



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.

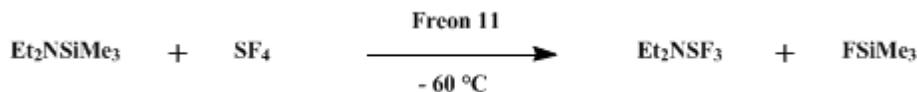
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 6, p.440 (1988); Vol. 57, p.50 (1977).

DIETHYLAMINOSULFUR TRIFLUORIDE

[Sulfur, (diethylamino)trifluoro-]



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1. Procedure

Caution! This procedure should be conducted in a good hood to avoid exposure to sulfur tetrafluoride. Protective gloves should be worn when handling diethylaminosulfur trifluoride since this material can cause severe HF burns.

A dry, 1-l., three-necked, round-bottomed flask is equipped with a thermometer (−100° to 50°), a magnetic stirrer, and two dry-ice condensers (one condenser is capped with a drying tube, the other with a gas-inlet tube). The apparatus is flushed with dry nitrogen, and 300 ml. of trichlorofluoromethane (Note 1) is added to the flask. As the nitrogen atmosphere is maintained, the trichlorofluoromethane is cooled to −70° with an acetone–dry ice bath, and 119 g. (1.10 moles) of sulfur tetrafluoride (Note 2) is added from a cylinder through the gas-inlet tube (Note 3), which is then replaced with a 250-ml., pressure-equalizing dropping funnel charged with a solution of 145 g. (1.00 mole) of *N,N*-diethylaminotrimethylsilane (Note 4) in 90 ml. of trichlorofluoromethane. This solution is added dropwise, with stirring, to the sulfur tetrafluoride solution at a rate slow enough to keep the temperature of the reaction mixture below −60° (about 40 minutes). The cooling bath is removed, and the reaction mixture is allowed to warm gradually to room temperature. The apparatus is prepared for distillation with a simple distillation head, and the solvent (b.p. 24°) and by-product fluorotrimethylsilane (b.p. 17°) are distilled into a well-cooled receiver by warming the reaction mixture gently to 45° with a heating mantle. The yellow to dark-brown residual liquid is transferred and distilled at reduced pressure through a spinning-band column, yielding 131 g. (81%) of diethylaminosulfur trifluoride as a light yellow liquid, b.p. 46–47° (10 mm.) (Note 5). This product can be stored for several months at room temperature in an inert plastic bottle (such as one made of polypropylene or Teflon FEP), or for short periods of time in a dry, glass bottle.

2. Notes

1. Trichlorofluoromethane (Freon 11) is available from E. I. duPont de Nemours and Company, Inc., or Matheson Gas Products.
2. Sulfur tetrafluoride is available from Air Products and Chemicals, Inc., or Matheson Gas Products.
3. If it is inconvenient to add sulfur tetrafluoride directly from a cylinder, it may first be condensed in a calibrated trap containing a boiling chip and cooled in an acetone–dry ice bath. When cooled to −78°, 119 g. of sulfur tetrafluoride has a volume of about 62 ml. The sulfur tetrafluoride can be added to the cooled flask by allowing it to distil slowly from the trap.
4. *N,N*-Diethylaminotrimethylsilane is available from PCR, Inc., or it can be prepared by the following procedure. A solution of 292 g. (413 ml.) of diethylamine in 1000 ml. of diethyl ether is cooled in an ice bath, and a solution of 216 g. (252 ml.) of chlorotrimethylsilane in 200 ml. of ether is added dropwise with mechanical stirring over a period of 1 hour. The precipitated solid is removed by filtration, thoroughly washed with ether, and the filtrate is fractionally distilled, yielding 175 g. (60%) of *N,N*-diethylaminotrimethylsilane as a colorless liquid, b.p. 124–125°.
5. The reaction of diethylaminosulfur trifluoride with water is highly exothermic; clean-up procedures should be carried out with caution.

3. Discussion

Diethylaminosulfur trifluoride is a useful and convenient reagent for replacing primary, secondary, and tertiary hydroxyl and aldehyde and ketone carbonyl oxygen^{2,3} with fluorine, even in the presence of other halogens and other functional groups, such as carboxylic esters. In contrast to sulfur tetrafluoride, this reagent is a liquid easily measured and used in standard glass equipment at moderate temperatures and atmospheric pressure, and can be used on acid-sensitive compounds (such as pivaldehyde) to convert them into the fluorinated derivative. In contrast to other reagents such as SF₄, SeF₄, pyridine HF, HF.pyridine, and (C₂H₅)₂NCF₂CFHCl, this reagent can replace hydroxyl groups with fluorine in primary alcohols such as 2-methyl-1-propanol without causing extensive rearrangement or dehydration.

This preparation of diethylaminosulfur trifluoride is an adaptation of a procedure first described by von Halasz and Glemser.⁴ The same procedure can also be used to prepare other dialkylaminosulfur trifluorides by the substitution of the diethylaminotrimethylsilane with other dialkylaminotrimethylsilanes.²

This preparation is referenced from:

- Org. Syn. Coll. Vol. 6, 628
- Org. Syn. Coll. Vol. 6, 835

References and Notes

1. Central Research and Development Department, Experimental Station, E. I. duPont deNemours and Co., Wilmington, Del. 19898.
 2. W. J. Middleton, *J. Org. Chem.*, **40**, 574 (1975); W. J. Middleton and E. M. Bingham, *Org. Synth., Coll. Vol. 6*, 835 (1988).
 3. L. N. Markovskij, V. E. Pashinnik, and A. V. Kirsanov, *Synthesis*, 787 (1973).
 4. S. P. von Halasz and O. Glemser, *Chem. Ber.*, **104**, 1247 (1971).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

Sulfur, (diethylamino)trifluoro-

Freon 11

ether,
diethyl ether (60-29-7)

nitrogen (7727-37-9)

diethylamine (109-89-7)

2-methyl-1-propanol (78-83-1)

trichlorofluoromethane (75-69-4)

sulfur tetrafluoride (7783-60-0)

CHLOROTRIMETHYLSILANE (75-77-4)

Diethylaminosulfur trifluoride (38078-09-0)

fluorotrimethylsilane (420-56-4)

diethylaminotrimethylsilane,
N,N-diethylaminotrimethylsilane (996-50-9)