



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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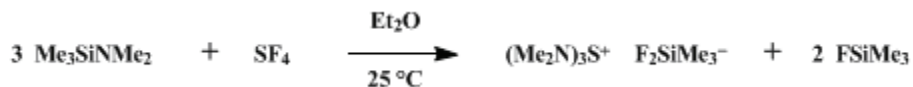
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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TRIS(DIMETHYLAMINO)SULFONIUM DIFLUOROTRIMETHYLSILICATE

[Sulfur(1+), tris(*N*-methylmethanaminato)-, difluorotrimethylsilicate(1-)]



Submitted by William J. Middleton¹

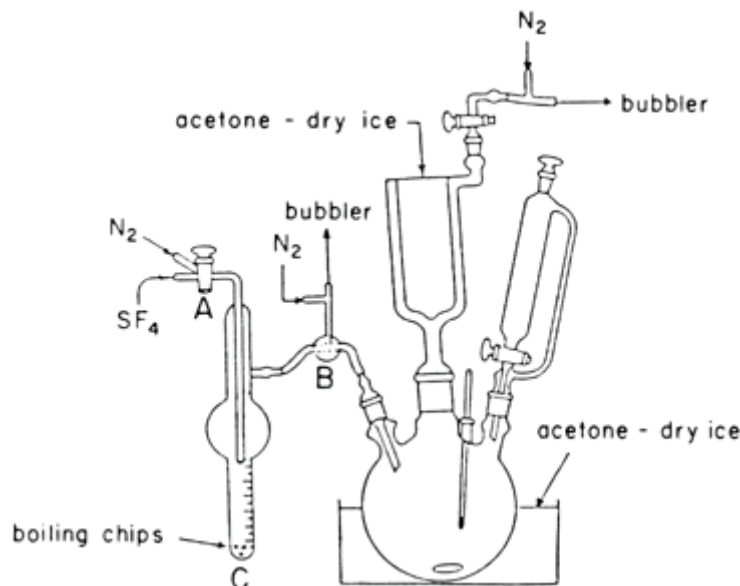
Checked by Fred G. West and Edwin Vedejs.

1. Procedure

Caution! This procedure should be conducted in an efficient hood to avoid exposure to the toxic gas sulfur tetrafluoride.

A dry, 500-mL, four-necked flask equipped with a magnetic stirrer, dry ice condenser, thermometer ($-100^\circ - 50^\circ\text{C}$) and a gas inlet tube is assembled as shown in Figure 1 (connections were all-glass or polyethylene tubing). The system is flushed with nitrogen through three-way stopcocks A and B, the four-necked flask is charged with 150 mL of dry ether (Note 1), and the dropping funnel is charged with 46.9 g (0.40 mol) of *N,N*-dimethylaminotrimethylsilane (Note 2). The reaction vessel is maintained under a positive nitrogen pressure using a bypass nitrogen stream and bubbler. Stopcock A is connected to the sulfur tetrafluoride (SF_4) tank (Note 3) and stopcock B is turned to vent directly into a nitrogen bypass line and bubbler. While the graduated cylinder C is cooled in acetone-dry ice, SF_4 is slowly passed into the cylinder until 7 mL (13 g at -70°C , 0.12 mol) of liquid SF_4 have condensed. Stopcock A is closed and B is vented directly into the three-necked flask. Removal of the cooling bath from graduated cylinder C allows distillation of SF_4 into the cooled reaction vessel.

Figure 1



A slow stream of nitrogen is passed into the reaction vessel through stopcock B and the *N,N*-dimethylaminotrimethylsilane is added to the stirred SF_4 solution at a rate sufficiently slow to keep the temperature below -60°C (about 30 min). The cooling bath is removed, the mixture is allowed to warm to room temperature, and the entire system is placed inside a nitrogen-flushed glove bag. The dropping funnel and condenser are replaced by stoppers, stopcock B is closed, and the closed system is stirred for

3 days with constant nitrogen flow through the glove bag (Note 4). During this time, the product separates as fine crystals. The crystals are collected in a nitrogen pressure filter, washed with 50–100 mL of dry ether, and dried by passing a stream of dry nitrogen through them to give 23–26 g (71–78% yield) of tris(dimethylamino)sulfonium difluorotrimethylsilicate as hygroscopic (Note 5), colorless needles, mp 98–101°C (Note 6).

2. Notes

1. It is important that the ether be very dry (distilled from Na/benzophenone). Otherwise, the quality of the product and the yield will be substantially lower.
2. *N,N*-Dimethylaminotrimethylsilane is available from Petrarch Systems, Inc. Care should be taken to assure that there is no free dimethylamine present. Commercial samples can be purified by distillation through a 6-in. Vigreux column, bp 86–87°C. The submitters used a spinning band column for removal of hexamethyl-disiloxane, bp 99–100°C, which is present as a contaminant.
3. Sulfur tetrafluoride is available from Air Products and Chemicals, Inc. or Matheson Gas Products. Commercial SF₄ was used without purification. In a more convenient modification of this procedure, dimethylaminosulfur trifluoride (methyl DAST), available from Carbolabs, Inc., can be substituted for SF₄. Dimethylaminosulfur trifluoride (1 mol) is mixed with dry ether and dimethylaminotrimethylsilane (2.1 mol) is added over a one-half–2 hr period with the temperature held below 20°C. After this addition, all other aspects of the run are carried out in the same manner as those of the procedure using SF₄.
4. The submitters obtained good yields without a glove bag, but the checkers encountered 30–40% yield reduction without this precaution. A drybox is also suitable. More than 3 days may be required for the reaction to go to completion if the laboratory temperature drops below 20°C.
5. Because tris(dimethylamino)sulfonium difluorotrimethylsilicate is very hygroscopic, it is best transferred in a dry atmosphere of nitrogen or argon (dry box or glove bag).
6. Even a brief exposure to moist air will cause the product to react with the available water vapor to give (Me₂N)₃S⁺ HF₂⁻ and (Me₃Si)₂O, and the presence of these products will appreciably lower the melting point. A melting point as low as 58–62°C can be obtained after a brief exposure.

3. Discussion

Tris(dimethylamino)sulfonium difluorotrimethylsilicate is a source of soluble organic fluoride ion of high anionic reactivity. Fluoride ion from this salt and other tris(dialkylamino)sulfonium difluorotrimethylsilicates has been used to displace halogen from carbon² and to cleave Si-O^{3,4,5,6,7} and Si-C=O^{7,8} bonds. Since these salts can be prepared in a rigorously anhydrous state, they have an advantage over quaternary ammonium fluorides, which usually contain some water. Tris(dialkylamino)sulfonium difluorotrimethylsilicates have also been used to prepare other sulfonium salts with high nucleophilic reactivity, including (R₂N)₃S⁺ enolates,⁶ phenoxide,⁵ cyanide, azides, and cyanates.²

This method has been used to prepare several different tris(dialkylamino)sulfonium difluorotrimethylsilicates, including salts with greater organic solubility such as the tris(diethylamino)sulfonium^{2,3} and tris(pyrrolidino)sulfonium² difluorotrimethylsilicates. The tris(dimethylamino)sulfonium salt, however, is highly crystalline and thus has an advantage in ease of preparation and purification over these other salts.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 8, 326

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References and Notes

1. E. I. du Pont de Nemours and Company, Central Research and Development Department, Experimental Station, Wilmington, DE 19898. Present address: Department of Chemistry,

Ursinus College, Collegeville, PA 19426.

2. Middleton, W. J. U.S. Patent 3940402, 1976; *Chem. Abstr.* **1976**, 85, P6388j.
 3. Noyori, R.; Nishida, I.; Sakata, J. *J. Am. Chem. Soc.* **1981**, 103, 2106.
 4. Noyori, R.; Nishida, I.; Sakata, J. *Tetrahedron Lett.* **1980**, 21, 2085.
 5. Noyori, R.; Nishida, I.; Sakata, J. *Tetrahedron Lett.* **1981**, 22, 3993.
 6. Noyori, R.; Nishida, I.; Sakata, J.; Nishizawa, M. *J. Am. Chem. Soc.* **1980**, 102, 1223.
 7. Brinkman, K. C.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1980**, 1260.
 8. Blakeney, A. J.; Johnson, D. J.; Donovan, P. W.; Gladysz, J. A. *Inorg. Chem.* **1981**, 20, 4415.
 9. Farnham, W. B.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, 103, 4608.
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

Sulfur(1+), tris(N-methylmethanaminato)-, difluorotrimethylsilicate(1-)

SF₄

ether (60-29-7)

nitrogen (7727-37-9)

carbon (7782-42-5)

Benzophenone (119-61-9)

Na (13966-32-0)

dimethylamine (124-40-3)

sulfur tetrafluoride (7783-60-0)

argon (7440-37-1)

hexamethyl-disiloxane (107-46-0)

Tris(dimethylamino)sulfonium difluorotrimethylsilicate (59218-87-0)

dimethylaminotrimethylsilane,
N,N-dimethylaminotrimethylsilane (2083-91-2)

phenoxide

dimethylaminosulfur trifluoride (3880-03-3)