



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.

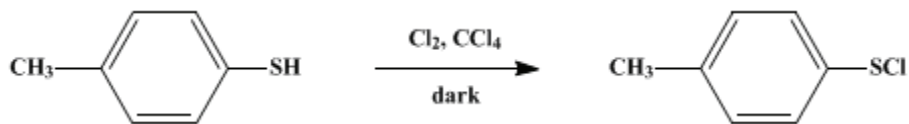
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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. 4, p.934 (1963); Vol. 35, p.99 (1955).

p-TOLUENESULFENYL CHLORIDE



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1. Procedure

Caution! This preparation should be conducted in a good hood.

Chlorine (Note 1) is passed into 300 ml. of anhydrous carbon tetrachloride (Note 2) contained in a 500-ml. three-necked round-bottomed flask equipped with a mechanical stirrer, a dropping funnel protected from atmospheric moisture by a calcium chloride tube, and a gas-inlet tube equipped with a sintered-glass tip (Note 3). The amount of chlorine contained in the resulting yellow-green liquid, estimated volumetrically (Note 4), varies between 25 and 32 g. The gas-inlet tube is replaced by a calcium chloride tube, and the reaction vessel is cooled externally with ice water and protected from light by being covered with a towel.

One or two crystals of iodine are added to the chlorine solution, and a solution of *p*-toluenethiol (7.3 g. per 10 g. of dissolved chlorine, i.e., halogen in 140% excess) (Note 5) in 50 ml. of anhydrous carbon tetrachloride (Note 2) is added dropwise over a period of approximately 1 hour. The initial slight turbidity disappears gradually, a bright orange solution being formed (Note 6). After an additional 30 minutes' stirring, the solvent and excess chlorine are rapidly removed under reduced pressure at the lowest possible temperature (Note 7), the crude sulfonyl chloride being left as an orange-red mobile liquid (Note 8). For batches starting with 24.8 g. (0.2 mole) of *p*-toluenethiol, the yield varies between 27 and 30.5 g. (85–96%).

Rapid distillation under reduced pressure affords *p*-toluenesulfonyl chloride as a red mobile liquid boiling at 66–68°/0.8 mm. (74–76°/1.5 mm.; 82–84°/3.5 mm.) (Note 9). The yield of redistilled material varies between 24.5 and 28 g. (77–88%).

2. Notes

1. The checkers used tank chlorine obtained from the Ohio Chemical and Surgical Equipment Company, Detroit, Michigan. The gas was dried with concentrated sulfuric acid and used with no further purification. The rate of chlorine addition was regulated so that no chlorine escaped from the carbon tetrachloride solution. After 1.5–2.0 hours, 27–33 g. of chlorine was absorbed. The submitters generated chlorine by the action of concentrated hydrochloric acid on potassium permanganate.

2. The carbon tetrachloride is treated with a small quantity of phosphorus pentoxide, and the suspension is set aside for 1–2 hours. The clear supernatant liquid is first decanted into a dry flask and gently shaken. Any droplets of phosphoric acid are retained on the walls of this vessel; the anhydrous solvent is then easily decanted.

3. During the slow absorption of chlorine, the solution is satisfactorily protected from atmospheric moisture by means of a plug of cotton wool through which the gas-inlet tube passes. The temperature of the solution does not rise, and external cooling is not required.

4. A 2-ml. aliquot of the solution, withdrawn by means of a safety pipet, is added to 20 ml. of water containing 2 g. of potassium iodide, and the liberated iodine is titrated with good shaking with standard sodium thiosulfate solution.

5. When a smaller excess of chlorine is used poorer yields of sulfonyl chloride are obtained, a larger proportion of *p*-tolyliddisulfide being formed.

6. The checkers found that the turbidity persisted throughout the addition of the *p*-toluenethiol and that a small amount of an orange-yellow solid was present at the end of the addition. This material dissolved during the concentration under reduced pressure.
7. Since traces of sulfenyl chloride are carried over with the carbon tetrachloride, the distillate varies from light to deep yellow during the concentration. Recovery of this material by repeated distillation is not economical.
8. This material is suitable for use in further synthesis without purification by distillation, particularly if the presence of a few per cent of *p*-tolyl disulfide is of no consequence.
9. The checkers found that 76% of the product boiled at 64–66°/1.1 mm. and 24% boiled at 66–74°/1.1 mm.; however, the index of refraction of the two fractions was constant (n_D^{20} 1.6018–1.6019). As the first few drops of distillate were green, they were discarded.

3. Discussion

p-Toluenesulfenyl chloride has been prepared by the action of chlorine on a solution of *p*-toluenethiol or *p*-tolyl disulfide in anhydrous carbon tetrachloride.^{2,3,4} Benzenesulfenyl chloride has also been obtained by the interaction of hydrogen chloride and *N,N*-diethylbenzenesulfenamide⁵ and by reaction of benzenethiol with *N*-chlorosuccinimide.⁶ A comprehensive review dealing with sulfenyl halides and related compounds is available.⁷

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 6, 981*

References and Notes

1. University of London, London, England.
2. Lecher, Holschneider, Koberle, Speer, and Stocklin, *Ber.*, **58**, 409 (1925).
3. Lecher and Holschneider, Ger. pat. 423,232 (*Brit. C. A.*, **1926**, B, 386).
4. Montanari, *Gazz. chim. ital.*, **86**, 406 (1956).
5. Lecher and Holschneider, *Ber.*, **57**, 755 (1924).
6. Emde, Ger. pat. 804,572 [*C. A.*, **46**, 529 (1952)].
7. Kharasch, Potempa, and Wehrmeister, *Chem. Revs.*, **39**, 269 (1946).

Appendix

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

sulfenyl chloride

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrogen chloride,
hydrochloric acid (7647-01-0)

potassium permanganate (7722-64-7)

carbon tetrachloride (56-23-5)

potassium iodide (7681-11-0)
sodium thiosulfate (7772-98-7)
iodine (7553-56-2)
chlorine (7782-50-5)
phosphoric acid (7664-38-2)
N-chlorosuccinimide (128-09-6)
Benzenethiol (108-98-5)
Benzenesulfonyl chloride (931-59-9)
N,N-diethylbenzenesulfenamide
phosphorus pentoxide (1314-56-3)
p-Toluenesulfonyl chloride (933-00-6)
p-toluenethiol (106-45-6)
p-tolyl disulfide,
p-tolyldisulfide (103-19-5)