

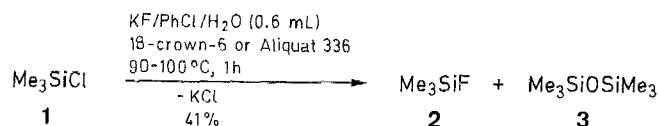
A One-Pot Synthesis of Trimethylsilyl Fluoride¹

E. V. Dehmlow,* U. Fastabend, M. Keßler

Fakultät für Chemie, Universität Bielefeld, Universitätsstr. 25, D-4800
Bielefeld 1, Federal Republic of Germany

Trimethylsilyl fluoride (**2**) is prepared in a most simple way from trimethylsilyl chloride and solid potassium fluoride in the presence of a phase-transfer catalyst and a few drops of water.

Trimethylsilyl fluoride (**2**) is formed and lost in many protective group cleavage reactions, but if it is needed as reagent relatively complicated procedures are advocated: treatment of trimethylsilyl chloride (**1**) with antimony trifluoride,² or intermediate formation of very reactive trimethylsilyl triflate.³ We record here a much simpler approach, which we found in an attempt to improve the preparation of trimethylsilyl iodide.⁴ The energetically "uphill" process from the chloride by phase-transfer catalysis in a non-polar medium proved to be inefficient, whereas the "downhill" product (**2**) could be prepared easily.



When heating trimethylsilyl chloride (**1**) with solid potassium fluoride in the presence of 18-crown-6 and a few drops of water in chlorobenzene, **2** can be distilled directly into a cold trap. These facts are pertinent to the execution of the reaction:

Highly dried potassium fluoride (650 °C) gives almost no product. Apparently a small surface layer of water on the crystals facilitates the anion exchange.⁵ Maximum yield is around 40% because of the formation of hexamethyldisiloxane (**3**).

Too much water results in the formation of lower yields because more **3** is formed.

Aliquat 336⁶ is almost as efficient a catalyst as 18-crown-6.

Trimethylsilyl Fluoride (**2**):

Dry KF (10 g, 0.17 mol), trimethylsilyl chloride (20 g, 0.18 mol), 18-crown-6 (200 mg, 0.76 mmol) and H₂O (0.6 ml) are heated in chlorobenzene (70 mL) under intensive stirring at 90–100 °C in a two-necked flask with a reflux condenser being connected to a cold trap cooled to between –50 °C and –60 °C. After 1 h, more KF (10 g) and H₂O (0.6 mL) are added, and this is repeated after the second hour. The liquid collected in the cold trap is purified by trap-to-trap distillation. Bp 15–16 °C (Lit.⁴ 15–16 °C). Yield: 6.9 g (41%).

This work was supported in part by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Received: 23 July 1988

- (1) Applications of Phase-Transfer Catalysis, Part 44. Part 43: Dehmlo, E. V., Vehre, B. *New Journ. Chem.*, in press.
- (2) West, R., Gornowicz, G. A. *J. Organomet. Chem.* **1971**, 28, 25.
- (3) Della, E. W., Tsanaktsidis, J. *Synthesis* **1988**, 407.
- (4) Sakurai, H., Shirahata, A., Sasaki, K., Hosomi, H. *Synthesis* **1979**, 740.
- (5) The influence of water traces on solid/liquid fluoride phase-transfer catalysis is well documented:
Dermeik, S., Sasson, Y. *J. Org. Chem.* **1985**, 50, 879.
Dermeik, S., Sasson, Y. *J. Fluorine Chem.* **1983**, 22, 431.
Tordeuk, T., Wakselman, C. *Synth. Commun.* **1982**, 12, 513.
Alper, H., Damude, L. C. *Organometallics* **1982**, 1, 579; *C. A.* **1982**, 96, 143040.
Bram, G., Loupy, A., Sansoulet, J. *Isr. J. Chem.* **1985**, 26, 291.
Dehmlo, E. V., Rathis, H.-C. *J. Chem. Res.*, in press.
- (6) Technical methyltrioctylammonium chloride.