The Acid-Induced Rearrangement of 1-Hydroxyalkyltris(trimethylsilyl)silanes

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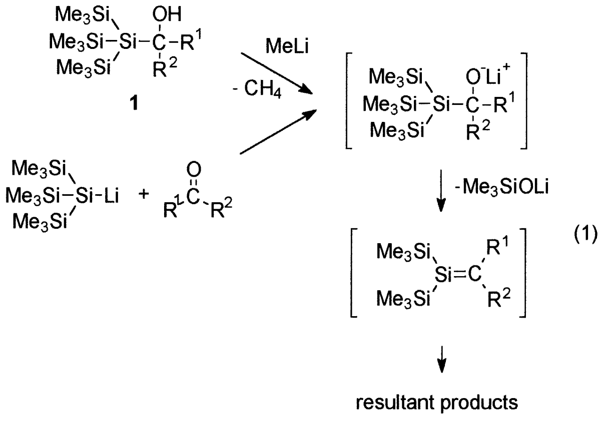
In the presence of strong acids, such as HCl or H_2SO_4, 1-hydroxyalkyltris(trimethylsilyl)silanes $(Me_3Si)_3Si-C(OH)R^1R^2$ (**1a−f**) isomerize by 1,2-Me_3Si/OH exchange to give the trimethylsilylmethylsilanols $(Me_3Si)_2Si(OH)-C(SiMe_3)R^1R^2$ (**4a−f**) [R^1,R^2: **a**: Me, Me; **b**: H, 4-MeC_6H_4; **c**: H, 4-*i*PrC_6H_4; **d**: H, Mes; **e**: H, 2-$Me_2NC_6H_4$; **f**: H, 2,4,6-$(MeO)_3C_6H_2$]. A mechanism for the isomerization is proposed. In the case of the reaction of **1d** with sulfuric acid, the silylsulfate $(Me_3Si)_2Si(OSO_3H)-C(SiMe_3)HMes$ (**5**) was isolated. **5** is the intermediate in the H_2SO_4-catalyzed isomerization of **1d** and was converted in situ with methanol, acetic anhydride, HF or HCl to give the respective methoxysilane **6**, acetoxysilane **7**, fluorosilane **8**, or chlorosilane **9**. Deprotonation of **4a, d, f** with sodium hydride causes a further rearrangement, a 1,3-C,O-trimethylsilyl migration, to give the siloxanes $(Me_3Si)_2(Me_3SiO)Si-CHR^1R^2$ (**11a, d, f**).

The base-induced elimination of trimethylsilanolate from 1-hydroxyalkyltris(trimethylsilyl)silanes (**1**) proved to be a suitable method for the synthesis of silaethenes. The mechanism of the process is interpreted as a variation of the Peterson reaction, in such a way that a carbon atom in the original Peterson product is replaced by a silicon atom. The polysilanylalcohols **1** are readily available by the addition of tris(trimethylsilyl)silylmagnesium bromide to the carbonyl group of aldehydes or ketones[1], and the isolated polysilanylalcohols are deprotonated with organolithium compounds, initiating the elimination of trimethylsilanolate to give transient silenes, which were characterized by trapping reactions and as different kinds of dimers (Eq. 1)[2]. The generation of silenes by the Peterson mechanism can also be performed in an in situ reaction from $(Me_3Si)_3SiLi$ and carbonyl compounds[3], and recently Apeloig et al. successfully applied this method to the synthesis of new stable silenes[4].

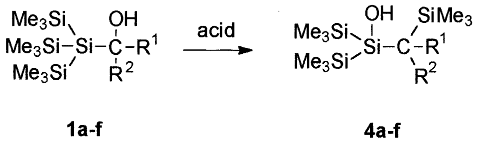


(1)

The Peterson reaction, originally the formation of olefins by a base-induced elimination of trimethylsilanol from 2-trimethylsilyl alcohols, can also be performed under acidic conditions[5]. During the course of our studies on the synthetic utility of 1-hydroxyalkyltris(trimethylsilyl)silanes (**1**) we therefore explored their conversion by strong acids which, in contrast to the base-promoted sila-Peterson reaction, did not give elimination and silene formation but an interesting rearrangement of the hydroxyalkylpolysilanes **1** into 1-trimethylsilylalkylsilanols **4**.

The Reaction of 1-Hydroxyalkyltris(trimethylsilyl)silanes (1) with Acids

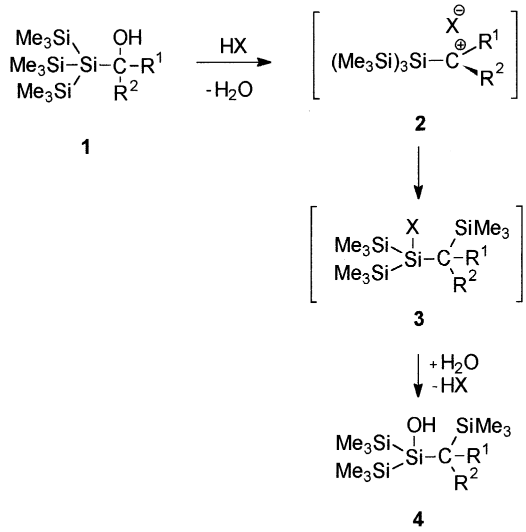
Strong acids, such as hydrochloric acid in ether, cause the 1-hypersilylalcohols **1a−f** to rapidly undergo a rearrangement to afford the bis(trimethylsilyl)-1-trimethylsilylalkylsilanols **4a−f**. The silanols **4a−f** are colorless solids. Their structures were elucidated on the basis of their IR, NMR and MS data (see Experimental Section).



(2)

a: $R^1 = R^2 = Me$
b: $R^1 = H$; $R^2 =$ 4-Me-C_6H_4
c: $R^1 = H$; $R^2 =$ 4-iPr-C_6H_4
d: $R^1 = H$; $R^2 =$ Mes
e: $R^1 = H$; $R^2 =$ 2-Me_2N-C_6H_4
f: $R^1 = H$; $R^2 =$ 2,4,6-$(MeO)_3C_6H_2$

The proposed pathway for the conversion of **1a−f** into **4a−f** is outlined in Eq. 3. The acid-catalyzed elimination of water from the alcohols **1a−f**, affording the carbenium ions **2a−f**, is followed by a migration of one trimethylsilyl group from the central silicon atom to the neighboring carbon atom and attack of X^-, the conjugate base of the acid used as the catalyst, at the electrophilic silicon. Hydrolysis of the Si−X bond of **3a−f** by the eliminated water gives the silanols **4a−f**.



(3)

As the subject of some mechanistic studies we have chosen compound **1d**. The kinetic control of its conversion into **4d** (^{1}H NMR, solvent - [D$_6$]acetone, equimolar quantities of trifluoroacetic acid) revealed that the consumption of the alcohol **1d**, as well as the generation of the silanol **4d**, is a first-order process. Additional water in the reaction mixture does not increase the rate of formation of **4d**. Thus, a bimolecular reaction, involving a direct attack of water at the central tetracoordinated silicon atom of **2d** facilitating the trimethylsilyl shift and increasing the rate of the silanolate formation, can be excluded − at least in the rate-determining step of the reaction.

1,2-Migrations of alkyl, aryl and also trimethylsilyl groups from a tetracoordinated silicon center to a neighboring carbenium center appear to be common and have been described in the literature. Kumada et al. studied the $AlCl_3$-catalyzed rearrangement of chloromethyldisilanes into chlorosilanes[6]. They suggested a mechanism involving a slow rate-determining step consisting of the ionization of the carbon-chlorine bond, followed by a fast step involving synchronous nucleophilic attack by the halide on silicon and migration of a Me_3Si group from silicon to carbon. A similar mechanism was reported by Brook et al.[7] for the closely related reaction, the boron trifluoride-induced rearrangement of (hydroxymethyl)silicon compounds to give fluorosilanes. The BCl_3-induced conversion of methoxymethyltris(trimethylsilyl)silanes $(Me_3Si)_3Si-CH(OMe)R$ into the chlorosilanes $(Me_3Si)_2Si(Cl)-CH(SiMe_3)R$, described by Märkl et al., is similarly discussed as a synchronous process[8].

Isomerizations of silyl-substituted carbenium ions with the simultaneous generation of a silylium-ion intermediate or transition state have been described more recently[9]. An important contribution to this area was made by Apeloig and Stanger, who provided evidence of a direct, solvent-unassisted 1,2-methyl migration of a solvolytically produced α-trimethylsilyl carbenium ion[10]. 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[10][11]. In our particular case the 1,2-trimethylsilyl shift is probably favored by the fact that the hyperconjugative stabilization of the silylium-ion transition-states by the $CR^1R^2SiMe_3$ groups is more effective than the stabilization of the carbenium ions **2a−f** by the hypersilyl substituent. Whereas an α-silyl group at a carbenium ion center destabilizes the system relative to a methyl group[11], trimethylsilylmethyl groups cause a small but significant stabilization of a silylium ion[12].

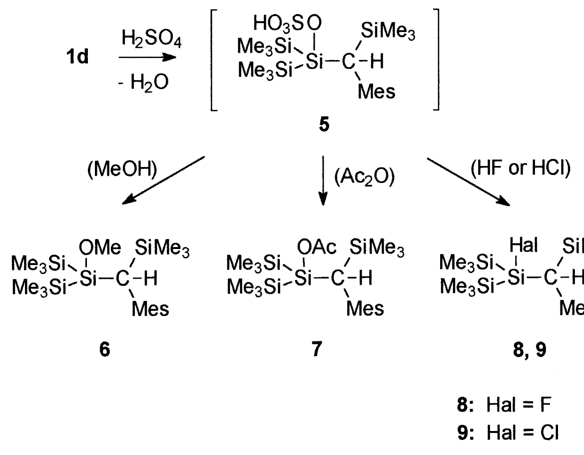
Both mechanisms, the synchronous process involving X^- in the trimethylsilyl shift and that involving a silylium-ion intermediate, fit the experimental results and agree with the proposed reaction path of the conversion of **1a−f** into **4a−f**. However, detailed information on the nature of the intermediates cannot be obtained from the data available and, in particular, the question of the existence of a silylium-ion intermediate remains unanswered.

Recently we became aware of a related rearrangement, the conversion of trimethylsiloxymethyl-chlorosilanes $(Me_3Si)_2Si(Cl)-C(OSiMe_3)R_2$ via chloromethyldisiloxanes $(Me_3Si)_2Si(OSiMe_3)-C(Cl)R_2$ into trimethylsilylmethylchlorodisiloxanes $Me_3Si(Me_3SiO)Si(Cl)-C(SiMe_3)R_2$, and it is very likely that this proceeds along a similar reaction path[13].

The polysilanylalcohols **1e** and **1f** were included in our studies with the aim of stabilizing the intermediate carbenium ion by introducing electron-donating substituents and thus preventing the 1,2-Si,C-trimethylsilyl shift. However, as demonstrated in Eq. 2, **1e** and **1f** follow the same isomerization pattern and give the silanols **4e** and **4f**, respectively.

When concentrated sulfuric acid is used as the catalyst for the rearrangement of **1a−f**, the water eliminated from the alcohols is not available and other nucleophiles present in the mixture can attack the electrophilic silicon center of **3a−f** to give the functionalized silanes **6−9**. For these experiments we have chosen to study **1d**. Thus, the addition of several drops of concentrated H_2SO_4 to a solution of **1d** in methanol results in the formation of the methoxysilane **6**. Under the same conditions **1e** and **1f** give **6e** and **6f**, respectively. The reaction of **1d** with sulfuric acid in acetic anhydride affords the acetoxysilane **7**. Similarly, when a mixture of HF and H_2SO_4 is added to an ethereal solution of **1d**, the fluorosilane **8** is formed almost quantitatively. The chlorosilane **9** is obtained by passing gaseous HCl through a solution of **1d** and H_2SO_4 in ether (Eq. 4).

All these reactions proceed through the silylsulfate **5**, and **6−9** are formed by replacement of the HSO_4 group of **5** by the appropriate nucleophile. This was demonstrated by the reaction of **1b** with sulfuric acid in ether in the absence of further nucleophiles, which allowed the isolation of **5** in the



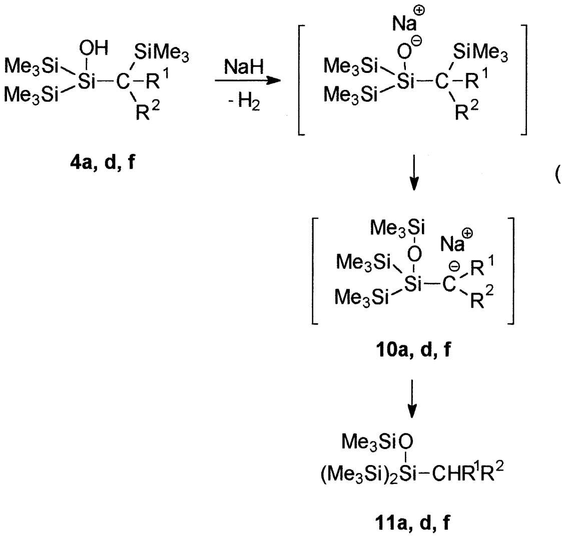
(4)

form of a colorless, crystalline, highly moisture-sensitive compound.

The structures of **4**–**9** were elucidated by a full spectral analysis [IR; ^1H-, ^{13}C- and ^{29}Si-NMR spectroscopy, MS and elemental analyses (see Experimental Section)].

The Base- Induced Rearrangement of the 1-Trimethylsilylalkylsilanols 4 into the Disiloxanes 11

Deprotonation of the silanols **4** with sodium hydride leads to a further rearrangement, with one trimethylsilyl group migrating from carbon to oxygen. The reaction was performed with **4a**, **4d** and **4f**, producing the disiloxanes **11a**, **11d** and **11f**, respectively (Eq. 5).



(5)

Such 1,3-C,O-trimethylsilyl migrations are well known, e.g. they are probably part of the Peterson olefination process[5]. Interestingly, the conversion of **4a, d, f** into **11a, d, f** is easily achieved by treatment with NaH in THF. In ether the reaction proceeds very slowly, and after deprotonation of **4a, d, f** with organolithium reagents, the silanols were recovered unchanged. This demonstrates the dependence of the nucleophilicity of the silanolate oxygen atom on the counter ion and the solvent. In the course of the Peterson reaction, the 1,3-Si,O-trimethylsilyl migration is followed by a trimethylsilanolate elimination to establish the olefinic double bond. In contrast, in the case of **10a, d, f** the high energy of the silicon oxygen bond, as expected, prevents a silanolate elimination and silaethene formation.

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Experimental Section

All reactions involving organometallic reagents were carried out under purified argon. – NMR: Bruker AC 250 or Bruker ARX 300, tetramethylsilane as internal standard. – IR: Nicolet 205 FT-IR. – MS: Intectra AMD 402, chemical ionization with isobutane as the reactant gas. – $(Me_3Si)_3SiLi \cdot 3$ THF[14], **1a**[1], **1c**[15], **1d**[1] and **1e**[2] were prepared as reported in the literature. – All yields given refer to amounts obtained after chromatographic separation and purification. – The syntheses and the spectral data characterizing the structures of **4a**, **4c**, **4d**, **6** and **8** were described previously[15].

Synthesis of the 1-Hydroxyalkyltris(trimethylsilyl)silanes **1b** and **1f**: As described previously[1], **1b** and **1f** were prepared by the reaction of tris(trimethylsilyl)silylmagnesium bromide, made from 14.7 g (0.03 mol) of $(Me_3Si)_3SiLi \cdot 3$ THF and an equimolar quantity of $MgBr_2$ and 3.6 g (0.03 mol) of 4-methylbenzaldehyde or 5.89 g (0.03 mol) of 2,4,6-trimethoxybenzaldehyde, respectively.

1b: The product was purified by column chromatography (silica gel, heptane/ethyl acetate 20/1) and recrystallization from acetonitrile; yield 7.2 g (65%), m.p. 78°C. – IR (nujol): $\tilde{\nu}$ = 3518.5 cm^{-1} (OH). – ^1H NMR ([D$_6$]benzene): δ = 0.26 (s, $SiCH_3$, 27 H), 1.12 (d, ^3J = 2.74 Hz, OH, 1 H), 2.12 (s, p-CH_3, 3 H), 4.81 (d, ^3J = 2.74 Hz, CH, 1 H), 6.97 (m, ArH, 2 H), 7.16 (m, ArH, 2 H). – ^{13}C NMR ([D$_6$]benzene): δ = 1.8 ($SiCH_3$), 21.0 (p-CH_3); 69.2 (CH), 125.8, 129.1 (arom. CH), 135.6, 145.0 (quart. arom. C). – ^{29}Si NMR ([D$_6$]benzene): δ = –13.1 ($SiMe_3$), –67.7 ($\mathit{Si}SiMe_3$). – MS: m/z (%) = 351 (100) [M^+ – OH], 295 (4) [M^+ – $SiMe_3$], 277 (6) [M^+ – $C_6H_4CH_3$], 247 (16) [$Si(SiMe_3)_3{}^+$], 121 (15) [M^+ – $Si(SiMe_3)_3$]. – $C_{17}H_{36}OSi_4$ (368.81): calcd. C 55.36, H 9.84; found C 55.13, H 9.81.

1f: Recrystallized from heptane, yield 12.0 g (90%), m.p. 115°C. – IR (nujol): $\tilde{\nu}$ = 3579.8 cm^{-1} (OH free), 3455.0 (OH ass.). – ^1H NMR ([D$_6$]benzene): δ = 0.31 (s, $SiCH_3$, 27 H), 3.23 (s, o-OCH_3, 6 H), 3.34 (s, p-OCH_3, 3 H), 3.45 (d, OH, 1 H, ^3J = 10.98 Hz), 5.93 (d, CH, 1 H, ^3J = 10.98 Hz), 6.0 (s, ArH, 2 H). – ^{13}C NMR ([D$_6$]benzene): δ = 1.7 ($SiCH_3$), 54.7 (o-OCH_3), 54.9 (p-OCH_3), 59.0 (CH), 127.6 (arom. CH), 115.6, 157.4, 160.1 (quart. arom. C). – ^{29}Si NMR ([D$_6$]benzene): δ = –12.6 ($SiMe_3$), –73.1 ($\mathit{Si}SiMe_3$). – MS: m/z (%) = 444 (0.6) [M^+]; 371 (3) [M^+ – $SiMe_3$]; 197 (100) [M^+ – $Si(SiMe_3)_3$]. – $C_{19}H_{40}O_4Si_4$ (444.87): calcd. C 51.30, H 9.06; found C 51.14, H 9.22.

Isomerization of **1b**, **1e** *and* **1f** *into the Silanols* **4b**, **4e** *and* **4f**:

4b: To an ethereal solution of 0.5 g (1.35 mmol) of **1b** was added an equimolar quantity of ethereal HCl at room temperature and the mixture was stirred for 5 h. After addition of aqueous $NaHCO_3$ solution, the organic phase was separated, dried and the solvent evaporated. Kugelrohr distillation and chromatographic purification (silica gel, heptane/ethyl acetate 20/1) of the residue gave 0.25 g (50%) of colorless crystals, m.p. 48°C. – IR (nujol): $\tilde{\nu}$ = 3647 and 3676 cm^{-1} (OH), 3427 (OH ass.). – ^1H NMR ([D]$_6$benzene): δ = 0.12, 0.14 and 0.18 (3 s, $SiCH_3$, 3 × 9 H), 2.05 (s, CH, 1 H), 2.10 (s, Ar–CH_3, 3 H), 6.93 (m, ArH, 4 H). – ^{13}C NMR

($[D_6]$benzene): δ = −0.4, 0.0 and 0.6 (SiCH$_3$), 20.9 (ArCH$_3$), 30.1 (CH), 129.4, 129.5, 133.3 and 138.6 (arom. C). − ^{29}Si NMR ($[D_6]$benzene): δ = −19.2 and −18.7 (Si*Si*Me$_3$), 1.9 (CSiMe$_3$), 10.4 (SiOH). − MS: *m*/*z* (%) = 368 (3) [M$^+$], 353 (5) [M$^+$ − CH$_3$], 295 (40) [M$^+$ − SiMe$_3$], 279 (80) [M$^+$ − Me$_3$SiOH], 73 (100) [SiMe$_3$$^+$]. − $C_{17}H_{36}OSi_4$ (368.81): calcd. C 55.36, H 9.84; found C 56.10, H 10.20.

4e: 0.04 ml (0.75 mmol) of conc. H_2SO_4 was added to a solution of 0.3 g (0.75 mmol) of **1e** in heptane and the mixture was stirred for 3 h. Workup as described above and chromatographic purification (silica gel, heptane/ethyl acetate 10/1) gave 0.12 g (40%) of a colorless solid, m.p. 60°C. − IR (nujol): $\tilde{\nu}$ = 3613 and 3655 cm^{-1} (OH), 3400 (OH ass.). − ^{1}H NMR ($[D_6]$benzene): δ = 0.04, 0.23 and 0.24 (3 s, SiCH$_3$, 3 × 9 H), 0.92 (br. s, OH, 1 H), 2.45 (s, NCH$_3$, 6 H), 3.12 (s, CH, 1 H), 6.92−7.35 (m, ArH, 4 H). − ^{13}C NMR ($[D_6]$benzene): δ = −0.5, −0.3 and 1.3 (SiCH$_3$), 22.8 (CH), 45.3 (NCH$_3$), 120.6, 124.4, 125.1, 130.5 139.6 and 151.9 (arom. C). − ^{29}Si NMR ($[D_6]$benzene): δ = −19.5 and −19.2 (Si*Si*Me$_3$), 2.3 (CSiMe$_3$), 14.0 (SiOH). − MS: *m*/*z* (%) = 397 (100) [M$^+$], 353 (3) [M$^+$ − NMe$_2$], 338 (100) [M$^+$ − NMe$_2$ − CH$_3$]. − $C_{18}H_{39}NOSi_4$ (397.86): calcd. C 54.34, H 9.88, N 3.52; found C 54.52, H 9.94, N 3.60.

4f: As described for **4e**, 0.3 g (0.67 mmol) of **1f** and 0.04 ml (0.75 mmol) of H_2SO_4 gave, after chromatographic separation (silica gel, heptane/ethyl acetate 5/1), 0.2 g (66%) of colorless crystals, m.p. 53°C. − IR (nujol): $\tilde{\nu}$ = 3557 and 3675 cm^{-1} (OH), 3390 (OH ass.). − ^{1}H NMR ($[D_6]$benzene): δ = 0.08, 0.24 and 0.33 (3 s, SiCH$_3$, 3 × 9 H), 1.54 (s, OH, 1 H), 2.70 (s, CH, 1 H), 3.24, 3.34 and 3.39 (3 s, OCH$_3$, 3 × 3 H), 6.06 and 6.10 (2 d, ^4J = 2.45 Hz, ArH, 2 H). − ^{13}C NMR ($[D_6]$benzene): δ = −0.5, −0.3 and 1.6 (SiCH$_3$), 16.1 (CH), 54.5, 54.9 and 55.2 (OCH$_3$), 90.9, 91.3, 112.8, 157.4, 158.2 and 158.2 (arom. C). − ^{29}Si NMR ($[D_6]$benzene): δ = −19.5 and −19.3 (Si*Si*Me$_3$), 2.3 (CSiMe$_3$), 11.8 (SiOH). − MS: *m*/*z* (%) = 445 (1) [M$^+$ + H], 429 (5) [M$^+$ − CH$_3$], 371 (100) [M$^+$ − SiMe$_3$]. − $C_{19}H_{40}O_4Si_4$ (444.87): calcd. C 51.30, H 9.06; found C 51.16, H 9.02.

Reaction of **1d** *with Sulfuric Acid*: 0.1 ml (1.9 mmol) of conc. H_2SO_4 was added to a solution of 0.3 g (0.75 mmol) of **1d** in 30 ml of ether at room temperature. After 3 h the solvent was evaporated and the colorless, slowly crystallizing residue was washed with pentane to give 0.26 g (72%) of **5**; m.p. 84−88°C. − IR (cap.): $\tilde{\nu}$ = 2224 and 2477 cm^{-1} (SOH), 840 (SO$_2$ symm.), 941 (SO$_2$ asymm.). − ^{1}H NMR ($[D_6]$benzene): δ = 0.21, 0.24 and 0.36 (3 s, SiCH$_3$, 3 × 9 H), 2.10, 2.31 and 2.39 (3 s, ArCH$_3$, 3 × 3 H), 2.77 (s, CH, 1 H), 6.75 (s, ArH, 2 H). − ^{13}C NMR ($[D_6]$benzene): δ = 0.2, 0.3 and 2.0 (SiCH$_3$), 20.7, 22.6 and 23.2 (ArCH$_3$), 25.0 (CH), 129.7, 130.0, 133.6, 135.7 136.0 and 137.3 (arom. C). − ^{29}Si NMR ($[D_6]$benzene): δ = −15.1 and −14.1 (Si*Si*Me$_3$), 3.6 (CSiMe$_3$), 32.6 (SiOSO$_3$H). − MS: *m*/*z* (%) = 475 (35) [M$^+$ − H], 379 (100) [M$^+$ − HSO$_4$], 403 (25) [M$^+$ − SiMe$_3$], 306 (40) [M$^+$ − HSO$_4$ − SiMe$_3$]. − $C_{19}H_{40}O_4SSi_4$ (476.93): calcd. C 47.85, H 8.45, S 6.72; found C 47.26, H 8.36, S 6.28.

Synthesis of the Methoxysilanes **6e** and **6f**: A 2.5-fold molar excess of H_2SO_4 was added to a solution of **1e** or **1f** in methanol at room temperature. After 5−8 h the solvent was evaporated and the residue was separated by column chromatography.

6e: A solution of 0.3 g (0.75 mmol) of **1e** and 0.1 ml (1.9 mmol) of H_2SO_4 in 30 ml of methanol gave, after evaporation of the solvent and chromatographic purification (silica gel, heptane/ethyl acetate 20/1), 0.2 g (65%) of a colorless solid, m.p. 125−130°C. − ^{1}H NMR ($[D_6]$benzene): δ = 0.05, 0.26 and 0.30 (3 s, SiCH$_3$, 3 × 9 H), 2.47 (s, NCH$_3$, 6 H), 3.09 (s, CH, 1 H), 3.38 (s, OCH$_3$, 3 H), 6.93−6.98 and 7.39−7.42 (2 m, ArH, 4 H). − ^{13}C NMR ($[D_6]$benzene): δ = 0.5, 0.6 and 1.1 (SiCH$_3$), 21.9 (CH), 45.2 (NCH$_3$), 53.7 (OCH$_3$), 120.5, 124.1, 124.9, 127.5, 139.7 and 150.0 (arom. C). − ^{29}Si NMR ($[D_6]$benzene): δ = −19.8 and −19.5 (Si*Si*Me$_3$), 2.9 (CSiMe$_3$), 18.4 (SiOMe). − MS: *m*/*z* (%) = 410 (1) [M$^+$ − H], 396 (20) [M$^+$ − CH$_3$], 338 (100) [M$^+$ − SiMe$_3$]. − $C_{19}H_{41}NOSi_4$ (411.88): calcd. C 55.41, H 10.03, N 3.40; found C 55.07, H 9.85, N 3.35.

6f: 0.3 g (0.67 mmol) of **1f** and 0.01 ml (1.7 mmol) of H_2SO_4 in methanol gave, after chromatographic purification, 0.22 g (70%) of colorless crystals, m.p. 121°C. − ^{1}H NMR ($[D_6]$benzene): δ = 0.20, 0.27 and 0.28 (3 s, SiCH$_3$, 3 × 9 H), 3.00 (s, CH, 1 H), 3.33, 3.35, 3.39 and 3.50 (4 s, OCH$_3$, 4 × 3 H), 6.08 and 6.10 (2 d, ^4J = 2.4 Hz, ArH, 2 H). − ^{13}C NMR ($[D_6]$benzene): δ = 0.3, 0.8 and 1.3 (SiCH$_3$), 14.0 (CH), 53.8, 54.4, 54.8 and 55.0 (OCH$_3$), 90.7, 90.8, 110.9, 157.6, 158.3 and 158.4 (arom. C). − ^{29}Si NMR ($[D_6]$benzene): δ = −18.9 and −18.8 (Si*Si*Me$_3$), 2.2 (CSiMe$_3$), 14.9 (SiOMe). − MS: *m*/*z* (%) = 458 (40) [M$^+$], 443 (10) [M$^+$ − CH$_3$], 427 (100) [M$^+$ − OMe], 385 (50) [M$^+$ − SiMe$_3$]. − $C_{20}H_{42}O_4Si_4$ (458.89): calcd. C 52.35, H 9.23; found C 52.42, H 9.14.

Reaction of **1d** *with Sulfuric Acid in Acetic Anhydride:* 0.3 g (0.76 mmol) of **1d** and 0.1 ml (1.9 mmol) of conc. H_2SO_4 were dissolved in 30 ml of acetic anhydride and the solution was refluxed for 10 h. After evaporation of the acetic anhydride, chromatographic separation (silica gel, heptane/ethyl acetate 5/1) gave 0.27 g (82%) of **7**, m.p. 125°C. − IR (KBr): $\tilde{\nu}$ = 1712 cm^{-1} (CO). − ^{1}H NMR ($[D_6]$benzene): δ = 0.10, 0.16 and 0.31 (3 s, SiCH$_3$, 3 × 9 H), 1.78 (s, OCOCH$_3$, 3 H), 2.13 and 2.27 (2 s, Ar-*o*-CH$_3$, 2 × 3 H), 2.36 (s, Ar-*p*-CH$_3$, 3 H), 2.60 (s, CH, 1 H), 6.77 and 6.78 (2 s, Ar-H, 2 × 1 H). − ^{13}C NMR ($[D_6]$benzene): δ = 0.3, 0.5 and 2.0 (SiCH$_3$), 20.7, 21.2 and 22.2 (ArCH$_3$), 22.8 (CH), 129.6, 130.1, 133.2, 135.5, 135.6 and 138.2 (arom. C), 149.2 (OCO*C*H$_3$), 171.2 (O*C*OCH$_3$). − ^{29}Si NMR ($[D_6]$benzene): δ = −16.0 and −15.2 (Si*Si*Me$_3$), 2.9 (CSiMe$_3$), 12.9 (SiOCOCH$_3$). − MS: *m*/*z* (%) = 438 (100) [M$^+$], 423 (40) [M$^+$ − CH$_3$], 365 (100) [M$^+$ − SiMe$_3$], 233 (80) [(Me$_3$Si)$_2$SiOC(O)CH$_3$$^+$]. − $C_{21}H_{42}O_2Si_4$ (438.91): calcd. C 57.47, H 9.65; found C 57.23, H 9.44.

Synthesis of **9**: Gaseous HCl was passed through a solution of 0.3 g (0.76 mmol) of **1d** and 0.1 ml (1.9 mmol) of H_2SO_4 in 30 ml of ether. The reaction was monitored by TLC and continued until all the alcohol **1d** had been consumed. The solvent was evaporated and the ether was replaced by pentane. After the addition of Na_2CO_3 the solution was filtered and the pentane evaporated to give a colorless solid, 0.19 g (60%), m.p. 45°C. − IR (cap.): $\tilde{\nu}$ = 690 cm^{-1} (SiCl). − ^{1}H NMR ($[D_6]$benzene): δ = 0.16 (s, SiCH$_3$, 18 H), 0.19 (s, SiCH$_3$, 9 H), 2.09, 2.20 and 2.33 (3 s, ArCH$_3$, 3 × 3 H), 2.65 (s, CH, 1 H), 6.72 (s, ArH, 2 H). − ^{13}C NMR ($[D_6]$benzene): δ = −0.6, 0.1 and 2.0 (SiCH$_3$), 20.7, 22.6 and 23.6 (ArCH$_3$), 24.0 (CH), 129.7, 130.0, 133.6, 135.2, 135.5 and 137.6 (arom. C). − ^{29}Si NMR ($[D_6]$benzene): δ = −21.8 (Si*Si*Me$_3$), 4.0 (CSiMe$_3$), 13.1 (SiCl). − MS: *m*/*z* (%) = 414 (10) [M$^+$], 399 (30) [M$^+$ − CH$_3$], 379 (2) [M$^+$ − Cl], 341 (60) [M$^+$ − SiMe$_3$]. − $C_{19}H_{39}ClSi_4$ (415.31): calcd. C 54.95, H 9.47, Cl 8.54; found C 54.36, H 9.42, Cl 8.20.

Isomerization of the Silanols **4a, d, f** *into the Disiloxanes* **11a, d, f**: A two-fold molar excess of sodium hydride was added to a solution of the appropriate silanol in THF at room temperature. After stirring for 3−8 h (monitored by chromatography) water was added and the product was extracted with ether. After drying with $MgSO_4$ the ether was evaporated and the residue was purified by column chromatography (silica gel, heptane/ethyl acetate 20/1).

11a: 0.3 g (1.0 mmol) of **4a** and 0.05 g (2 mmol) of NaH gave 0.19 g (65%) of a colorless oil. − IR (cap.): ṽ = 1050 cm^{-1} (SiOSi). − ^{1}H NMR ([D$_6$]benzene): δ = 0.28 (s, SiSiCH$_3$, 18 H), 0.31 (s, OSiCH$_3$, 9 H), 1.15 (d, ^3J = 6.7 Hz, CCH$_3$, 6 H), 1.31 (sept, ^3J = 6.7 Hz, CH, 1 H). − ^{13}C NMR ([D$_6$]benzene): δ = 1.3 (SiSiCH$_3$), 2.7 (OSiCH$_3$), 21.0 (CCH$_3$), 23.0 (CH). − ^{29}Si NMR ([D$_6$]benzene): δ = −20.4 (Si*Si*Me$_3$), 6.1 and 6.3 (*Si*SiMe$_3$ and OSiMe$_3$). − MS: *m*/*z* (%) = 306 (42) [M$^+$], 305 (100) [M$^+$ − CH$_3$], 263 (15) [M$^+$ − C$_3$H$_7$]. − C$_{12}$H$_{34}$OSi$_4$ (306.74): calcd. C 46.99, H 11.17; found C 46.76, H 11.12.

11d: 0.3 g (0.75 mmol) of **4d** and 0.04 g (1.7 mmol) of NaH afforded 0.15 g (50%) of a colorless oil. − IR (nujol): ṽ = 1054 cm^{-1} (SiOSi). − ^{1}H NMR ([D$_6$]benzene): δ = 0.12 (s, SiSiCH$_3$, 18 H), 0.13 (s, OSiCH$_3$, 9 H), 2.18 (s, *p*-ArCH$_3$, 3 H), 2.26 (s, *o*-ArCH$_3$, 6 H), 2.45 (s, CH$_2$, 2 H), 6.80 (s, ArH, 2 H). − ^{13}C NMR ([D$_6$]benzene): δ = −1.1 (SiSiCH$_3$), 2.3 (OSiCH$_3$), 20.9 (*p*-ArCH$_3$), 21.6 (CH$_2$), 22.0 (*o*-ArCH$_3$), 129.1, 133.2, 134.6 and 135.8 (arom. C). − ^{29}Si NMR ([D$_6$]benzene): δ = −19.5 (Si*Si*Me$_3$), 3.3 (*Si*SiMe$_3$), 6.9 (OSiMe$_3$). − MS: *m*/*z* (%) = 396 (40) [M$^+$ − H], 381 (95) [M$^+$ − CH$_3$], 323 (75) [M$^+$ − SiMe$_3$], 307 (20) [M$^+$ − OSiMe$_3$], 277 (100) [M$^+$ − C$_6$H$_2$Me$_3$]. − C$_{19}$H$_{40}$OSi$_4$ (396.87): calcd. C 57.50, H 10.16; found C 57.24, H 10.10.

11f: 0.3 g (0.7 mmol) of **4f** and 0.035 g (1.5 mmol) of NaH gave 0.22 g (75%) of a colorless oil. − IR (cap.): ṽ = 1062 (SiOSi). − ^{1}H NMR ([D$_6$]benzene): δ = 0.22 (s, SiSiCH$_3$, 18 H), 0.29 (s, OSiCH$_3$, 9 H), 2.73 (s, CH$_2$, 2 H), 3.39 (s, *o*-OCH$_3$, 6 H), 3.42 (s, *p*-OCH$_3$, 3 H), 6.12 (s, ArH, 2 H). − ^{13}C NMR ([D$_6$]benzene): δ = −1.2 (SiSiCH$_3$), 2.3 (OSiCH$_3$), 12.9 (CH$_2$), 54.8 (*o*-OCH$_3$), 54.9 (*p*-OCH$_3$), 90.6, 109.1, 157.9 and 158.8 (arom. C). − ^{29}Si NMR ([D$_6$]benzene): δ = −19.6 (Si*Si*Me$_3$), 0.9 (*Si*Si*Me*$_3$), 6.3 (OSiMe$_3$). − MS: *m*/*z* (%) = 445 (10) [M$^+$ + H], 429 (35) [M$^+$ − CH$_3$], 371 (100) [M$^+$ − SiMe$_3$], 355 (10) [M$^+$ − OSiMe$_3$]. − C$_{19}$H$_{40}$O$_4$Si$_4$ (444.87): calcd. 51.30, H 9.06; found C 51.22, H. 9.14.

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