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Note

A Convenient Preparation of Organofluorosilanes. A Possible Involvement of Tetracoordinated Siliconium Ion Pairs*

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Organofluorosilanes and their complexes with weakly coordinating fluorine containing salts are frequently used in mechanistic studies of organosilicon compounds.[1] Examples include studies of nucleophilic attack at silicon[2] and attempts to generate silicenium ions of type R_3Si^+.[3,4] Silyl fluorides are also used in key steps in the synthesis of sterically hindered tetraalkylsilanes[5,6] or of highly congested trialkylsilyl halides (chlorides, bromides and iodides).[5,7]

In view of these important applications, it is surprising that until very recently the available synthetic methods for preparing silyl fluorides were limited and used quite inconvenient chemicals, procedures and reaction conditions. Thus, organofluorosilanes were prepared by the treatment of the corresponding silyl halides with anhydrous hydrofluoric acid,[8] antimony trifluoride,[9] or zinc fluoride.[7,10] Only one report in the older literature indicated that triphenylfluorosilane can be prepared under much milder conditions. *i.e.*, by the reaction of the corresponding chloride with sodium fluoroborate in acetone at room temperature.[11] The lack of simple straightforward methods for preparing silyl fluorides is especially intriguing in view of the fact that the Si–F bond is the strongest known bond to silicon, and consequently fluorosilanes are expected to exhibit high thermodynamic stability.[12]

Progress towards a more simple synthesis of fluorosilanes was made in recent years. Bassindale and Stout noted that the reaction of Me_3SiCl with silver tetrafluoroborate yields trimethylfluorosilane[13a] (not trimethylsilyl tetrafluoroborate as previously suggested).[13b] Della and Tsanaktidis reported in 1988 that silyl triflates react at 25–70 °C with potassium fluoride in DMF in the presence of 18-crown-6 to produce the corresponding silyl fluorides.[14] However, this procedure suffers from the disadvantage that silyl triflates are generally quite expensive and only a few are com-

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* Dedicated to Professor Dionis E. Sunko on the occasion of his seventieth birthday.

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mercially available. More recently Olah *et al.*[15] reported on the high yield fluorination of triorganylsilanes with nitrosonium tetrafluoroborate in acetronitrile. White *et al.*[16] have reported in 1991 that the reaction of Me_3SiCl or Me_3SiI with $AgBF_4$ or $AgSiF_6$ in acetonitrile produces the corresponding silyl fluorides even at –50 °C. These recently reported methods[14-16] are significantly more facile and convenient than the older methods,[8-10] but their generality has not yet been established.

We wish to report that chlorosilanes react with sodium tetrafluoroborate or with sodium fluoride in acetonitrile at room temperature to produce the corresponding silyl fluorides in very high yield (Eq. 1). This halogen-exchange reaction presents a very convenient and efficient method for the preparation of a variety of organofluorosilanes and some representative examples are presented in Table I.

$$R_3SiCl \xrightarrow[CH_3CN]{NaF\ (or\ NaBF_4)} R_3SiF + NaCl\downarrow\ (+\ CH_3CN{:}BF_3) \tag{1}$$

(1) Reaction (1) is best carried out by mixing the chlorosilane with 3 eqivalents of $NaBF_4$ in acetonitrile at room temperature. Sodium chloride immediately begins to precipitate and the reaction is complete after 1–3 days.[17] The fluorosilane can be isolated from the reaction mixture by aqueous workup. The fluoride exchange reactions are essentially quantitative (based on gas-chromatography and ^1H NMR analyses), and no detectable by-products are formed. The halogen-exchange reaction may also be carried out with sodium fluoride as the source for fluoride ions, but in this case it proceeds at a slower rate than with $NaBF_4$. The addition of chloroform to the acetonitrile solvent, which might be necessary to solubilize the inorganic fluoride salt, also lowers the

TABLE I

The preparation of fluorosilanes by the reaction at 25 °C of chlorosilanes with $NaBF_4$ or NaF in acetonitrile.

substrate	product	reaction time (days)	yield[a]	^1H NMR (fluorosilane)
$(t\text{-}Bu)_2SiHCl$	$(t\text{-}Bu)_2SiHF$	2^b, 3^c, 5^d	> 97	1.10 (d, 18H, $J_{H-F} = 1.1$ Hz); 4.22 (d, 1H, $J_{H-F} = 48$ Hz)
$t\text{-}Bu(CH_3)_2SiCl$	$t\text{-}Bu(CH_3)_2SiF$	2^b, 3^c, 3^d,7^e	> 97	0.23 (d, 6H, $J_{H-F} = 7.6$ Hz); 0.99 (d, 9H, $J_{H-F} = 0.7$ Hz)
$Tx(CH_3)_2SiCl^f$	$Tx(CH_3)_2SiF$	1^b	> 97	0.38 (d, 6H, $J_{H-F} = 8$ Hz); 1.0 (m, 12H), 1.6(m, 1H);
Ph_2CH_3SiCl	Ph_2CH_3SiF	2^b	> 97	0.62 (d, 3H, $J_{H-F} = 8$ Hz); 7–7.4 (m, 10H);
$Ph_2(t\text{-}Bu)SiCl$	$Ph_2(t\text{-}Bu)SiF$	2^b	> 97	1.22 (s, 9H); 7.2–7.4 (m, 6H); 7.5–7.7 (m, 4H);
$Ph(CH_3)_2SiCl$	$Ph(CH_3)_2SiF$	2^b	> 97	0.2 (d, 6H, $J_{H-F} = 7.0$ Hz); 7.00–7.45 (m, 5H)
$(t\text{-}Bu)_3SiCl$	–	6^b (reflux)	< 3	–
$(CH_3)_3SiCH_2Cl$	–	3^b	< 3	–

a. Based on gas-chromatography and ^1H NMR.
b. With $NaBF_4$.
c. With NaF.
d. With $NaBF_4$ in 10% CH_3CN: 90% $CHCl_3$.
e. With $NaBF_4$ in 2% CH_3CN: 98% $CHCl_3$.
f. Tx = Thexyl = $H(CH_3)_2C(CH_3)_2C$ –

reaction rate. The highly congested tri-*tert*-butylsilyl chloride failed to undergo fluoride exchange even under reflux for six days, most likely because of the high steric congestion around the silicon atom. However, other relatively bulky chlorosilanes with somewhat smaller steric congestion, such as $Ph_2(t\text{-}Bu)SiCl$ did undergo the fluoride exchange reaction (Table I). Interestingly, trimethyl(chloromethyl)silane, remains unchanged under our reaction conditions, while it was reported that with KF in the presence of 18-crown-6 (in toluene at 70 °C) this compound undergoes fluorination accompanied by methyl rearrangement to produce $CH_3CH_2Si(CH_3)_2F$.[18]

We believe that the method presented here for the preparation of silyl fluorides is superior to the available literature methods, because of its convenience, simplicity, mild conditions and the fact that it uses relatively inexpensive and easy-to-handle chemicals. Furthermore, many chlorosilanes which can serve as precursors are commercially available.

The high strength of the Si–F bond which is formed in the reaction supplies the thermodynamic driving force for the halogen-exchange process. Thus, the average strength of a Si–F bond is 170 kcal mol^{-1}, compared to only 140 kcal mol^{-1} for the Si–Cl bond.[12] The fact that NaCl is practically insoluble in acetonitrile (or acetonitrile-chloroform mixtures) probably also assists the reaction (see below).

Our present observations support a two-step mechanism (Eq. 2) for the halogen exchange reaction (Eq. 1), according to which an electrophilic intermediate **1** is formed in the rate determining step. Electrophilic coordination of sodium ions to chloride ions probably assists the ionization. In the ion-pair **1** the silyl moiety is coordinated to an acetonitrile molecule, and it can be regarded as a complex between a silicenium ion (R_3Si^+) and acetonitrile. *Ab initio* calculations at the 6-31G*//3-21G$^{(*)}$ level[19] estimate that the dissociation energy of the complex **1** is surprisingly high, *i.e.*, 50.5 kcal mol^{-1}, compared to 42.0 kcal mol^{-1} for the $[Me_3Si\text{-}OH_2]^+$ complex.[20] The first step of the reaction is made practically irreversible by the fact that the chloride ions are »captured« by the sodium ions, forming the insoluble sodium chloride which precipitates. In the second, fast step of the process, the siliconium ion intermediate **1** collapses to product by attack of F^- or of BF_4^-.

$$R_3SiCl \xrightarrow[NaBF_4]{slow} \underset{\mathbf{1}}{[R_3Si{-}N{\equiv}C{-}CH_3]^+\,[BF_4^-]} + NaCl \xrightarrow{fast} R_3SiF + CH_3C{\equiv}N{:}BF_3 \quad (2)$$

A similar mechanism and the involvement of a silicenium ion-acetonitrile complex **1** were proposed in similar reactions.[16,21] At this stage we cannot, however, totally exclude a more simple one-step mechanism, involving direct nucleophilic attack of fluoride ion or of the tetrafluoroborate ion on the silicon atom of the chlorosilane. This mechanistic question may be resolved by kinetic studies and by using optically active silyl chlorides. Such experiments are underway in our laboratory.

EXPERIMENTAL

NMR spectra were obtained on a Bruker AM 200 MHz and gas-chromatography analyses were carried out on a Packard 427 instrument on a 25M capillary Carbowax column. $NaBF_4$, NaF, and all the chlorosilanes used in this work (except $t\text{-}Bu_3SiCl$) are commercialy avaliable from Aldrich Chemicals. Tri-*t*-butylchlorosilane was prepared following a literature procedure.[4] Acetonitrile was refluxed for 2 hrs over CaH_2 and then distilled from fresh CaH_2 and was used immediately. $CHCl_3$ was dried over molecular sieves 4A, and passed through a basic alumina column into the reaction vessel. All fluorosilanes obtained were characterized by ^1H NMR (Table I) and by gas-chromatography.

A typical procedure for reaction (1) is as follows:

t-*Butyldimethylsilyl fluoride:*

$NaBF_4$ (540 mg, 3×10^{-3} mol) was added to 5 ml of dry freshly distilled CH_3CN. The fluoride salt does not fully dissolve. *t*-Butylmethylchlorosilane (150 mg, 1×10^{-3} mol) was added to the reaction mixture. A white precipitate of NaCl appears immediately, and thickens with time. After stirring for 2 days at room temperature, the product is extracted from the mixture into ether, and the ethereal solution is washed twice with 10 ml portions of water. The ethereal solution is dried over $MgSO_4$, and the solvent is evaporated. The product consists according to GC and NMR of more than 97% of *t*-butyldimethylfluorosilane (in practice no other products were observed.). The product can be further purified by distillation.

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Note Added in Proofs. After this work was submitted for publication we learned that Kira, Hino and Sakurai observed by NMR complexes, similar to **1**, between silicenium ions and ethers, *i. e.*, of the type $[R_3Si{-}OEt_2]^+ [TFPB]^-$. See: M. Kira, T. Hino, and H. Sakurai, *J. Amer. Chem. Soc.*, in press (1992). We thank these authors for discussions and for a reprint of their paper.

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SAŽETAK

Novi postupak priprave organofluorsilana. Indicije za uključenje tetrakoordiniranih silikonium ionskih parova.

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Opisan je novi, vrlo efikasan postupak priprave sterički nesmetanih organofluorsilana polazeći od odgovarajućih organosililklorida. Kao fluorirajući agens koristi se $NaBF_4$ ili NaF. Ukratko je diskutiran mehanizam reakcije.