

# Nucleophilic fluorination of alkoxy silane with alkali metal salts of perfluorinated complex anions.<sup>1a</sup> Part 2<sup>1b</sup>

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Alkali metal salts of perfluorinated complex anions have been used to effect nucleophilic fluorination of alkyl-, arylalkyl- and arylalkoxy-silanes both in the presence and absence of solvent. Near-quantitative yields of fluorinated silanes are obtained using equimolar quantities of fluoride ion equivalents and alkoxy silanes. In certain cases, intermediate organoboron and organophosphorus compounds derived from the corresponding complex anions and alkoxy silanes are identified in the reaction mixtures, and based on these intermediates a mechanism of reaction has been proposed.

Several methods exist in the literature for the preparation of fluorosilanes. Antimony trifluoride and pentafluoride and anhydrous hydrogen fluoride have been used<sup>1c,2</sup> for the preparation of aromatic fluorosilanes from appropriate halo precursors while fluorosulfonic acid at low to ambient temperatures has been used for the conversion of alkylalkoxy silanes to the corresponding fluorosilanes.<sup>3a</sup> Alkoxy- and siloxy-silanes react with alkyl- and aryl-fluorophosphoranes to give fluorosilanes in high yield.<sup>3b,4</sup> Metal fluorides have been used<sup>5</sup> for the preparation of fluorosilanes by an exchange reaction of alkoxy-, halo-, hydroxy-, amino-, cyano-, thio- or siloxy-organosilanes in the presence of HCl or H<sub>2</sub>SO<sub>4</sub>. Carbonyl fluorides are used as fluorinating reagents in organosilicon chemistry and thus, alkyl- and phenyl-silanol and alkoxyalkylsilanes are converted to the corresponding fluorosilanes in respectable yields.<sup>6</sup>

Other literature methods include the boron trifluoride-diethyl ether conversion of oligomeric organosiloxanes under heating, to organofluorosilanes,<sup>7a</sup> boron trifluoride-diethyl ether fluorinations of functionalized organosilanes R<sub>4-n</sub>SiX<sub>n</sub> (X = H, OR, Cl, Br),<sup>7b,c</sup> graphite-intercalated SbF<sub>5</sub> fluorination of organosilicon compounds containing Si-O and Si-Cl bonds<sup>7d</sup> and, under mild conditions, phosphorus pentafluoride fluorination of the Si-H bond in (SiH<sub>3</sub>)<sub>2</sub>O.<sup>8a,b</sup> Boron trifluoride-diethyl ether has also been used in the fluorination of the Si-H bond, e.g. in  $\alpha$ -naphthyl(ferrocenyl)fluorosilane ( $\alpha$ -NpFcSiHF).<sup>8c</sup>

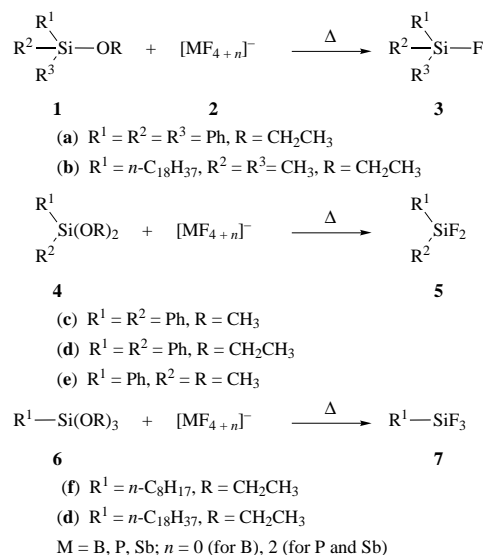
Perfluorinated complex anions, e.g. BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup> and AsF<sub>6</sub><sup>-</sup>, have been regarded as non-nucleophilic and inert or 'innocent' anions. Electrochemical experiments<sup>9</sup> from several controlled-potential oxidations have demonstrated that these anions are not truly inert and that high yields of fluorinated products result from the participation of these anions in the 'follow-up' reactions of electrode intermediates. Some of these anions were used<sup>10</sup> as their (expensive) silver salts for halogen-exchange fluorination of chlorosilicon and chlorogermanium transition metal complexes. In these reactions, silver-ion assisted rapid elimination of halogen is seemingly obvious in accounting for the reasonable yields of the fluorinated products. As its triphenylmethyl salt, under mild reaction conditions, tetrafluoroborate anion has been reported<sup>11</sup> to fluorinate Si-H bond(s) of trialkyl- and dialkyl-silanes. The reagent was further used for successful fluorination of HSiMe<sub>2</sub>CH<sub>2</sub>Fe(CO)<sub>2</sub>Cp (Cp =  $\pi$ -cyclopentadienyl).<sup>11</sup> Potassium tetrafluoroborate, under similar conditions, failed to fluorinate the Si-H bond in trialkylsilanes.<sup>11</sup>

To our knowledge, alkali metal salts of 'non-nucleophilic' anions have not been used for fluorination of functionalized organosilicon compounds. We have recently reported the use of

alkali metal salts of perfluorinated complex anions for the conversion of halosilanes<sup>12</sup> and haloboranes<sup>13</sup> to the corresponding fluorosilanes and fluoroboranes in high yield. Recently, we have also reported the action of alkali metal hexafluorophosphate on some selected alkoxy silanes.<sup>14</sup> We now report the use of commonly used alkali metal salts of perfluorinated complex anions as potential sources of fluoride ions for the effective conversion of alkoxy silanes to the corresponding fluorosilanes.

## Results and discussion

When a heterogeneous mixture of triphenylethoxysilane **1a** (Scheme 1) and sodium tetrafluoroborate in a 1:1 molar ratio



Scheme 1

in tetraglyme was heated to about 200 °C for 5 h, a brown reaction mixture resulted. The <sup>29</sup>Si NMR spectrum of the reaction mixture showed a doublet (1:1) at  $\delta_{\text{Si}}$  -3.25 (d, *J*<sub>Si-F</sub> 281 Hz) and a singlet at  $\delta_{\text{Si}}$  -12.54 (s) in the ratio 43:57. The former <sup>29</sup>Si NMR signal is due to triphenylfluorosilane **3a** and the latter is due to the unreacted starting material as was confirmed by comparison with <sup>29</sup>Si NMR chemical shifts of authentic samples. When the reaction was repeated for 16 h, the <sup>29</sup>Si NMR spectrum shows the two components in the ratio 95:5 in the reaction mixture. Appropriate work-up of the reaction mixture

**Table 1** Fluorination of alkoxysilanes with fluoride salts

Alkoxysilane	Alkali metal salt	Alkoxysilane: salt	Reaction time (h)	Fluorosilane	Yield (%)
Ph <sub>3</sub> SiOEt <b>1a</b>	NaBF <sub>4</sub>	1:1	16	Ph <sub>3</sub> SiF	92
	NaPF <sub>6</sub>	1:1	0.5		96
Ph <sub>2</sub> Si(OEt) <sub>2</sub> <b>4d</b>	NaSbF <sub>6</sub>	1:2	2	Ph <sub>2</sub> SiF <sub>2</sub>	72
	NaPF <sub>6</sub>	1:2	0.5		93
		1:1	2		98 <sup>a</sup>
		3:1	5		95 <sup>a</sup>
		1:2	5	Ph <sub>2</sub> SiF <sub>2</sub> <sup>a</sup>	93 <sup>a</sup>
Ph <sub>2</sub> Si(OMe) <sub>2</sub> <b>4c</b>	NaBF <sub>4</sub>	1:1	16		82 <sup>a</sup>
	NaPF <sub>6</sub>	1:2	0.25		92 <sup>a</sup>
		3:1	6		96 <sup>a</sup>
	LiPF <sub>6</sub>	1:2	0.5		98
	NaPF <sub>6</sub>	1:2	0.75	MePhSiF <sub>2</sub>	98
<i>n</i> -C <sub>8</sub> H <sub>17</sub> Si(OEt) <sub>3</sub> <b>6f</b>		3:1	9		93 <sup>a</sup>
	NH <sub>4</sub> PF <sub>6</sub>	1:2	0.5		98
	NaSbF <sub>6</sub>	1:2	0.75	<i>n</i> -C <sub>8</sub> H <sub>17</sub> SiF <sub>3</sub>	73
		2:1	8		81 <sup>a</sup>
		1:3	0.33		88
<i>n</i> -C <sub>18</sub> H <sub>37</sub> Si(Me) <sub>2</sub> OEt <b>1b</b>	NaPF <sub>6</sub>	1:3	0.5		96
	NaPF <sub>6</sub>	1:3	1		98
		2:1	12		94 <sup>a</sup>
	NaBF <sub>4</sub>	1:1	3	<i>n</i> -C <sub>18</sub> H <sub>37</sub> (OMe) <sub>2</sub> SiF	92
	NaPF <sub>6</sub>	6:1	6		92 <sup>a</sup>
<i>n</i> -C <sub>18</sub> H <sub>37</sub> Si(OEt) <sub>3</sub> <b>6g</b>	NaPF <sub>6</sub>	2:1	5	<i>n</i> -C <sub>18</sub> H <sub>37</sub> SiF <sub>3</sub>	90 <sup>a</sup>
	NaPF <sub>6</sub>	2:1	20	PhSi(OMe) <sub>2</sub> F <sub>2</sub>	73
	NaSbF <sub>6</sub>	2:1	7		68

<sup>a</sup> In the absence of solvent.

followed by vacuum distillation gave triphenylfluorosilane **3a** in 92% yield (Table 1).

When a heterogeneous mixture of diphenyldimethoxysilane **4c** and sodium tetrafluoroborate in a 1:2 ratio in tetraglyme was allowed to react for 5 h under the above discussed reaction conditions, a similar reaction mixture was obtained. Distillation at 760 Torr gave a mixture of products with bp 60–80 °C. <sup>1</sup>H and <sup>11</sup>B NMR spectra of the distillate showed a proton signal at δ<sub>H</sub> 3.47 and a boron signal at δ<sub>B</sub> 18.45 due to methoxyboron difluoride (*vide infra*). The reaction mixture after appropriate work-up, was analyzed by <sup>29</sup>Si NMR spectroscopy. A triplet (1:2:1) at δ<sub>Si</sub> –28.84 (t, *J*<sub>Si-F</sub> 290 Hz) and doublets at δ<sub>Si</sub> –28.40 (d, *J*<sub>Si-F</sub> 285 Hz) and –35.35 (d, *J*<sub>Si-F</sub> 280 Hz) were identified in the ratio 40:43:17. The three <sup>29</sup>Si NMR signals are due to diphenyldifluorosilane, diphenylmethoxyfluorosilane and diphenylfluorosilanol, as was confirmed by comparison with authentic samples.<sup>14</sup> The reaction was repeated in the absence of solvent for 5 h to obtain diphenyldifluorosilane and diphenylmethoxyfluorosilane in the ratio 95:5. <sup>11</sup>B NMR spectroscopy of this reaction mixture showed a singlet at δ<sub>B</sub> 18.45 due to methoxyboron difluoride (*vide infra*).<sup>9</sup> Diphenyldifluorosilane, obtained by vacuum distillation in 93% yield, was free from any boron component as ascertained by <sup>11</sup>B NMR spectroscopy. With sodium hexafluorophosphate, diphenyldimethoxysilane under similar reaction conditions gave 92% yield of the corresponding fluorosilane after 0.25 h reaction.

Sodium tetrafluoroborate was allowed to react with an aliphatic alkoxysilane, *e.g.* *n*-octadecyldimethylethoxysilane **1b** in a 1:1 molar ratio for 3 h under the described reaction conditions to afford *n*-octadecyldimethylfluorosilane **3b** in 92% yield (Table 1) by vacuum distillation.

Use of tetrafluoroborate salts as a source of fluoride ion for high conversion of alkoxysilanes to the corresponding fluorosilanes suggests the use of other salts of perfluorinated complex anions for this application. These alkali metal salts are relatively cheap and can easily be made available from commercial sources.

Under the described conditions, reaction of diphenyldiethoxysilane **4d** with sodium hexafluoroantimonate in a 1:2 molar ratio for 2 h in tetraglyme gave a 72% yield (Table 1) of

diphenyldifluorosilane after usual work-up of the reaction mixture. Use of sodium hexafluorophosphate in the same reaction gave a 93% yield of the fluorinated silane.

In the reaction of an alkylaryldialkoxysilane, *e.g.* methylphenyldimethoxysilane **4e** with sodium tetrafluoroborate in the ratio 1:2 in tetraglyme for 15 h, several fluorosilicon products were identified in the reaction mixture by <sup>29</sup>Si NMR spectroscopy. A triplet (1:2:1) at δ<sub>Si</sub> –9.66 (t, *J*<sub>Si-F</sub> 293 Hz) and doublets (1:1) at δ<sub>Si</sub> –10.85 (d, *J*<sub>Si-F</sub> 287 Hz), –18.43 (d, *J*<sub>Si-F</sub> 282 Hz) and –19.49 (d, *J*<sub>Si-F</sub> 288 Hz) were identified in the ratio 31:36:23:10. These signals are due to methylphenyldifluorosilane, methylphenylmethoxyfluorosilane, methylphenylfluorosilanol and methylfluorosilane diol. In the <sup>29</sup>Si NMR spectra were also identified methylphenylsilane diol and unreacted starting material at δ<sub>Si</sub> –22.23 (s) and –13.12 (s) respectively. Formation of these fluorosilicon compounds was further ascertained by their mass spectra. In the mass spectra was also identified MePhSi(OSiFPhMe)<sub>2</sub>. When the same reaction was repeated replacing sodium tetrafluoroborate by the corresponding hexafluorophosphate, methylphenyldifluorosilane was obtained as the single product in 98% yield (Table 1).

To identify some of the alkoxyboron intermediates, the reaction of methylphenyldimethoxysilane **4e** with sodium tetrafluoroborate in tetraglyme was repeated for a short time, *e.g.* 3 h. The same fluorosilicon components were formed in the same ratio as described above. <sup>19</sup>F NMR spectroscopy of the clear solution part of the reaction mixture (after filtration) showed three <sup>19</sup>F NMR signals at δ<sub>F</sub> –136.87 (septet, *J*<sub>F-H</sub> 6.1 Hz), –143.35 (q, *J*<sub>F-H</sub> 5.3 Hz) and –155.93 (s) which were assigned to difluorodimethylborate, trifluoromethylborate and tetrafluoroborate anions respectively. <sup>19</sup>F NMR spectroscopy of the solid part of the reaction mixture analyzed in deuterium oxide showed three <sup>19</sup>F NMR signals at δ<sub>F</sub> –121.97 (s), –143.42 (septet, *J*<sub>F-H</sub> 6.2 Hz) and –154.93 (s) which were assigned to sodium fluoride, difluorodimethylborate and tetrafluoroborate anions respectively.

The reaction of *n*-octyltriethoxysilane **6f** and sodium tetrafluoroborate in the ratio 1:3 in tetraglyme for 4 h gave four components consisting of unreacted *n*-octyltriethoxy-, *n*-octyldiethoxyfluoro-, *n*-octylethoxydifluoro- and *n*-octyltrifluorosilane in the ratio 34:41:20:5. Repeating the reaction for 20 h,

in the absence of solvent, gave the same product distribution in the ratio 12:24:36:18. Fractional distillation allowed the separation of different fractions which were characterized by their  $^{29}\text{Si}$  NMR spectra. Repeating the reaction with sodium hexafluoroantimonate in a 1:2 molar ratio for 0.75 h gave di- and tri-fluorinated silane in the ratio 24:76. Repeating the same reaction with a 1:3 molar ratio for 0.33 h gave the trifluorinated silane in 88% yield (Table 1). *n*-Octyltriethoxysilane **6f** with sodium hexafluorophosphate in the molar ratio 1:3 reacted smoothly to give 96% yield (Table 1) of the trifluorinated product in a 0.5 h reaction. Hexafluorophosphate salts of other alkali metals, e.g. lithium and potassium, also smoothly reacted with this trialkoxysilane to provide 98% yield of the desired product.<sup>14</sup>

It is not only the sodium salt of perfluorinated complex anions but also the other alkali metal salts of the same anion which show equal efficiency towards fluorination of the alkoxy-silanes under discussion. Thus, using lithium, ammonium and potassium hexafluorophosphates, near-quantitative conversions of diphenyldimethoxy-, methylphenyldimethoxy- and *n*-octyltriethoxy-silanes to the corresponding fluorosilanes have been achieved under the described reaction conditions.<sup>14</sup>

We have previously investigated the reactions of a few selected alkoxy-silanes with alkali metal hexafluorophosphates to obtain high yields of fluorosilane in the presence and absence of polar solvents.<sup>14</sup> Reactions in a multifunctional ethereal solvent, e.g. tetraglyme, gave ether complexes of the fluorophosphoric acids and in acetonitrile gave nitrilium salts of fluorophosphates in the absence of silicon precursors.<sup>14</sup> In tetraglyme, reaction of an alkoxy-silane, e.g. methylphenyldimethoxy-silane, with sodium hexafluorophosphate in the ratio 3:1 (fluoride equivalent) is slow and usually gives a wide distribution of the fluorinated products in lower relative abundance.<sup>14</sup> Reactions leading to fluorosilicon products in acetonitrile are also slow. Thus, the reaction of diphenyldimethoxysilane with sodium tetrafluoroborate in the ratio 1:2 in acetonitrile for 24 h gave diphenyldifluorosilane, diphenylmethoxyfluorosilane and diphenylfluorosilanol in the ratio 3:1:8. The same reaction with sodium hexafluorophosphate in a 1:1 ratio for 20 h gave diphenylmethoxyfluorosilane and diphenylfluorosilanol in the ratio 28:4.

In an effort to prepare diphenylmethoxyfluorosilane from diphenyldimethoxysilane, reaction of diphenyldimethoxysilane and sodium tetrafluoroborate in the ratio 1:1 was carried out for 16 h and the products were separated by fractional distillation. The product mixture consisted of two fractions—the first fraction was collected within bp 55–60 °C/760 Torr and the second fraction was collected within bp 180–190 °C/760 Torr. The first fraction did not show any  $^{29}\text{Si}$  NMR signals but showed a  $^{11}\text{B}$  NMR signal at  $\delta_{\text{B}}$  18.28. This compound was identified as methoxyboron difluoride.<sup>9</sup> The second fraction showed diphenyldifluorosilane and diphenylmethoxyfluorosilane in the ratio 85:15 by  $^{29}\text{Si}$  NMR spectroscopy. In this fraction some boron component was also carried along from the first fraction. This fraction, after the usual work up, gave diphenyldifluorosilane in 82% yield (Table 1). The formation of methoxyboron difluoride and the high yield of diphenyldifluorosilane shows that more than one fluoride ion from tetrafluoroborate anion can be used for fluorination of alkoxy-silane.

At a 1:1 molar ratio diphenyldimethoxysilane **4c** reacted with sodium hexafluorophosphate in the absence and presence of solvent (tetraglyme) to give diphenyldifluorosilane as the single product in 98% yield.<sup>14</sup>  $^{31}\text{P}$  NMR spectroscopy of the distillate showed a doublet and a triplet at  $\delta_{\text{P}}$  –5.51 (d,  $J_{\text{P-F}}$  979 Hz) and –17.62 (t,  $J_{\text{P-F}}$  1014 Hz) due to dimethylfluorophosphate and methyl difluorophosphate.<sup>15</sup> Diphenyldimethoxysilane **4c** also reacts with sodium hexafluorophosphate in the molar ratio 3:1 (fluoride equivalent) to give diphenyldifluorosilane as the only product (96% yield, Table 1).<sup>14</sup>

It was of interest to see if all the fluoride ion from a complex anion can be used for fluorination. Accordingly, diphenyldiethoxysilane **4d** was reacted with sodium hexafluorophosphate in the ratio 3:1 (fluoride equivalent) in the absence of solvent for 3 h and diphenyldifluorosilane and diphenylmethoxyfluorosilane were formed in the ratio 82:18.  $^{31}\text{P}$  NMR spectroscopy showed a doublet at  $\delta_{\text{P}}$  –8.93 (d,  $J_{\text{P-F}}$  972 Hz) and a singlet at  $\delta_{\text{Si}}$  0.81 (s) due to diethylfluorophosphate and triethylphosphate in the ratio 10:90. Continuing the reaction for 5 h showed 98% conversion to diphenyldifluorosilane which was vacuum distilled in 95% yield (Table 1).

The complex anion provides a ready source of anhydrous fluoride ion. In order to investigate further whether all the available fluoride ions in a complex anion can be utilized we examined a few other organoalkoxy-silanes. Methylphenyldimethoxysilane **4e** and *n*-octadecyldimethylethoxysilane were heated with sodium hexafluorophosphate for 9 and 6 h in the absence of any solvent and the corresponding fluorosilanes were obtained as the only products (Table 1).

When *n*-octyltriethoxysilane **6f** was reacted with sodium hexafluorophosphate under the reaction conditions previously described in the molar ratio 4:1 for 16 h, a mixture of fluorinated silicon products were obtained as identified by their  $^{29}\text{Si}$  NMR spectra. These components were identified as unreacted *n*-octyltriethoxysilane, *n*-octyldiethoxyfluorosilane, *n*-octylethoxydifluorosilane and *n*-octyltrifluorosilane in the ratio 20:50:26:4. From the  $^{29}\text{Si}$  NMR spectra, the silicon chemical shifts were assigned as  $\delta_{\text{Si}}$  –43.85 (s), –47.28 (d,  $J_{\text{Si-F}}$  277 Hz), –52.03 (t,  $J_{\text{Si-F}}$  282 Hz) and –58.40 (q,  $J_{\text{Si-F}}$  275 Hz). The reaction was repeated using the silane and hexafluorophosphate in the molar ratio 2:1 for 12 h. Usual aqueous work up and subsequent vacuum distillation gave *n*-octyltrifluorosilane in 94% yield (Table 1). Repeating the reaction for 8 h with sodium hexafluoroantimonate similarly gave *n*-octyltrifluorosilane in 81% yield (Table 1).

Reaction of an aliphatic trialkoxy-silane, e.g. *n*-octadecyltriethoxysilane **6g**, with sodium hexafluorophosphate in a 2:1 ratio (fluoride equivalent) and in the absence of any solvent, for a 3 h reaction, gave *n*-octadecyltrifluoro- and *n*-octadecylethoxydifluoro-silane in the ratio 75:25. Continuing the reaction for another 2 h gave trifluorosilane in 90% yield.  $^{31}\text{P}$  NMR spectroscopy of this reaction mixture showed diethylfluorophosphate and triethylphosphate at  $\delta_{\text{P}}$  –8.85 (d,  $J$  979 Hz) and 0.81 (s) respectively in the ratio 20:80. Reaction of an aromatic trialkoxy-silane, e.g. phenyltrimethoxysilane, with sodium hexafluorophosphate in the ratio 2:1 (fluoride equivalent) in tetraglyme for a 20 h reaction, gave phenylmethoxydifluorosilane and phenyldimethoxyfluorosilane in the ratio 75:25.

As a part of our comparison, reaction of an alkoxy-silane with sodium hexafluorosilicate salt was carried out under identical reaction conditions. Reaction of *n*-octadecyldimethylethoxysilane **1b** with sodium hexafluorosilicate in a 1:1 ratio in tetraglyme for 4 h gave *n*-octadecyldimethylfluorosilane and *n*-octadecyldimethylsilanol in the ratio 10:3. The same reaction in the absence of any solvent gave the same products in the ratio 22:3 for a 20 h reaction.

We previously reported<sup>12</sup> that when alkyl- or aryl-halosilanes were heated with alkali metal salts of perfluorinated complex anions in the presence or absence of any ethereal solvent, the corresponding fluorosilane was formed in near quantitative yield. The reactions in the absence of solvent have shown the evolution of boron trifluoride gas and the release of fluoride ion from the thermal decomposition of the complex anion  $[\text{BF}_4]^-$ . The fluoride ion causes nucleophilic halogen-exchange fluorination in the halosilanes. In the present reactions, under similar conditions, evolution of any boron trifluoride has not been observed when the reactions were carried out in the absence of any solvent. The thermally liberated Lewis acid undergoes complexation with oxygen in the alkoxy-silane where in the silicon center becomes more polarized for nucleophilic



about 200 °C for 45 min. The reaction mixture, on cooling down to room temperature, was worked up as described previously. The product was distilled *in vacuo* (bp 112–118 °C/760 Torr) to obtain 1.7 g (98%) (Table 1) methylphenyldifluorosilane. The reaction was repeated using 6 g (65.4 mmol) methylphenyldimethoxysilane and 3.8 g (22.9 mmol) sodium hexafluorophosphate in the absence of tetraglyme and worked up as usual. Methylphenyldifluorosilane was obtained in 72 and 93% yield for 5 and 9 h reactions respectively (Table 1).  $\delta_{\text{H}}$ (400 MHz,  $\text{CDCl}_3$ ) 7.45 (d,  $J$  8.1; dd,  $J$  1.5), 7.42 (t,  $J$  7.5; tt,  $J$  2.2), 7.32 (t,  $J$  7.5), 0.49 (t,  $J$  7.5);  $\delta_{\text{Si}}$ (400 MHz,  $\text{CDCl}_3$ ) –12.95 (t,  $J_{\text{Si-F}}$  291) [lit.,<sup>18</sup>  $\delta_{\text{Si}}$  –12.40 (t,  $J_{\text{Si-F}}$  289)].

#### *n*-Octyltrifluorosilane

To a solution of 1 g (3.6 mmol) *n*-octyltriethoxysilane in 1 g tetraglyme was added 2.8 g (10.8 mmol) sodium hexafluoroantimonate and the heterogeneous mixture was heated to about 200 °C as described above. Usual work-up and subsequent vacuum distillation gave *n*-octyltrifluorosilane 0.63 g (88%) (Table 1). The reaction was repeated using 3 g (10.8 mmol) *n*-octyltriethoxysilane and 0.9 g (5.4 mmol) sodium hexafluorophosphate in the absence of tetraglyme for 5 h to obtain *n*-octylethoxydifluorosilane in 80%. The reaction was repeated for 12 h to obtain *n*-octyltrifluorosilane in 94% yield (Table 1);  $\delta_{\text{Si}}$ (400 MHz,  $\text{CDCl}_3$ ) –57.42 (q,  $J_{\text{Si-F}}$  285).

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