

Preliminary communication

The acid promoted rearrangement of
1-hydroxyalkyl-tris(trimethylsilyl) silanes into
bis(trimethylsilyl)-1-trimethylsilylalkylsilanols: generation of a transient
silylium ion

Katrin Sternberg ^a, Manfred Michalik ^b, Hartmut Oehme ^{a,*}

^a Fachbereich Chemie der Universität Rostock, Rostock D-18051, Germany

^b Institut für Organische Katalyseforschung an der Universität Rostock e.V., Rostock D-18055, Germany

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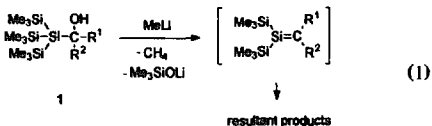
Abstract

In the presence of strong acids, 1-hydroxyalkyl-tris(trimethylsilyl)silanes (**1a–c**) undergo a rearrangement under formation of bis(trimethylsilyl)-1-trimethylsilylalkylsilanols (**4a–c**). The conversion is interpreted as proceeding through a silylium ion intermediate, which can be trapped with methanol or hydrofluoric acid to give the methoxysilane **5** or the fluorosilane **6** respectively.

Keywords: Silylium ions; Tris(trimethylsilyl)silylcarbenium ions; Hypersilylcarbenium ions; Peterson reaction

1. Introduction, results and discussion

1-Hydroxyalkyl-tris(trimethylsilyl)silanes (**1**), easily accessible by the reaction of tris(trimethylsilyl)silylmagnesium bromide with carbonyl compounds [1], proved to be suitable precursors for the synthesis of transient silenes. The conversion of these alcohols into Si=C systems is discussed in terms of a modified Peterson reaction, where the alcohol **1** is deprotonated with strong bases, e.g. organolithium derivatives, and after spontaneous elimination of trimethylsilanolate the respective silenes formed are indicated by different kinds of dimerization products or by trapping reactions (Eq. (1)) [1,2].

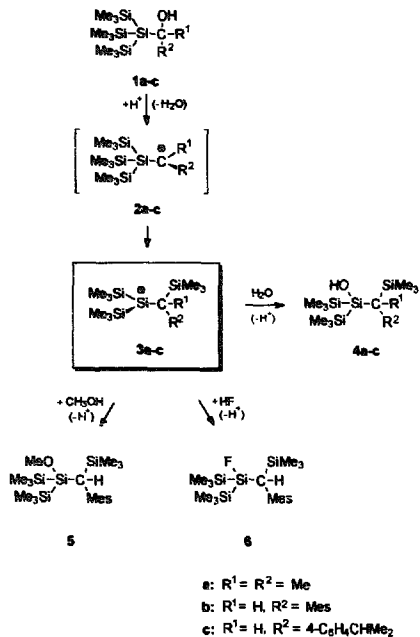


The Peterson reaction, i.e. originally the formation of olefins by elimination of trimethylsilanol from 2-hydroxyalkyltrimethylsilanes, can also be performed under acidic conditions [3]. Attempts to apply this reaction principle to the hypersilyl alcohols **1a–c** surprisingly did not lead to silenes or their resultant products, but after reaction of **1a–c** with strong acids, such as hydrochloric acid, we obtained in good yields the bis(trimethylsilyl)-1-trimethylsilylalkylsilanols **4a–c**. The structures of **4a–c** were elucidated on the basis of their IR, NMR and MS data (see Section 2).

The course of the conversion of **1a–c** into **4a–c** is demonstrated in Scheme 1. The acid catalyzed elimination of water from the alcohols **1a–c** leads to the carbenium ions **2a–c**. The migration of one trimethylsilyl group from silicon to the neighbouring carbon atom results in the formation of the silylium ions **3a–c**, which immediately add water to give the silanols **4a–c**.

1,2-Migrations of alkyl, aryl and also trimethylsilyl groups from tetracoordinated silicon to a neighbouring carbenium centre under simultaneous generation of a silylium ion have already been described [4]. These experimental observations confirm expectations deduced from theoretical work, according to which α -silyl carbenium ions should generally be less stable than the isomeric silylium ions [5]. In our particular case the

* Corresponding author.



Scheme 1. The acid catalyzed elimination of water from the 1-hydroxyalkyltris(trimethylsilyl)silanes **1a–c** and the generation of the silylium ions **3a–c**. The re-addition of water to **3a–c** affords the silanols **4a–c** and trapping reactions of **3b** with methanol and HF give the methoxysilane **5** and the fluorosilane **6** respectively.

1,2-trimethylsilyl shift is probably favoured by the fact that the hyperconjugative stabilization of the silylium ions **3a–c** by the $\text{CR}^1\text{R}^2\text{SiMe}_3$ groups is more effective than the stabilization of the carbenium ions **2a–c** by the hypersilyl rest. Whereas an α -silyl group at a carbenium ion centre is destabilizing the system relative to a methyl group [6], trimethylsilylmethyl groups cause a small but effective stabilization of a silylium ion [7].

For some mechanistic studies of the acid promoted rearrangement of 1-hydroxyalkyltris(trimethylsilyl)silanes we have chosen **1b**. The kinetic control of the conversion of **1b** into **4b** (^1H NMR, solvent acetone- d_6 , equimolar quantities of trifluoroacetic acid) revealed that the consumption of the alcohol **1b** as well as the generation of the silanol **4b** proceed with first order. Additional water in the reaction mixture does not increase the reaction rate of the formation of **4b**. Thus, a bimolecular reaction **2b** \rightarrow **3b**, involving an attack of water at the central tetracoordinated silicon atom of **2b**

facilitating the trimethylsilyl shift and increasing the rate of generation of the silylium ion, can be excluded – at least in the rate determining step of the reaction.

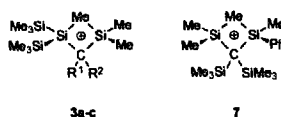
When the water, eliminated from **1a–c**, is fixed by suitable reagents, it should be also possible to trap the generated silylium ions with other nucleophiles. This could easily be achieved by using concentrated sulphuric acid as the catalyst and dehydrating agent, and in this paper we describe the behaviour of **1b** towards methanol and hydrofluoric acid.

When some drops of H_2SO_4 are added to a solution of **1b** in methanol, the methoxysilane **5** is obtained in good yield. Similarly, when a mixture of HF and H_2SO_4 is given to an ethereal solution of **1b**, the fluorosilane **6** is formed almost quantitatively.

Of course, in principle, **5** and **6** can also be formed by the interaction of the silanol **4b** with methanol or HF respectively. But carefully controlled experiments showed that under conditions applied for the conversion of **1b** into **5** or **6**, the silanol **4b** with methanol or HF gives only traces of the methoxysilane or the fluorosilane respectively. Only the addition of considerable quantities of conc. H_2SO_4 to the methanolic solution of **4b** or to the ethereal HF-containing solution of **4b** respectively gradually shifts the equilibria of the methoxysilane **5** or to the fluorosilane **6**.

In conclusion, the conversion of **1c** into the methoxysilane **5** or the fluorosilane **6** can best be interpreted by the existence of more or less free silylium ions, which are trapped by methanol or HF (Scheme 1). Thus, we may also exclude a concerted intramolecular shift of the OH and the Me_3Si groups, comparable with the AlCl_3 catalyzed rearrangement of arylchloromethylsilanes $\text{ArMe}_2\text{SiCH}_2\text{Cl}$ into benzylchlorosilanes $\text{Me}_2\text{Si}(\text{Cl})\text{CH}_2\text{Ar}$, described by Eaborn and coworkers [8].

Information about the structure of the transient silylium ions cannot be taken from the material available. In particular, methyl-bridged forms of **3**, showing a remarkable similarity to the cations **7**, obtained by Eaborn and coworkers by the treatment of trisilyl-iodosilanes with silver salts [9], cannot be excluded. On the contrary, isomeric products formed by the attack of the nucleophiles at the $\text{CSiMe}_3\text{–Si}$ atom could not be detected.



2. Experimental details

1c. As described previously [1,2], **1c** is prepared by the reaction of tris(trimethylsilyl)silylmagnesium bromide, made from 14.7 g (0.03 mol) $(\text{Me}_3\text{Si})_3\text{SiLi} \cdot 3\text{THF}$ [10] and an equimolar quantity of MgBr_2 , and 4.6 g (0.03 mol) 4-isopropylbenzaldehyde. The product is purified by Kugelrohr distillation and recrystallization from acetonitrile, yield 8.35 g (68%), m.p. 70°C [11]. IR (Nujol): $\nu = 3525$ (OH_{free}), 3431 cm^{-1} (OH_{ass}). ^1H NMR (250 MHz, benzene- d_6): $\delta = 0.26$ (s, SiCH_3 , 27H), 1.15 (d, $^3J = 3.05 \text{ Hz}$, COH, 1H), 1.16 (d, $^3J = 7.03 \text{ Hz}$, $\text{CH}(\text{C}_6\text{H}_5)_2$, 6H), 2.73 (sept, $^3J = 7.03 \text{ Hz}$, $\text{Me}_2\text{C}(\text{H}, 1\text{H})$, 4.86 (d, $^3J = 3.05 \text{ Hz}$, CHO, 1H), 7.13 (m, Ar-H, 4H). ^{13}C NMR (62.9 MHz, CDCl_3 , DEPT): $\delta = 1.5$ (SiCH_3), 24.10 and 24.12 (CHMe_2), 33.8 (CHMe_2), 69.2 (COH), 125.5, 126.3, 144.7 and 147.1 (arom. C). ^{29}Si NMR (79.5 MHz, CDCl_3): $\delta = -13.1$ (SiMe_3), -67.7 (SiSiMe_3). MS m/z (%): 395 (0.7) [$\text{M}^+ - \text{H}$], 379 (100) [$\text{M}^+ - \text{OH}$], 307 (15) [$\text{M}^+ - \text{OSiMe}_3$]. Anal. Found: C, 57.09; H, 10.08. $\text{C}_{19}\text{H}_{40}\text{OSi}_4$ (396.87) Calc.: C, 57.50; H, 10.16%.

4a. To an ethereal solution of 0.5 g (1.6×10^{-3} mol) **1a** [1] an equimolar quantity of ethereal HCl is added and the mixture is stirred for 5 h. After addition of aqueous NaHCO_3 solution, the organic phase is separated, dried and evaporated. Kugelrohr distillation (75°C, 0.5 Torr) and chromatographic purification (silica gel, hexane/ethylacetate 20:1) gave a colourless oil (0.3 g, 60%). IR (Nujol): $\nu = 3461$ (OH_{ass}), 3650 and 3678 cm^{-1} (OH_{free}). ^1H NMR (250 MHz, benzene- d_6): $\delta = 0.05$ (s, CSiCH_3 , 9H), 0.19 (s, SiSiCH_3 , 18H), 1.13 (s, CCH_3 , 6H). ^{13}C NMR (100.6 MHz, benzene- d_6 , DEPT): $\delta = -2.9$ (CSiCH_3), 0.0 (SiSiCH_3), 11.4 (CCH_3), 20.4 (CCH_3). ^{29}Si NMR (79.5 MHz, benzene- d_6): $\delta = -19.6$ (SiSiMe_3), 7.0 (CSiMe_3), 17.6 (SiOH). MS (Cl, isobutane) m/z (%): 305 (6) [$\text{M}^+ - \text{Si}$], 291 (100) [$\text{M}^+ - \text{CH}_3$], 289 (60) [$\text{M}^+ - \text{OH}$]. Anal. Found: C, 46.87; H, 11.39. $\text{C}_{12}\text{H}_{24}\text{OSi}_4$ (306.75) Calc.: C, 46.99; H, 11.17%.

4b. As described above, the reaction of 0.5 g (1.3×10^{-3} mol) **1b** [1] with ethereal HCl leads to a product which is purified by recrystallization from acetonitrile and chromatography (silica gel, hexane/ethylacetate 20:1). Yield 0.35 g (70%), m.p. 85°C. IR (Nujol): $\nu = 3410$ (OH_{ass}), 3652 and 3678 cm^{-1} (OH_{free}). ^1H NMR (250 MHz, benzene- d_6): $\delta = -0.03$, 0.19 and 0.24 (3s, SiCH_3 , 3 \times 9H), 1.56 (s, OH, 1H), 2.13, 2.19 and 2.40 (3s, ArCH_3 , 3 \times 3H), 2.31 (s, CH, 1H), 6.77 and 6.78 (2s, ArH, 2 \times 1H). ^{13}C NMR (100.6 MHz, benzene- d_6 , DEPT): $\delta = -0.2$, 0.0 and 2.5 (SiCH_3), 20.9, 22.9 and 23.2 (ArCH_3), 25.0 (CH), 129.5, 130.3, 132.9, 134.7, 135.9 and 139.4 (aromat. C). ^{29}Si NMR (79.5 MHz, benzene- d_6): $\delta = -19.6$ and -18.5 (SiSiMe_3), 2.6 (CSiMe_3), 11.0 (SiOH). MS (Cl, isobutane) m/z (%): 395 (30) [$\text{M}^+ - \text{H}$], 381 (38) [$\text{M}^+ - \text{CH}_3$], 379 (100)

[$\text{M}^+ - \text{OH}$]. Anal. Found: C, 57.44; H, 10.15. $\text{C}_{19}\text{H}_{40}\text{OSi}_4$ (396.87) Calc.: C, 57.50; H, 10.16%.

4c. Similarly 0.5 g (1.26×10^{-3} mol) **1c** and ethereal HCl give, after chromatographic purification (silica gel, hexane/ethylacetate 20:1), 0.25 g (50%) of a colourless oil. IR (cap.): $\nu = 3647$ and 3676 (OH_{free}), 3441 cm^{-1} (OH_{ass}). ^1H NMR (250 MHz, benzene- d_6): $\delta = 0.12$, 0.13 and 0.19 (3s, SiCH_3 , 3 \times 9H), 1.14 (d, $^3J = 6.70 \text{ Hz}$, $\text{CH}(\text{C}_6\text{H}_5)_2$, 6H), 2.07 (s, SiCH_3 , 1H), 2.71 (sept, $^3J = 6.70 \text{ Hz}$, 1H), 7.02 (m, Ar-H, 4H). ^{13}C NMR (100.6 MHz, benzene- d_6): $\delta = -0.6$, -0.1 and 0.5 (SiCH_3), 24.4 (CHMe_2), 30.3 (SiCH_3), 34.1 (CHMe_2), 127.0 and 129.8 (arom. CH), 139.4 and 144.9 (arom. quart. C). ^{29}Si NMR (79.5 MHz, benzene- d_6): $\delta = -18.9$ and -21.9 (SiSiMe_3), 1.9 (CSiMe_3), 10.3 (SiOH). MS m/z (%): 396 (10) [M^+], 323 (50) [$\text{M}^+ - \text{SiMe}_3$], 307 (100) [$\text{M}^+ - \text{OSiMe}_3$]. Anal. Found: C, 57.02; H, 10.15. $\text{C}_{19}\text{H}_{40}\text{OSi}_4$ (396.87) Calc.: C, 57.50; H, 10.16%.

5. At room temperature 0.1 ml conc. H_2SO_4 is given to a stirred solution of 0.3 g (7.6×10^{-4} mol) of **1b** in 30 ml of methanol. After 4 h the solid precipitate of **5** is separated and recrystallized from acetonitrile. Yield 0.27 g (87%), m.p. 110°C. IR (Nujol): $\nu = 1088 \text{ cm}^{-1}$ (SiOC). ^1H NMR (250 MHz, benzene- d_6): $\delta = -0.17$, 0.21 and 0.28 (3s, SiCH_3 , 3 \times 9H), 2.14, 2.22 and 2.45 (3s, Aryl CH_3 , 3 \times 3H), 3.37 (s, OCH, 3H), 6.77 and 6.80 (2s, ArH, 2 \times 1H). ^{13}C NMR (100.6 MHz, benzene- d_6 , DEPT): $\delta = 0.1$, 0.5 and 1.1 (SiCH_3), 20.8, 22.7 and 22.8 (Ar CH_3), 23.4 (CH), 53.4 (OCH $_3$), 129.3, 130.2, 132.8, 134.7, 136.2 and 139.0 (aromat. C). ^{29}Si NMR (79.5 MHz, benzene- d_6): $\delta = -19.8$ and -18.8 (SiSiMe_3), 2.8 (CSiMe_3), 15.3 (SiOMe). MS (Cl, isobutane) m/z (%): 395 (80) [$\text{M}^+ - \text{CH}_3$], 379 (60) [$\text{M}^+ - \text{OCH}_3$], 306 (100) [$\text{M}^+ - \text{MeOSiMe}_3$]. Anal. Found: C, 58.33; H, 10.38. $\text{C}_{20}\text{H}_{42}\text{OSi}_4$ (410.89) Calc.: C, 58.46; H, 10.30%.

6. To a solution of 0.3 g (7.6×10^{-4} mol) **1b** in 30 ml of ether, a 2.5 molar excess of HF (0.04 g) in 0.1 ml H_2SO_4 is given at room temperature. After standing for 5 h the ethereal solution is separated and evaporated. The residue is washed with hexane to give a colourless oil which gradually crystallizes. Yield 0.25 g (83%). IR (cap.): $\nu = 1019 \text{ cm}^{-1}$ (SiF). ^1H NMR (250 MHz, benzene- d_6): $\delta = -0.03$, 0.20 and 0.25 (3s, SiCH_3 , 3 \times 9H), 2.12, 2.16 and 2.39 (3s, Aryl CH_3 , 3 \times 3H), 2.34 (d, $^2J_{\text{FH}} = 19.1 \text{ Hz}$, FSiCH, 1H), 6.76 (s, Ar-H, 2H). ^{13}C NMR (62.9 MHz, benzene- d_6): $\delta = -0.7$ (d, $^3J_{\text{FC}} = 2.0 \text{ Hz}$, SiSiCH $_3$), -0.3 (d, $^3J_{\text{FC}} = 2.0 \text{ Hz}$, SiSiCH $_3$), 2.1 (CSiCH_3), 20.7, 22.5 and 22.6 (Aryl CH_3), 25.6 (d, $^2J_{\text{FC}} = 13.4 \text{ Hz}$, FSiCH), 129.4, 130.3, 131.4, 133.2, 135.9 and 138.5 (arom. C). ^{19}F NMR (235.4 MHz, benzene- d_6): $\delta = -191.1$ (SiF). ^{29}Si NMR (79.5 MHz, benzene- d_6): $\delta = -19.7$ (d, $^2J_{\text{SiF}} = 23.1 \text{ Hz}$, SiSiMe $_3$), -18.4 (d, $^2J_{\text{SiF}} = 22.3 \text{ Hz}$, SiSiMe $_3$), 2.7 (CSiMe_3), 35.4 (d, $^1J_{\text{SiF}} = 343.4 \text{ Hz}$,

FSi). MS (70 eV) m/z (%): 398 (12) $[M^+]$, 383 (11) $[M^+ - CH_3]$, 325 (70) $[M^+ - SiMe_3]$, 73 (100) $[SiMe_3^+]$. Anal. Found: C, 57.00; H, 9.64. $C_{19}H_{39}FSi_4$ (398.86) Calc.: C, 57.22; H, 9.86%.

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