Synthesis of difunctional organooxasilacycloalkanes

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2,8-Dichloro-2,4,4,6,6,8,10,10,12,12-decamethyl-5-carbacyclohexasiloxane, 4,7-dichloro-2,2,4,7-tetramethyl-1,3-dioxa-2,4,7-trisilacycloheptane, and 4,8-dichloro-2,2,4,8-tetramethyl-1,3-dioxa-2,4,8-trisilacyclooctane were prepared for the first time by heterofunctional condensation of 1,1,7,7-tetrachloro-1,3,3,5,5,7-hexamethyl-4-carbatetrasiloxane with 1,3-dihydroxy-1,1,3,3-tetramethyldisiloxane, of 2,2,5,5-tetrachloro-2,5-disilahexane with dihydroxydimethylsilane, and of 2,2,6,6-tetrachloro-2,6-disilaheptane with dihydroxydimethylsilane, respectively. Hydrolysis of the resulting compounds afforded the corresponding dihydroxy derivatives, and *trans*-isomers of some of these derivatives were isolated in individual form.

Key words: difunctional methyloxasilacycloalkanes, substitution reactions, heterofunctional condensation, hydrolysis.

Previously, the synthesis of difunctional organocyclosiloxanes which differ in the number of siloxane groups in the ring and are characterized by different organic framing has been reported[1,2] and the effect of their structures on the ability of cyclolinear polyorganosiloxanes (CLPOS) to undergo self-organization in ultrathin Langmuir—Blodgett (LB) films has been investigated.[3] However, the mechanism of interaction of LB films of CLPOS with surfaces of different liquids is still poorly understood. To elucidate the role of individual R_2SiO and $R_2SiO_{1,5}$ fragments in the CLPOS unit, it is necessary to compare these units with cyclolinear polyorganocarbosiloxanes in which one or two oxygen atoms or R_2SiO fragments are replaced by $(CH_2)_n$ fragments. The aim of this work was to synthesize difunctional organocyclocarbosiloxanes which differ in the number of $SiCH_2Si$ groups and in the length of $(CH_2)_n$ fragments between silicon atoms. These compounds are of interest as monomers for the preparation of organosilicon polymers.

Synthesis of tetrachloroorganocarbosiloxane. The synthesis of difunctional organocyclocarbosiloxanes (Scheme 1) was carried out with the use of carbotetrasiloxane **2**, which was prepared by heterofunctional condensation of compound **1b** with trichloromethylsilane.

Scheme 1

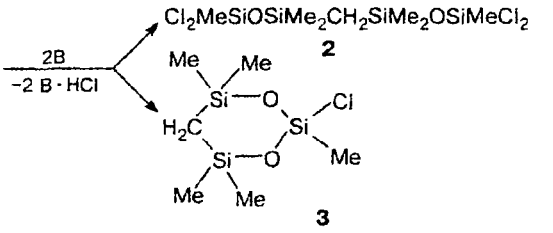
$$ClCH_2SiMe_2Cl + Me_2SiCl_2 + Mg \longrightarrow$$

$$\longrightarrow \underset{\mathbf{1a}}{ClMe_2SiCH_2SiMe_2Cl} \qquad (a)$$

$$\mathbf{1a} + 2\,H_2O \xrightarrow[-2\,PhNH_2\cdot HCl]{2\,PhNH_2}$$

$$\longrightarrow \underset{\mathbf{1b}}{HOMe_2SiCH_2SiMe_2OH} \qquad (b)$$

$$\mathbf{1b} + n\,MeSiCl_3 \longrightarrow \qquad (c)$$



B = $PhNH_2$, C_5H_5N

Depending on the reaction conditions, the reaction of compound **1b** with $MeSiCl_3$ (stage *c*) afforded either linear or cyclic products (**2** and **3**, respectively). Unlike the goals pursued in studies carried out previously,[4,5] a distinguishing feature of the conditions chosen by us for the synthesis of compound **2** is the suppression of the formation of cyclic product **3**.

The results of studies of the effects of the solvent, the acceptor, the ratio between the initial compounds, and their concentrations on the composition of the final reaction products are summarized in Table 1, from which it can be seen that the yield of compound **2** depends on the concentration of disilapentane **1b** and on the excess of $MeSiCl_3$, the latter being governed by the reagent ratio.

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Table 1. Effect of the reaction conditions of heterofunctional condensation of **1b** and $MeSiCl_3$ on the ratio of products **2** and **3**

Run	Ratio **1b** : CH_3SiCl_3 /mol mol^{-1}	Concentration of the reagents in the initial solutions/mol L^{-1}		Acceptor	Solvent	Ratio of reaction products based on GLC data		Yield of reaction products (%)	
		1b	CH_3SiCl_3			**2**	**3**	**2**	**3**
1	1 : 4	0.34	1.00	C_5H_5N	PhMe	0.33	0.67		
2	1 : 4	0.34	12.00	C_5H_5N	PhMe	0.37	0.63		
3	1 : 4	0.12	1.00	C_5H_5N	PhMe	0.60	0.40		
4	1 : 4	0.12	1.00	$C_6H_5NH_2$	PhMe	0.60	0.40		
5	1 : 4	0.82	1.96	$C_6H_5NH_2$	PhMe	0.20	0.80	11.9	49.1
6	1 : 4	0.82	1.96	C_5H_5N	PhMe	0.29	0.71		
7	1 : 4	0.82	1.96	C_5H_5N	Et_2O	0.44	0.56	35.7	40.1
8	1 : 4	0.30	1.00	C_5H_5N	Et_2O	0.72	0.28	48.6	18.3
9	1 : 6	0.30	1.50	C_5H_5N	Et_2O	0.68	0.32		
10	1 : 6	0.10	0.50	$C_6H_5NH_2$	Et_2O	0.00	1.00		
11	1 : 4	0.15	0.30	$C_6H_5NH_2$	Et_2O	0.00	1.00		
12	1 : 7	0.30	1.64	C_5H_5N	Et_2O	0.80	0.20	59.6	28.3

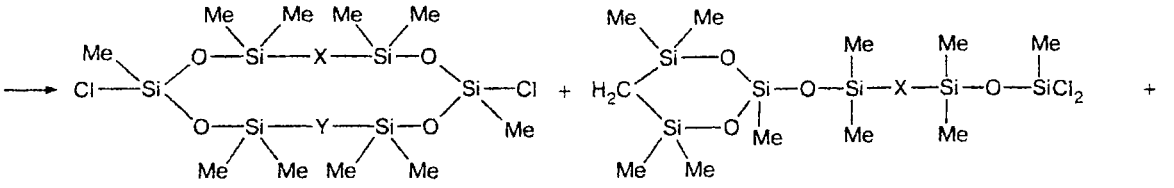
Synthesis of dichloroorganocyclocarbosiloxanes containing $SiCH_2Si$ fragments. Dichloroorganocyclocarbosiloxanes containing one or two $SiCH_2Si$ groups were synthesized according to Scheme 2.

Judging from the GLC data, an attempt to synthesize cyclocarbosiloxane **4** containing two $SiCH_2Si$ fragments resulted in a mixture of four compounds in a ratio of 24.5 : 18.5 : 33.5 : 23.5. The ^1H and ^{29}Si NMR spectra (Tables 2 and 3, respectively) of the product isolated by distillation have four groups of signals characteristic of protons and Si atoms, respectively, of the $SiCH_2Si$, $CH_3SiO_{1.5}$, $(CH_3)_2SiO$, and CH_3SiCl groups as well as of CH_3SiCl_2. According to the data from GLC-mass spectrometry (*m/z* 411, 465, and 557), this product is a mixture of compounds, which may be assigned to compounds **4**—**7**. The formation of compounds **5** and **6** is highly probable taking into account the characteristic structural features of disilapentane **1b**. In this compound, the Si—C—Si angle is 118°,[6] unlike the Si—O—Si angle in 1,1,3,3-tetramethyl-1,3-dihydroxydisiloxane (**13**)

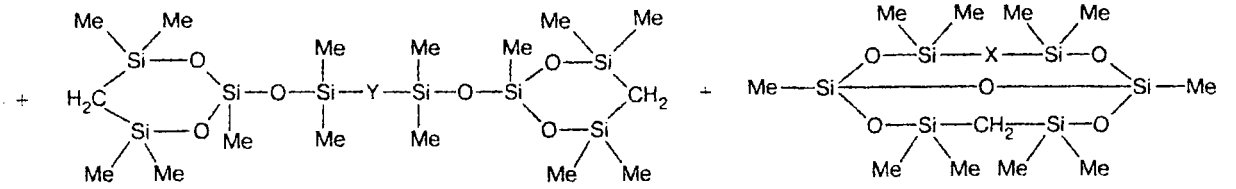
Scheme 2

$Cl_2MeSiOSiMe_2$—X—$SiMe_2OSiMeCl_2$ + $HOMe_2Si$—Y—$SiMe_2OH$ $\xrightarrow[-2\,B\cdot HCl]{2\,B}$

2, 8 **1b, 13**



4, 9a **5, 10**



6, 12 **7, 11**

1b: Y = CH_2; **2**: X = CH_2; **4**: X = Y = CH_2; **5**: X = CH_2; **6**: Y = CH_2; **7**: X = CH_2; **8**: X = O; **9a**: X = O, Y = CH_2; **10**, **11**: X = O; **12**, **13**: Y = O

Table 2. Data of ^{1}H NMR spectroscopy

Compound	Solvent	δ					
		CH_3SiCl_2	CH_3SiCl*	$(CH_3)_nSiCH_2$ (n = 1, 2)	$(CH_3)_nSiO$ (n = 1, 2)	$Si(CH_2)_nSi$ (n = 1, 2, 3)	$CH_3SiO_{1.5}$
2	C_6D_6	0.70 (d, 6 H)			0.26 (s, 12 H)	0.14 (s, 2 H)	
3	C_6D_6		0.41, 0.42 (both s, 3 H)		0.27 (s, 6 H)	0.22 (s, 2 H)	
4—7	C_6D_6	0.65, 0.67 (both s, 3 H)	0.41—0.47 (m, 6 H)	0.23—0.34 (m, 24 H)		−0.2—0.06 (m, 4 H)**	0.14—0.18 (m, 6 H + 3 H)**
9—12 (mixture)	C_6D_6	0.71, 0.72 (both s, 3 H)	0.42, 0.44 (both s, 6 H)	0.19, 0.20, 0.22, 0.23 (all s, 12 H)	0.17 (s, 6 H) 0.24, 0.25, 0.28, 0.29 (all s, 12 H)**	−0.04—0.03 (m, 4 H)**	0.15 (s, 3 H)
9a	$CDCl_3$		0.40, 0.41 (both s, 6 H)	0.12, 0.13, 0.17, 0.18 (all s, 12 H)	0.18, 0.19, 0.22, 0.23 (all s, 12 H)	−0.09 (q, 2 H)	
trans-**9b**	$(CD_3)_2CO$		4.96 (br.s, 2 H)	0.08, 0.10 (both br.s, 12 H)	0.13, 0.15 (all br.s, 12 H)		0.04 (br.s, 6 H)
11	$CDCl_3$			0.09, 0.11 (both s, 12 H)	0.14, 0.16 (both s, 12 H)	−0.06 (q, 2 H)	0.07 (s, 6 H)
16a	C_6D_6		0.38, 0,40 (both s, 6 H)		0.18, 0.23 (both s, 6 H)	0.96, 1.16 (AA′BB′ system, 4 H)	
16b	$(CD_3)_2CO$		4.21 (br.s, 2 H)	0.02 (*trans*), 0.04 (*cis*) (both s, 6 H)	0.05, 0.08 (both s, 6 H)	0.64, 0.72 (AA′BB′ system, 4 H)	
17a			0.38, 0.39 (both s, 6 H)		0.23, 0.25 (both s, 6 H)	0.99, 1.10 (2 m, AA′BB′X_2 system)	
17b	$(CD_3)_2CO$		2.99 (br.s, 2 H)	0.07 (*trans*), 0.09 (*cis*) (both s, 6 H)	0.04, 0.08 (both s, 6 H)	0.75, 0.81 (2 m, AA′BB′X_2 system)	

* For dihydroxy derivatives, CH_3SiOH.

** In cyclic and linear fragments of compounds **5**, **6**, **10**, and **12**.

(140.1°).[7] We failed to isolated compound **4** in the individual state.

The reaction of tetrachloride **8** with dihydroxy derivative **1b** afforded a product in 15% yield. According to the GLC data, this product consisted of two compounds in a ratio of 22 : 78. We failed to separate these compounds by additional distillation due to their similar boiling points. The GLC-mass spectrum of this mixture has an ion with m/z 467 with an intensity distribution in the isotope pattern characteristic of compounds containing two chlorine atoms. This peak may be assigned to structural isomers, *viz.*, to carbosiloxane **9a** and compound **10** with the molecular weight of 482. In addition, the mass spectrum has peaks of ions at m/z 413 and 561 corresponding to compounds **11** and **12**, respectively. This is supported by the ^{1}H NMR spectrum (see Table 2), which has signals for the protons of the CH_3SiCl_2 and CH_3SiCl groups, signals assigned to the methyl protons of the $(CH_3)_2SiCH_2Si(CH_3)_2$ and $(CH_3)_2SiOSi(CH_3)_2$ fragments, and signals characteristic of the CH_2 group in the cyclic and linear fragments of compounds **9a—12**.

We succeeded in preparing carbosiloxane **9a** by the reaction of tetrachloride **2** with disiloxane **13**. When aniline was used as an acceptor of HCl, chromatographically pure compound **11** was isolated in 25% yield. Its structure was established based on the data from GLC-mass spectrometry and ^{1}H NMR spectroscopy. When pyridine was used instead of aniline, compound **9a** was obtained in 39.9% yield. The resulting product contained an admixture of **11**, but the content of the latter was no higher than 7.0%.

Synthesis of difunctional organooxasilacycloalkanes containing $Si(CH_2)_nSi$ fragments. Organooxasilacycloalkanes containing $-(CH_2)_2-$ and $-(CH_2)_3-$ groups between silicon atoms were synthesized by heterofunctional condensation of tetrachlorides **14** or **15** with dihydroxydimethylsilane. As a result, dichlorotrisilacycloheptane (**16a**) and dichlorotrisilacyclooctane (**17a**) were prepared (Scheme 3).

The starting disilahexane **14** and disilaheptane **15** were synthesized by the addition of dichloromethylsilane to vinyl- or allyldichloromethylsilanes, respectively, in the presence of the Speyer catalyst.[8,9]

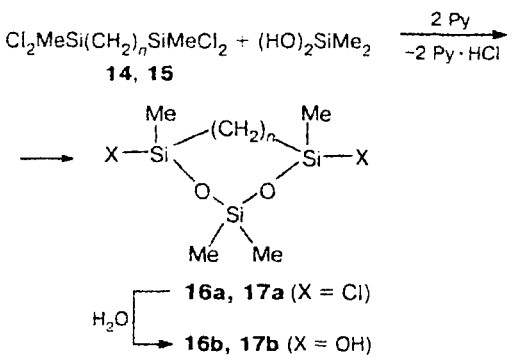
Fractionation of a mixture of heterofunctional condensation products gave compounds **16a** and **17a** in 20 and 30% yields (with respect to the total amount of distillate), respectively, as well as fractions whose ^{1}H NMR spectra have signals characteristic of $CH_3SiO_{1.5}$ fragments. These signals belong, apparently, to bicyclic

Table 3. Data of ^{29}Si NMR spectroscopy

Compound	Solvent	δ			
		$SiO_{1.5}$	CH_3SiCl (CH_3SiOH)	$OSi(CH_3)_2$	$CH_2Si(CH_3)_2$
4, **5**, **6**, **7**	$CDCl_3$	−64.27, −63.25, −61.95 (all s, 3 Si)	−56.85, −56.68 (both s, 2 Si)		6.37—7.25, 9.88—10.64* (both m, 10 Si) 28.89—29.01** (both s, 4 Si)
9a	$CDCl_3$		−45.5 (s, 2 Si)	−18.96, 18.71 (both s, 2 Si)	10.49 (br.s, 2 Si)
9b	$(CD_3)_2CO$		−63.02 (s, 2 Si)	−19.5 (s, 2 Si)	6.59 (s, 2 Si)
16b	$(CD_3)_2CO$		−11.48 (s, 2 Si)	−16.32 (s, 2 Si)	
17b	$(CD_3)_2CO$		−12.28 (s, 2 Si)	−18.42 (s, 2 Si)	

* In compound **4** and cyclic fragments of compounds **5** and **6**.
** In linear fragments of compounds **5** and **6**.

Scheme 3



n = 2 (**14**, **16**), 3 (**15**, **17**)

compounds in which chlorine atoms of molecules **16a** and **17a** reacted with a second dihydroxydimethylsilane molecule.

Dihydroxy derivatives **9b**, **16b**, and **17b** were prepared by hydrolysis of compounds **9a**, **16a**, and **17a**, respectively, in Et_2O in the presence of aniline as an acceptor of HCl. The structures of the products were established by ^1H and ^{29}Si NMR spectroscopy (Tables 2 and 3, respectively) and IR spectroscopy. For compound **9b**, the *trans*-isomer was isolated from hydrolysis products of compound **9a** by fractional crystallization from a hexane—Et_2O mixture. The structure of this isomer was confirmed by IR spectroscopy. The IR spectrum of compound *trans*-**9b** in a solution in CCl_4 (C = 0.1 mol L^{-1}) has a broad band at 3050—3600 cm^{-1} characteristic of hydrogen bonds of associated OH groups. The IR spectrum of a solution diluted to C = 0.005 mol L^{-1} has a narrow band at 3690 cm^{-1} characteristic of free OH groups. Unlike the *trans*-isomer, the *cis*-isomer retains intramolecular hydrogen bonds. The ^1H NMR spectrum of *trans*-**9b** is analogous to that of compound **11**. In the ^1H NMR spectrum of *trans*-**9b**, the protons of the methyl groups bound to the silicon atoms are observed as five signals. In the spectrum of compound **9b**, unlike that of bicyclic compound **11**, the signals for the protons of the methylene groups are shifted downfield and overlap with intense signals of the methyl groups.

Fractional crystallization of compounds **16b** and **17b** from a hexane—Et_2O mixture afforded their *trans*-isomers in 18.6 and 31.6% yields, respectively. The ^1H NMR spectrum of *trans*-isomer **16b** has two signals with equal integral intensities, which belong to the methyl protons of the $(CH_3)_2SiO$ and CH_3SiOH groups. The protons of the CH_2CH_2 fragment give a multiplet characteristic of the AA′BB′ spin system. The region of signals of the CH_3SiOH and $(CH_3)_2SiO$ groups in the ^1H NMR spectrum of *trans*-**17b** is to a great extent analogous to that of *trans*-**16b**, and the chemical shifts of the protons of the $-(CH_2)_3-$ group are observed as two multiplets characteristic of the AA′BB′X_2 spin system.

Experimental

The IR spectra were recorded on a Specord M-82 spectrophotometer.

The ^1H and ^{29}Si NMR spectra were measured on a Bruker AMX-400 spectrometer (400.13 MHz) in CCl_4—$CDCl_3$, CCl_4—$(CD_3)_2CO$, and CCl_4—C_6D_6 solutions. The ^{29}Si NMR spectra were recorded in the absence of the Overhauser effect; the delay time between pulses was 25 s. Chromatographic analysis was carried out on an LKhM-80 instrument (the length and the diameter of the column were 3 m and 3 mm, respectively; Chromaton as the sorbent; SE-30 as the liquid phase; helium as the carrier gas (30 mL min^{-1}); the evaporator temperature was 270 °C; a katharometer as the detector; the temperature-programming mode from 50 to 300 °C at a rate of 25 deg min^{-1}). The GLC-mass spectrometric analysis (EI) was carried out on a Kratos MS-890 spectrometer (Great Britain) (70 eV, the temperature of the ionization chamber was 250 °C) equipped with a Carlo Erba Meda Series gas-liquid chromatograph with a capillary column (15 m) coated with methylsiloxane elastomer. The operating mode: 4 deg min^{-1} from 30 to 250 °C, 10 deg min^{-1} from 250 to 400 °C, and 15 min at 400 °C. Helium was used as the carrier gas (2 mL min^{-1}).

The reactions were carried out in anhydrous solvents.

Dihydroxydimethylsilane was prepared according to a known procedure.[10] The yield was 79.3%, m.p. 98—99 °C (hexane) (*cf.* lit. data[10]: m.p. 99—100 °C). **Allyldichloromethylsilane** was synthesized as described previously.[9] The yield was 33.9%, b.p. 118—122 °C (*cf.* lit. data[9]: b.p. 120 °C). **1,1,7,7-Tetrachloro-1,3,3,5,5,7-hexamethyltetrasiloxane (8)** was prepared according to a procedure reported previously.[2] The chromatographically pure product was isolated in 35.7% yield, b.p. 247—250 °C. **1,3-Dihydroxy-1,1,3,3-tetramethyldisiloxane (13)** was prepared according to a known procedure.[11] The crystalline product was obtained in 56.6% yield, m.p. 68 °C (*cf.* lit. data[11]: m.p. 68.5 °C). **2,4-Dichloro-2,4-dimethyl-2,4-disilapentane (1a).** A mixture of dimethylchloromethylchlorosilane (43.84 g, 0.306 mol) and Me_2SiCl_2 (102.12 g, 0.920 mol) in THF (65 mL) was added dropwise to a solution of Mg (chips, 8.10 g, 0.333 g-at.) in THF (20 mL) at 60 °C. The reaction mixture was refluxed with stirring for 20 h. The precipitate was filtered off. The solvent and unconsumed Me_2SiCl_2 were distilled off. Then the reaction mixture was distilled and the fraction with b.p. 140—180 °C was fractionated once again on a rectification column with metal ring packing. The fraction with b.p. 170—178 °C was collected (*cf.* lit. data[11]: b.p. 177—178 °C). Disilapentane **1a** was isolated in a yield of 22.7 g (36.8%). ^1H NMR ($CDCl_3$—CCl_4), δ: 0.51 (s, 12 H, $C\underline{H}_3(Cl)SiCH_2$); 0.56 (s, 2 H, $SiCH_2Si$).

1,1,6,6-Tetrachloro-2,5-disilahexane (14) was prepared according to a known procedure.[12] Dichloromethylsilane (44.24 g, 0.385 mol) was added dropwise to a mixture of dichloromethylvinylsilane (54.25 g, 0.385 mol) and $H_2PtCl_6 \cdot 6H_2O$ (0.155 g, $0.3 \cdot 10^{-3}$ mol) in THF at 60 °C. Chromatographically pure product **14** was obtained in a yield of 86.7 g (88.0%), b.p. 139 °C (80 Torr) (*cf.* lit. data[12]: b.p. 109—111 °C (30 Torr)).

1,1,7,7-Tetrachloro-2,6-disilaheptane (15) was prepared according to a procedure reported previously.[13] Dichloromethylsilane (11.8 g, 0.1 mol) was added dropwise to a mixture of allyldichloromethylsilane (15.9 g, 0.102 mol) and $H_2PtCl_6 \cdot 6H_2O$ (0.518 g, $1.0 \cdot 10^{-3}$ mol) at 60 °C. The reaction mixture was heated at 70—80 °C for 4 h. Chromatographically pure compound **15** was isolated by fractionation in a yield of 18.95 g (50.8%), b.p. 58—66 °C (1 Torr) (*cf.* lit. data[13]: b.p. 132—136 °C (33 Torr)).

2,4-Dihydroxy-2,4-dimethyl-2,4-disilapentane (1b). A solution of disilapentane **1a** (9.50 g, 0.047 mol) in Et_2O (150 mL) was added dropwise with intense stirring to a mixture of $PhNH_2$ (9.22 g, 0.099 mol) and H_2O (1.70 g, 0.094 mol) in Et_2O (190 mL) cooled to from −5 to −8 °C. The reaction mixture was filtered from a precipitate of $PhNH_2 \cdot HCl$, the solvent was distilled off under reduced pressure, and the crystals that precipitated were twice recrystallized. Disilapentane **1b** was obtained in a yield of 4.4 g (56.7%), m.p. 85—86 °C (pentane). Found (%): C, 36.46; H, 9.75; Si, 34.39. $C_5H_{16}O_2Si_2$. Calculated (%): C, 36.53; H, 9.83; Si, 34.17. ^1H NMR ($(CD_3)_2CO$), δ: −0.08 (s, 2 H, CH_2Si); 0.10 (s, 12 H, CH_3Si); 4.10 (s, 2 H, $\underline{H}OSiCH_3$).

1,1,7,7-Tetrachloro-1,3,3,5,5,7-hexamethyl-4-carbatetrasiloxane (2). *A.* A solution of disilapentane **1b** (4.7 g, 0.029 mol) in Et_2O (95 mL) and Py (4.74 g, 0.060 mol) were added dropwise with intense stirring to a solution of $MeSiCl_3$ (17.10 g, 0.114 mol) in Et_2O (114 mL) at −4 °C. The reaction mixture was kept at this temperature for 1 h. Then the reaction mixture was allowed to warm to ~20 °C and filtered under a flow of argon. The solvent was distilled off. The reaction products were isolated first by distillation and then by rectification. Compound **3** was obtained in a yield of 1.21 g (18.3%), b.p. 170—180 °C. Tetrasiloxane **2** was obtained in a yield of 3.21 g (48.6%), b.p. 246—256 °C. IR of **3** (CCl_4), ν/cm^{-1}: 1032, 1064 (SiOSi); 1266, 1256 ($SiCH_2$).

B. The synthesis was carried out analogously to procedure *A* starting from a solution of $MeSiCl_3$ (80.19 g, 0.536 mol) in Et_2O (450 mL), a solution of compound **1b** (22.40 g, 0.134 mol) in Et_2O (150 mL), and a solution of $PhNH_2$ (26.92 g, 0.282 mol) in Et_2O (150 mL). Tetrasiloxane **2** was obtained in a yield of 18.8 g (35.7%), b.p. 247—250 °C. Compound **3** was obtained in a yield of 21.10 g (40.1%), b.p. 172—181 °C.

C. The synthesis was carried out analogously to procedure *A* starting form a solution of $MeSiCl_3$ (44.2 g, 0.296 mol) in Et_2O (180 mL) and a solution of compound **1b** (7.4 g, 0.045 mol) and Py (7.2 g, 0.091 mol) in Et_2O (150 mL). Chromatographically pure tetrasiloxane **2** was obtained in a yield of 10.7 g (59.6%).

An attempt to synthesize **2,8-dichloro-2,4,4,6,6,8,10,10,12,12-decamethyl-5,11-dicarbacyclohexasiloxane (4)**. A mixture of disilapentane **1b** (1.47 g, $0.896 \cdot 10^{-2}$ mol) and $PhNH_2$ (1.75 g, $0.188 \cdot 10^{-1}$ mol) in Et_2O (37.4 mL) and a solution of tetrasiloxane **2** (3.36 g, $0.896 \cdot 10^{-2}$ mol) in Et_2O (37.4 mL) were added simultaneously dropwise at the same rate to Et_2O (10 mL) at −8 °C. The reaction mixture was kept at this temperature for 1 h. Then the mixture was filtered from a precipitate of $PhNH_2 \cdot HCl$ and the solvent was distilled off. A mixture of compounds **4**—**7** was isolated by fractionation in a yield of 0.83 g (20.1%), b.p. 120—160 °C (1 Torr). IR (CCl_4), ν/cm^{-1}: 830, 853 (SiMe); 1020, 1059 (SiO); 1255, 1266 (SiMe). GLC/MS, *m/z* (I_{rel} (%)). **6**: 557 $[M - Me]^+$ (20); **4** and **5** (for ^{35}Cl isotope): 465 $[M - Me]^+$ (53); **7**: 411 $[M - Me]^+$ (34).

2,8-Dichloro-2,4,4,6,6,8,10,10,12,12-decamethyl-5-carbahexacyclosiloxane (9a). *A.* A solution of tetrachloride **8** (6.51 g, 0.040 mol) in Et_2O (65 mL) and a solution of a mixture of $PhNH_2$ (7.38 g, 0.079 mol) and disilapentane **1b** (14.81 g, 0.038 mol) in Et_2O (45 mL) were added dropwise simultaneously using two dropping funnels to dry Et_2O (135 mL) at −4 °C. After 1 h, the reaction mixture was filtered from the precipitate, the solvent was distilled off under reduced pressure, and the reaction mixture was distilled. The fraction with b.p. 170—175 °C (1 Torr) was collected in a yield of 5.10 g (35%). GLC/MS, *m/z* (I_{rel} (%)). **11**: 413 $[M - Me]^+$; **9a** and **10** (for ^{35}Cl isotope): 467 $[M - Me]^+$; **12**: 561 $[M - Me]^+$.

B. The reaction was carried out analogously to procedure *A*. A solution of a mixture of compound **13** (1.81 g, 0.011 mol) and $PhNH_2$ (2.24 g, 0.024 mol) in Et_2O (47 mL) was added to a solution of compound **2** (4.25 g, 0.011 mol) in Et_2O (47 mL). Product **11** was obtained in a yield of 1.55 g (30.0%), b.p. 115—118 °C (1 Torr). GLC/MS, *m/z* (I_{rel} (%)): 413 $[M - Me]^+$ (70.6).

C. The synthesis was carried out analogously to procedure *A*. A solution of compound **2** (7.80 g, 0.020 mol) in Et_2O (87 mL) and a solution of a mixture of compound **13** (3.32 g, 0.020 mol) and Py (3.32 g, 0.042 mol) in Et_2O (87 mL) were added to Et_2O (48 mL). Chromatographically pure dichloride **9a** was obtained in a yield of 3.85 g (39.9%), b.p. 99—110 °C. GLC/MS (for ^{35}Cl isotope), *m/z* (I_{rel} (%)): 467 $[M - Me]^+$ (11.2).

2,8-Dihydroxy-2,4,4,6,6,8,10,10,12,12-decamethyl-5-carbacyclohexasiloxane (9b). The reaction was carried out as described above for compound **1b**. A solution of H_2O (0.083 g, $4.612 \cdot 10^{-3}$ mol) in Et_2O (17 mL) was added to a solution of compound **9a** (2.240 g, $4.612 \cdot 10^{-3}$ mol) in Et_2O (9 mL) and $PhNH_2$ (0.859 g, $9.255 \cdot 10^{-3}$ mol). Compound **9b** was obtained in a yield of 0.85 g (71.0%). *trans*-**9b** was isolated by recrystallization from a mixture of hexane and Et_2O in a yield of 0.61 g (51.0%), m.p. 80—82 °C. Found (%): C, 29.62; H, 7.63; Si, 37.01. $C_{11}H_{34}O_7Si_6$. Calculated (%): C, 29.56; H, 7.68; Si, 37.70. IR (Nujol mulls), ν/cm^{-1}: 3050—3600 (SiOH).

4,7-Dichloro-2,2,4,7-tetramethyl-1,3-dioxa-2,4,7-trisilacycloheptane (16a). A solution of tetrachloride **14** (30.50 g,

0.111 mol) in Et_2O (200 mL) and a solution of dihydroxydimethylsilane (10.21 g, 0.111 mol) in Et_2O (200 mL) were added dropwise simultaneously using two dropping funnels to a solution of Py (18.40 g, 0.234 mol) in Et_2O (100 mL). The temperature of the reaction mixture was maintained at about −5 °C. The reaction mixture was kept at ~20 °C for 2 days. The completion of the reaction was followed from the disappearance of the signal for the methyl proton in the CH_3SiCl_2 fragment of compound **14** at δ 0.5—0.6 in the ^1H NMR spectrum. The solvent was distilled off. The reaction product was distilled first *in vacuo* and then on a rectification column with metal ring packing. Product **16a** was obtained in a yield of 3.3 g (10.1%), b.p. 66.5—73.0 °C (4 Torr). The fraction with b.p. 90—130 °C (2 Torr) was isolated in a yield of 9.8 g (30%). Found (%): C, 25.82; H, 5.81; Si, 31.01; Cl, 25.75. $C_6H_{16}Si_3Cl_2$. Calculated (%): C, 26.18; H, 5.81; Si, 30.61; Cl, 25.76.

4,7-Dihydroxy-2,2,4,7-tetramethyl-1,3-dioxa-2,4,7-trisilacyclopentane (16b). The reaction was carried out as described above for compound **1b**. Water (0.65 g, 0.036 mol) in Et_2O (67 mL) was added to a solution of compound **16a** (4.40 g, 0.018 mol) in Et_2O (34 mL) and $PhNH_2$ (3.54 g, 0.038 mol). The products with b.p. 80—100 °C (5 Torr) and with b.p. 110—130 °C (5 Torr) obtained after fractionation crystallized. The total yield was 2.70 g (70.9%). *trans*-**16b**, m.p. 133—137 °C (hexane), *trans,cis*-**16b** (75—25%), m.p. 120—125 °C (hexane—Et_2O), *cis,trans*-**16b** (25—75%), m.p. 108—109 °C (hexane—Et_2O). Found (%): C, 29.98; H, 7.51; Si, 35.80. $C_6H_{18}O_4Si_3$. Calculated (%): C, 30.24; H, 7.55; Si, 35.35. IR (KBr), ν/cm^{-1}: 848, 880, 1253, 1259 (MeSiMe); 1053, 1076 (SiOSi); 1148 ($SiCH_2CH_2Si$); 3000—3550 (SiOH).

4,8-Dichloro-2,2,4,8-tetramethyl-1,3-dioxa-2,4,8-trisilacyclooctane (17a). The reaction was carried out as described above for compound **16a**. A solution of compound **15** (20.92 g, 0.105 mol) in Et_2O (127.6 mL) and a solution of dihydroxydimethylsilane (9.68 g, 0.105 mol) in Et_2O (127.6 mL) were added to a solution of Py (17.34 g, 0.221 mol) in Et_2O (127.6 mL). Rectification of the reaction mixture afforded compound **17a** in a yield of 4.81 g (22.5%), b.p. 61—69 °C (5 Torr), and a fraction of a product with b.p. 69—75 °C (5 Torr) in a yield of 4.3 g (20%). Found (%): C, 29.13; H, 6.30; Cl, 24.46; Si, 29.05. $C_7H_{18}Si_2O_2Cl_2$. Calculated (%): C, 29.13; H, 6.28; Cl, 24.50; Si, 29.11.

4,8-Dihydroxy-2,2,4,8-tetramethyl-1,3-dioxa-2,4,8-trisilacyclooctane (17b). The reaction was carried out as described above for compound **16b**. A solution of compound **17a** (1.86 g, 0.014 mol) in Et_2O (14.4 mL) was added dropwise to a mixture of $PhNH_2$ (1.32 g, 0.028 mol), H_2O (0.24 g, 0.028 mol), and Et_2O (28.8 mL) at a temperature from −5 to −8 °C. A precipitate of $PhNH_2 \cdot HCl$ was filtered off and Et_2O was distilled off. Then the crystalline product was recrystallized from a hexane—Et_2O mixture. A mixture of isomers **17b** was obtained in a yield of 0.65 g (40.3%). Repeated crystallization afforded *trans*-**17b**, m.p. 130—134 °C, and a mixture of *cis*-**17b** and *trans*-**17b**, m.p. 108—115 °C. Found (%): C, 33.01; H, 7.90; Si, 33.81. $C_7H_{20}O_4Si_2$. Calculated (%): C, 33.32; H, 7.93; Si, 33.39. IR (KBr), ν/cm^{-1}: 849, 876, 1246, 1263 (MeSiMe); 1035, 1065 (SiOSi); 1114 ($Si(CH_2)_nSi$); 3000—3550 (SiOH).

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