A Convenient Synthesis of Trimethylsilyl Fluoride

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Trimethylsilyl fluoride **1** is conveniently prepared by the reaction of trimethylsilyl trifluoromethanesulfonate with potassium fluoride in dimethylformamide containing 18-crown-6 ether.

A problem encountered in the synthesis of alkyltrimethylsilanes from coupling of organolithium reagents with trimethylsilyl chloride is the formation of the α-metallated silane, $LiCH_2Si(CH_3)_2Cl$, via a competing acid–base reaction. The situation becomes acute when the alkyllithium is hindered. In these cases West and Gornowicz[1,2] have demonstrated that yields of the required silanes can be increased substantially by using trimethylsilyl fluoride **(1)** as the electrophilic silylating reagent in what is believed to be a frontside displacement process.

$$R{-}Li + \underset{\mathbf{1}}{(CH_3)_3Si{-}F} \xrightarrow[15\text{-}30\ ^\circ C]{\text{Refs. 1,2, pentane/TMEDA}} R{-}Si(CH_3)_3 + LiF$$

Faced with the objective of synthesising a series of *tertiary* alkyltrimethylsilanes recently, we decided to employ the West procedure. Trimethylsilyl fluoride **(1)** is available commercially, but is expensive. It is also accessible by treatment of trimethylsilyl chloride with antimony trifluoride,[3] but this procedure suffers from the disadvantage that trimethylsilyl chloride itself is reasonably volatile and tends to contaminate the product. In the search for a comparable substitution process that would obviate these difficulties, we were attracted to the use of trimethylsilyl trifluoromethansulfonate (trimethylsilyl triflate), whose synthesis has been reported recently to be readily performed and to proceed in high yield.[4-6]

We find that conversion of the triflate to the fluoride **1** can be effected in excellent yield by treatment with potassium fluoride in dimethylformamide in the presence of 18-crown-6 ether. In the absence of the crown ether the rate is slowed considerably. Because trimethylsilyl fluoride is the only volatile substance present, it can be removed readily and collected in a cold trap in a high state of purity.

This procedure thus represents a convenient, reasonably inexpensive, two-step preparation of **1** from tetramethylsilane.

$$(CH_3)_4Si \xrightarrow{\text{Ref. 4}} (CH_3)_3Si{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}CF_3 \xrightarrow[90\ \%]{\text{KF/DMF/18-crown-6, r.t.}\rightarrow 70\ ^\circ C,\ 2\ h} \underset{\mathbf{1}}{(CH_3)_3Si{-}F}$$

Trimethylsilyl Fluoride (1):

Trimethylsilyl trifluoromethanesulfonate (34 g, 0.15 mol), prepared from tetramethylsilane as described,[4] is added over 30 min to a rapidly stirred suspension of dry KF (27 g, 0.47 mol) in DMF (75 mL) containing 18-crown-6 ether (4.5 g, 0.017 mol). The temperature rises to 40 °C and **1** is removed by a gentle stream of nitrogen and collected in a cold trap (−78 °C). When all of the triflate has been added, the mixture is warmed to 70 °C for 2 h. Distillation of the product gives **1** as a colourless liquid; yield: 12.4 g (90%); bp 15–16 °C (Lit.[3] bp 16.4 °C).

^{1}H-NMR (CCl_4, TMS): $\delta = 0.15$ (d, $J = 7.2$ Hz) (cf. Ref. 7).

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