# Application of Dialkylaminosulfur Trifluorides in the Synthesis of Fluoroorganic Compounds

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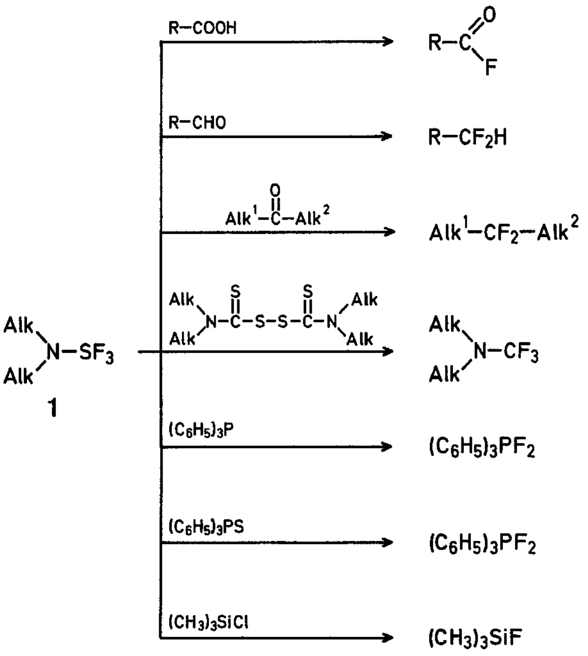
The chemical properties of dialkylaminosulfur trifluorides (**1**) are similar to those of sulfur(IV) fluoride. Thus the reactions of dialkylaminosulfur trifluorides with bis-[trimethylsilyl]-amines, bis-[trimethylsilyl]-carbodiimides, and other *N*,*N*-bis-trimethylsilyl derivatives yield compounds containing an S=N double bond[1]. Furthermore, dialkylaminosulfur trifluorides (**1**) as well as sulfur(IV) fluoride are good fluorinating agents. We have found that compounds **1** react readily with carboxylic acids, aldehydes, ketones, tetraalkylthiuram disulfides, triphenylphosphine, triphenylphosphine sulfide, and chlorotrimethylsilane to give fluorinated compounds.



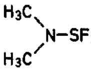
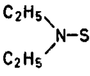
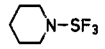
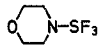
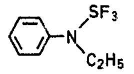
Fluorinations with dialkylaminosulfur trifluorides (**1**) are more convenient than those using sulfur(IV) fluoride. Fluorination reactions with sulfur(IV) fluoride are generally slow (reaction time: 7–14 hr); they usually begin at temperatures above 100° and require the use of pressure equipment; in many cases, a catalyst is necessary. The analogous fluorinations using dialkylaminosulfur trifluorides may be carried out in glass vessels at atmospheric pressure and at temperatures of 0–80°; the reactions are complete within 15–30 min, and the yields are better (except benzylidene fluoride) than those obtained using sulfur(IV) fluoride.

### Preparation of Dialkylaminosulfur Trifluorides (1a–d); General Procedure:

The solution of a dialkyl-trimethylsilylamine[7] (0.1 mol) in ether (50 ml) is added dropwise with stirring to a solution of sulfur(IV) fluoride (0.12 mol) in ether (150 ml) at −78°. The mixture is then allowed to gradually warm to 20° with stirring. Fluorotrimethylsilane, excess sulfur(IV) fluoride, and ether are evaporated and the residue is distilled at reduced pressure.

*N-Ethyl-N-phenylaminosulfur trifluoride* (**1e**) is prepared similarly.

**Table 1.** $N,N$-Disubstituted Aminosulfur Trifluorides (**1**) prepared from Secondary Amines and Sulfur(IV) Fluoride

| | Formula | Yield (%) | b.p./torr | $n_D^{20}$ | Elemental Analyses | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **1a** |  | 60 | 24–25°/12 (Ref.[8]) | 1.4018 | $C_2H_6F_3NS$<br>(133.6) | calc.<br>found | C 17.98<br>17.90 | H 4.53<br>4.52 | F 42.67<br>42.63 |
| **1b** |  | 70 | 43–44°/12 (Ref.[9]) | 1.4125 | $C_4H_{10}F_3NS$<br>(161.2) | calc.<br>found | C 29.80<br>29.76 | H 6.25<br>6.23 | F 35.36<br>35.37 |
| **1c** |  | 65 | 75–77°/12 (Ref.[1]) | 1.4515 | $C_5H_{10}F_3NS$<br>(173.2) | calc.<br>found | C 34.67<br>34.60 | H 5.82<br>5.82 | F 32.91<br>32.87 |
| **1d** |  | 68 | 41–42°/0.5 | 1.4538 | $C_4H_8F_3NOS$<br>(175.2) | calc.<br>found | C 27.42<br>27.40 | H 4.60<br>4.60 | F 32.54<br>32.53 |
| **1e** |  | 60 | 56–57°/0.3[a] | 1.4930 | $C_8H_{10}F_3NS$<br>(209.2) | calc.<br>found | C 45.92<br>45.70 | H 4.81<br>4.78 | F 27.24<br>27.37 |

[a] This compound slowly decomposed at 20°.

**Preparation of Carboxylic Acid Fluorides; General Procedure:**

The solution of a dialkylaminosulfur trifluoride (0.01 mol) in ether (10 ml) is added dropwise with stirring to a mixture of the carboxylic acid (0.01 mol) and ether (30 ml) at 0° (ice cooling). The mixture is then stirred at 20° for 15 min and the acyl fluoride isolated by crystallization or distillation.

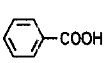
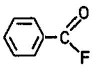
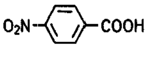
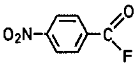
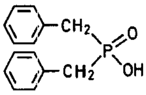
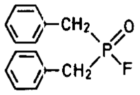
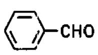
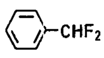
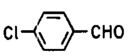
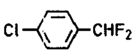
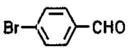
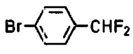
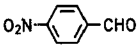
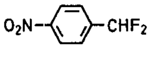
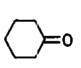
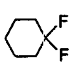
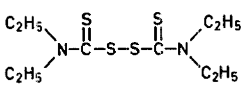
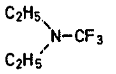
**Preparation of Benzylidene Fluorides; General Procedure:**

The mixture of an aromatic aldehyde (0.01 mol) and a dialkylaminosulfur trifluoride (0.01 mol) is heated carefully till incipient exothermic reaction, and then at 60° for 15 min. The resultant mixture is dissolved in carbon tetrachloride (15 ml) and the solution poured into ice water (20 ml) to remove the dialkylamine-$N$-sulfinyl fluoride formed in the reaction. The organic layer is dried with sodium sulfate, carbon tetrachloride is evaporated, and the residue distilled at reduced pressure.

**Preparation of *gem*-Difluoroalkanes; General Procedure:**

The dialkylaminosulfur trifluoride (0.01 mol) is mixed with the aldehyde or ketone (0.01 mol) with stirring and cooling. The mixture is then heated carefully till incipient exothermic reaction, whereupon the temperature is maintained at 80° for 30 min with stirring. The mixture is cooled to 20°, carbon tetrachloride (15 ml) is added, and the mixture poured into ice water (20 ml) to remove the dialkylamine-$N$-sulfinyl fluoride formed in the reaction. Carbon tetrachloride is evaporated and the residue distilled in vacuo.

**Table 2.** Fluoro Compounds obtained by Fluorination of Various Organic Compounds with Dialkylaminosulfur Trifluorides

| Educt | Product | Yield (%) | m.p. or b.p. | $n_D^{20}$ | Elemental Analyses | | | | |
|---|---|---|---|---|---|---|---|---|---|
|  |  | 85 | b.p. 43–44°/<br>12 torr (Ref.[2]) | 1.4960 | | | | | |
|  |  | 89 | m.p. 144–146° | | $C_7H_4FNO_3$<br>(169.2) | calc.<br>found | C 49.71<br>49.62 | H 2.38<br>2.24 | F 11.23<br>11.17 |
|  |  | 60 | m.p. 108–109° | | $C_{14}H_{14}FOP$<br>(248.2) | calc.<br>found | C 67.73<br>67.65 | H 5.68<br>5.65 | F 7.65<br>7.45 |
|  |  | 63 | b.p. 130–134°/<br>755 torr<br>(Ref.[2]) | | | | | | |
|  |  | 70 | b.p. 56–58°/<br>12 torr | 1.4895 | $C_7H_5ClF_2$<br>(162.6) | calc.<br>found | C 51.71<br>51.68 | H 3.10<br>3.09 | F 23.37<br>23.32 |
|  |  | 71 | b.p. 74–76°/<br>12 torr | 1.5045 | $C_7H_5BrF_2$<br>(207.0) | calc.<br>found | C 40.60<br>40.42 | H 2.43<br>2.41 | F 18.35<br>18.16 |
|  |  | 75 | b.p. 110–111°/<br>12 torr (Ref.[3]) | 1.5120 | | | | | |
| $n\text{-}C_6H_{13}\text{–}CHO$ | $n\text{-}C_6H_{13}\text{–}CHF_2$ | 65 | b.p. 120–121°/<br>755 torr<br>(Ref.[2]) | 1.3720 | | | | | |
|  |  | 55 | b.p. 98–99°/<br>755 torr<br>(Ref.[2]) | 1.3903 | | | | | |
|  |  | 70 | b.p. 71–72°/<br>755 torr<br>(Ref.[5]) | | | | | | |
| $(C_6H_5)_3P$ | $(C_6H_5)_3PF_2$ | 93 | m.p. 139–140°<br>(Ref.[6]) | | | | | | |
| $(C_6H_5)_3P{=}S$ | $(C_6H_5)_3PF_2$ | 83 | m.p. 139–140°<br>(Ref.[6]) | | | | | | |

**Diethyltrifluoromethylamine:**

Tetraethylthiuram disulfide (0.02 mol) is added portionswise with stirring to the dialkylaminosulfur trifluoride (0.03 mol) at 0–5°. The mixture is allowed to gradually warm to 20°. The product is isolated by distillation of the reaction mixture in vacuo; yield: 70%; b.p. 71–72°/755 torr[5].

**Difluorotriphenylphosphorane (Triphenylphosphine Difluoride):**

Method A; from Triphenylphosphine: The solution of a dialkylaminosulfur trifluoride (0.01 mol) in ether (15 ml) is added dropwise to a stirred solution of triphenylphosphine (0.01 mol) in ether (20 ml) at 20°. The precipitated product is isolated by filtration and recrystallized from benzene; yield: 93%; m.p. 139–140°.

Method B; from Triphenylphosphine Sulfide: The solution of a dialkylaminosulfur trifluoride (0.01 mol) in benzene (10 ml) is added dropwise to a stirred solution of triphenylphosphine sulfide (0.01 mol) in benzene (15 ml). The mixture is refluxed for 15 min, cooled, and the product isolated by filtration; yield: 82%; m.p. 139–140°.

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[1] S. P. von Halasz, O. Glemser, *Chem. Ber.* **104**, 1247 (1971).

[2] W. Hasek, W. C. Smith, *J. Amer. Chem. Soc.* **82**, 543 (1960).

[3] N. V. Kondratenko, G. I. Matyushicheva, L. M. Yagupolskii, *Zh. Org. Khim.* **6**, 1423 (1970).

[4] A. Henne, E. Plueddeman, *J. Amer. Chem. Soc.* **65**, 587 (1943).

[5] R. Hardek, W. C. Smith, *J. Amer. Chem. Soc.* **83**, 3422 (1961).

[6] W. C. Smith, *J. Amer. Chem. Soc.* **82**, 6176 (1960).

[7] K. Itoh, S. Sakai, I. Ishii, *J. Org. Chem.* **31**, 3948 (1966).

[8] G. Demitras, A. McDiarmid, *Inorg. Chem.* **6**, 1903 (1967).

[9] S. P. von Halasz, O. Glemser, *Chem. Ber.* **103**, 594 (1970).