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FC(SiMe$_3$)$_3$ and FC(SiMe$_3$)$_2$SnBu$_3$: a novel C$_1$ building block for fluoro olefins

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Abstract

Reaction of fluorotris(trimethylsilyl)methane and aldehydes is catalyzed by KF/18-Cr-6 to give 1,3-disubstituted 2-fluoro-2-propen-1-ols in one pot. On the other hand, Sn–Li exchange of bis(trimethylsilyl)-fluoro(tributylstannyl)methane with BuLi and subsequent treatment with an aldehyde afforded 1-fluoroalkenyltrimethylsilanes in moderate to good yields.

Keywords: fluorine; polysilylmethanes; silicon; fluoro olefins.

Since poly(triorganosilyl)methanes are useful precursors for vinylsilanes which are highly potential intermediates,[1] fluoropoly(triorganosilyl)methanes should be reliable precursors of fluorinated vinylsilanes which could be transformed in various ways into fluoro olefins[2] that are attracting much attention in the field of liquid crystalline materials, peptide isosteres, and enzyme inhibitors.[3] However, such fluorine-containing C$_1$ building blocks have remained yet to be explored.

We report herein that fluorotris(trimethylsilyl)methane (**1**) reacts with 2 mol of an aromatic aldehyde in the presence of KF/18-crown-6 to give 1,3-disubstituted 2-fluoro-2-propen-1-ols (**2**). In addition, treatment of bis(trimethylsilyl)fluoro(tributylstannyl)methane (**3**) with BuLi followed by addition of an aldehyde produces 1-fluoroalkenylsilane **4** in moderate to good yields (Scheme 1).

At first we examined fluoride ion-catalyzed reaction of **1** with benzaldehyde. Treatment of CFBr$_3$ (1 mol) with BuLi (3.2 mol) in the presence of Me$_3$SiCl (3.2 mol) in THF–Et$_2$O (2:1) at −130°C gave **1** in 97% yield.[4] To a THF solution of **1** (1.0 mol) and PhCHO (1.0 mol) was added Bu$_4$NF (TBAF, 0.1 mol) at 0°C, and the reaction mixture was allowed to warm to room temperature. Work-up and purification by silica gel chromatography gave in 35% yield 2-fluoro-1,3-diphenyl-2-propen-1-ol (**2a**, *E*:*Z*=66:34), a product derived from 1 mol of **1** and 2 mol of PhCHO (Table 1, run 1).[5] When 2.5 mol of PhCHO was used, the yield of **2a** slightly improved (run 2). The formation of the 1:2 adduct was much improved with a KF/18-Cr-6 reagent system (runs 5 and 6). The conditions of run 6[6] could

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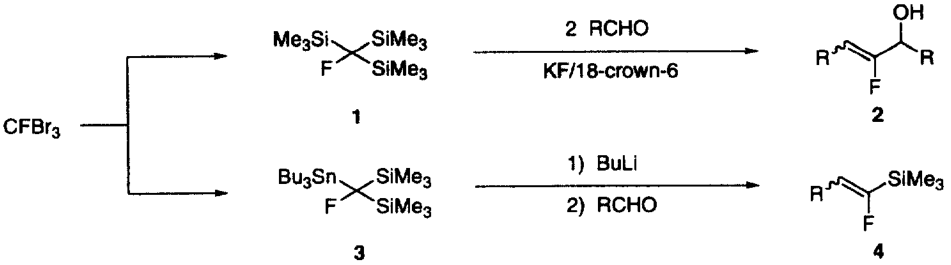


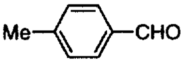
Scheme 1.

be applied to 4-MeC_6H_4CHO, 4-$MeOC_6H_4CHO$, 4-$C_6H_5C_6H_4CHO$, and 1-naphthaldhyde (vide infra), while cinnamaldehyde, 3-phenylpropanal, *p*-CF_3-C_6H_4CHO, *p*-CN-C_6H_4CHO, and C_6F_5CHO did not give the corresponding products. It is noteworthy that no alkenylsilane **4** could be isolated and that further carbonyl addition occurred smoothly in contrast to the fact that, in the presence of a fluoride catalyst, $(Me_3Si)_3CH$ reacts with an aldehyde, as reported, to give vinylsilanes $RCH{=}CH(SiMe_3)$.[1f]

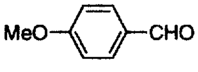
Table 1
Fluoride ion-catalyzed reaction of **1** with aldehydes

Run	PhCHO (mol)	F^- (mol)	Solvent	Temp	Yield (%)	*E* : *Z* [a]
1	1.0	Bu_4NF (0.1)	THF	0 °C to rt	35	66 : 34
2	2.5	Bu_4NF (0.1)	THF	0 °C to rt	46	67 : 33
3	2.5	Bu_4NF (0.5)	THF	0 °C to rt	12	63 : 37
4	2.5	KF/18-Cr-6 (0.1)	DMF	rt	26	56 : 44
5	2.5	KF/18-Cr-6 (0.5)	DMF	rt	72	66 : 34
6	2.5	KF/18-Cr-6 (1.0)	DMF	rt	74	65 : 35

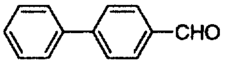
[a] Stereochemistry was assigned on the basis of ^{19}F NMR spectroscopy: $^3J_{H\text{-}F}$ = 20.4 Hz for (*E*)-isomer and 39.3 Hz for (*Z*)-isomer.



70% (68 : 32)



78% (65 : 35)



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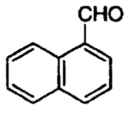
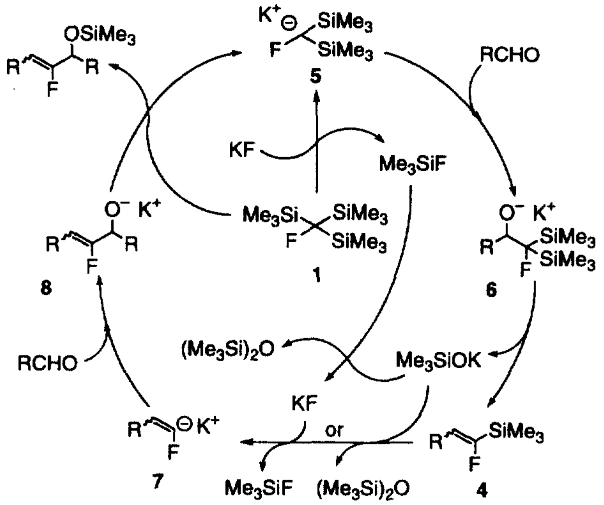


65% (61 : 39)

A reaction mechanism for the formation of **2** is tentatively proposed in Scheme 2.[1f] First, KF should activate **1** to generate fluoromethyl anion reagent **5** which reacts with an aldehyde, giving rise to potassium alkoxide **6**. The alkoxide undergoes the Peterson elimination to afford alkenylsilane **4** and Me_3SiOK which would react with Me_3SiF to produce KF and $Me_3SiOSiMe_3$. The alkenylsilane **4** is activated by the reproduced KF to generate alkenylpotassium reagent **7** which reacts with another aldehyde to give adduct **8**. Alternatively, activation of **4** by Me_3SiOK or alkoxide **8** might also be plausible. Finally, silicon–potassium exchange between adduct **8** and starting silane **1** affords a silyl ether of **2** and regenerates anion **5**.

Since the fluoride ion-catalyzed reaction of **1** with aldehydes gives fluorinated allylic alcohols in one pot, we examined an alternative route for the generation of a bis(trimethylsilyl)fluoromethyl anion reagent from **3** and its aldehyde addition in order to synthesize fluoroalkenylsilanes **4**, potential intermediates applicable to various kinds of transformations.[2] Treatment of $CFBr_3$ (1 mol) with BuLi (2.0 mol) in the presence of Me_3SiCl (2.0 mol) in THF–Et_2O (2:1) at −130°C followed by the addition of Bu_3SnCl (1.0 mol) and *s*-BuLi (1.0 mol) in this order at −130°C gave **3** in 67% yield.[7] Tin–lithium exchange[8] of **3** with BuLi in THF at −78°C followed by treatment with an aldehyde at −98°C[9] gave 1-



Scheme 2. Proposed mechanism

fluoroalkenylsilanes **4** in moderate to good yields as summarized in Table 2.[10,11] To this transformation, aldehydes that failed to give **2** were applicable (**4e**–**h**). The configuration of the resulting olefins varied markedly depending on the substituent R; the reason is not clear at present.

Table 2
Synthesis of **4** from **3**

RCHO	4	Yield (%)	*E* : *Z*
PhCHO	**4a**	51	24 : 76
4-Me-C_6H_4CHO	**4b**	69	24 : 76
4-MeO-C_6H_4CHO	**4c**	98	15 : 85
4-C_6H_5-C_6H_4CHO	**4d**	87	28 : 72
(*E*)-PhCH=CHCHO	**4e**	86	27 : 83
$Ph(CH_2)_2CHO$	**4f**	75	93 : 7
C_6F_5CHO	**4g**	53	>99 : <1
4-CF_3-C_6H_4CHO	**4h**	98	57 : 43

In summary, we have demonstrated that $FC(SiMe_3)_3$ and $FC(SiMe_3)_2SnBu_3$, both readily available from $CFBr_3$, can be conveniently transformed into fluoro olefins by activation and aldehyde addition. Elucidation of the origin of the stereoselectivity and synthetic applications are in progress.

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4. Compound **1** (bp 80°C/3 mmHg) ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.16 (s, 27H); ^{19}F NMR (188 MHz, $CDCl_3$) δ −263.7; MS (70 eV) *m/z* 252 (M^++2, 0.1), 251 (M^++1, 0.1), 250 (M^+, 0.6), 235 (20), 143 (100). HRMS Found: M^+, 250.1404. Calcd for $C_{10}H_{27}FSi_3$: *m/z* 250.1405.
5. *E*/*Z* isomers of **2a** were separated by silica gel column chromatography. (*E*)-**2a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.37 (d, *J*=7.5 Hz, 1H), 5.68 (dd, *J*=7.5, 26.7 Hz, 1H), 6.51 (d, *J*=20.4 Hz, 1H), 7.20–7.80 (m, 10H); ^{19}F NMR (188 MHz, $CDCl_3$) δ −120.1 (dd, *J*=20.4, 26.7 Hz). Found: C, 79.14; H, 5.79%. Calcd for $C_{15}H_{13}FO$: C, 78.93; H, 5.74%; (*Z*)-**2a**: ^{1}H NMR δ 2.45 (br s, 1H), 5.33 (dd, *J*=4.5, 12.0 Hz, 1H), 5.90 (d, *J*=39.3 Hz, 1H), 7.20–7.60 (m, 10H); ^{19}F NMR δ −115.6 (dd, *J*=12.0, 39.3 Hz). Found: C, 78.95; H, 5.69%. Calcd for $C_{15}H_{13}FO$: C, 78.93; H, 5.74%.
6. A typical procedure with the KF/18-Cr-6 reagent system: To a DMF (2 mL) solution of KF (1.0 mmol)/18-Cr-6 (1.0 mmol) were added aldehyde (2.5 mmol) and **1** (1.0 mmol) successively at room temperature. After stirring for 12 h, the reaction mixture was quenched with 3 M HCl (5 mL). The aqueous layer was extracted with Et_2O (20 mL×3); the combined organic layer was washed with brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The crude products were purified by silica gel column chromatography to give **2**.
7. Compound **3**: R_f 0.56 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.11 (s, 18H), 0.90 (t, *J*=7.5 Hz, 9H), 0.96–1.20 (m, 6H), 1.33 (q, *J*=7.2 Hz, 6H), 1.42–1.55 (m, 6H); ^{19}F NMR (188 MHz, $CDCl_3$) δ −263.7 (t, *J*=76.1 Hz). Found: C, 48.96; H, 9.88%. Calcd for $C_{19}H_{45}FSi_2Sn$: C, 48.82; H, 9.70%.
8. Bromine–lithium exchange of bis(trimethylsilyl)bromofluoromethane with BuLi followed by aldehyde addition failed to give the desired alkenylsilane.
9. When 3-phenylpropanal was added at −78°C, the *E*/*Z* ratio of product **4f** was 72:28.
10. A typical procedure: To a solution of **3** (1.0 mmol) in THF (2 mL) was added BuLi (1.05 mmol) at −78°C; the resulting mixture was stirred for 20 min at −78°C. An aldehyde (1.2 mmol) was added to the reagent solution at −98°C, and the resulting mixture was allowed to warm to room temperature before quenching with sat. aq. NH_4Cl solution. Work-up and purification by silica gel column chromatography gave **4**.
11. Data of **4f**: R_f 0.37 (hexane); ^{1}H NMR (200 MHz, $CDCl_3$) (*E*)-isomer: δ 0.13 (s, 9H), 2.30–2.70 (m, 4H), 5.06 (dt, *J*=7.4, 49.6 Hz, 1H), 7.10–7.40 (m, 5H); (*Z*)-isomer: δ 0.17 (s, 9H), 5.86 (dt, *J*=8.4, 36.8 Hz, 1H); ^{19}F NMR (188 MHz, $CDCl_3$) (*E*)-isomer: δ −123.2 (d, *J*=49.6 Hz); (*Z*)-isomer: δ −112.4 (d, *J*=36.8 Hz). Found: C, 70.28; H, 8.91%. Calcd for $C_{13}H_{19}FSi$: C, 70.22; H, 8.61%.