On the synthesis of siloxanes. XXIII ☆. Synthesis and spectroscopic characterization of 2-functional 1,3-dioxa-2,4,7-trisilacycloheptanes

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Abstract

A series of 2-functional 1,3-dioxa-2,4,7-trisilacycloheptanes was synthesized and characterized by means of ^{29}Si NMR spectroscopy, gas chromatography, high performance liquid chromatography and gas chromatography-mass spectrometry. The signals were assigned to the various configurational isomers. This assignment was confirmed by independent synthesis of individual isomers. The sequence of the NMR signals of the all-*cis* and *trans-trans* isomers required for the determination of stereochemistry was found to be the same as that of the respective cyclotrisiloxanes.

1. Introduction

Investigations of the stereochemistry of nucleophilic substitution reactions of silicon atoms in cyclotrisiloxanes have revealed that these reactions proceed with retention of configuration [1,2]. In addition, it is known that the stereochemistry of nucleophilic substitution reactions of cyclic silicon compounds depends on the ring size [3]. The smaller the bond angle on the functional silicon atom, the more the reactions tend to proceed with retention of configuration. In order to investigate the influence of the O–Si–O bond angle in the cyclosiloxanes on the stereochemistry of nucleophilic substitution reactions, one oxygen atom in cyclotrisiloxane may be replaced by $(CH_2)_n$ chains ($n = 2$ or 3). For this purpose, a series of 2-functional 1,3-dioxa-2,4,7-trisilacycloheptanes was synthesized.

Assignments of the NMR signals of the obtained isomeric mixtures were confirmed by a comparison of their chromatographic (GC and HPLC) and mass spectral data with those of individual isomers prepared by independent methods.

2. Experimental

2.1. Methods

2.1.1. Spectra, general details

The ^{29}Si NMR measurements ($CDCl_3$ solutions or neat substances with external lock) were run on a Bruker MSL 300 spectrometer at 59.627 MHz applying the inverse gated decoupling technique with a repetition time of 5 s and a 30° flip angle. The spectra were recorded with 0.2 Hz/point. ^{1}H and ^{13}C NMR measurements were obtained using a Bruker AC 200 P spectrometer at 200.13 and 50.323 MHz, respectively. The chemical shifts are given in ppm and referred to TMS.

2.1.2. GC

Using the Autosystem Perkin Elmer gas chromatograph, the products were analyzed under the following conditions: injector split 1:50; column PVMS/54-Permaspher, 50 m × 0.32 mm ID; film thickness 0.3 μm; carrier gas He; 129 or 200 kPa; injection volume 0.1 μl; isothermal.

2.1.3. HPLC

The following conditions were used for the HPLC measurements: eluent methanol/water 90:10 V%; flow

1 ml min^{-1}; concentration 10 μg ml^{-1} eluent; column Eurospher C 18 (5 μm), 250 mm × 4 mm; isocratic.

Detection: UV Chrom-A-Scope (wavelength 190–370 nm) at 254 nm; RI differential refractometer of the type 198.0.

Separation of diastereomers: eluent n-hexane/ethanol 88:12 V%; flow 0.5 ml min^{-1}; concentration 10 μg ml^{-1} eluent; column Chiralpak AD 250 mm × 4.6 mm; adsorbent Amylose Carbamate; isocratic.

Detection: UV Chrom-A-Scope (wavelength 190–370 nm) at 254 nm; RI differential refractometer of the type 198.0.

2.1.4. GC–MS

The GC–MS measurements were made using a Hewlett-Packard HP 5890, series II instrument, under the following conditions: injector splitless; column Anabond-225, 50 m × 0.32 mm, 1 μm film thickness; carrier gas He; 100 kPa; injection volume 0.1 μl.

MS: electron impact mode (EI-mode) or chemical ionization mode (CI-mode).

For compound 12 (CI-mode): column DB-5, 30 m × 0.25 mm, film thickness 0.25 μm.

2.1.5. Materials

The solvents were dried according to conventional methods. Chloromethylphenylsilane and chloromethylphenylvinylsilane were made from dichloromethylsilane or dichloromethylvinylsilane and phenylmagnesiumbromide according to the literature methods [6,7]. The chlorosiloxanes 1-chloro-1,3,3,3-tetramethyldisiloxane, 1-chloro-1,3,3,3-tetramethyl-1-vinyldisiloxane, 1,1-dichloro-3,3,3-trimethyldisiloxane and 1,1-dichloro-3,3,3-trimethyl-1-vinyldisiloxane used as starting materials were synthesized by equilibration of the respective chlorosilanes with hexamethyldisiloxane [4,5].

2.1.6. Preparations

2,2,5,5-Tetrachloro-2,5-disilahexane (1). A solution of 200 μl of H$_2$[PtCl$_6$] in iso-propanol was added to a mixture of 141.5 g (1 mol) dichloromethylvinylsilane and 11.5 g (0.1 mol) dichloromethylsilane. The reaction solution was heated to 80°C. After the reaction had started, as indicated by a temperature increase and discoloration of the catalyst, another 103.5 g (0.9 mol) dichloromethylsilane was added dropwise with stirring. The product was purified by distillation under reduced pressure.

Yield: 344 g (85%); b.p. 113°C/33 mbar; hydrolyzable chlorine found: 55.2%; Calc.: 55.37%.

2,5-Dichloro-2,5-bis(trimethylsiloxy)-2,5-disilahexane (2a). (a) A solution of 32.4 g (0.36 mol) trimethylsilanol in 100 ml diethyl ether was added dropwise to a stirred solution of 145.6 g (0.36 mol) 1 and 28.5 g (0.36

mol) pyridine in 100 ml diethyl ether. The mixture was allowed to stand overnight. The pyridine hydrochloride precipitate was filtered off, the ether evaporated, and the residue distilled under reduced pressure.

B.p. for the mixture of isomers (2a and 3) 60–63°C/ 0.13 mbar; hydrolyzable chlorine found: 21.7%; Calc.: 19.5%

(b) Compound 2a was prepared using the same procedure as for compound 1. 194.5 g (1 mol) 1-chloro-1,3,3,3-tetramethyl-1-vinyldisiloxane and 168.5 g (1 mol) 1-chloro-1,3,3,3-tetramethyldisiloxane were used.

Yield: 196 g (54%); b.p. 133°C/27 mbar; d_4^{25} 0.993 g cm^{-3}; hydrolyzable chlorine found: 19.15%; Calc.: 19.5%; ^{29}Si (CDCl$_3$): δ 12.27 (Me$_3$Si); 4.14 (MeClSiCH$_2$); ^{13}C (CDCl$_3$): δ 11.16 (CH$_2$); 1.87 (CH$_3$); 1.66 (Si(CH$_3$)$_3$).

1,1,4,4-Tetrachloro-1,4-bis(trimethylsiloxy)-1,4-disilabutane (2b). Compound 2b was prepared using the same procedure as for compound 1; 215 g (1 mol) 1,1-dichloro-3,3,3-trimethyl-1-vinyldisiloxane and 189 g (1 mol) 1,1-dichloro-3,3,3-trimethyldisiloxane were used.

Yield: 194 g (48%); b.p. 116°C/6 mbar; d_4^{25} 1.098 g cm^{-3}; hydrolyzable chlorine found: 35.1%; Calc.: 35.07%; ^{29}Si (CDCl$_3$): δ 12.10 (Me$_3$Si); 4.0 (Cl$_2$SiCH$_2$).

2,5-Dichloro-2,5-diphenyl-2,5-disilahexane (8). Compound 8 was synthesized using the same method as for compound 1; 182.45 g (1 mol) chloromethylphenylvinylsilane and 156.45 g (1 mol) chloromethylphenylsilane were used [8].

Yield: 271.5 g (80%); b.p. 170°C/0.665 mbar; hydrolyzable chlorine found: 19.6%; Calc.: 20.89%; ^{29}Si (CDCl$_3$): δ 22.02 (MePhClSiCH$_2$).

3,6-Dichloro-2,2,7,7-tetramethyl-3,6-bis(trimethylsiloxy)-3,6-disilaoctane (2c). A 1.7 M solution (100 ml) of tert-butyllithium in diethyl ether was added dropwise to a stirred solution of 40.4 g (0.1 mol) of 2b in 100 ml diethyl ether. The mixture was heated under reflux for 1 h, the precipitate LiCl filtered off, the diethyl ether evaporated and the residue distilled under reduced pressure.

Yield: 19.7 g (44%); b.p. 113–117°C/12 mbar; d_4^{25} 0.93 g cm^{-3}; hydrolyzable chlorine found: 14.5%; Calc.:15.86%; ^{29}Si (CDCl$_3$): δ 11.62; 11.56 (Me$_3$Si); 5.27 (^{t}BuClSiCH$_2$); ^{13}C (CDCl$_3$): δ 6.46; 6.39 (CH$_2$); 1.43 (Si(CH$_3$)$_3$); 25.5 (C(CH$_3$)$_3$); 20.41 (C(CH$_3$)$_3$).

2,5-Dihydroxy-2,5-bis(trimethylsiloxy)-2,5-disilahexane (10a) and 2,5-dimethyl-2,5-bis(trimethylsiloxy)-1-oxa-2,5-disilacyclopentane (9a). A solution of 73 g (0.2 mol) 2a in 200 ml diethyl ether was added dropwise to a vigorously stirred suspension of 50 g (0.59 mol)

NaHCO$_3$ in 400 ml water. The mixture was stirred for an additional hour. The organic phase was separated, washed three times with water and dried over Na$_2$SO$_4$. After evaporation of the diethyl ether the residue was distilled under reduced pressure.

10a. Yield: 24 g (36.6%); b.p. 90°C/0.27 mbar; ^{29}Si (CDCl$_3$): δ 7.30; 7.40 (Me$_3$Si); −12.20 (Me(OH)SiCH$_2$).

9a. Yield: 23 g (37%); b.p. 40°C/0.27 mbar; ^{29}Si (CDCl$_3$): δ 8.46; 8.36 (Me$_3$Si); −7.69; −8.43 (MeSiCH$_2$)

^{1}H (CDCl$_3$): δ 0.6–0.8 (m, 4H, CH$_2$); 0.16; 0.10 (2s, 6H, CH$_3$); 0.09; 0.07 (2s, 18H, Si(CH$_3$)$_3$); ^{13}C (CDCl$_3$): δ 8.80; 8.79 (CH$_2$); −0.75 (CH$_3$); 1.70; 1.65 (Si(CH$_3$)$_3$); GC–MS (CI-mode, methane): [M$^+$ + 1] 309.0 (27%); [M$^+$-CH$_3$] 293.1 (100%).

3,6-Dihydroxy-2,2,7,7-tetramethyl-3,6-bis(trimethyl-siloxy)-3,6-disilaoctane (10c) and 2,5-di-tert-butyl-2,5-dimethyl-1-oxa-2,5-disilacyclopentane (9c). Compounds **9c** and **10c** were prepared and worked up according to the same procedure as for **9a** and **10a**, using 89.5 g (0.2 mol) of **2c**. The reaction mixture was fractionated by distillation under reduced pressure. Compound **10c** crystallized after distillation and was purified by recrystallization from n-hexane.

10c. Yield: 17.5 g (22.5%); b.p. 140°C/1.34 mbar; m.p. 115°C/192.5–198°C; ^{29}Si (CDCl$_3$): δ 7.01; 6.98 (Me$_3$Si); −14.48; −14.74 (^{t}Bu(OH)SiCH$_2$); ^{1}H (CDCl$_3$): δ 0.4–0.7 (m, 4H, CH$_2$); 0.09; 0.12 (2s, 18H, OSi(CH$_3$)$_3$); 0.90; 0.91 (2s, 18H, C(CH$_3$)$_3$).

9c. Yield: 30.3 g (38.6%); b.p. 95°C/1.34 mbar; ^{29}Si (CDCl$_3$): δ 8.09; 8.02 (Me$_3$Si); −8.42; −8.58 (^{t}BuSiCH$_2$).

2,5-Dimethyl-2,5-diphenyl-1-oxa-2,5-disilacyclopentane (9b). Compound **8** (20 g, 59 mmol) in 100 ml diethyl ether and 1.06 g (59 mmol) water in 100 ml 1,4-dioxane were added dropwise and simultaneously to a stirred solution of 9.3 g (0.118 mol) pyridine in 200 ml diethyl ether. The solution was stirred for another 2 h. The precipitated pyridine hydrochloride was filtered off, the solvents evaporated, and the residue distilled under reduced pressure.

Yield: 14.1 g (84%); b.p. 135°C/0.67 mbar; ^{29}Si (CDCl$_3$): δ 15.0 (MePhSiCH$_2$); ^{1}H (CDCl$_3$): δ 0.9–1.31 (m, 4H, CH$_2$); 0.55 (s, 6H, CH$_3$); 7.27–7.78 (m, 10H, C$_6$H$_5$). GC–MS (EI-mode): [M$^+$] 284 (9%); m/z 269 (50%); 254.9 (76.5%); 240.9 (100%); 205.9 (79%); 197 (50%); 177.9 (51%); 134.9 (30%); 105 (34%); 89.1 (68%).

meso-2,5-Dihydroxy-2,5-diphenyl-2,5-disilahexane (10b). Aqueous NaOH (0.5 ml, 0.1 N) was added to a stirred solution of 6.5 g (23 mmol) **9b** in 5 ml 1,4-di-

oxane. The compound **10b** crystallized on standing at ambient temperature for 48 h.

Yield: 3.2 g (46%); m.p. 60–128°C (dec.); ^{29}Si (CDCl$_3$): δ 7.04 ppm (shoulder at 7.01 ppm) (MeSi(OH)CH$_2$); ^{1}H (CDCl$_3$): δ 0.9 (s, 4H, CH$_2$); 0.384 (s, 6H, CH$_3$).

2,4,7-Trimethyl-4,7-bis(trimethylsiloxy)-1,3-dioxa-2,4,7-trisilacycloheptane (11). Compound **10a** (32.7 g, 0.1 mol) and 11.5 g (0.1 mol) dichloromethylsilane, each in 100 ml diethyl ether, were added dropwise and simultaneously to a stirred solution of 15.8 g (0.2 mol) pyridine in 200 ml diethyl ether. The mixture was stirred for another 2 h. The pyridine hydrochloride was separated by filtration and the ethereal solution was washed with water several times. After solvent evaporation the residue was distilled under reduced pressure.

Yield: 7.4 g (20%); b.p. 50°C/0.13 mbar; d_4^{25} 0.90 g cm^{-3}; ^{29}Si (C$_6$D$_6$ ext.): δ 8.09; 7.98; 7.84 (Me$_3$Si); −17.92; −17.99; −18.07; −18.10 (MeSiCH$_2$); −31.83; −31.98; −32.25 (MeSiH).

2,4,7-Trimethyl-4,7-diphenyl-1,3-dioxa-2,4,7-trisilacycloheptane (12). Compound **12** was prepared using the same procedure as for **11**, using 4 g (13 mmol) of **10b**.

Yield: 0.67 g (15%); b.p. 110°C/1.3 × 10^{-4} mbar; d_4^{25} 1.05 g cm^{-3}; ^{29}Si (CDCl$_3$): δ 2.98; 2.92; 2.90 (MePhSiCH$_2$); −28.16; −28.44; −28.97 (MeSiH); trans–trans and all-cis isomer 2.87; 2.86 (MePhSiCH$_2$); −28.22; −29.04 (MeSiH).

^{1}H (CDCl$_3$): δ 1.05 (d, 4H, CH$_2$); 0.3–0.4 (4s, 6H, PhSiCH$_3$); 0.25–0.3 (m, 3H, HSiCH$_3$); 4.9 (m, 1H, SiH); 7.3–7.7(m, 10H, C$_6$H$_5$); GC–MS (EI-mode): [M$^+$] 344.1 (24%); m/z 329.1 (85%); 315.0 (89%); 266.1 (100%); 238 (77%); 223 (45%); 197.1 (45%); 179 (65%); 158.1 (19%); 135.1 (31%); 119.1 (24%); 105.1 (10%); GC–MS (CI-mode, isobutane): [M$^+$-1] 343.0 (49%); [M$^+$-C$_6$H$_5$] 266.8 (100%).

4,7-Di-tert-butyl-2-methyl-4,7-bis(trimethylsiloxy)-1,3-dioxa-2,4,7-trisilacycloheptane (13). Compound **13** was prepared using the same procedure as for **11**, using 4.5 g (11 mmol) of **10a**.

Yield: 0.59 g (12%); b.p. 84°C/0.26 mbar; ^{29}Si (CDCl$_3$): δ 7.51; 7.49; 7.38; 7.35 (Me$_3$Si); −19.14; −19.24; −19.62 (^{t}BuSiCH$_2$); −30.44; −30.82; −32.34 (MeSiH); cis–trans isomer: 7.48; 7.33 (Me$_3$Si); −19.15; −19.25 (^{t}BuSiCH$_2$); −30.82 (MeSiH).

2-Chloro-2,4,7-trimethyl-4,7-bis(trimethylsiloxy)-1,3-dioxa-2,4,7-trisilacycloheptane (14). A solution of 1.14 g (16 mmol) chlorine in carbon tetrachloride was added dropwise to a stirred solution of 6 g (16 mmol) **11** in carbon tetrachloride and 1.26 g (16 mmol) pyridine. The precipitated pyridine hydrochloride was filtered off, the
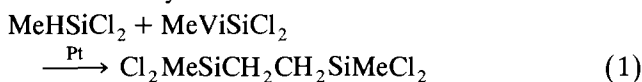
solvent evaporated and the residue distilled under reduced pressure.

B.p. 65°C/0.065 mbar; ^{29}Si (CDCl$_3$): δ 8.84; 8.75; 8.61 (Me$_3$Si); -16.94; -16.99; -18.34; -18.48 (MeSiCH$_2$); -39.80; -40.06 (MeSiCl).
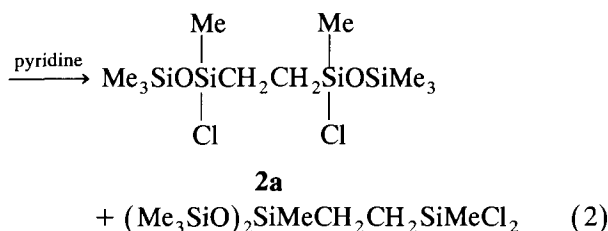
3. Results and discussion

Dioxatrisilacycloheptanes were synthesized according to the preparation of cyclotrisiloxanes [2] by the condensation of a silanediol with methyl dichlorosilane in the presence of pyridine as HCl acceptor and diethyl ether as solvent. The silanediols were made by hydrolyzing the respective chlorosilanes. Attempts were first carried out to synthesize 2,2,5,5-tetrachloro-2,5-disilahexane 1 by the reaction of dichloromethylsilanes and dichloromethylvinylsilanes (Eq. (1)).

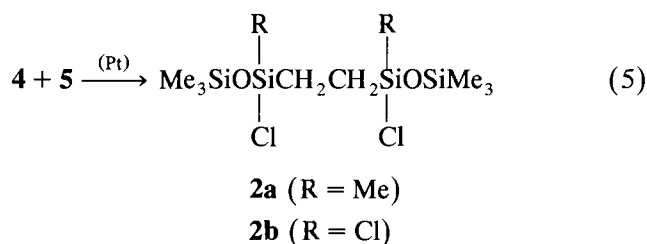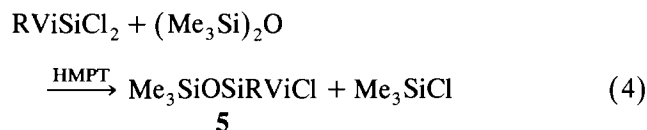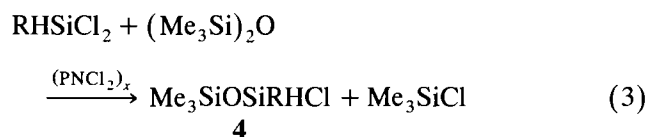The subsequent reaction of 1 with trimethylsilanol in the presence of pyridine (Eq. (2)) however, gave mixture of the isomers 2a and 3, which could not be fractionated by distillation.
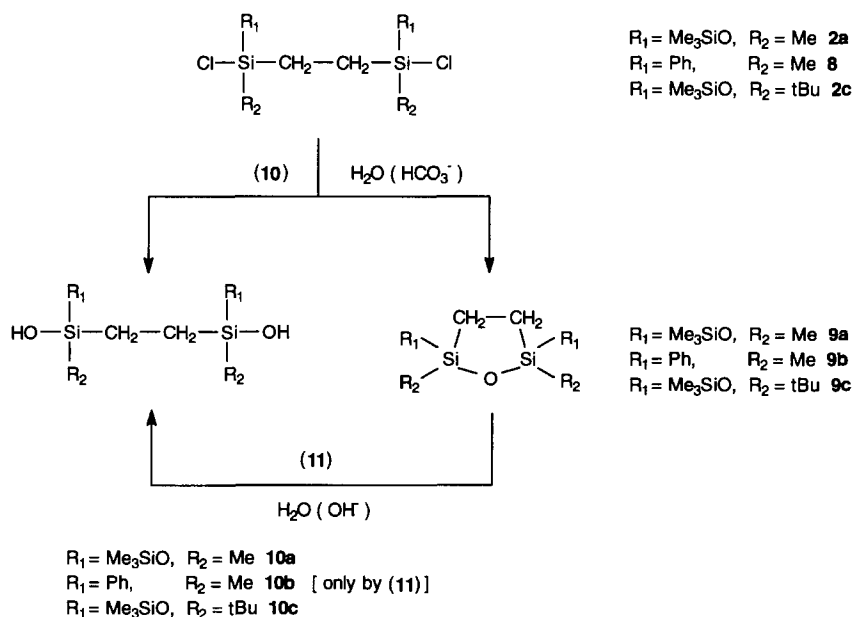
$$\text{MeHSiCl}_2 + \text{MeViSiCl}_2$$

$$\xrightarrow{\text{Pt}} \text{Cl}_2\text{MeSiCH}_2\text{CH}_2\text{SiMeCl}_2 \tag{1}$$
$$\mathbf{1}$$

$$+ 2 \text{ Me}_3\text{SiOH}$$

$$\xrightarrow{\text{pyridine}} \begin{array}{c} \text{Me} \quad\quad \text{Me} \\ | \quad\quad\quad | \\ \text{Me}_3\text{SiOSiCH}_2\text{CH}_2\text{SiOSiMe}_3 \\ | \quad\quad\quad | \\ \text{Cl} \quad\quad\quad \text{Cl} \end{array}$$

$$\mathbf{2a}$$

$$+ (\text{Me}_3\text{SiO})_2\text{SiMeCH}_2\text{CH}_2\text{SiMeCl}_2 \tag{2}$$
$$\mathbf{3}$$

Therefore, it was necessary to select a reaction where the substituents were introduced before hydrosilylation. For this purpose 4 was obtained by the reaction of dichloromethylsilane with hexamethyldisiloxane in the presence of $(\text{PNCl}_2)_x$ in 1,2-dichloroethane (Eq. (3); R = Me) [4]. The reaction of dichloromethylvinylsilane and hexamethyldisiloxane in the presence of HMPT in methylene chloride resulted in the formation of 5 (Eq. (4); R = Me) [5]. Hydrosilylation then gave the desired product cleanly (Eq. (5).

$$\text{RHSiCl}_2 + (\text{Me}_3\text{Si})_2\text{O}$$

$$\xrightarrow{(\text{PNCl}_2)_x} \text{Me}_3\text{SiOSiRHCl} + \text{Me}_3\text{SiCl} \tag{3}$$
$$\mathbf{4}$$

$$\text{RViSiCl}_2 + (\text{Me}_3\text{Si})_2\text{O}$$

$$\xrightarrow{\text{HMPT}} \text{Me}_3\text{SiOSiRViCl} + \text{Me}_3\text{SiCl} \tag{4}$$
$$\mathbf{5}$$

$$\mathbf{4 + 5} \xrightarrow{(\text{Pt})} \begin{array}{c} \text{R} \quad\quad \text{R} \\ | \quad\quad\quad | \\ \text{Me}_3\text{SiOSiCH}_2\text{CH}_2\text{SiOSiMe}_3 \\ | \quad\quad\quad | \\ \text{Cl} \quad\quad\quad \text{Cl} \end{array} \tag{5}$$

$$\mathbf{2a} \ (\text{R} = \text{Me})$$
$$\mathbf{2b} \ (\text{R} = \text{Cl})$$

An analogous procedure was used for the synthesis of the phenyl-substituted compounds. First, the respective phenyl-substituted silanes 6 and 7 were obtained by the reaction of dichloromethylsilane and dichloromethylvinylsilane with phenylmagnesiumbromide (Eqs. (6)

R$_1$ = Me$_3$SiO, R$_2$ = Me 2a
R$_1$ = Ph,   R$_2$ = Me 8
R$_1$ = Me$_3$SiO, R$_2$ = tBu 2c

R$_1$ = Me$_3$SiO, R$_2$ = Me 9a
R$_1$ = Ph,   R$_2$ = Me 9b
R$_1$ = Me$_3$SiO, R$_2$ = tBu 9c

R$_1$ = Me$_3$SiO, R$_2$ = Me 10a
R$_1$ = Ph,   R$_2$ = Me 10b [only by (11)]
R$_1$ = Me$_3$SiO, R$_2$ = tBu 10c

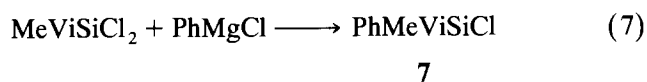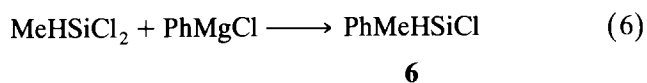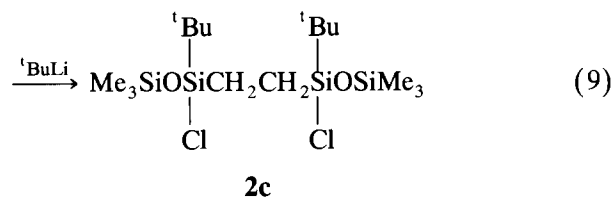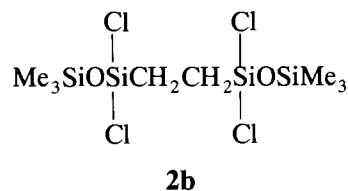Scheme 1. Hydrolysis of the 2,5-dichloro-2,5-disilahexanes 2a, 2c and 8.
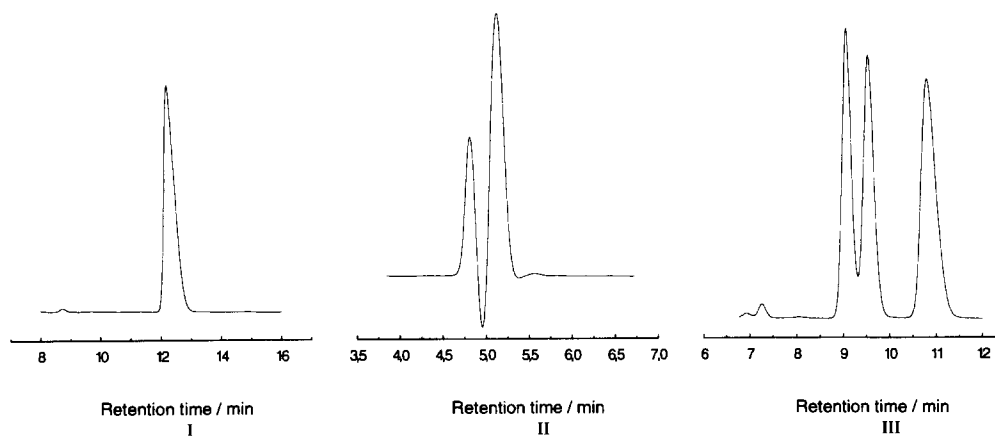
Fig. 1. HPLC Chromatograms of the compounds **10b** (I), **10c** (II) and 1,3-dihydroxy-1,3-dimethyl-1,3-diphenyldisiloxanes (III).

and (7)), followed by hydrosilylation to yield **8** (Eq. (8)).

$$MeHSiCl_2 + PhMgCl \longrightarrow PhMeHSiCl \qquad (6)$$

$$\mathbf{6}$$

$$MeViSiCl_2 + PhMgCl \longrightarrow PhMeViSiCl \qquad (7)$$

$$\mathbf{7}$$

$$\mathbf{6 + 7} \xrightarrow{(Pt)} \underset{\overset{|}{Cl}}{\overset{Me}{Ph\overset{|}{Si}CH_2CH_2}}\underset{\overset{|}{Cl}}{\overset{Me}{\overset{|}{Si}Ph}} \qquad (8)$$

$$\mathbf{8}$$
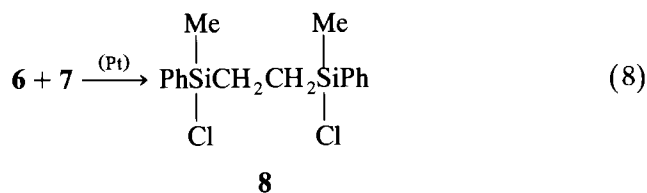
In contrast to the synthesis described in Eq. (2), compound **2c** could be made from 1,1,4,4-tetrachloro-1,4-bis(trimethylsiloxy)-1,4-disilabutane **2b** and tert-butyllithium (Eq. 9). Obviously, this monosubstitution

is caused by the steric hindrance of the bulky tert-butyl group.

$$Me_3SiO\underset{\overset{|}{Cl}}{\overset{Cl}{\overset{|}{Si}}}CH_2CH_2\underset{\overset{|}{Cl}}{\overset{Cl}{\overset{|}{Si}}}OSiMe_3$$

$$\mathbf{2b}$$

$$\xrightarrow{{}^tBuLi} Me_3SiO\underset{\overset{|}{Cl}}{\overset{{}^tBu}{\overset{|}{Si}}}CH_2CH_2\underset{\overset{|}{Cl}}{\overset{{}^tBu}{\overset{|}{Si}}}OSiMe_3 \qquad (9)$$

$$\mathbf{2c}$$

The starting compound **2b** was prepared by hydrosilylation of the chlorosiloxanes 1,1-dichloro-3,3,3-trimethyldisiloxane and 1,1-dichloro-3,3,3-trimethyl-1-

R₁ = Me₃SiO, R₂ = Me   **11**
R₁ = Ph,   R₂ = Me   **12**
R₁ = Me₃SiO, R₂ = tBu   **13**

(12)
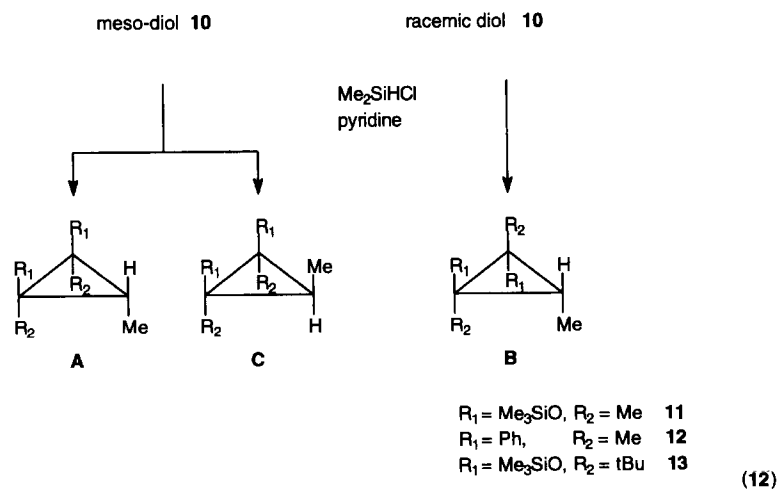
Scheme 2. Synthesis of the dioxatrisilacycloheptanes.
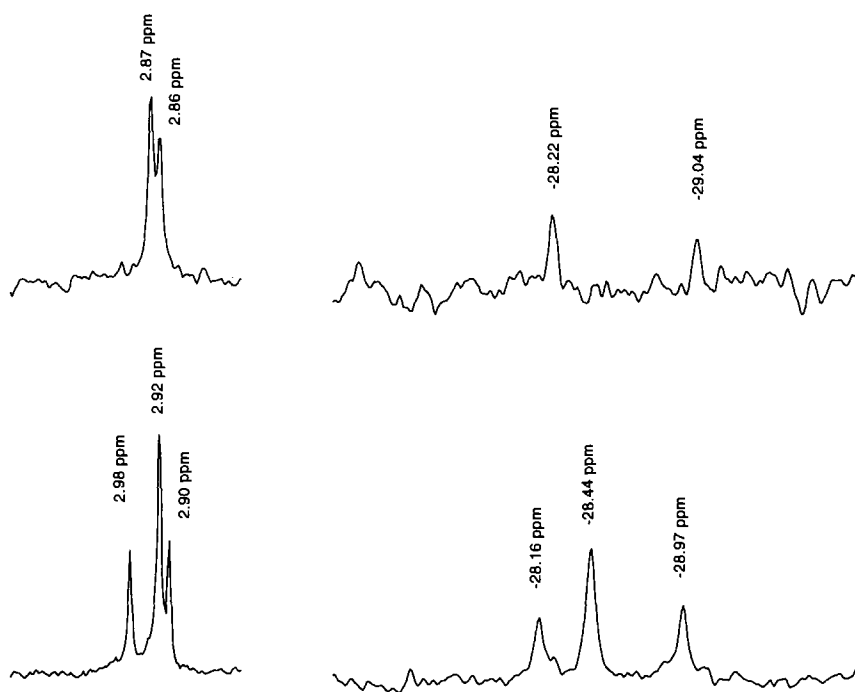
Fig. 2. ^{29}Si NMR spectra of compound 12. (a) A and C; (b) A, B and C.

vinyldisiloxane (Eq. (5), R = Cl). These chlorosiloxanes were obtained by equilibration of trichlorosilane (Eq. (3), R = Cl) or trichlorovinylsilane (Eq. (4), R = Cl) with hexamethyldisiloxane in the presence of $(PNCl_2)_x$ in 1,2-dichloroethane.

The hydrolysis of the chlorosilanes 2a, 2c and 8 resulted in the formation of the dihydroxy compounds 10a and 10c (reaction (10). Additionally, various quantities of the respective intramolecular condensation products (oxadisilacyclopentanes 9a-c) and higher-condensed products were obtained (Scheme 1).

Hydrolysis of 8 gave the five-membered ring 9b along with large quantities of polymeric products. Therefore 2,5-dimethyl-2,5-diphenyl-1-oxa-2,5-disil-acyclopentane 9b was synthesized first by adding a stoichiometric quantity of water to a dilute solution of chlorosilane 8 in the presence of pyridine as HCl-accep-

tor. The dihydroxy compound 10b was obtained by the cleavage of 9b using water in the presence of a catalytic amount of sodium hydroxide (reaction (11), Scheme 1).

HPLC investigations using a chiral column showed that only the meso-product was formed (Fig. 1). Since 9b was present in a 1:1 cis: trans ratio, the exclusive formation of the meso-product can only be explained by isomerization. This isomerization is probably caused by the catalyst and the displacement of equilibrium due to the crystallization of only one isomer.

We succeeded in separating the isomers by crystallization in the case of the tert-butyl-substituted compound 10c. HPLC investigations using a chiral column showed that in the case of the compound 10c the racemic diastereomers were obtained (Fig. 1).

Before analyzing the diastereomers of 10c by means of HPLC the experimental conditions were optimized.

Table 1
Chromatographic results of the compounds 9

Compound	GC				HPLC			
	Retention time (min)	Percentage	Retention time (min)	Percentage	Retention time (min)	Percentage	Retention time (min)	Percentage
9a	6.43 [a]	49%	6.57	51%	9.37 [b]	46.5%	9.97	53.5%
9b	12.25 [c]	48%	13.67	52%	5.96 [d]	45%	6.28	55%
9c	5.78 [e]	56%	6.04	44%				

[a] 130°C, 130 kPa.
[b] MeOH/H$_2$O 90:10 V%, 1 ml min^{-1}.
[c] 200°C, 130 kPa.
[d] MeOH/H$_2$O 90:10 V%, 1 ml min^{-1}.
[e] 200°C, 130 kPa.

For this purpose a mixture of diastereomers of 1,3-dihydroxy-1,3-dimethyl-1,3-diphenyldisiloxane was used as a model system (Fig. 1).

For the preparation of dioxatrisilacycloheptanes the dihydroxy compounds **10** were treated with dichloromethylsilane in the presence of pyridine as HCl-acceptor and diethyl ether as solvent. The isomers

with trans–trans-(**A**) or all-cis-(**C**) configuration were formed from the meso-diol, whereas from the racemic diols a racemic mixture of the cis–trans isomer **B** was obtained (Scheme 2).

The cyclization of the pure isomers meso-**10b** and rac-**10c** resulted in the formation of the expected isomers **12A**, **12C** and **13B**, respectively; thus the assign-

Table 2
^{29}Si NMR results for the compounds **9**

Compound	Si in the ring		Si in R¹	
	δ (ppm) (intensity)	δ (ppm) (intensity)	δ (ppm) (intensity)	δ (ppm) (intensity)
9a	−7.69 (53%)	−8.43 (47%)	8.46 (47%)	8.36 (53%)
9b	15.0 (100%)			
9c	−8.42 (64%)	−8.58 (36%)	8.09	8.02

Table 3
GC results for the compounds **11–13**

Compound	Retention time (min)	Percentage	Retention time (min)	Percentage	Retention time (min)	Percentage
11 [a]	9.48	27%	9.88	73%		
12 [b]	10.61	25%	11.11	25%	11.64	50%
13 [c]	6.68	38.8%	6.75	25.4%	6.92	35.8%
14 [d]	14.68	23%	15.33	77%		

[a] 130°C, 130 kPa.
[b] 200°C, 200 kPa.
[c] 200°C, 200 kPa.
[d] 130°C, 130 kPa.

Table 4
HPLC results for the compounds **11** and **12**

Compound	Retention time (min)	Percentage	Retention time (min)	Percentage	Retention time (min)	Percentage
11 [a]	12.81	23%	13.21	77%		
12 [b]	20.40	24%	21.10	23%	22.03	53%

[a] MeOH/H$_2$O 95:5, 0.5 ml min^{-1}.
[b] MeOH/H$_2$O 85:15, 1 ml min^{-1}.

Table 5
^{29}Si NMR results for the isomers **A**, **B**, **C** [a] of trisilacycloheptanes **11–14** and of the analogous cyclotrisiloxanes (region MeSiX)

Compound	Isomer	δ (ppm) (percentage)	Compound	Isomer	δ (ppm)
11	A	−31.98 (28%)	(MT)$_2$D^H [2]	A	−23.37
	C	−32.25 (24%)		C	−23.77
	B	−31.83 (48%)		B	−23.91
13	A	−30.44 (35%)			
	C	−32.34 (22%)			
	B	−30.82 (43%)			
14	A + C	−39.80 (50%)	(MT)$_2$D^{Cl} [2]	A	−31.18
				C	−31.68
	B	−40.06 (50%)		B	−31.76
12	A	−28.16 (25%)	(D^{Ph})$_2$D^H [1]	A	−22.13
	C	−28.97 (27%)		C	−22.27
	B	−28.44 (48%)		B	−22.41

[a] A trans–trans; B cis–trans; C all-cis.

ments found by means of HPLC were substantiated. However, the cyclization of *meso*-**10b** sometimes gave three isomers unexpectedly. It is likely that traces of acid in the ethereal solution of the dihydroxy compound caused isomerization of the dihydroxy compound before cyclization. In fact, when the presence of a trace of acid was omitted, the cyclization resulted exclusively in the expected isomers **12A** and **12C**. The formation of the three isomers **12A**, **12B** and **12C** in the former case (Fig. 2(b)) and the two isomers **12A** and **12C** in the latter (Fig. 2(a)) was proved by means of ^{29}Si NMR spectroscopy.

Finally, the chlorosilanes required for the stereochemical investigations were obtained by the reaction of the respective H-silanes with chlorine in the presence of pyridine as HCl-acceptor (Eq. (13)).

$$(13)$$
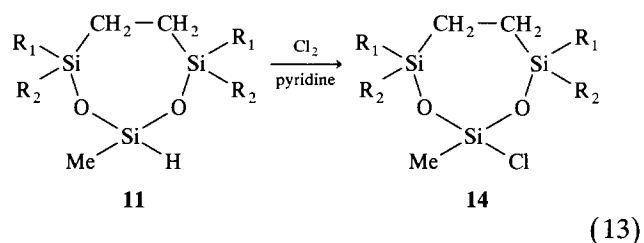
$(R_1 = Me_3SiO, R_2 = Me)$

The obtained cyclic compounds were investigated by means of GC, HPLC and ^{29}Si NMR spectroscopy (Tables 1–5).

The compounds **9** and **11–14** showed several peaks in their gas chromatograms. For selected compounds GC–MS confirmed that these peaks can be assigned to isomers of one compound. The respective mass spectra were in accord with this. The distribution of isomers was determined from the areas (GC integrations), with the assumption that the individual isomers are detected with the same sensitivity. The isomer with the shortest retention time should be that with the greatest number of substituents on a silicon atom located *cis* to each other. By means of the isomeric distribution determined

in this way, the signals of the ^{29}Si NMR spectra were assigned. The assignment coincides with those obtained for the correspondingly substituted cyclotrisiloxanes [1,2]. However, the signal position for the *cis–trans* isomer relative to that for the other isomers differed from the results obtained for the cyclotrisiloxanes. However, the *cis–trans* isomer can be assigned unequivocally by means of proportion formed. In comparison with the two other isomers, it will be formed from the racemic mixture with a twofold statistical probability.

As in the case of cyclotrisiloxanes [1,2], the signal due to the functional silicon atom in the all-*cis* isomers of the dioxatrisilacycloheptanes was shifted to a higher field when compared with that of the *trans–trans* isomer.

Acknowledgment

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