

CHEMISTRY OF ORGANOSILICON COMPOUNDS

CCXVI. STERICALLY CROWDED SILANES

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Summary

Some highly crowded silanes, such as tri-*t*-butylphenyl, tri-*iso*-propylphenyl, tris(trimethylsilyl)methyl, *t*-butyl and mesityl substituted silanes, have been prepared and the order of steric bulkiness of these substituents is estimated.

Introduction

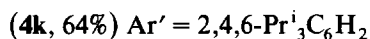
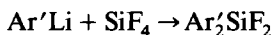
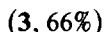
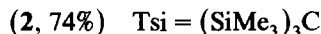
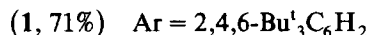
Along with the unique chemistry of compounds containing the tris(trimethylsilyl)methyl group [(Me₃Si)₃C = trisyl = Tsi] developed by Eaborn and co-workers [1], recent success in the isolation of kinetically stabilized organosilicon reactive intermediates has aroused interest in sterically crowded silanes [2]. We have prepared some fluorosilanes with sterically bulky substituents, using tetrafluorosilane as a starting material [3]. After completion of the present study [3a], we received a paper by Weidenbruch and Kramer [3b] which described the preparation of 2,4,6-tri-*t*-butylphenylfluorosilanes. In the present paper, we report our results together with some information on the relative steric bulkiness. The order of steric bulkiness of some of the substituents has been estimated by means of solvolysis.

Results and discussion

Preparations of sterically crowded fluorosilanes

The trisyl group was introduced first on a silicon atom by the reaction of trisyllithium with appropriate chlorosilanes [4]. Recently another very bulky group, 2,4,6-tri-*t*-butylphenyl (denoted by Ar), has been introduced in the chemistry of diphosphenes [5].

Tetrafluorosilane is the most compact in size among the halosilanes and is therefore expected to be a good precursor for the preparation of a sterically very



crowded silane. However, only a few reactions of SiF_4 have been reported so far [6]; in fact, trisyltrifluorosilane (1) and 2,4,6-tri-*t*-butylphenyltrifluorosilane (2) are found to be readily obtained in good yields by the reaction of the corresponding organolithium with SiF_4 in THF at -78°C .

Another bulky substituent, 2,4,6-tri-isopropylphenyl (denoted by Ar') is readily introduced into the silicon centre by using SiF_4 ; namely, the reaction of 2,4,6-tri-isopropylphenyllithium with SiF_4 under similar conditions affords bisphenylated difluorosilane 4 \mathbf{k} in 64% yield. *t*-Butyltrifluorosilane (3) is conveniently prepared from *t*-butyltrichlorosilane by the halogen exchange reaction using cupric fluoride [7,8]. Using these trifluorosilanes, some bulky difluorosilanes have been prepared as shown in Table 1.

Alcoholysis of the difluorosilane in the presence of potassium hydroxide

To prepare sterically crowded silanols and alkoxy silanes, alcoholysis of the difluorosilanes in the presence of potassium hydroxide was carried out at ambient temperature under various conditions. The results obtained are summarized in Table 2.

From the alcoholysis four types of product were obtained, namely, a silanol 5, an alkoxy silane 6, and alkoxy silanol 7, and a dialkoxy silane 8, depending on the bulkiness of the substituent on the silicon atom and on the alcohol employed. The product distribution observed here can be accounted for in terms of the stepwise

TABLE 1
PREPARATIONS OF CROWDED DIFLUOROSILANES 4

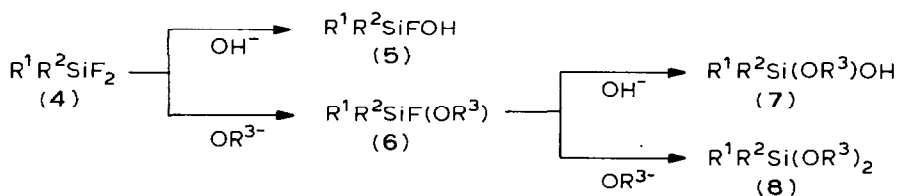
Run	Trifluoro- silane	Reagent	Solvent	Difluoro- silane	Yield (%) ^a
1	ArSiF_3 ^b (1)	MeLi	Et_2O	ArMeSiF_2 (4d)	62
2	1	EtMgBr	THF	ArEtSiF_2 (4e)	81
3	1	Pr^iLi	Et_2O	$\text{ArPr}^i\text{SiF}_2$ (4f)	85
4	1	MesLi	Et_2O	ArMesSiF_2 (4g)	39
5	1	Bu^tLi	Et_2O	$\text{ArBu}^t\text{SiF}_2$ (4h)	52
6	TsiSiF_3 ^c (2)	MesLi	Et_2O	TsiMesSiF_2 (4i)	59
7	Bu^tSiF_3 (3)	TsiLi	THF	$\text{TsiBu}^t\text{SiF}_2$ (4j)	52
8	3	$\text{Ar}'\text{Li}$ ^d	THF	$\text{Ar}'\text{Bu}^t\text{SiF}_2$ (4c)	38

^a Isolated yield. ^b $\text{Ar} = 2,4,6\text{-Bu}^t_3\text{C}_6\text{H}_2$. ^c $\text{Tsi} = \text{C}(\text{SiMe}_3)_3$. ^d $\text{Ar}' = 2,4,6\text{-Pr}^i_3\text{C}_6\text{H}_2$.

TABLE 2
ALCOHOLYSIS OF DIFLUORODISILANE 4

Run	Difluoro-silane	Alcohol (R ₃ OH)	Product yield (%) ^a			
			5	6	7	8
1	Ar'Bu ¹ SiF ₂ (4c)	MeOH				56
2	ArMeSiF ₂ (4d)	MeOH				47
3	ArPr ¹ SiF ₂ (4f)	MeOH				46
4	ArMesSiF ₂ (4g)	MeOH		34		
5	ArBu ¹ SiF ₂ (4h)	MeOH		83		
6	TsiMesSiF ₂ (4i)	MeOH		67		
7	TsiBu ¹ SiF ₂ (4j)	MeOH	<i>b</i>	44		
8	Ar ₂ SiF ₂ (4k)	MeOH				46
9	Ar'Bu ¹ SiF ₂ (4c)	EtOH			31	2
10	TsiMesSiF ₂ (4i)	EtOH		61		
11	TsiBu ¹ SiF ₂ (4j)	EtOH	<i>b</i>			
12	Ar'Bu ¹ SiF ₂ (4c)	Pr ¹ OH	35			
13	ArMeSiF ₂ (4d)	Pr ¹ OH	39			
14	ArPr ¹ SiF ₂ (4f)	Pr ¹ OH	46			
15	ArMesSiF ₂ (4g)	Pr ¹ OH	28			
16	ArBu ¹ SiF ₂ (4h)	Pr ¹ OH	38			
17	Ar ₂ SiF ₂ (4k)	Pr ¹ OH	62			

^a Isolated yield by TLC on silica gel. ^b Trace.



SCHEME 1

mechanism depicted in Scheme 1. This enables us to estimate the bulkiness of the substituent on the silicon atom.

When isopropyl alcohol was used as the solvent, only silanol **5** was obtained. In the ethanolysis, **4j** (R¹ = Tsi, R² = Bu¹) gave only a trace amount of silanol **5j** (R¹ = Tsi, R² = Bu¹) but **4i** (R¹ = Tsi, R² = Mes) afforded ethoxysilane **6i** (R¹ = Tsi, R² = Mes, R³ = Et), and **4c** (R¹ = Ar', R² = Bu¹) yielded ethoxysilanol **7c** (R¹ = Ar', R² = Bu¹, R³ = Et) together with diethoxysilane **8c** (R¹ = Ar', R² = Bu¹, R³ = Et). This suggests that the *t*-butyl group is bulkier than the mesityl, and the trisyl group is much larger than 2,4,6-tri-isopropylphenyl. Examination of the table in this way shows that the substituents can be arranged qualitatively in order of decreasing bulkiness as follows: Tsi = Ar > Ar' > Bu¹ > Mes > Pr¹ > Et > Me.

Experimental

General remarks

NMR spectra were obtained using Varian EM-90, JEOL FX-90Q and Varian XL-200 instruments. Mass spectra were obtained on a JEOL JMS D-300 GC-MS

instrument. NMR spectra were recorded in CDCl_3 and chemical shift data are given in δ values unless otherwise noted. All reactions were performed under an atmosphere of argon.

*Preparation of 2,4,6-tri-*t*-butylphenyltrifluorosilane (1)*

In a 200-ml, three-necked flask equipped with a mechanical stirrer, a gas inlet, a reflux condenser and a dropping funnel, 3.30 g (10.1 mmol) of 2,4,6-tri-*t*-butylphenyl bromide in THF (50 ml) was placed. A hexane solution of BuLi (1.5 *N*, 7.0 ml) was added at -78°C , the resultant reaction mixture was stirred at -78°C for 2 h, and then SiF_4 was introduced from the gas inlet for 15 min. The solution was then allowed to warm gradually to ambient temperature. After having been left a day, the reaction mixture was distilled to give 2.36 g (71%) of **1**. **1**: b.p. $77\text{--}83^\circ\text{C}/0.4$ Torr; ^1H NMR 1.48 (s, 9H, Bu^t), 1.63 (q_F, J_{F} 1.0 Hz, 18H, Bu^t), 7.56 (s, 2H, ArH); ^{13}C NMR 30.94 (q), 32.38 (q), 34.99 (s), 38.45 (s), 111.46 (s, q_F, J_{F} 22.1 Hz), 123.05 (d), 153.60 (s), 161.37 (s); ^{29}Si NMR -71.30 (q, J_{F} 261.8 Hz); MS *m/e* (%) M^+ 330 (6), 259 (75), 57(100); Exact mass found: 330.1815. $\text{C}_{18}\text{H}_{29}\text{F}_3\text{Si}$ calcd.: 330.1812.

Preparation of trifluoro[tris(trimethylsilyl)methyl]silane (2)

A 500-ml, three-necked flask equipped with a mechanical stirrer, a reflux condenser and a dropping funnel was charged with 22.9 g (98.7 mmol) of tris(trimethylsilyl)methane in THF (220 ml). MeLi in ether (1.2 *N*, 85 ml) was added and the resulting mixture was stirred for 6 h at ambient temperature. After the dropping funnel was replaced by a gas inlet, SiF_4 was bubbled into the reaction mixture slowly through the gas inlet for 1.5 h at ambient temperature. The solution was then refluxed for 3 h. After removal of the solvent, hexane was added to the residue and insoluble materials were filtered out. The filtrate was condensed in vacuum and sublimed at $100^\circ\text{C}/1.0$ Torr to give 23.2 g (74.4%) of **2**. **2**: m.p. $250\text{--}253^\circ\text{C}$; ^1H NMR 0.30 (t_F, J_{F} 0.5 Hz, 27H, SiMe); ^{13}C NMR 3.39 (q), 3.72 (s, q_F, J_{F} 14.7 Hz); ^{29}Si NMR -60.35 (q_F, J_{F} 277.7 Hz); MS *m/e* (%) ($M^+ - 15$) 301 (82), 209 (100), 73 (42); Exact mass found: 301.0912. $\text{C}_9\text{H}_{27}\text{F}_3\text{Si}_4$ calcd.: 301.0907.

*Preparation of *t*-butyltrifluorosilane (3)*

In a 200-ml, two-necked flask equipped with a reflux condenser and a dropping funnel, 43.0 g (0.313 mol) of CuF_2 in butyl ether (100 ml) was placed. After addition of a butyl ether solution containing 32.6 g (0.170 mol) of *t*-butyltrichlorosilane at 0°C , the reaction mixture was stirred magnetically overnight, and was distilled directly to give 16.0 g (66.2%) of **3**. **3**: b.p. $35\text{--}36^\circ\text{C}$; ^1H NMR 1.14 (q_F, J_{F} 1.0 Hz, 9H); ^{13}C NMR 15.2 (s, q_F, J_{F} 3.8 Hz), 24.7 (q); ^{29}Si NMR -62.13 (q_F, J_{F} 304.0 Hz).

*Preparation of *t*-butyldifluoro(2,4,6-triisopropylphenyl)silane (4c)*

In a 300-ml, three-necked flask equipped with a reflux condenser and a dropping funnel, 30.0 g (0.106 mol) of 2,4,6-tri-isopropylbenzene in THF (100 ml) was placed. After Bu^tLi in pentane (1.88 *N*, 65 ml) was added and the solution was stirred at -78°C for 1 h, **3** (15.1 g, 0.106 mol) in THF was added to it. The reaction mixture was refluxed gently for 1 h, left for a day, and hydrolysed with dilute HCl, followed by extraction with ether. The ether fraction was evaporated and the residue was crystallized from ethanol to give 13.1 g (37.9%) of **4c**. **4c**: m.p. $72\text{--}73^\circ\text{C}$; ^1H NMR

(CCl₄) 1.09 (t_F, J_F 0.8 Hz, 9H, Bu^t), 1.24 (d, J 6.9 Hz, 18 H, CHMe₂), 2.83 (sep, J 6.9 Hz, 1H, CHMe), 3.05 (sep, J 6.9 Hz, 2H, CHMe₂), 6.95 (s, 2H, ArH); ¹³C NMR 19.19 (s, t_F, J_F 14.7 Hz), 23.76 (q), 25.20 (q), 25.72 (q), 34.47 (d), 34.66 (d), 121.81 (d), 122.26(s), 152.23 (s), 157.06 (s); ²⁹Si NMR -9.83 (t_F, J_F 310.3 Hz); MS *m/e* (%) M⁺ 326 (45), 269 (84), 203 (49); Exact mass found: 326.2224. C₁₉H₃₂F₂Si calcd.: 326.2242.

*Preparation of difluoromethyl(2,4,6-tri-*t*-butylphenyl)silane (4d)*

A 50-ml, two-necked flask equipped with a reflux condenser and a dropping funnel was charged with 1.22 g (3.69 mmol) of **1** in ether (10 ml). After addition of MeLi in ether (0.70 N, 5.3 ml) at 0°C, the reaction mixture was stirred for 30 min and allowed to warm to ambient temperature. After 1 h, the reaction mixture was hydrolysed with dilute HCl and extracted with ether. The ether fraction was condensed and subjected to TLC to give 751 mg (62.4%) of **4d**. **4d**: m.p. 133–134°C; ¹H NMR 0.52 (t_F, J_F 4.1 Hz, 3H, SiMe), 1.41 (s, 27H, Bu^t), 7.37 (s, 2H, ArH); ¹³C NMR 2.55 (q, t_F, J_F 17.7 Hz), 31.14 (q), 33.36 (q), 34.79 (s), 39.10 (s), 123.18 (d), 123.53 (s), 152.10 (s), 161.10 (s); ²⁹Si NMR -13.39 (t_F, J_F 280.9 Hz); MS *m/e* (%) 326 (5), 270 (9), 255 (100); Exact mass found: 326.2232. C₁₉H₃₂F₂Si calcd.: 326.2242.

*Preparation of ethyldifluoro(2,4,6-tri-*t*-butylphenyl)silane (4e)*

A 50-ml, two-necked flask equipped with a reflux condenser and a dropping funnel was charged with 3.08 g (9.33 ml) of **1** in THF. After addition of a THF solution of ethyl Grignard reagent (1.2 N, 7.8 ml) at 0°C, the reaction mixture was stirred magnetically for 30 min. After 8 h at ambient temperature, it was hydrolysed with dilute HCl followed by extraction with ether. The ethereal fraction was passed through a short silica gel column and was evacuated to give 2.59 g (81.3%) of **4e**. **4e**: m.p. 97–98°C; ¹H NMR 1.20 (m, 2H, SiCH₂), 1.39 (t, J 5.3 Hz, 3H, CH₂CH₃), 1.46 (s, 9H, Bu^t), 1.60 (s, 18H, Bu^t), 7.48 (s, 2H, ArH); ¹³C NMR 7.44 (q) 11.10 (t, t_F, J_F 18.7 Hz), 31.27(q), 33.42(q), 34.86 (s), 39.04 (s), 123.18 (d), 151.97 (s), 161.04 (s); ²⁹Si NMR -14.62 (t_F, J_F 289.0 Hz); MS *m/e* (%) M⁺ 340 (2), 269 (79), 57 (100); Exact mass found: 340.2399. C₂₀H₃₄F₂Si calcd.: 340.2398.

*Preparation of difluoroisopropyl(2,4,6-tri-*t*-butylphenyl)silane (4f)*

A 50-ml, two-necked flask equipped with a reflux condenser and a dropping funnel was charged with 3.34 g (10.1 mmol) of **1** in 20 ml of ether. After addition of a hexane solution of Pr^tLi (1.5 N, 6.7 ml) at 0°C, the reaction mixture was stirred for 30 min and left for 1 h. Then, it was hydrolysed with dilute HCl and extracted with ether. The ethereal fraction was passed through a short silica gel column and condensed to give 3.04 g (84.4%) of **4f**. **4f**: m.p. 83–84°C; ¹H NMR 0.97 (m, 1H, CHMe₂), 1.26 (d, J 6.9 Hz, 6H, CHMe₂), 1.53 (s, 9H, Bu^t), 1.67 (s, 18H, Bu^t), 7.56 (s, 2H, ArH); ¹³C NMR 17.30 (d, t_F, J_F 14.7 Hz), 17.30 (q), 31.14 (q), 32.90 (q), 34.66 (s), 38.64 (s), 120.43 (s, t_F, J_F 13.7 Hz), 122.65 (d), 151.70 (s), 160.58 (s); ²⁹Si NMR -17.10 (t_F, J_F 300.0 Hz); MS *m/e* (%) M⁺ 354 (2), 283 (100), 57 (72); Exact mass found: 354.2579. C₂₁H₃₆F₂Si calcd.: 354.2555.

*Preparation of difluoromesityl(2,4,6-tri-*t*-butylphenyl)silane (4g)*

In a 100-ml, three-necked flask equipped with a mechanical stirrer, reflux condenser, and a dropping funnel. MesLi prepared from 3.56 g (17.9 mmol) of

mesityl bromide in ether was placed. After addition of 5.65 g (17.1 mmol) of **1** in ether at -30°C , the reaction mixture was left for a day and hydrolysed with dilute HCl followed by ether extraction. The extract was passed through a short silica gel column and evaporated to a residue, which was crystallized from ethanol to give 2.84 g (38.6%) of **4g**. **4g**: $^1\text{H NMR}$ (CCl_4) 1.27 (s, 18H, Bu^t), 1.30 (s, 9H, Bu^t), 1.85 (s, 6H, Me), 2.19 (s, 3H, Me), 6.60 (s, 2H, ArH), 7.26 (s, 2H, ArH); $^{13}\text{C NMR}$ (C_6D_6) 21.08 (q), 22.19 (q), 31.20 (q), 32.83 (q), 35.12 (s), 39.23 (s), 123.40 (s, t_{F} , J_{F} 19.9 Hz), 123.51 (d), 129.57 (s, t_{F} , J_{F} 17.0 Hz), 129.77 (d), 140.67 (s), 144.79 (s), 152.75 (s), 161.10 (s); $^{29}\text{Si NMR}$ (C_6D_6) -31.23 (t_{F} , J_{F} 301.5 Hz); MS m/e (%) M^+ 430 (2), 359 (47), 57 (100); Exact mass found: 430.2845. $\text{C}_{27}\text{H}_{40}\text{F}_2\text{Si}$ calcd.: 430.2867.

*Preparation of *t*-butyldifluoro(2,4,6-tri-*t*-butylphenyl)silane (4h)*

A 50-ml, two-necked flask equipped with a reflux condenser and a dropping funnel was charged with 2.45 g (7.42 mmol) of **1** in 20 ml of ether. After addition of a pentane solution of Bu^tLi (1.5 N, 4.8 ml) at 0°C , the reaction mixture was allowed to stand for 3 h at ambient temperature and hydrolysed with dilute HCl followed by ether extraction. The ethereal fraction was evaporated to a residue, which was crystallized from ethanol to give 1.42 g (52.0%) of **4h**. **4h**: $104\text{--}105^{\circ}\text{C}$; $^1\text{H NMR}$ 1.35 (t_{F} , J_{F} 2.0 Hz, SiBu^t), 1.43 (s, 9H, Bu^t), 1.57 (s, 18H, Bu^t), 7.46 (s, 2H, ArH); $^{13}\text{C NMR}$ 22.65 (s, t_{F} , J_{F} 15.5 Hz), 29.64 (q), 31.14 (q), 33.16 (q), 34.66 (s), 38.06 (s), 122.46 (s, t_{F} , J_{F} 14.7 Hz), 122.78 (d), 151.38 (s), 160.58 (s); $^{29}\text{Si NMR}$ -16.44 (t_{F} , J_{F} 305.9 Hz); MS m/e (%) M^+ 368 (1), 297 (72), 57 (100); Anal. Found: C, 71.86; H, 10.55. $\text{C}_{22}\text{H}_{38}\text{F}_2\text{Si}$ calcd.: C, 71.68; H, 10.39%.

Preparation of difluoromesityl[tris(trimethylsilyl)methyl]silane (4i)

A three-necked flask equipped with a mechanical stirrer, a reflux condenser and a dropping funnel was charged with an ether solution of MesLi prepared from 3.02 g (15.2 mmol) of mesityl bromide. After addition of 4.80 g (15.1 mmol) of **2** in ether at -30°C , the reaction mixture was stirred for 2 h at ambient temperature and refluxed for 3 h, followed by hydrolysis with dilute HCl and then ether extraction. The ethereal fraction was condensed and recrystallized from ethanol to yield 3.69 g (58.7%) of **4i**. **4i**: m.p. $94\text{--}96^{\circ}\text{C}$; $^1\text{H NMR}$ 0.35 (t_{F} , J_{F} 0.6 Hz, 27H, SiMe_3), 2.30 (s, 3H, Me), 2.55 (t_{F} , J_{F} 3.0 Hz, 6H, Me), 6.84 (s, 2H, ArH); $^{13}\text{C NMR}$ 6.14 (q), 6.14 (s, t_{F} , J_{F} 26.5 Hz), 21.02 (q), 25.52 (q), 128.53 (s, t_{F} , J_{F} 23.5 Hz), 129.57 (d), 140.80 (s), 145.05 (s); $^{29}\text{Si NMR}$ -12.14 (t_{F} , J_{F} 305.2 Hz), 0.42 (t_{F} , J_{F} 8.8 Hz); MS m/e (%) M^+ 416 (1), 401 (86), 309 (100); Exact mass found: 401.1794. $\text{C}_{18}\text{H}_{35}\text{F}_2\text{Si}_4$ calcd.: 401.1784.

*Preparation of *t*-butyldifluoro[tris(trimethylsilyl)methyl]silane (4j)*

In a 200-ml, three-necked flask equipped with a mechanical stirrer, a reflux condenser and a dropping funnel, tris(trimethylsilyl)methyl lithium prepared from 7.83 g (33.7 mmol) of tris(trimethylsilyl)methane in THF was placed. After addition of 4.69 g (33.0 mmol) of **3**, the reaction mixture was refluxed for 5 h and hydrolysed with dilute HCl followed by ether extraction. The ether layer was passed through a short silica gel column and was distilled to give 6.09 g (52.1%) of **4j**. **4j**: b.p. $150^{\circ}\text{C}/1.0$ Torr; $^1\text{H NMR}$ 0.33 (t_{F} , J_{F} 0.6 Hz, 27H, SiMe), 1.13 (t_{F} , J_{F} 1.5 Hz, 9H, Bu^t); $^{13}\text{C NMR}$ 5.35 (q), 5.35 (s, t_{F} , J_{F} 26.5 Hz), 23.04 (s, t_{F} , J_{F} 16.9 Hz), 29.05

(q); ^{29}Si NMR -4.51 (t_{F} , J_{F} 319.9 Hz), -1.40 , -1.16 , -0.83 ; MS m/e (%) ($M^+ - 15$) 339 (32), 297 (36), 205 (100); Exact mass found: 339.1628. $\text{C}_{13}\text{H}_{33}\text{F}_2\text{Si}_4$ calcd.: 339.1628.

Preparation of difluorobis(2,4,6-tri-isopropylphenyl)silane (4k)

A 500-ml, three-necked flask equipped with a mechanical stirrer, a reflux condenser and a dropping funnel was charged with 38.0 g (0.134 mmol) of 2,4,6-tri-isopropylbenzene in THF (200 ml). After addition of Bu^tLi in pentane (1.8 N, 150 mmol) at -78°C , the dropping funnel was replaced by a gas inlet and SiF_4 was bubbled for 40 min. The reaction mixture was allowed to warm gradually to ambient temperature and left for a day. Then it was hydrolysed with dilute HCl followed by extraction with ether and condensed to give 20.4 g (64.4%) of **4k**. **4k**: ^1H NMR 1.33 (d, J 7.0 Hz, 24H, CHMe_2), 1.45 (d, J 7.0 Hz, 12H, CHMe_2), 3.06 (sep, J 7.0 Hz, 2H, CHMe_2), 3.59 (sep, J 7.0 Hz, 4H, CHMe_2), 7.23 (s, 4H, ArH); ^{13}C NMR 23.83 (q) 24.61 (q), 33.42 (d), 34.47 (d), 121.55 (d), 126.25 (s, t_{F} , J_{F} 16.9 Hz), 152.10 (s), 155.55 (s); ^{29}Si NMR -24.37 (t_{F} , J_{F} 301.5 Hz); MS m/e (%) M^+ 472 (27), 268 (42), 253 (53), 204 (100); Exact mass found: 472.3329. $\text{C}_{30}\text{H}_{46}\text{F}_2\text{Si}$ calcd.: 472.337.

Solvolysis of difluorosilanes in the presence of potassium hydroxide

Methanolysis of 4c

In a 30-ml, two-necked flask equipped with a reflux condenser, 118 mg (0.362 mmol) of **4c** and 294 mg of KOH in 10 ml of MeOH were placed and stirred magnetically for 1 h at ambient temperature. After addition of water, the reaction mixture was extracted with ether and the ethereal fraction was condensed to give 70.6 mg (55.7%) of **8c** ($R^3 = \text{Me}$): ^1H NMR (C_6D_6) 1.10 (s, 9H, Bu^t), 1.18 (d, J 6.8 Hz, 6 H, CHMe_2), 1.31 (d, J 6.8 Hz, 12H, CHMe_2), 2.75 (sep, J 6.8 Hz, 1H, CHMe_2), 3.42 (s, 6H, OMe), 3.72 (sep, J 6.8 Hz, 2H, CHMe_2), 7.12 (s, 2H, ArH); ^{13}C NMR (C_6D_6) 20.82 (s), 24.02 (q), 26.11 (q), 27.68 (q), 33.42 (d), 34.66 (d), 51.24 (q), 122.13 (d), 126.14 (s), 150.53 (s), 157.71 (s); ^{29}Si NMR (C_6D_6) -13.13 ; MS m/e (%) ($M^+ - 15$) 335 (0.4), 293 (100), 261 (83); Exact mass found: 335.2392. $\text{C}_{20}\text{H}_{35}\text{O}_2\text{Si}$ calcd.: 335.2406.

The following methoxysilanes were obtained from the corresponding difluorosilanes under similar conditions.

8d ($R^3 = \text{Me}$). ^1H NMR (C_6D_6) 0.54 (s, 3H, SiMe), 1.16 (s, 9H, Bu^t), 1.36 (s, 18H, Bu^t), 2.96 (s, 6H, OMe), 7.22 (s, 2H, ArH); ^{13}C NMR (C_6D_6) 0.13 (q), 31.40 (q), 33.55 (q), 34.60 (s), 39.82 (s), 49.02 (q), 122.07 (d), 129.05 (s), 149.88 (s), 161.24 (s); ^{29}Si NMR (C_6D_6) -15.12 ; MS m/e (%) M^+ 350 (1), 279 (23), 105 (100); Exact mass found: 350.2640. $\text{C}_{21}\text{H}_{38}\text{O}_2\text{Si}$ calcd.: 350.2641.

8f ($R^3 = \text{Me}$). ^1H NMR 1.16 (d, J 6.3 Hz, CHMe_2), 1.36 (s, 9H, Bu^t), 1.47 (s, 18H, Bu^t), 3.35 (s, 6H, OMe), 7.27 (s, 2H, ArH); ^{13}C NMR 16.97 (d), 19.45 (q), 31.14 (q), 33.03 (q), 34.40 (s), 39.04 (s), 50.20 (q), 121.61 (d), 125.92 (s), 149.29 (s), 160.84 (s); ^{29}Si NMR -17.35 ; MS m/e (%) M^+ 378 (1), 335 (10), 133 (100); Exact mass found: 378.2964. $\text{C}_{23}\text{H}_{42}\text{O}_2\text{Si}$ calcd.: 378.2954.

7g ($R^3 = \text{Me}$). ^1H NMR (C_6D_6) 1.14 (s, 9H, Bu^t), 1.21 (s, 18H, Bu^t), 1.78 (d_F, J_{F} 1.1 Hz, 6H, ArMe), 1.89 (s, 3H, ArMe), 3.09 (s, 3H, OMe), 6.43 (s, 2H, ArH), 7.18 (s, 2H, ArH); ^{13}C NMR (C_6D_6) 21.15 (q), 22.29 (q, d_F, J_{F} 4.4 Hz), 31.40 (q),

33.03 (q), 34.79(s), 39.65 (s), 49.61 (q), 123.05 (d), 125.56 (s, d_F , J_F 22.1 Hz), 129.83 (d), 130.88 (s, d_F , J_F 20.6 Hz), 139.82 (s), 145.05 (s), 151.64 (s), 161.23 (s, d_F , J_F 3.0 Hz); ^{29}Si NMR (C_6D_6) -30.41 (d_F , J_F 305.91 Hz); MS m/e (%) M^+ 442 (3), 231 (38), 217 (100); Exact mass found: 442.3110. $\text{C}_{28}\text{H}_{43}\text{FOSi}$ calcd.: 442.3067.

7h ($R^3 = \text{Me}$). ^1H NMR (C_6D_6) 1.23 (s, 18H, Bu^t), 1.24 (d_F , J_F 2.0 Hz, SiBu^t), 1.44 (s, 18H, Bu^t), 2.84 (s, 3H, OMe), 7.35 (s, 2H, ArH); ^{13}C NMR (C_6D_6) 22.81 (s, d_F , J_F 13.2 Hz), 30.29 (q), 31.27 (q), 33.36 (s), 33.49 (q), 34.66 (s), 38.71 (s), 50.23 (q, d_F , J_F 4.4 Hz), 122.46 (d), 125.96 (s, d_F , J_F 15.6 Hz), 150.66 (s), 161.43 (s); ^{29}Si NMR (C_6D_6) -16.56 (d_F , J_F 298.6 Hz); MS m/e (%) M^+ 380 (1), 323 (15), 267 (48), 57 (100); Exact mass found: 380.2882. $\text{C}_{23}\text{H}_{41}\text{FOSi}$ calcd.: 380.2911.

6i ($R^3 = \text{Me}$). ^1H NMR (C_6D_6) 0.42 (d_F , J_F 1.0 Hz, SiMe), 2.07 (s, 3H, ArMe), 2.60 (s, 3H, ArMe), 2.68 (d_F , J 6.8 Hz, 3H, ArMe), 3.23 (s, 3H, OMe), 6.73 (s, 2H, ArH); ^{13}C NMR (C_6D_6) 6.46 (q), 7.05 (s, d_F , J_F 26.5 Hz), 20.95 (q), 25.13 (q), 26.40 (q, d_F , J_F 13.2 Hz), 49.15 (q), 129.74 (s, d_F , J_F 16.2 Hz), 131.14 (d), 140.35 (s), 144.39 (s); ^{29}Si NMR (C_6D_6) -12.56 (d_F , J_F 297.1 Hz), -0.08 (d_F , J_F 5.9 Hz); MS m/e (%) ($M^+ - 15$) 413 (100), 217 (41), 73 (44); Exact mass found: 413.1975. $\text{C}_{19}\text{H}_{38}\text{FOSi}_4$ calcd.: 413.1984.

6j ($R^3 = \text{Me}$). ^1H NMR (C_6D_6) 0.27 (d_F , J_F 0.6 Hz, 27H, SiMe), 1.05 (d_F , J_F 1.6 Hz, 9H, Bu^t), 3.34 (s, 3H, OMe); ^{13}C NMR (C_6D_6) 6.07 (q), 24.49 (s, d_F , J_F 18.0 Hz), 30.09 (q), 51.96 (q, d_F , J_F 3.0 Hz); ^{29}Si NMR (C_6D_6) -8.55 (d_F , J_F 316.2 Hz), -1.53 (d_F , J_F 4.4 Hz); MS m/e (%) ($M^+ - 15$) 351 (35), 309 (100), 217 (32); Exact mass found: 351.1828. $\text{C}_{14}\text{H}_{36}\text{FOSi}_4$ calcd.: 351.1827.

8k ($R^3 = \text{Me}$). ^1H NMR (C_6D_6) 1.05 (d, J 6.9 Hz, 24H, CHMe_2), 1.11 (d, J 6.9 Hz, 12H, CHMe_2), 2.69 (sep, J 6.9 Hz, 2H, CHMe_2), 3.36 (s, 6H, OMe), 3.85 (sep, J 6.9 Hz, CHMe_2), 6.97 (s, 4H, ArH); ^{13}C NMR (C_6D_6) 24.15 (q), 24.94 (q), 32.51 (d), 34.73 (d), 50.20 (q), 121.81 (d), 129.05 (s), 150.79 (s), 156.08 (s); ^{29}Si NMR (C_6D_6) -21.48; MS m/e (%) M^+ 496 (0.1), 292 (100), 260 (33); Exact mass found: 496.3783. $\text{C}_{32}\text{H}_{52}\text{O}_2\text{Si}$ calcd.: 496.3736.

Ethanolysis of **4c**

In a 50-ml, two-necked flask equipped with a reflux condenser, 425 mg (1.30 mmol) of **4c** and 286 mg of KOH in 10 ml of EtOH were placed and stirred magnetically for 1 h at ambient temperature. After addition of water, the reaction mixture was extracted with ether. The ethereal fraction was condensed and subjected to silica gel TLC. This gave 142 mg (31.2%) of **7c** ($R^3 = \text{Et}$) together with a small amount of **8c** ($R^3 = \text{Et}$, 3.4 mg). **7c** ($R^3 = \text{Et}$): ^1H NMR 1.05 (s, 9H, Bu^t), 1.20 (t, J 7.0 Hz, 3H, CH_2CH_3), 1.24 (d, J 6.8 Hz, 6H, CHMe_2), 1.26 (d, J 6.8 Hz, 12H, CHMe_2), 2.30 (s, 1H, OH), 2.86 (sep, J 6.8 Hz, 1H, CHMe_2), 3.61 (sep, 6.8 Hz, 2H, CHMe_2), 3.85 (q, J 6.7 Hz, 1H, $\text{CH}_a\text{H}_b\text{CH}_3$), 3.86 (q, J 7.1 Hz, $\text{CH}_a\text{H}_b\text{CH}_3$), 7.02 (s, 2H, ArH); ^{13}C NMR 20.04 (s), 23.76 (q), 25.33 (q), 25.85 (q), 26.89 (q), 33.23 (d), 34.14 (d), 58.49 (t), 121.68 (d), 126.90 (s), 150.01 (s), 156.93 (s); ^{29}Si NMR -13.30; MS m/e (%) ($M^+ - 15$) 335 (0.3), 293 (100), 347 (71); Exact mass found: 335.2420. $\text{C}_{20}\text{H}_{35}\text{O}_2\text{Si}$ calcd.: 335.2406.

The following ethoxysilanes were obtained from the corresponding difluorosilanes under similar conditions.

8c ($R^3 = \text{Et}$). ^1H NMR 0.88 (t, J 7.0 Hz, 6H, CH_2CH_3), 0.98 (s, 9H, Bu^t), 1.19 (d, J 6.5 Hz, 6H, CHMe_2), 1.20 (D, J 6.5 Hz, 6H, CHMe_2), 1.22 (d, J 6.5 Hz, 6H, CHMe_2), 2.82 (sep, J 6.5 Hz, 1H, CHMe_2), 3.65 (sep, J 6.5 Hz, 2H, CHMe_2), 3.87

(q, J 7.0 Hz, 2H, CH_2CH_3), 3.88 (q, J 7.0 Hz, 2H, CH_2CH_3), 6.99 (s, 2H, ArH); MS m/e (%) ($M^+ - 15$) 363 (0.2), 321 (100), 275 (56); Exact mass found: 363.2719. $\text{C}_{22}\text{H}_{39}\text{O}_2\text{Si}$ calcd.: 363.2719.

6i ($R^3 = Et$). ^1H NMR (C_6D_6) 0.41 (s, 27H, SiMe), 1.09 (t, J 6.8 Hz, 3H, CH_2CH_3), 2.05 (s, 3H, Me), 2.59 (s, 3H, Me), 2.64 (d_F, J_F 8.6 Hz, 3H, ArMe), 3.52 (m, 2H, CH_2CH_3), 6.72 (s, 2H, ArH); ^{13}C NMR (C_6D_6) 6.53 (q), 18.08 (q), 21.02 (q), 25.46 (q), 26.44 (q, d_F, J_F 14.7 Hz), 58.44 (t), 131.14 (d), 140.35 (s), 144.46 (s), 144.74 (s); MS m/e (%) ($M^+ - 15$) 427 (100), 231 (20), 73 (48); Exact mass found: 427.2135. $\text{C}_{20}\text{H}_{40}\text{FOSi}_4$ calcd.: 427.2140.

iso-Propanolysis of 4c

In a 50-ml, two-necked flask equipped with a reflux condenser, 775 mg (2.38 mmol) of **4c** and 212 mg of KOH in 20 ml of 2-propanol were placed and stirred magnetically for 1 h at ambient temperature. After addition of water, the reaction mixture was extracted with ether. The ether layer was condensed and subjected to silica gel TLC. This gave 494 mg (64.1%) of **5c**. **5c**: m.p. 105–106°C; ^1H NMR (C_6D_6) 1.09 (d_F, J_F 0.9 Hz, 9H, Bu^t), 1.20 (d, J 7.0 Hz, 6H, CHMe_2), 1.26 (d, J 7.0 Hz, 6H, CHMe_2), 1.33 (d, J 7.0 Hz, 6H, CHMe_2), 2.51 (s, 1H, OH), 2.76 (sep, J 7.0 Hz, 1H, CHMe_2), 3.46 (sep, J 7.0 Hz, 2H, CHMe_2), 7.11 (s, 2H, ArH); ^{13}C NMR 19.35 (s, d_F, J_F 16.2 Hz), 23.70 (q), 25.26 (q), 25.39 (q), 26.11 (q), 33.94 (d), 34.21 (d), 121.81 (d), 125.58 (s, d_F, J_F 18.47 Hz), 151.25 (s), 153.93 (s); ^{29}Si NMR –8.38 (d_F, J_F 301.49 Hz); MS m/e (%) M^+ 324 (7), 267 (33), 249 (100); Exact mass found: 324.2278. $\text{C}_{19}\text{H}_{33}\text{FOSi}$ calcd.: 324.2285.

The following silanols were obtained from the corresponding difluorosilanes under similar conditions.

5d. ^1H NMR (C_6D_6) 0.60 (d_F, J_F 5.4 Hz, 3H, SiMe), 1.19 (s, 9H, Bu^t), 1.36 (s, 18H, Bu^t), 1.86 (s, 1H, OH), 7.30 (s, 2H, ArH); ^{13}C NMR (C_6D_6) 3.13 (s, d_F, J_F 17.7 Hz), 31.33 (q), 33.49 (q), 34.73 (s), 39.36 (s), 122.85 (d), 127.45 (s, d_F, J_F 16.2 Hz), 150.79 (s), 161.04 (s); ^{29}Si NMR (C_6D_6) –13.22 (d_F, J_F 276.5 Hz); MS m/e (%) M^+ 324 (3), 268 (9), 253 (100); Exact mass found: 324.2252. $\text{C}_{19}\text{H}_{33}\text{FOSi}$ calcd.: 324.2285.

5f. ^1H NMR (C_6D_6) 0.64 (m, 1H, CHMe_2), 0.96 (m, 6H, CHMe_2), 1.17 (s, 18H, Bu^t), 1.33 (s, 9H, Bu^t), 7.14 (s, 2H, ArH); ^{13}C NMR (C_6D_6) 17.62 (q), 18.05 (d, d_F, J_F 19.1 Hz), 31.27 (q), 33.36 (q), 34.66 (s), 39.17 (s), 122.00 (d), 124.84 (s, d_F, J_F 16.2 Hz), 150.92 (s), 160.84 (s); ^{29}Si NMR (C_6D_6) –16.23 (d_F, J_F 286.8 Hz); MS m/e (%) M^+ 352 (2), 296 (10), 281 (86), 57 (100); Exact mass found: 352.2600. $\text{C}_{21}\text{H}_{37}\text{FOSi}$ calcd.: 352.2598.

5g. ^1H NMR (C_6D_6) 1.16 (s, 9H, Bu^t), 1.23 (s, 18H, Bu^t), 1.82 (s, 6H, Me), 1.90 (s, 3H, Me), 2.84 (s, 1H, OH), 6.44 (s, 2H, ArH), 7.22 (s, 2H, ArH); ^{13}C NMR (C_6D_6) 21.08 (q), 22.46 (q), 31.33 (q), 33.10 (q), 34.73 (s), 39.43 (s), 123.18 (d), 126.54 (s, d_F, J_F 19.1 Hz), 129.83 (d), 132.28 (s, d_F, J_F 22.1 Hz), 139.76 (s), 144.85 (s), 151.57 (s), 160.78 (s); ^{29}Si NMR (C_6D_6) –29.37 (d_F, J_F 289.7 Hz); MS m/e (%) M^+ 428 (2), 231 (100), 57 (55); Exact mass found: 428.2909. $\text{C}_{27}\text{H}_{41}\text{FOSi}$ calcd.: 428.2910.

5h. ^1H NMR (C_6D_6) 1.22 (d_F, J_F 2.0 Hz, 9H, Bu^t), 1.28 (s, 9H, Bu^t), 1.48 (s, 18H, Bu^t), 1.73 (d_F, J_F 1.0 Hz, OH), 7.34 (s, 2H, ArH); ^{13}C NMR (C_6D_6) 22.45 (s, d_F, J_F 14.7 Hz), 30.29 (q), 31.33 (q), 33.62 (q), 34.73 (s), 38.71 (s), 122.91 (d), 127.91 (d), 127.91 (s, d_F, J_F 19.1 Hz), 150.66 (s), 161.17 (s); ^{29}Si NMR (C_6D_6) –15.20 (d_F,

J_F 297.1 Hz; MS m/e (%) M^+ 366 (5), 309 (22), 295 (100); Exact mass found: 366.2783. $C_{22}H_{39}FOSi$ calcd.: 366.2754.

5k. 1H NMR (C_6D_6) 1.15 (d, J 7.0 Hz, 12H, $CHMe_2$), 1.16 (d, J 7.0 Hz, 12H, $CHMe_2$), 1.18 (d, J 7.0 Hz, 12H, $CHMe_2$), 2.75 (sep, J 7.0 Hz, 2H, $CHMe_2$), 3.74 (sep, J 7.0 Hz, 4H, $CHMe_2$), 7.04 (s, 4H, ArH); ^{13}C NMR 24.02 (q), 24.81 (q), 24.94 (q), 33.10 (d), 33.23 (d), 34.73 (d), 121.74 (d), 151.57 (s), 155.68 (s); ^{29}Si NMR (C_6D_6) -52.76 (d, J_F , J_F 292.6 Hz); MS m/e (%) M^+ 470 (1), 266 (45) 204 (100); Exact mass found 470.3379. $C_{30}H_{47}FOSi$ calcd.: 470.3380.

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