



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.

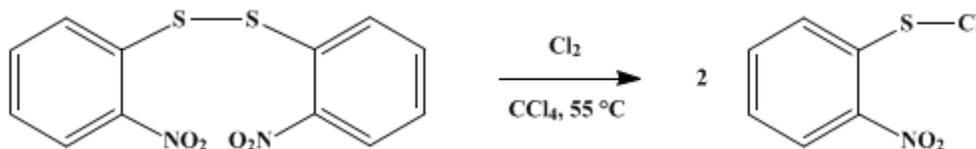
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries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

Organic Syntheses, Coll. Vol. 2, p.455 (1943); Vol. 15, p.45 (1935).

***o*-NITROPHENYLSULFUR CHLORIDE**

[Benzenesulfenyl chloride, *o*-nitro-]



Submitted by Max H. Hubacher
Checked by Louis F. Fieser and D. J. Potter.

1. Procedure

In a 1-l. three-necked flask, fitted with a thermometer, a reflux condenser, and an inlet tube extending to the bottom of the flask and drawn out to a small opening, are placed 600 cc. of dry **carbon tetrachloride**, 154 g. (0.5 mole) of **di-*o*-nitrophenyl disulfide**, m.p. 193–195° (*Org. Syn. Coll. Vol. I, 1941, 220*), and 0.25 g. of **iodine**. To the upper end of the condenser is attached a glass tube which dips below the surface of a little **carbon tetrachloride** contained in a test tube. A current of **chlorine**, dried with **sulfuric acid**, is passed into the reaction mixture, the temperature of which is maintained at 50–60°. The rate of flow of the **chlorine** (about 16–17 g. per hour) is regulated so that little or no gas escapes through the carbon tetrachloride trap. The yellow **di-*o*-nitrophenyl disulfide** gradually disappears, and after two to two and one-half hours a homogeneous, dark yellow solution is obtained (*Note 1*). The warm solution is filtered from a small amount of dark residue through a warm Büchner funnel, the flask and filter being rinsed with 30 cc. of warm **carbon tetrachloride**. The yellow filtrate (*Note 2*) is cooled to 5° and the product allowed to crystallize. The cake of crystals is broken with a rod, collected on a Büchner funnel, and drained well. The product is dried rapidly (two hours) at 50° and bottled (*Note 3*). This material melts at 73–74.5° and weighs 126–135 g. (66–71 per cent of the theoretical amount). A further crop is obtained by removing the solvent from the mother liquor by distillation from a water bath (*Note 4*), the dark, residual oil being poured into an evaporating dish. The last traces of **carbon tetrachloride** are removed by drying at 50°, during which process the oil crystallizes. This material melts at 67–72° and weighs 48–58 g. It is pure enough for most purposes (*Note 5*). The total yield is 183–184 g. (96–97 per cent of the theoretical amount) (*Note 6*) and (*Note 7*).

2. Notes

1. An excess of **chlorine** will do no harm.
2. For many purposes this filtered solution can be used without purification after distilling about 100 cc. of the solvent to remove the excess **chlorine**. The yield of material in solution is considered as 98 per cent of the theoretical amount.
3. The pure material melts at 74.5–75°. When in contact with moist air, ***o*-nitrophenylsulfur chloride** decomposes within a few days, giving off **hydrogen chloride**. Stored in a brown, glass-stoppered bottle and sealed well, the material can be kept for many months.
4. Since ***o*-nitrophenylsulfur chloride** decomposes spontaneously when heated to about 170°, it is advisable to use a water bath when removing the solvent.
5. This material may be crystallized from hot **carbon tetrachloride** (2 cc. per gram), the filtered solution being cooled to 5°. The recovery of a product melting at 70–73° is 75 per cent.
6. Practically the same method can be used for the preparation of ***o*-nitro-*p*-chlorophenylsulfur chloride** (m.p. 95–97°); the chlorination of the disulfide (m.p. 212–213°) in this case proceeds much more slowly. **2,4-Dinitrophenylsulfur chloride** can be prepared by the chlorination of the corresponding disulfide in **nitrobenzene** suspension at 120–130°. As the chloride is explosive the solvent must be removed by distillation in vacuum at 130°. The crude material melts at 89–92°. After crystallization from **carbon tetrachloride** it melts at 94–95°.
7. The arylsulfur chlorides are used for the introduction of the ArS- group, their reactions being

analogous to those of acid chlorides.

3. Discussion

o-Nitrophenylsulfur chloride has always been prepared by the chlorination of the disulfide.¹

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 5*, 843

References and Notes

1. Zincke, *Ber.* **44**, 770 (1911); Zincke and Farr, *Ann.* **391**, 63 (1912).
-

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

sulfuric acid (7664-93-9)

hydrogen chloride (7647-01-0)

carbon tetrachloride (56-23-5)

iodine (7553-56-2)

chlorine (7782-50-5)

Nitrobenzene (98-95-3)

2,4-Dinitrophenylsulfur chloride (528-76-7)

Di-*o*-nitrophenyl disulfide (1155-00-6)

o-Nitrophenylsulfur chloride,
Benzenesulfenyl chloride, *o*-nitro- (7669-54-7)

o-Nitro-*p*-chlorophenylsulfur chloride (4153-06-4)