



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.

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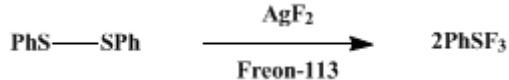
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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PHENYLSULFUR TRIFLUORIDE

[Benzenesulfenyl trifluoride]



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Checked by E. S. Glazer and John D. Roberts.

1. Procedure

Caution! Phenylsulfur trifluoride and by-products (e.g., hydrogen fluoride from hydrolysis) are toxic, and all manipulations should be carried out in a good hood. Silver difluoride is a powerful oxidative fluorinating agent and reacts vigorously with many organic materials. These reagents should not be allowed to come in contact with the skin.

A 1-l., four-necked, round-bottomed flask equipped with reflux condenser, sealed stirrer, thermometer, and solid addition funnel² and protected from atmospheric moisture with a Drierite® guard tube is carefully dried and flushed with a dry inert gas (Note 1). The flask is charged with 453 g. (3.1 moles) of silver difluoride (Note 2) and 500 ml. of 1,1,2-trichloro-1,2,2-trifluoroethane (Note 3), and phenyl disulfide (100 g., 0.458 mole) (Note 4) is weighed into the solid addition funnel. The stirrer is started, and phenyl disulfide is added to the slurry in small portions. An exothermic reaction occurs, and after the addition of several portions the reaction mixture reaches a temperature of 40° (Note 5). By intermittent use of a cooling bath and by adjusting the rate of addition of the disulfide, the reaction temperature may be maintained between 35° and 40°. The addition of the phenyl disulfide requires 45–60 minutes. On completion of the addition the suspension of black silver difluoride has been converted to yellow silver monofluoride, and the exothermic reaction gradually subsides. The reaction mixture is stirred for an additional 15–30 minutes without external cooling and then quickly heated to reflux.

The reaction mixture is filtered hot through a fluted filter paper under a blanket of dry nitrogen into a dry, 1-l., round-bottomed flask. The residue of solid silver fluoride is washed with a total of 500 ml. of boiling 1,1,2-trichloro-1,2,2-trifluoroethane in portions (Note 6). The filtrates are combined and distilled through a short Vigreux column, an oil bath not heated over 70° being used (Note 7). The residue of phenylsulfur trifluoride is transferred to a 200-ml. round-bottomed flask and distilled, b.p. 47–48° (2.6 mm.), through a Claisen-type distillation column, discarding a small fore-run. The product is obtained in a yield of 84–92 g. (55–60%) as a colorless liquid, m.p. –10° (Note 8). Since phenylsulfur trifluoride slowly attacks Pyrex® glass, it should be used immediately. It can be stored for several days in glass at –80° or in polyethylene, however, and may be stored indefinitely at room temperature in bottles of Teflon® polytetrafluoroethylene resin or aluminum (Note 9).

2. Notes

1. The equipment should be dried carefully by the techniques normally employed when preparing for a Grignard reaction. Dry nitrogen gas was normally employed to flush the apparatus, but any dry inert atmosphere, or dry air, could be employed.
2. A technical grade of silver difluoride (approximately 85%) is available from Harshaw Chemical Company. Better grades of silver difluoride are available and may be employed. It is important that the silver difluoride be a black powder. If the material is light brown and lumpy, a lower yield of product may be obtained. Normally, the contents of a 1-lb. can (approximately 435–470 g.) are employed.
3. 1,1,2-Trichloro-1,2,2-trifluoroethane (trademark "Freon-113"), b.p. 47°, is available from the Organic Chemicals Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware.
4. Eastman's white label grade phenyl disulfide is suitable.

5. Caution must be exercised in the addition of the phenyl disulfide. There is a short induction period between the addition of disulfide and the exothermic reaction. If the disulfide is added too rapidly, a vigorous exothermic reaction, which is difficult to control, will result. The extensive use of a cooling bath should be avoided because the reaction rate is sufficiently slow at lower temperatures to allow buildup of reactants and the development of a vigorous, uncontrollable reaction.
6. Etching of the glass equipment is reduced to a minimum if all equipment used in the preparation and subsequent manipulation is rinsed with water and acetone *immediately* after use.
7. The Freon® solvent may be removed under reduced pressure in order to shorten the distillation time. Since phenylsulfur trifluoride attacks glass, the total time involved in the preparation and distillation in the glass equipment should be kept to a maximum of a few hours. It is recommended that the column be changed after distillation of the Freon®. If the preparation cannot be completed within a day, the Freon® solution of crude phenylsulfur trifluoride may be stored in polyethylene bottles overnight.
8. In contact with moisture of glass, phenylsulfur trifluoride develops pink, green, or bluish colors. A small amount of discoloration does not appear to affect the quality. Phenylsulfur trifluoride prepared in glass equipment always contains a few percent of phenylsulfinyl fluoride. The amount of this impurity depends on the care taken to exclude moisture during preparation and manipulation.
9. Phenylsulfur trifluoride slowly oozes through polyethylene bottles after storage for several days. However, a sample of phenylsulfur trifluoride has been stored in a bottle of Teflon® for several years without decomposition. Storage in a dry atmosphere in a well-ventilated area is recommended.

3. Discussion

Phenylsulfur trifluoride has been prepared only by the present method.^{3,4}

4. Merits of the Preparation

This procedure illustrates a fairly general method for the preparation of alkyl- and arylsulfur trifluorides. The method has also been applied to the synthesis of nitrophenyl-, tolyl-, and fluorobutylsulfur trifluorides,^{3,4} and it is probably applicable to any disulfide that does not contain groups reactive with silver difluoride. 2,4-Dinitrophenyl- and perfluoroalkylsulfur trifluorides have been prepared by reaction of disulfides with fluorine or by electrolytic fluorination.^{5,6} These other routes to sulfur trifluoride compounds are not general or convenient, and they often give low yields.

The sulfur trifluoride compounds are useful as selective agents for conversion of carbonyl and carboxyl groups to difluoromethylene⁷ and trifluoromethyl groups,^{3,4} respectively, and as intermediates for synthesis of arylsulfur pentafluorides.^{3,8}

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 396

References and Notes

1. Contribution No. 670 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company.
2. R. C. Fuson, E. C. Horning, S. P. Rowland, and M. L. Ward, *Org. Syntheses, Coll. Vol. 3*, 549 (1955); see (Note 7).
3. W. A. Sheppard, *J. Am. Chem. Soc.*, **82**, 4751 (1960).
4. W. A. Sheppard, *J. Am. Chem. Soc.*, **84**, 3058 (1962).
5. D. L. Chamberlain and N. Kharasch, *J. Am. Chem. Soc.*, **77**, 1041 (1955).
6. J. Burdon and J. C. Tatlow in M. Stacey, J. C. Tatlow, and A. G. Sharpe, "Advances in Fluorine Chemistry," Academic Press, Inc., New York, 1960, p. 151.
7. W. A. Sheppard, *this volume*, p. 396.
8. W. A. Sheppard, *J. Am. Chem. Soc.*, **84**, 3064 (1962).

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

nitrogen (7727-37-9)

hydrogen fluoride (7664-39-3)

phenylsulfinyl fluoride

Phenylsulfur trifluoride (672-36-6)

Fluorine (7782-41-4)

silver fluoride,
silver monofluoride (7775-41-9)

phenyl disulfide (882-33-7)

Benzenesulfonyl trifluoride

Silver difluoride

1,1,2-trichloro-1,2,2-trifluoroethane (76-13-1)