Effect of the temperature on the composition and ratio of hydrolysis products of 1,2-dichlorotetramethyldisilane

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The hydrolysis of 1,2-dichlorotetramethyldisilane was studied at different temperatures. At reduced temperatures, the hydrolysis gave permethylcyclo(oxadisilanes) $[(Me_2Si)_2O]_n$ (n = 2 and 3) and α,ω-dihydroxypermethyloligo(oxadisilanes) $HO[(SiMe_2)_2O]_mH$ (m = 1—5). The formation of the latter was proved by the GC-MS method.

Key words: 1,2-dichlorotetramethyldisilane, permethylcyclo(oxadisilanes), α,ω-dihydroxypermethyloligo(oxadisilanes), α,ω-bis(trimethylsilyloxy)permethyloligo(oxadisilanes), GC-MS analysis.

α,ω-Dihydroxypermethyloligosilanes are of great interest as the starting building blocks for the synthesis of copolymers of various macromolecular designs with oligosilane fragments in the backbone chain. However, in contrast to α,ω-dihydroxypermethyloligosiloxanes, the literature data on α,ω-dihydroxypermethyloligosilanes are virtually lacking. The sole documented dihydroxypermethyloligosilane (1,6-dihydroxydodecamethylhexasilane) has been obtained in 40% yield by hydrolysis of 1,6-dichlorododecamethylhexasilane at reduced temperatures.[1] Its molecular and crystal structures have been studied by X-ray diffraction analysis.[2] It is known[1,3,4] that α,ω-dihydroxypermethyloligosilanes containing fewer than six Si atoms in the oligomer chain are very unstable compounds, which undergo easy condensation during their synthesis or isolation to give cyclooxasilanes. Attempts to obtain the simplest dihydroxy oligosilane 1,2-dihydroxytetramethyldisilane (**2a**) by hydrolysis of 1,2-dichlorotetramethyldisilane (**1**), 1,2-difluorotetramethyldisilane, or 1,2-diethoxytetramethyldisilane have failed:[3] in all cases, the hydrolysis yields octamethyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane (**3a**), whose molecular[5,6] and crystal structures[6] have been studied later by X-ray diffraction analysis. At the same time, dihydroxydisilane **2a** is of great interest as the starting material for the preparation of amphiphilic organosilicon polymers with hydrophilic-hydrophobic units in the inorganic backbone chain.

Here we studied the hydrolysis of dichlorodisilane **1** at different temperatures and the composition of the resulting products was determined by the GC-MS method.

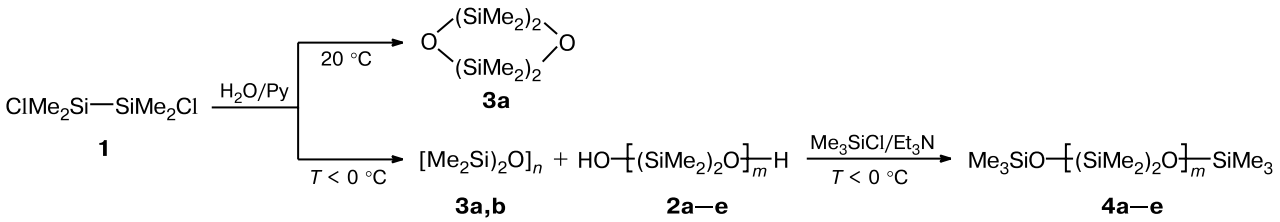
Results and Discussion

Hydrolysis of disilane **1** was carried out in ether at 20, −(5—10), and −(70—80) °C (Scheme 1).

At room temperature, only heterocycle **3a** was obtained in 72% yield. Apparently, its formation is due to intramolecular cyclization of compounds **1b** and **2b** (Scheme 2).

At reduced temperatures, after the hydrolysis was completed, Me_3SiCl and Et_3N were added to block the terminal OH groups of the resulting disilanediol **2a** for preven-

Scheme 1



n = 2 (**a**), 3 (**b**); m = 1 (**a**), 2 (**b**), 3 (**c**), 4 (**d**), 5 (**e**)

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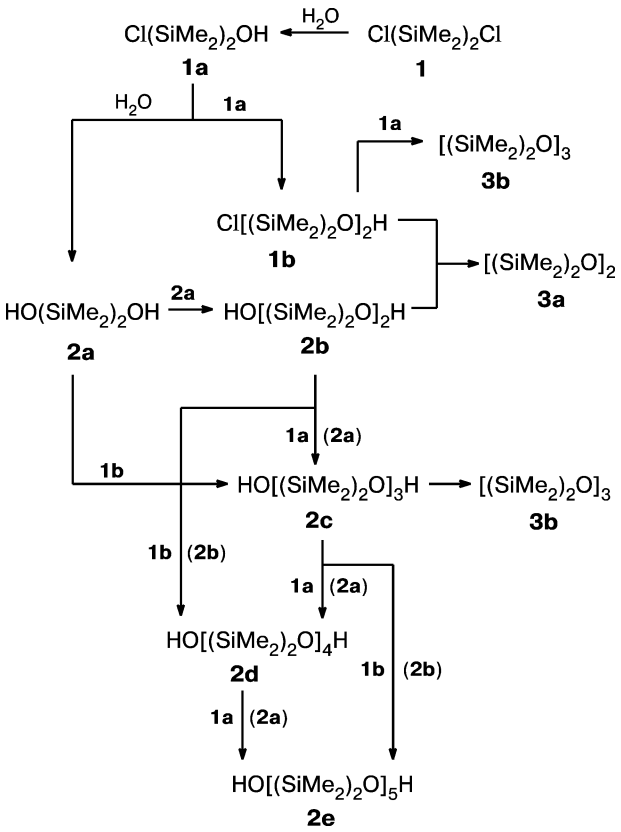
tion of further condensation. However, it turned out that the low-temperature hydrolysis gives not only heterocycle **3a** but also its homolog dodecamethyl-1,4,7-trioxa-2,3,5,6,8,9-hexasilacyclononane (**3b**) and linear α,ω-dihydroxypermethyloligo(oxadisilanes) $HO[(SiMe_2)_2O]_nH$, which was confirmed by the mass spectra* of the corresponding trimethylsilyloxy derivatives of these oligomers, namely, $Me_3SiO[(SiMe_2)_2O]_nSiMe_3$ (**4a—e**) (Table 1). Apparently, the room-temperature hydrolysis of dichlorodisilane **1** and subsequent condensation and cyclization occur so rapidly that addition of Me_3SiCl/Et_3N to the reaction mixture is virtually ineffective: only heterocycle **3a** was obtained. In the hydrolysis at −5 to −10 °C, the ratio of heterocycles **3** to oligomers **4** was 1.69 : 1 (GC-MS data; see Table 1). At −70 to −80 °C, this ratio was 0.90 : 1 (see Table 1); the content of oligomer **4a** with $n = 1$ was doubled, mainly because of a decrease in the content of heterocycle **3a**. Therefore, the low-temperature cyclization is less rapid, which allows linear products to be formed in significant amounts. A probable reaction sequence leading to compounds **3a,b** and **2b—e** is shown in Scheme 2.

Scheme 2



* Cyclic structure **3a** was identified by comparing its mass spectrum to the mass spectral library.[7] Compounds **3b** and **4a—e** were identified from empirical MS—structure correlations.

Table 1. Composition of the products of the hydrolysis of dichlorodisilane **1** according to GC-MS data

T/°C	Major hydrolysis products* (%)						
	3a	**3b**	**4a**	**4b**	**4c**	**4d**	**4e**
20	100	—	—	—	—	—	—
−(5—10)	59.70	3.08	18.30	8.09	6.26	3.12	1.45
−(70—80)	45.90	1.59	42.45	6.40	2.81	0.71	0.14

* By-products are not included.

Thus, according to GC-MS data, the low-temperature hydrolysis of dichlorodisilane **1** gives cyclic and linear permethyl(oxadisilanes).

Experimental

^{29}Si NMR spectra were recorded on a Bruker WP-400 SY spectrometer (79.46 MHz) with Me_4Si as the internal standard. An IR spectrum in the 400—3700 cm^{-1} range was recorded on a Specord M-82 spectrophotometer (thin film between KBr plates). An UV spectrum was recorded on a Specord M-40 spectrophotometer. GLC analysis was carried out on an LKhM-8MD chromatograph (stainless steel column 0.3×100 cm, 5% SE-30 on Chromaton N-AW-DMCS, a katharometer, a temperature rise from 30 to 300 °C at a rate of 12 deg min^{-1}; helium as a carrier gas). GC-MS analysis was carried out on an HP-5890 instrument (capillary column 20 000×0.32 mm, SE-30 liquid phase, helium as a carrier gas, temperature of the injector and the transfer lines 250 °C, ionizing voltage 70 eV, a temperature rise from 60 to 300 °C at a rate of 7 deg min^{-1}).

Dichlorodisilane **1** was prepared as described earlier.[8] Ether was dehydrated by refluxing over metallic Na in the presence of benzophenone and then distilled in a flow of argon. Triethylamine and pyridine were distilled in a flow of argon over granulated NaOH; Me_3SiCl was used freshly distilled under argon.

Hydrolysis of 1,2-dichlorodisilane (1) at 20 °C. A solution of disilane **1** (2.0 g, 10.7 mmol) in anhydrous ether (10 mL) was added dropwise to a vigorously stirred mixture of water (0.385 g, 21.4 mmol), acetone (1 mL), and pyridine (1.69 g, 21.4 mmol) in Et_2O (15 mL). The reaction mixture was kept for 1 h. The precipitate was filtered off and washed with anhydrous ether. The solvent was removed *in vacuo* at room temperature and the residue was recrystallized from EtOH—H_2O (4 : 1) to give cyclooxadisilane **3a** (1.02 g, 72%), m.p. 44 °C. ^{29}Si NMR ($CDCl_3$), δ: 2.96. IR, ν/cm^{-1}: 2954, 2892 (CH); 1405, 1257, 1245, 869, 855 (Me); 1083, 1030 (SiOSi); 801, 774 (SiC). UV (*n*-hexane), λ_{max}/nm: 215, 234.

Hydrolysis of 1,2-dichlorodisilane (1) at reduced temperatures. A solution of disilane **1** (2.0 g, 10.7 mmol) in anhydrous ether (10 mL) was added dropwise to a vigorously stirred, cooled mixture of water (0.385 g, 21.4 mmol), acetone (5 mL), and pyridine (1.69 g, 21.4 mmol) in ether (15 mL). The reaction mixture was kept for 1 h. Solutions of Me_3SiCl (2.32 g, 21.4 mmol) in anhydrous ether (5 mL) and of Et_3N (2.16 g, 21.4 mmol) in anhydrous ether (5 mL) were simultaneously added dropwise from two dropping funnels. The reaction mix-

ture was kept for 1 h, warmed to room temperature, and stirred for 0.5 h. The precipitate was filtered off and washed with anhydrous ether. The solvent was removed *in vacuo* at room temperature. The residue (2.8 g, 89%) was analyzed by GLC and GC-MS (see Table 1). MS (EI, 70 eV), m/z (I_{rel} (%)): **3a**: 264 $[M]^+$ (5.4), 249 $[M - Me]^+$ (20.6), 205 (66.7), 191 (17.3), 175 (22.9), 147 (13.3), 131 (13.2), 117 (12.2), 73 $[SiMe_3]^+$ (100); **3b**: 381 $[M - Me]^+$ (15.2), 323 (6.8), 249 (5.3), 174 (18.3), 147 (15.2), 131 (84.8), 117 (63.2), 73 $[SiMe_3]^+$ (100); 1,2-bis(trimethylsilyloxy)tetramethyldisilane (**4a**): 279 $[M - Me]^+$ (30.1), 221 (26.8), 191 (22.2), 147 (49.8), 131 (14.3), 117 (12.2), 73 $[SiMe_3]^+$ (100); 1-trimethylsilyl-6-trimethylsilyloxycatena-bis(oxatetramethyldisilane) (**4b**): 411 $[M - Me]^+$ (18.2), 279 (13.3), 265 (9.2), 205 (16.3), 191 (71.1), 147 (28.2), 131 (22.3), 117 (15.2), 73 $[SiMe_3]^+$ (100); 1-trimethylsilyl-9-trimethylsilyloxycatena-tris(oxatetramethyldisilane) (**4c**): 543 $[M - Me]^+$ (3.3), 279 (5.4), 265 (4.8), 205 (24.9), 191 (46.5), 147 (27.3), 131 (41.5), 117 (16.3), 73 $[SiMe_3]^+$ (100); 1-trimethylsilyl-12-trimethylsilyloxycatena-tetrakis(oxatetramethyldisilane) (**4d**): 675 $[M - Me]^+$ (2.1), 411 (2.3), 337 (8.3), 279 (7.1), 265 (15.3), 205 (53.4), 191 (55.6), 147 (36.6), 131 (58.4), 117 (16.7), 73 $[SiMe_3]^+$ (100); 1-trimethylsilyl-15-trimethylsilyloxycatena-pentakis(oxatetramethyldisilane) (**4e**): 807 $[M - Me]^+$ (1.8), 469 (4.8), 411 (5.3), 397 (5.5), 337 (33.2), 323 (14.5), 279 (23.2), 265 (33.6), 249 (28.9), 205 (77.3), 191 (70.5), 147 (36.3), 131 (67.3), 117 (19.2), 73 $[SiMe_3]^+$ (100).

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