 75–76° is 108–120 g. (58–64%).

2. Notes

1. The reaction mixture should not be heated too strongly as the temperature nears the boiling point, since the initial reaction is quite vigorous.
2. Some *p*-chloroaniline is removed by steam distillation during the concentration.
3. At first the solution becomes cloudy, and later large yellow globules begin to accumulate. Frequent cooling is required to maintain the temperature within the specified range.

3. Discussion

The procedure outlined is essentially that of Lantz¹ except for the use of hydrogen peroxide rather than air in the final oxidation. *p*-Aminophenyl disulfide has also been prepared by heating a mixture of aniline, aniline hydrochloride, and sulfur,² by the reduction of *p*-nitrophenyl disulfide with stannous chloride,^{3,4} and by the action of potassium hydroxide upon *p*-acetamidobenzenesulfonic acid (autoclave) followed by hydrolysis.⁵

References and Notes

1. Lantz, Fr. pat. 714,682 (*Chem. Zentr.*, **1932**, I, 1828).
 2. Hinsberg, *Ber.*, **38**, 1131 (1905).
 3. Shukla, *J. Indian Inst. Sci.*, **10**, 33 (1927).
 4. Danielsson, Christian, and Jenkins, *J. Pharm. Assoc., Sci. Ed.*, **36**, 261 (1947).
 5. Goldberg, *J. Chem. Soc.*, **1945**, 826.
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

ethanol (64-17-5)

aniline (62-53-3)

aniline hydrochloride (142-04-1)

sodium hydrosulfite (7775-14-6)

stannous chloride

sulfur (7704-34-9)

potassium hydroxide (1310-58-3)

hydrogen peroxide (7722-84-1)

sodium sulfide nonahydrate (1313-84-4)

p-chloronitrobenzene (100-00-5)

p-chloroaniline (106-47-8)

p-acetamidobenzenesulfonic acid (710-24-7)

p-Aminophenyl disulfide,
Aniline, *p,p'*-dithiodi- (722-27-0)

p-nitrophenyl disulfide (100-32-3)

