



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.

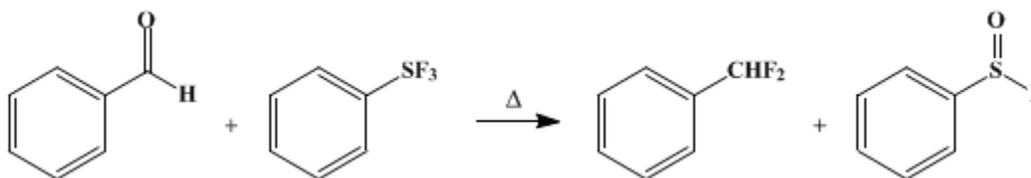
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.396 (1973); Vol. 44, p.39 (1964).

α,α -DIFLUOROTOLUENE AND BENZENESULFINYL FLUORIDE

[Toluene, α,α -difluoro-]



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

1. Procedure

Caution! Phenylsulfur trifluoride is toxic, and this reaction should be carried out in a good hood. The reagent should not be allowed to come in contact with the skin.

Phenylsulfur trifluoride² (16.6 g., 0.10 mole) is placed in a two-necked 50-ml. flask equipped with a dropping funnel and connected to a dry distillation column (Note 1). The flask is heated to 50–70° in an oil bath, and 10.6 g. (0.10 mole) of benzaldehyde is added in small portions over 30 minutes. A mild exothermic reaction occurs. After the addition is completed, the reaction flask is heated to 100° with an oil bath, and the pressure on the column is reduced until α,α -difluorotoluene distills. The major portion of product distills at 68° (80 mm.), but a small final cut, b.p. 45° (15 mm.), is obtained. The yield of α,α -difluorotoluene is 9.2–10.2 g. (71–80%) (Note 2). The pressure is reduced and the distillation is continued. An intermediate cut of 1–2 g., b.p. 45° (15 mm.) to 60° (2.5 mm.), is discarded, and benzenesulfinyl fluoride, 11.7–13.2 g. (81–91%), b.p. 60° (2.5 mm.), is collected. Since the benzenesulfinyl fluoride slowly attacks glass and may be unstable to storage at room temperature, it is recommended that this product be stored at –80°.

2. Notes

1. A 45-cm. spinning band column was employed by the submitter, but any distillation column with a low holdup may be used. Since the products have widely different boiling points, careful fractionation during distillation is not needed. Because the phenylsulfur trifluoride and benzenesulfinyl fluoride slowly attack glass, all equipment should be rinsed with water and acetone immediately after use to minimize etching.

2. The product attacks glass slowly on standing, and a moderate increase in pressure takes place. The product can be stored for a period of several days in a polyethylene bottle, but it is best to prepare the material shortly before use. If prolonged storage is required, a stainless steel cylinder or a bottle fabricated from Teflon[®] polytetrafluoroethylene resin is suggested.

3. Discussion

α,α -Difluorotoluene has been prepared by the reaction of α,α -dichlorotoluene with antimony (III) fluoride,³ by the hydrogenation of α -chloro- α,α -difluorotoluene,⁴ by the action of sulfur tetrafluoride on benzaldehyde,⁵ and by the present method.^{6,7}

4. Merits of the Preparation

Sulfur tetrafluoride provides an inexpensive method for selectively converting a carbonyl to a difluoromethyl group. However, the reactions involving sulfur tetrafluoride, in general, require pressure equipment constructed of fluorine-resistant material such as "Hastelloy-C" bombs.⁸ Phenylsulfur

[trifluoride](#) may be used to advantage for the same reaction, where small amounts are involved, since the reaction may be run at atmospheric pressure in glass, polyethylene, or metal containers.

Although the [sulfur trifluoride](#) compounds are generally useful as selective agents for conversion of carbonyl and carboxyl groups to difluoromethylene and trifluoromethyl groups, variations in reaction conditions are often necessary.⁷ Thus the reaction of aromatic ketones requires heating at 150°. Since the reaction with aliphatic aldehydes and ketones is exothermic, it is advantageous to run it in a solvent such as [methylene chloride](#) or [acetonitrile](#) containing a small amount of [sodium fluoride](#) powder (with ketones an induction period of several hours may be observed). Reactions with carboxylic acids should be carried out in a container resistant to [hydrogen fluoride](#), and they require heating at 120° to 150°.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 959](#)

References and Notes

1. Contribution No. 669 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company.
2. [W. A. Sheppard, this volume, p. 959.](#)
3. T. Van Hove, *Bull. Classe Sci. Acad. Roy. Belg.*, 1074 (1913).
4. F. Swarts, *Bull. Classe Sci. Acad. Roy. Belg.*, 410 (1920).
5. W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 543 (1960).
6. W. A. Sheppard, *J. Am. Chem. Soc.*, **82**, 4751 (1960).
7. W. A. Sheppard, *J. Am. Chem. Soc.*, **84**, 3058 (1962).
8. [W. R. Hasek, this volume, p. 1082.](#)

Appendix

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

[polytetrafluoroethylene](#)

[acetonitrile \(75-05-8\)](#)

[hydrogen fluoride \(7664-39-3\)](#)

[benzaldehyde \(100-52-7\)](#)

[acetone \(67-64-1\)](#)

[methylene chloride \(75-09-2\)](#)

[\$\alpha,\alpha\$ -dichlorotoluene \(98-87-3\)](#)

[sodium fluoride \(7681-49-4\)](#)

[BENZENESULFINYL FLUORIDE](#)

[Phenylsulfur trifluoride \(672-36-6\)](#)

antimony (III) fluoride

sulfur tetrafluoride (7783-60-0)

sulfur trifluoride

α,α -Difluorotoluene,
Toluene, α,α -difluoro- (455-31-2)

α -chloro- α,α -difluorotoluene