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Fluoridative degradation of cyclosiloxanes with alkali metal salts of perfluorinated complex anion. Part 5[☆]

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Abstract

Alkali metal salts of perfluorinated 'non-nucleophilic' complex anions were used for fluoridative degradation of cyclosiloxanes under thermal conditions in the absence and presence of high boiling multifunctional etheral solvent. The degradative products consist of fluorosilanes and fluorosiloxanes in low to moderate yields. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Procedures for the preparation of aryl, alkyl, aralkyl fluorosilanes from appropriate functionalized silicon compounds are known. These procedures include the use of antimony trifluoride with antimony pentachloride [1,2], fluorosulfonic acid [3], alkyl- and arylfluorophosphoranes [4] and metal fluorides with mineral acids [5]. Carbonyl fluorides were used as fluorinating reagent in organosilicon chemistry. Thus, alkyl- and phenylsilanols and alkoxyalkylsilanes were converted to the corresponding fluorosilanes in respectable yields [6].

Reaction of boron trifluoride-etherate with oligomeric organosiloxanes under heating gives organofluorosilanes [7a]. The former was also used in the fluorinations of such functionalized organosilanes as $R_{4-n}SiX_n$ [X = H, OR, Cl, Br] [7b,c]. Graphite-intercalated SbF_5 was used to fluorinate organo-silicon compounds involving Si–O and Si–Cl bonds [7d].

Under mild conditions, phosphorus pentafluoride was also found to fluorinate the Si–H bond in $(SiH_3)_2O$ [8a,b]. Boron trifluoride-etherate has also been used in the fluorination of the Si–H bond, e.g. in α-naphthyl ferrocenylfluorosilane (α-NpFcSiHF) [8c].

Perfluorinated complex anions, e.g. BF_4^-, PF_6^-, SbF_6^-, and AsF_6^-, have been regarded as non-nucleophilic and inert or 'innocent' anions. Electrochemical experiments [9] from several controlled-potential oxidations, have demonstrated that the anion, $[BF_4]^-$, is not truely inert and that high yields of fluorinated products result from the participation of this anion in the 'follow-up' reactions of electrode intermediates. Some of these anions were used [10] 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 the halogen is seemingly obvious in accounting for the reasonable yields of the fluorinated products. Tetrafluoroborate anion as its triphenylmethyl salt, under mild reaction conditions, has been reported [11] to fluorinate Si–H bond(s) of trialkyl- and dialkylsilanes. The reagent was further used for succesful fluorination of $HSiMe_2CH_2Fe(CO)_2Cp$ [Cp = π-cyclopentadienyl] [11]. Potassium tetrafluoroborate, under similar conditions, failed to fluorinate the Si–H bond in trialkylsilane [11].

To our knowledge, alkali metal salts of 'non-nucleophilic' perfluorinated complex anions have not been used for fluorination and degradation of such functionalized organosilicon compounds as cyclosiloxanes. We

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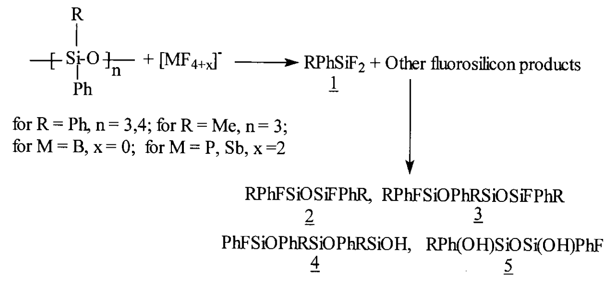

Scheme 1.

have recently reported the use of alkali metal salts of perfluorinated complex anions for the conversion of halo- and alkoxysilanes [12–16] to the corresponding fluorosilanes and haloboranes [17] to the corresponding fluoroboranes in high yield. We have also reported the use of the same reagents for the conversion of organochlorophosphorus compounds to their corresponding fluoro-derivatives in respectable yield [18–20]. We now want to report the use of these salts as potential sources of fluoride ions for the fluoridative degradation of cyclosiloxanes leading to fluorosilanes and fluorosiloxanes.

2. Results and discussion

When a mixture of hexaphenylcyclotrisiloxane and sodium tetrafluoroborate (Scheme 1) in the ratio 1:6 was heated to about 200°C for 45 min, a semi-solid resulted on cooling. Vacuum distillation gave a mixture of distillate which were identified by the NMR analysis. ^{29}Si-NMR spectra shows multiple signals due to diphenyldifluorosilane and monofluorinated organo-silicons together with other products in the ratio 80:20. Careful redistillation (b.p. 70–74°C/0.5 Torr)[1] gave diphenyldifluorosilane in 60% yield[2]. The monofluorinated organo-silicon products were idenfied by ^{29}Si-NMR and by mass spectra as 1,3-difluoro-1,1,3,3-tetraphenyldisiloxane, 1,5-difluoro-1,1,3,3,5,5-hexaphenyltrisiloxane and 1-fluoro-5-hydroxy-1,1,3,3,5,5-hexaphenyltrisiloxane in the ratio 50:40:10. ^{29}Si-NMR analysis (vide infra) of the residue of the reaction mixture shows all the four products in the ratio 26:20:16:12. An additional product, 1,5-dihydroxy-1,1,3,3,5,5-hexaphenyltrisiloxane, as identified by its ^{29}Si-NMR and mass spectra was formed in 26% relative abundance. Repeating the reaction, quenching the reaction products in water and appropriate work-up gave the same products. Mass spectral analysis of the discussed reaction mixture also identified 1,3,3,-trifluoro-1,1,3-triphenyldisiloxane which was formed by disproportionation of 1,1-difluoro-1,1,3,3-tetraphenyldisiloxane under the reaction conditions used. The solid residue of the reaction mixture was analyzed in deuterium oxide. ^{11}B-NMR spectra shows two signals at δ^{11}B 2.92 (q, J_{B-F} 16 Hz) and 1.10 (s) and ^{19}F-NMR spectra shows two signals at δ^{19}F −142.3(s) and −146.8(s). These NMR signals were assigned to $[FPh_2SiOBF_3]^-$ and $[BF_4]^-$, respectively.

The reaction of hexaphenylcyclotrisiloxane with tetrafluoroborate was repeated in 1:1 molar ratio for 2 h. Analysis of the products after work-up show unreacted starting material and the same five products (**1**–**5**) altogether in the ratio 30:70. The fluorinated products have almost similar distributions and none of them was formed in a higher ratio worth of isolation by distillation. The reaction was repeated with sodium hexafluorophosphate in the same ratio (1:1) for 1.5 h and the same five products were found to be formed in the ratio 10:35:25:12:18. On work-up the reaction mixture in water, extraction in methylene chloride, drying on anhydrous magnesium sulfate and removal of solvent, the same five products in the ratio 33:33:17:4:13 were obtained.

When the above discussed reaction of hexaphenylcyclotrisiloxane was repeated with potassium tetrafluoroborate in 1:6 molar ratio, a rather slow reaction was observed. For a reaction of 45 min, no diphenyldifluorosilane was formed. Other products viz., 1,3-difluoro-1,1,3,3-tetraphenyldisiloxane, 1,5-difluoro-1,1,3,3,5,5-hexaphenyltrisiloxane and 1-fluoro-5-hydroxy-1,1,3,3,5,5-hexaphenyltrisiloxane were formed in 70% in the ratio 3:2:11, the remaining being unreacted starting material. When the reaction was prolonged for about 2 h, about 6% diphenyldifluorosilane was found to be formed.

When a reaction mixture of octaphenylcyclotetrasiloxane and sodium tetrfluoroborate in the ratio 1:8 was heated for 45 min, a similar reaction mixture resulted. Vacuum distillation gave a mixture of products which were identified by their ^{29}Si-NMR spectra as diphenyldifluorosilane, 1,3-difluoro-1,1,3,3-tetraphenyldisiloxane, 1,5-difluoro-1,1,3,3,5,5-hexaphenyltrisiloxane and 1-fluoro-5-hydroxy-1,1,3,3,5,5-hexaphenyltrisiloxane in the ratio 21:54:15:10. Redistillation gave 1,3-difluoro-1,1,3,3-tetraphenyldisiloxane in 15% yield. The reaction was repeated for 1.5 h and the same five products were found to be formed in the ratio 40:30:10:15:5. Diphenyldifluorosilane was distilled in 35% yield. The residue of this reaction mixture was analyzed, after appropriate work-up, by ^{29}Si-NMR and mass spectra and was found to consist of the same reaction products in the ratio 3:16:21:18 together with the same additional product as identified in the reaction of hexaphenylcyclotrisiloxane in 42% relative abundance.

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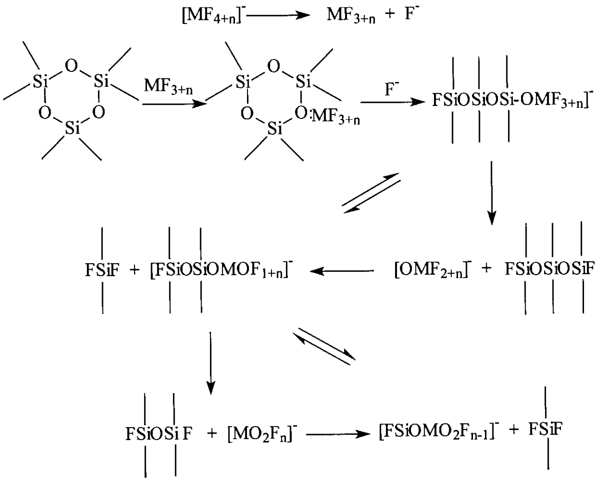
[1] B.p. 66–70°C/0.4 Torr: see Ref. [12].

[2] Yield is based on the assumption that all the silicons are difluorinated.



M = B, P, Sb; n = 0 (for B), 2 (for P, Sb)

Scheme 2.

When the above reaction was repeated in tetraglyme with sodium hexafluorophosphate in the same molar ratio for 15 min, the same products **1**–**5** were identified in the ratio.50:5:5:8:32 after appropriate work-up. Redistillation gave diphenyldifluorosilane in 42% yield. The reaction was repeated in the absence of solvent for 30 min to obtain the same products in the ratio 60:22:9:7:2. Diphenyldifluorosilane was distilled in 50% yield. The solid residue of the reaction mixture was analyzed in deuterium oxide and ^{29}Si-NMR spectra shows the products **1**–**3** in the ratio 5:17:22. ^{31}P-NMR spectra shows a doublet and a singlet at δ^{31}P -11.24 (d, J_{P-F} 1288 Hz) and -18.48 (s). These NMR signals were assigned to tris(fluorodiphenylsilyl) phosphate and tris(fluorotetraphenylsiloxysilyl)phosphate. The reaction of octaphenylcyclotetrasiloxane with sodium tetrafluoroborate was repeated, in the absence of any solvent, in 1:1 ratio for 2 h. Analysis of the reaction products, after appropriate aqueous work-up, by ^{29}Si-NMR and mass spectra shows the same compounds **1**–**5** in the ratio 20:17:10:15:38. The same reaction was repeated, in the absence of any solvent, with sodium hexafluorophosphate in the ratio 1:1 for 3 h. The reaction mixture was found to consist of the same products **1**–**5** in the ratio 17:30:20:20:10.

Reaction of trimethyltriphenylcyclotrisiloxane with sodium hexafluoroantimonate in the ratio 1:6 was also investigated under the same reaction conditions as described above. Aqueous work-up of the reaction mixture shows two main products viz., methylphenyldifluorosilane and 1,3-dihydroxy-1,3-dimethyl-1,3,-diphenyldisiloxane in the ratio 50:50. Vacuum distillation gave methylphenyldifluorosilane in 45% yield. When the same reaction was repeated, in the absence of any solvent, using sodium hexafluorophosphate in the ratio 1:1 for 45 min, all the five products **1**–**5** (for R = Me) were obtained in the ratio 8:40:24:16:12. Redistillation gave 1,3-difluoro-1,3-dimethyl-1,3-diphenyldisiloxane in 30% yield.

The reactivity of cyclosiloxanes is different from that of alkoxysilanes. We have recently reported [13–16] that the later reacts with alkali metal salts of perfluorinated complex anions even in a fluoride-equivalent ratio of the complex salts leading to near-quantitative yield of fluoro-silanes. Thus, diphenyldiethoxysilane, methylphenyldimethoxysilane and *n*-octadecyl dimethylethoxysilane react with alkali metal salts of complex anions in the fluoride-equivalent ratio to give near-quantitative yield of the fluorinated silanes. The cyclosiloxanes with the complex salts at even siloxy-equivalent ratio, generally, gives poor yield of the fluorosilanes and fluorosiloxanes. Lower ratio of salt:cyclosiloxane provides lower yield of fluorinated products.

It should be mentioned here that alkali metal fluorides, e.g. sodium fluoride does not react with cyclosiloxanes in the presence or absence of solvents. Therefore, salts of perfluorinated complex anions provide a route to the fluorinated silanes and -siloxanes from the cyclosiloxane precursors albeit reduced in yield.

In the discussed cases, that the reaction of cyclosiloxane with the complex salt gives poor yield of the expected fluorosilane may be attributed to poor polarization of the Si–O–Si bond by the in situ generated Lewis acid. In some reactions of cyclosiloxane with alkali metal complex salts monitored for a short time, silylfluorophosphate or -fluoroborate intermediates could be identified in the reaction mixture.

We previously reported [12,17] that when alkyl- or arylhalosilane or -haloborane was heated with alkali metal salts of perfluorinated complex anion in the presence or absence of any etheral solvent, corresponding fluorosilane or fluoroborane was formed in near quantitative yield. The reactions in the absence of solvent have shown the evolution of boron trifluoride gas [17] and the release of fluoride ion from the thermal decomposition of the complex anion, $[BF_4]^-$. The fluoride ion causes nucleophilic halogen-exchange fluorination in the halosilanes or haloboranes. We have further reported that alkoxysilanes [13,14] also react with the salts of ‘non-nucleophilic’ anions to give fluorosilanes and that the reactions provide a source of anhydrous fluoride ions and thermally liberated Lewis acids which undergo complexation with the alkoxysilane. In the present reactions, under similar conditions, thermally liberated Lewis acid undergoes complexation with oxygen in cyclosiloxane wherein the silicon center becomes polarized for nucleophilic attack by the liberated anhydrous fluoride ion (Scheme 2). The fluorinated ate anion undergoes further thermal decomposition forming difluorosilane, fluorinated siloxanes and fluorosilylfluoroborates, -phosphates and -antimonates which undergo further thermal decomposition leading to more difluorosilanes and fluorosiloxanes. Thermal decomposition of the fluorinated siloxanes also leads to the formation of difluorosilanes. This decomposition may involve participation of any intermediate complex fluoride ion or even the parent perfluorinated complex anion itself.

'Non-nucleophilic' perfluorinated complex anions are thermally labile and can be used as a source of anhydrous fluoride ions for nucleophilic fluorination of cyclosiloxanes. The process further involves fluoridative degradation of cyclosiloxanes leading to fluoro- and fluorosiloxy-silanes.

3. Experimental

Hexaphenylcyclotrisiloxane, octaphenylcyclotetracylosiloxane, methylphenylcyclotrisiloxanes (from Petrarch/Gelest), sodium salts of perfluorinated complex anions (from Aldrich) were of reagent grade and were used as received. Tetraglyme was dried over sodium under reflux. Boiling and melting points are uncorrected. ^{1}H-, ^{13}C-, ^{31}P- and ^{19}F-NMR spectra were recorded on a Varian superconducting NMR spectrometer at 400 MHz operating frequency for the ^{1}H-, 100.58 MHZ for the ^{13}C-, 162 MHz for the ^{31}P- and 376 MHz for the ^{19}F-NMR spectroscopy. In these experiments, TMS (internal) was used for ^{1}H- and ^{13}C-, 85% phosphoric acid (external) for ^{31}P- and $CFCl_3$ (external) for ^{19}F-NMR spectroscopy as references, respectively.

3.1. Reaction of hexaphenylcyclotrisiloxane

A mixture of 4 g (6.6 mmol) of hexaphenylcyclotrisiloxane and 4.8 g (44.0 mmol) of sodium tetrafluoroborate was heated for 45 min at about 200°C. Vacuum distillation at 80–90°C/0.5 Torr gave 2.4 g of distillate consisting of diphenyldifluorosilane and other difluorinated siloxanes together in the ratio 80:20. Redistillation gave diphenyl-difluorosilane in 45% yield (b.p. 70–74°C/0.5 Torr) in 99% purity. The yield is based on difluorination of each silicon moiety. The residue in the reaction flask was diluted with methylene chloride, filtered and dried over anhydrous magnesium sulfate. Removal of solvent gave a semi-solid which was analyzed by ^{29}Si-NMR and mass spectra. Reactions with potassium tetrafluoroborate and sodium hexafluorophosphate were similarly carried out.

Ph_2SiF_2 (**1**): ^{1}H-NMR [400 MHz, $CDCl_3$]: δ 7.87 (d, 8.1 Hz; dd, 1.4 Hz), 7.66 (t, 7.5 Hz), 7.56 (t, 7.5 Hz) [Lit. [12] 7.90(m), 7.28 (t), 7.14(t)]; ^{29}Si-NMR [400 MHz, $CDCl_3$]: δ -28.70 (t, $J_{\text{Si–F}}$ 290 Hz) [Lit. [12–14] -28.65 (t, $J_{\text{Si–F}}$ 292), -28.50 (t, $J_{\text{Si–F}}$ 290 Hz), -29.53 (t, $J_{\text{Si–F}}$ 291 Hz].

$FPh_2SiOSiPh_2F$ (**2**): ^{29}Si-NMR [400 MHz, $CDCl_3$]: δ -35.15 (d, $J_{\text{Si–F}}$ 278 Hz) [Lit. [12] -36.15 (d, $J_{\text{Si–F}}$ 286 Hz).

$FPh_2SiOSi(Ph_2)OSiPh_2F$ (**3**): ^{29}Si-NMR [400 MHz, $CDCl_3$]: δ -36.10 (d, $J_{\text{Si–F}}$ 284 Hz), -42.00 (s).

$FPh_2SiOSi(Ph_2)OSiPh_2OH$ (**4**): ^{29}Si-NMR [400 MHz, $CDCl_3$]: δ -36.51 (d, $J_{\text{Si–F}}$ 284 Hz), -42.50 (s), -32.90 (s).

3.1.1. Mass spectra

Ph_2SiF_2 (**1**): *m*/*e* 220–222 (Ph_2SiF_2, 86%), 154–156 (Ph_2SiF_2–SiF_2, 99%), 77 (Ph. from Ph–Ph).

$FPh_2SiOSiPh_2F$ (**2**): *m*/*e* 418–420 ($Ph_2FSiOSiFPh_2$, 55%), 341–343 ($Ph_2FsiOSiFPh$–Ph, 25%), 340–342 ($Ph_2FSiOSiFHPh$, 25%), 263–265 ($Ph_2FSiOSiFHPh$–Ph, 99%), 154 (Ph–Ph), 77 (Ph from Ph–Ph).

$FPh_2SiOSi(Ph_2)OSiPh_2F$ (**3**): *m*/*e* 616–618 [$FPh_2SiOSi(Ph_2)OSiPh_2F$, 32%], 415–417 [$FPh_2SiOSi(Ph_2)OSiPh_2F$–$SiPh_2F$, 52%], 402–404 [$(SiPhF)_2$, 20%], 201 (SiPhF, 40%), 154 (Ph–Ph, 40%), 77 (Ph from Ph–Ph, 20%).

$F_2PhSiOSiPh_2F$: *m*/*e* 360–362 [$F_2PhSiOSiPh_2F$, 45%], 282–284 [$F_2PhSiOSiPhF$, 10%], 205–207 [$F_2SiOSiPhF$, 100%), 154 [Ph–Ph, 65%].

3.2. Reaction of octaphenylcyclotetrasiloxane

A mixture of 4 g (5.02 mmol) octaphenylcyclotetrasiloxane and 4.82 g (44.2 mmol) sodium tetrafluoroborate was heated for 1.5 h as described above. Vacuum distillation gave a mixture of products consisting of diphenyldifluorosilane, 1,4-difluoro-1,1-3,3-tetraphenyldisiloxane and other fluorinated siloxanes in the ratio 21:54:25. Redistillation gave 1,3-difluoro-1,1,3,3-tetraphenyldisiloxane in 35% yield. The residue in the reaction flask was similarly analyzed as described above. Reaction with sodium hexafluorophosphate was similarly carried out for 30 min to obtain diphenyldifluorosilane in 50% yield. NMR and mass spectra of the products are similar as described above.

3.3. Reaction of trimethyltriphenylcyclotrisiloxane

To a solution of 4 g (8.74 mmol) of trimethyltriphenylcyclotrisiloxane in 4 g of tetraglyme was added 12.34 g (52.42 mmol) of sodium hexafluoroantimonate and the mixture was heated for 30 min as described above. The reaction mixture was analyzed by ^{29}Si-NMR and mass spectra. Vacuum distillation gave methylphenyldifluorosilane in 45% yield (b.p. 115–120°C/760 Torr). Reaction with sodium hexafluorophosphate was similarly carried out and analyzed.

$PhMeSiF_2$: ^{1}H-NMR [400 MHz, $CDCl_3$]: δ 7.64 (d, 8 Hz, dd, 1.6 Hz), 7.52 (t, 8 Hz, tt, 2 Hz), 7.43 (t, 8 Hz), 0.58 (t, 9 Hz) [Lit. [12] 7.45 (d, 8.1 Hz; dd, 1.5 Hz), 7.42 (t, 7.5 Hz, tt, 2.2 Hz), 7.32 (t, 7.5 Hz), 0.49 (t, 7.5 Hz); ^{29}Si-NMR [400 MHz, $CDCl_3$]: δ -11.80 (t, J_{Si-F} 287 Hz) [Lit. [13,14] -10.95 (t, J_{Si-F} 291 Hz), -10.94 (t, J_{Si-F} 289 Hz)]

FPhMeSiOMePhF: ^{29}Si-NMR [400 MHz, $CDCl_3$]: δ -20.5 (d, J 280 Hz).

FPhMeSiOSi(Ph)(Me)OSiMePhF: ^{29}Si-NMR [400 MHz, $CDCl_3$]: δ -21.56 (d, J 280 Hz), -31.47 (s).

FPhMeSiOSi(Ph)(Me)OSi(OH)MePh: ^{29}Si-NMR [400 MHz, $CDCl_3$]: δ -21.89 (d, J, 278 Hz), -31.94 (s), 30.65 (s).

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