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Trimethyltin fluoride: A new fluorinating reagent for the preparation of silicon fluorides [1]

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Abstract

A new fluorinating reagent for the preparation of silicon fluorides is described. The preparation of Me_2SiF_2, $(CH_2{=}CH)MeSiF_2$, $EtSiF_3$, $CH_2{=}CHSiF_3$, *n*-$PrSiF_3$, *n*-$HexSiF_3$($Hex = C_6H_{13}$) and $PhSiF_3$ using Me_3SnF is reported. The products are formed in high yield. The resulting Me_3SnCl can be easily recovered and again converted to the fluorinating reagent.

Keywords: Fluorinating reagent; Silicon fluorides; Recycling

1. Introduction

Silicon fluorides are a well established class of compounds and numerous reviews can be found in the literature. A most recent compilation appeared in the Gmelin handbook containing SiF compounds and their appropriate references [1,2]. Recently, we reported in a short note on the preparation of SiF_4 and Me_3SiF using Me_3SnF **1** as a fluorinating reagent [3]. An almost quantitative conversion was observed. Moreover, Me_3SnF turned out to be an efficient reagent for the preparation of organometallic fluorides [4]. Herein, we report on the preparation of several di- and trifluorides of silicon.

2. Results and discussion

Me_3SnF (**1**) has been known since 1918 [5–7] and has a polymeric structure containing Sn–F–Sn intermolecular bonds. It is easily prepared from the corresponding chloride using NaF in aqueous solution. Prior to use **1** should be thoroughly dried in vacuo. Otherwise oxofluorides are formed as by-products in the reaction mixture.

The difluorides Me_2SiF_2 (**2**) and $(CH_2{=}CH)MeSiF_2$ (**3**) have been prepared without using any solvents. The products are recovered by trap-to-trap distillation. The yields are almost quantitative (see Table 1). The trifluorides $EtSiF_3$ (**4**), $CH_2{=}CHSiF_3$ (**5**), *n*-$PrSiF_3$ (**6**), *n*-$HexSiF_3$ (**7**) and $PhSiF_3$ (**8**) are formed in high yields using the corresponding chlorides and Me_3SnF in a molar ratio of 1:3. The nonoptimized yields vary between 86% and 96%. Only in the case of

Table 1
Numbering scheme, yields, and physical data of compounds **2–8**

Reactant	Product	Compound no.	Yield (%)	bp (°C)	MS (EI)	^{19}F NMR $\delta(C_6D_6)$ ppm[a]	J(F–Si) (Hz)
Me_2SiCl_2	Me_2SiF_2 [8]	**2**	97	2	96	32.55	289.6
$(CH_2{=}CH)MeSiCl_2$	$(CH_2{=}CH)MeSiF_2$	**3**	97	24	108	25.93	286.7
$EtSiCl_3$	$EtSiF_3$ [9]	**4**	96	−4	114	22.27	283.7
$CH_2{=}CHSiCl_3$	$CH_2{=}CHSiF_3$ [10]	**5**	94	−10	112	20.35	263.2
n-$PrSiCl_3$	*n*-$PrSiF_3$ [1,2,9]	**6**	94	25	128	24.86	285.0
n-$HexSiCl_3$	*n*-$HexSiF_3$ [1,2]	**7**	88	92	170	25.59	286.0
$PhSiCl_3$	$PhSiF_3$ [1,2,11]	**8**	86	101	162	21.85	268.0

[a] External standard C_6F_6.

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[1] Dedicated to Professor K. Kühlein on the occasion of his 60th birthday.

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$PhSiF_3$ was a small amount of nonvolatile solvent added for a smooth reaction.

The compounds have been characterized by EI (electron ionisation) mass spectroscopy and ^{19}F NMR spectroscopy. Compounds **2–8** exhibit their molecular ions as the highest mass peak (see Table 1). The ^{19}F NMR chemical shifts are in the range of 20–32 ppm using C_6F_6 as an external standard.

These few experiments demonstrate that almost all organometallic halides of silicon may be converted to the corresponding fluorides using Me_3SnF or any other R_3SnF compound as a fluorinating reagent.

3. Experimental section

All experiments were performed under a dry nitrogen atmosphere using a glass reactor equipped with a Teflon valve. Me_3SnF was synthesized by published methods [5–7] and sublimed at 100°C/10^{-4} mbar prior to use. The organometallic silicon chlorides were obtained from Aldrich, ABCR, Fluka and Janssen Chimica.

^{19}F NMR spectra were recorded by means of a Bruker AM 250 instrument using TMS and C_6F_6 as external standards. Mass spectroscopic analyses were performed with a Finnigan MAT 8230 instrument. IR spectra were recorded in the gas phase using a BIO-RAD FTS-7 instrument.

4. Preparations

Me_2SiF_2 (**2**): 3.84 g (21 mmol) Me_3SnF were placed in a 30-ml reactor. After evacuation of the reactor on a vacuum line, 1.29 g (10 mmol) of Me_2SiCl_2 were condensed onto the Me_3SnF under cooling with liquid nitrogen. The reactor was slowly warmed to room temperature, kept at this temperature for 30 min, and the resulting product **2** purified by trap-to-trap distillation. Yield 0.9 g (97%). IR 2984, 1273, 947, 913, 827, 816, 331 cm^{-1}.

$(CH_2{=}CH)MeSiF_2$: (**3**) 3.84 g (21 mmol) Me_3SnF and 1.41 g (10 mmol) $(CH_2{=}CH)MeSiCl_2$ were reacted as described for **2**. Yield 1.05 g (97%) of **3**. IR 2985, 1604, 1415, 1276, 1015, 935, 888, 811, 629, 403, 318 cm^{-1}.

$EtSiF_3$ (**4**): 5.7 g (31 mmol) of Me_3SnF were reacted with 1.64 g (10 mmol) of $EtSiCl_3$ to yield 1.1 g (96%) of **4**. IR 2985, 1265, 993, 955, 890, 877, 420, 389, 355 cm^{-1}.

$CH_2{=}CHSiF_3$ (**5**): 5.7 g (31 mmol) Me_3SnF and 1.61 g (10 mmol) $CH_2{=}CHSiCl_3$ were reacted to yield 1.05 g (94%) of **5**. IR 2985, 1610, 1420, 1006, 958, 880, 542, 424, 359 cm^{-1}.

n-$PrSiF_3$ (**6**): To 5.7 g (31 mmol) Me_3SnF were added 1.77 g (10 mmol) *n*-$PrSiCl_3$ using a syringe. 1.2 g (94%) of **6** were obtained after distillation. IR 2973, 1468, 1227, 1069, 1021, 947, 905, 872, 439, 367, 330 cm^{-1}.

n-$HexSiF_3$ (**7**): 5.7 g (31 mmol) of Me_3SnF were placed in a 30-ml reactor cooled with liquid nitrogen under an atmosphere of dry nitrogen and finally 2.2 g (10 mmol) of *n*-$HexSiCl_3$ were added using a syringe. The reactor is closed and slowly warmed to 50°C, and kept at this temperature for 30 min. After cooling to room temperature and trap-to-trap distillation, 1.5 g (88%) of **7** were obtained. IR 2971, 2940, 1199, 1029, 971, 890, 734, 481, 428, 389 cm^{-1}.

$PhSiF_3$ (**8**): 5.7 g (31 mmol) of Me_3SnF and methylnaphthalin (5 ml) were placed in a reactor, which was then cooled with liquid nitrogen, and 2.11 g (10 mmol) of $PhSiCl_3$ were added. 1.4 g (86%) of **8** were obtained after trap-to-trap distillation. IR 3083, 1598, 1434, 1140, 949, 854, 784, 741, 696 cm^{-1}.

Recycling of Me_3SnF: After removal of the products the residue containing Me_3SnCl and a small amount of Me_3SnF is treated with water. Me_3SnF is not dissolved and separated by filtration. The resulting solution is treated with excess of a 15% solution of KF. Immediately Me_3SnF precipitates and is recovered by filtration and washed three times with water. Both quantities of Me_3SnF are combined, dried and finally sublimed in vacuo.

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