Organic Syntheses

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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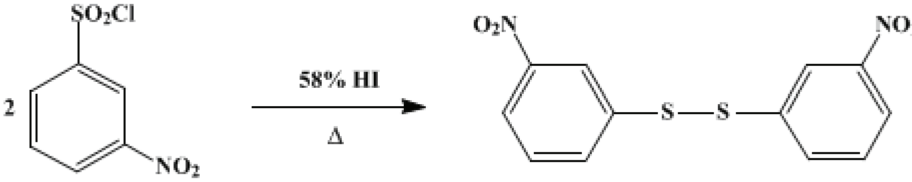
m-NITROPHENYL DISULFIDE

[Disulfide, bis-(*m*-nitrophenyl)]



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1. Procedure

A 5-l. three-necked round-bottomed flask equipped with a reflux condenser, a sealed mechanical stirrer, and a dropping funnel is set up in a hood and charged with 333 g. (1.50 moles) of *m*-nitrobenzenesulfonyl chloride (Note 1). The stirrer is started and 1033 ml. (7.5 moles) of 55–58% hydriodic acid (Note 2) is rapidly added dropwise over a period of 30–45 minutes (Note 3). After the addition is complete, the reaction mixture is stirred and refluxed on a steam bath for 3 hours. It is then cooled to room temperature, and the dropping funnel is replaced with an open powder funnel. Solid sodium bisulfite powder (Note 4) is added in portions until all the iodine has been reduced, and the reaction mixture is a suspension of pale yellow *m*-nitrophenyl disulfide in an almost colorless solution. The reaction mixture is filtered through a coarse-grade sintered-glass funnel to separate the disulfide, which is washed thoroughly with warm water to remove all inorganic salts. There is obtained 210–221 g. (91–96%) of crude *m*-nitrophenyl disulfide, m.p. 81–83°. This material is purified by dissolving it in approximately 800 ml. of boiling acetone, which is filtered hot and cooled to give 170–183 g. (74–79%) of the disulfide in the form of pale yellow prisms, m.p. 82–83°. By concentration of the mother liquor an additional 30–40 g. (13–17%) of disulfide, m.p. 82–83°, is obtained, so that the total yield of satisfactory product is 200–210 g. (86–91%).

2. Notes

1. Eastman Kodak white label *m*-nitrobenzenesulfonyl chloride was used.
2. Reagent grade hydriodic acid was generally employed, but material of lower purity may be used without decreasing the yield. The calculated amount of 45–47% hydriodic acid may also be employed[2] with only a slight diminution in yield.
3. The reaction of the hydriodic acid with *m*-nitrobenzenesulfonyl chloride is mildly exothermic, and iodine crystals precipitate as the reaction proceeds.
4. Approximately 3 lb. of sodium bisulfite is required to reduce the iodine. Technical grade bisulfite may be used satisfactorily. Caution should be observed in adding the bisulfite, since evolution of sulfur dioxide can cause excessive foaming. This foaming occurs a short time after each addition and is most noticeable when the iodine is almost neutralized. Iodine and product clinging to the upper walls of the flask and in the condenser may be conveniently rinsed into the reaction mixture with a stream of water from a wash bottle.

3. Discussion

The described method of preparation of *m*-nitrophenyl disulfide is essentially that of Foss and co-workers[2] and is a modification of that reported by Ekbom.[3] The disulfide has been prepared by reaction of potassium ethyl xanthate with *m*-nitrobenzenediazonium chloride solution, followed by hydrolysis to yield the mercaptan, which is subsequently oxidized with potassium ferrocyanide or dilute nitric acid to the disulfide.[4]

The usual method of preparing aromatic disulfides is to treat an aryl halide with Na_2S_2.[5] However, this method is limited to compounds where the halogen is strongly activated by electronegative groups (for example, *o*- or *p*-nitrochlorobenzene). The reaction of diazonium salts with xanthate is unsatisfactory for large-scale preparations because dilute solutions must be employed to reduce the hazard of explosion. Aromatic sulfonyl chlorides (not containing nitro groups) are also reduced with zinc and mineral acid to mercaptans,[6] which must be subsequently oxidized to the disulfide. The present method has been used to prepare nitronaphthalene disulfides,[7,8] naphthalene disulfide, and phenyl disulfide[8] and should be applicable to the preparation of any symmetrical aromatic disulfides containing substituents stable to hydriodic acid.

4. Use of *m*-Nitrophenyl Disulfide

The disulfides are useful intermediates in the preparation of sulfenyl chlorides.[2,9]

References and Notes

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6. Th. Zinke and O. Krüger, *Ber.*, **45**, 3468 (1912).
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9. M. H. Hubacher, *Org. Syntheses*, Coll. Vol. **2**, 455 (1943).

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

o- or p-nitrochlorobenzene

nitric acid (7697-37-2)

sulfur dioxide (7446-09-5)

sodium bisulfite,
sodium bisulfite powder (7631-90-5)

iodine (7553-56-2)

acetone (67-64-1)

zinc (7440-66-6)

hydriodic acid (10034-85-2)

potassium ferrocyanide

potassium ethyl xanthate (140-89-6)

xanthate

phenyl disulfide (882-33-7)

naphthalene disulfide

m-nitrobenzenediazonium chloride

m-Nitrophenyl disulfide,
Disulfide, bis-(m-nitrophenyl) (537-91-7)

m-nitrobenzenesulfonyl chloride (121-51-7)