Chemistry of Heterocyclic Compounds, Vol. 32, Nos. 11-12, 1996

ON THE SYNTHESIS OF SILOXANES. XXIV.* NUCLEOPHILIC SUBSTITUTION REACTIONS OF 2-FUNCTIONAL 1,3-DIOXA-2,4,7-TRISILACYCLOHEPTANES AND 1,3-DIOXA-2,4,8-TRISILACYCLOOCTANES†

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2-Hydrogen-1,3-dioxa-2,4,7-trisilacycloheptanes and 2-hydrogen-1,3-dioxa-2,4,8-trisilacyclooctanes, each as a mixture of three configurational isomers, were synthesized and halogenated with chlorine and bromine in the presence of pyridine. The stereochemical course of the halogenation reactions was studied by gas chromatography. 2-Chloro-2,4,7-trimethyl-4,7-bis(trimethyl-siloxy)-1,3-dioxa-2,4,7-trisilacycloheptanes and 2-chloro-2,4,7-trimethyl-4,7-diphenyl-1,3-dioxa-2,4,7-trisilacycloheptanes reacted with alcohols in the presence of pyridine, triethylamine, or 2,6-dimethylpyridine. Gas chromatography, and ^1H NMR and ^{29}Si NMR spectroscopy were used to investigate the stereochemistry of these substitution reactions. It has been found that all reactions proceed with retention of configuration and that the differences of the relative reactivities of the configurational isomers were distinctly smaller than those observed for reactions of the configurational isomers of functional cyclotrisiloxanes.

1. INTRODUCTION

Investigations on the stereochemistry of nucleophilic substitution reactions of silicon atoms in cyclotrisiloxanes revealed that all these reactions proceed with retention of configuration [2, 3], often in contrast to the stereochemical results of reactions with other types of silicon compounds [2]. One possible explanation for the unusual behavior of cyclic silicon compounds was found in the dependence of the stereochemical course of nucleophilic substitution reactions upon the ring size [4]. 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). So, recently, we described the preparation of substituted 2-functional 1,3-dioxa-2,4,7-trisilacycloheptanes [1]. The compounds prepared were characterized by ^{29}Si NMR spectroscopy, gas chromatography, high performance liquid chromatography, and gas chromatography-mass spectroscopy. The signals could be assigned to the configurational isomers. The sequence of the NMR signals of the configurational isomers was found to be the same as that of the respective cyclotrisiloxanes [2, 3]. In our actual studies we completed the series of cyclosiloxanes by the preparation of eight-membered rings and studied some substitution reactions of functional seven- and eight-membered cyclic compounds containing trisiloxane units.

*For part XXIII see [1].

†Dedicated to Professor É. Lukevits on the occasion of his 60th birthday.

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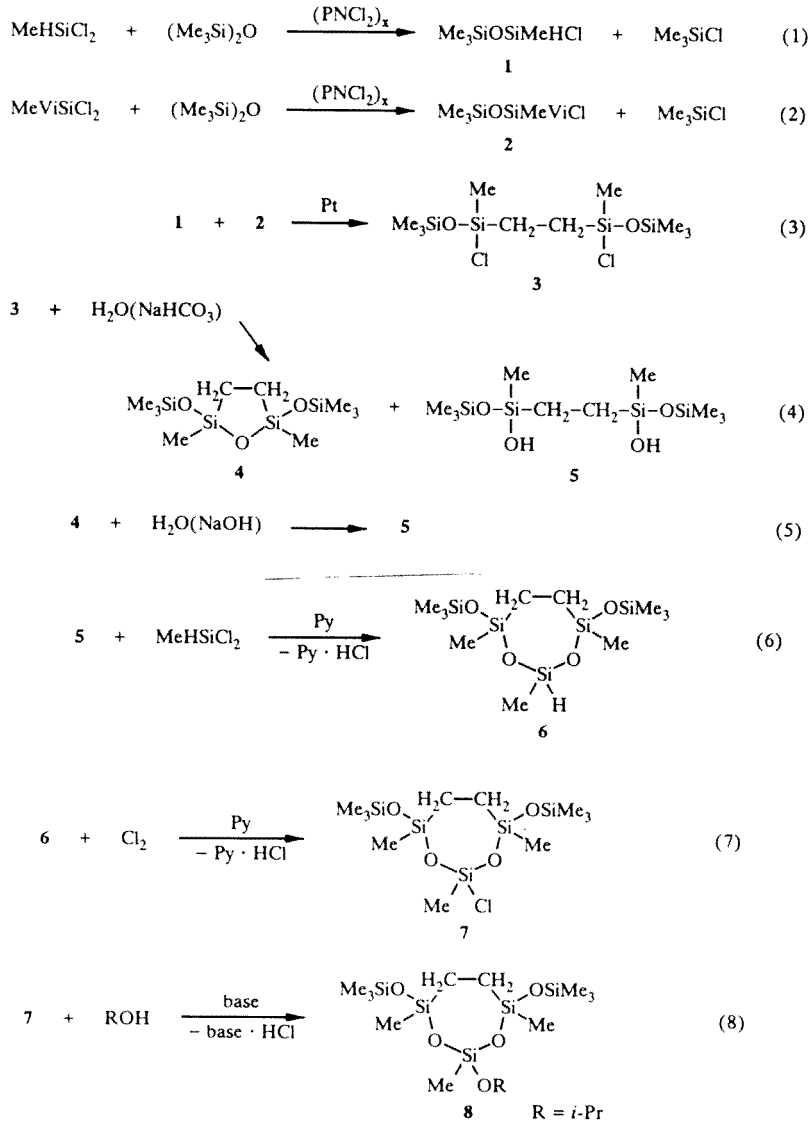
0009-3122/96/1112-1367$15.00

2. RESULTS AND DISCUSSION

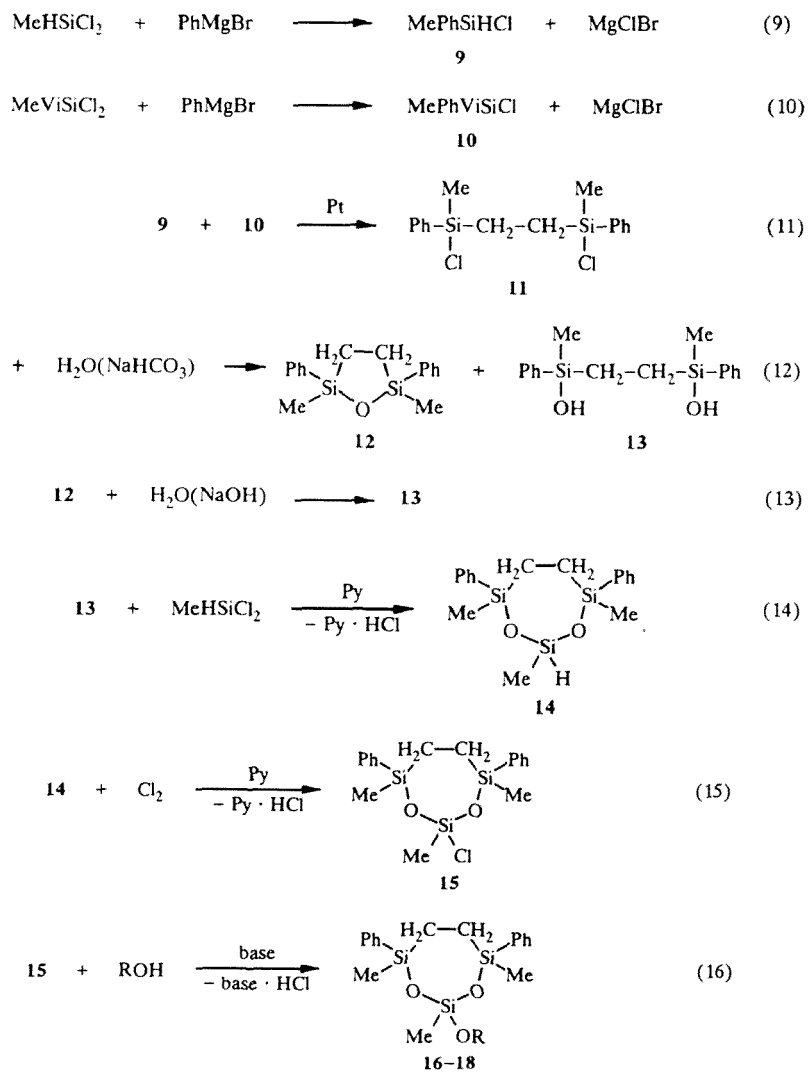
2.1. Preparation of the Model Compounds

Dioxatrisilacycloheptanes were synthesized according to Schemes 1 and 2 [1]. The first steps were either two equilibration reactions between dichlorosilanes and hexamethyldisiloxane (equations 1 and 2) using the $(PNCl_2)_x$ catalyst [5] or two Grignard reactions (9), (10). In the following dichlorodisilahexanes were obtained by hydrosilylation reactions (3), (11). Hydrolysis of chlorosilanes **3** or **11** with aqueous solutions of sodium hydrogen carbonate (4), (12) led to the mixtures of oxadisilacylopentanes **4** or **12** with the intended disilanols **5** or **13**. The overall yield of the end products could be raised by a definite synthesis of the oxadisilacyclopentanes, followed by the cleavage of these compounds with water and catalytic amounts of sodium hydroxide (5), (13). In most cases the disilanols obtained are forming mixtures of *meso* and *racemic* derivatives. But when **12** was cleaved with water-sodium hydroxide and the mixture was kept at room temperature for some days only the *meso*-**13** crystallized out. Ring closure to dioxatrisilacycloheptanes **5** and **14** was successfully done with methyldichlorosilane in the presence of pyridine as the HCl acceptor (6), (14).

Scheme 1



Scheme 2



base = pyridine, triethylamine or 2,6-dimethylpyridine;

16 R = Me; **17** R = *i*-Pr; **18** R = *t*-Bu

The same series of reactions could be used for the synthesis of dioxatrisilaoctanes (Schemes 3 and 4). But in this case vinyl groups had to be substituted by allyl residues. In this way at first oxadisilacyclohexanes **22** and **25** were obtained by reactions (17)-(20) or (21)-(23), respectively. But it was impossible to cleave bis(trimethylsiloxy) derivative **22**. Neither in acidic nor in basic medium the ring could be opened without splitting off the trimethylsiloxy groups. Fortunately, the diphenylderivative could be cleaved with a potassium hydroxide-potassium ethoxide mixture (24). Dipotassium disilanolate **26** further could be cyclized with dichloromethylsilane to 2,4,8-trimethyl-4,8-diphenyl-1,3-dioxa-2,4,8-trisilacylooctane **27** (25).

Scheme 3

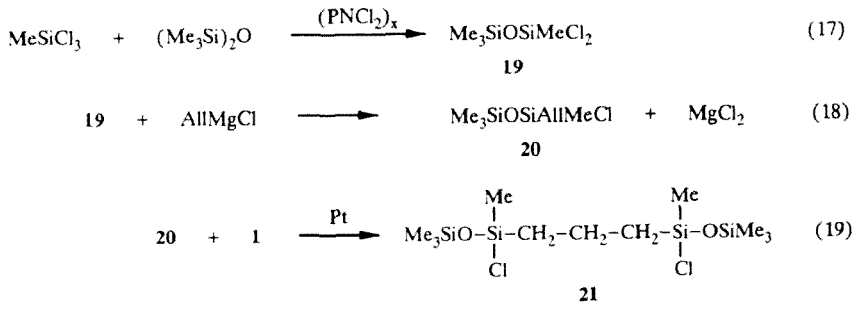


TABLE 1. ^{29}Si NMR Shifts δ (ppm) of Dioxatrisilacycloheptanes and -octanes

Compound	R	X	n	A (*trans, trans*)	B (*cis, trans*)	C (all-*cis*)
6	$OSiMe_3$	H	2	-31,98	-31,83	-32,25
7	$OSiMe_3$	Cl	2	-39,80	-40,06	-39,80
8	$OSiMe_3$	OPr-*i*	2	-56,50	-55,87	-55,56
14	Ph	H	2	-28,16	-28,44	-28,97
15	Ph	Cl	2	-36,64	-36,72	-37,18
16	Ph	OMe	2	-50,99	-50,69	-50,43
17	Ph	OPr-*i*	2	-53,69	-53,44	-53,39
18	Ph	OBu-*t*	2	-57,78	-57,73	-57,70
27	Ph	H	3	-29,50	-29,99	-30,42
28	Ph	Cl	3	-38,23	-38,27	-38,60

TABLE 2. Percentage (%) of Configurational Isomers in the Reaction Mixtures of Dioxatrisilacycloheptanes and -octanes

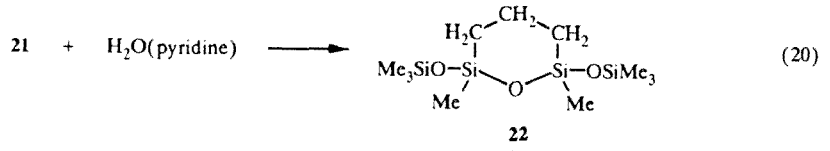
Compound	R	X	n	Method	A (*trans, trans*)	B (*cis, trans*)	C (all-*cis*)
6	$OSiMe_3$	H	2	GC	*	*	27
7	$OSiMe_3$	Cl	2	^{29}Si NMR	*	50	*
				GC	*	*	23
				calc.	27	50	23
8	$OSiMe_3$	OPr-*i*	2	^{29}Si NMR	33	48	19
14	Ph	H	2	^{29}Si NMR	25	48	27
				GC	25	50	25
15	Ph	Cl	2	^{1}H NMR	33	50	17
				^{29}Si NMR	35	48	18
				GC	30	52	18
16	Ph	OMe	2	^{1}H NMR	29	50	21
				^{29}Si NMR	38	51	12
				GC	38	51	11
17	Ph	OPr-*i*	2	^{1}H NMR	37	47	16
				^{29}Si NMR	34	52	14
				GC	33	*	*
18	Ph	OBu-*t*	2	^{1}H NMR	30	51	19
				^{29}Si NMR	32	45	23
				GC	33	*	*
27	Ph	H	3	^{29}Si NMR	23	46	31
				GC	22,5	49	28,5
28	Ph	Cl	3	^{29}Si NMR	33	48	19

*Signals not separable.

TABLE 3. Relative Reactivities of the Configurational Isomers of Dioxatrisilacycloheptanes and -octanes

Compound	R	X	n	Reagent	Method	Conversion, %	A (*trans, trans*)	B (*cis, trans*)	C (all-*cis*)
6	$OSiMe_3$	H	2	Cl_2	^{29}Si NMR	50	3,5	1,7	1
7	$OSiMe_3$	Cl	2	MeOH	^{1}H NMR	50	3,2	2,4	1
				i-PrOH	^{1}H NMR	50	4,3	2,5	1
14	Ph	H	2	Cl_2	GC	40	2,25	1,9	1
				Br_2	GC	40	4,6	2,0	1
15	Ph	Cl	2	MeOH	^{29}Si NMR	50	1,2	1	1
27	Ph	H	3	Cl_2	GC	53	3,7	1,8	1
				Br_2	GC	50	2,4	1,4	1

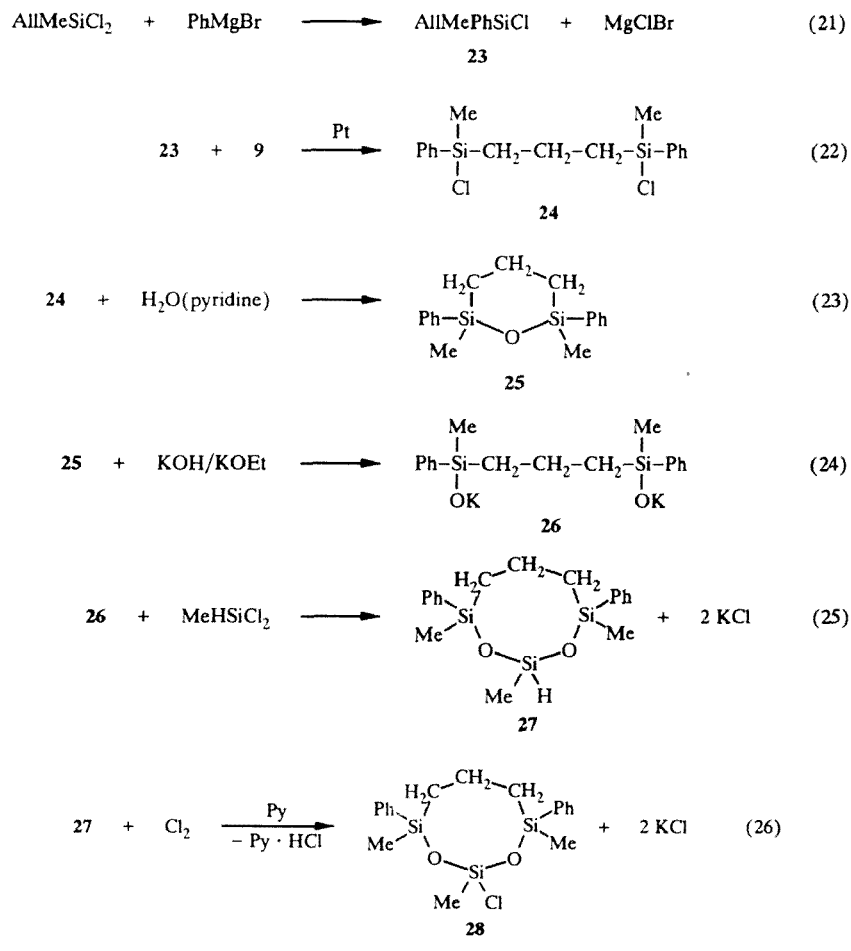
Scheme 3 (continued)



(20)

22

Scheme 4



(21)

23

(22)

24

(23)

25

(24)

26

(25)

27

(26)

28

2.2. Assignment of Spectroscopic Signals to the Configurational Isomers

Substituted cyclotrisiloxanes [2, 3], also substituted dioxatrisilacycloheptanes and dioxatrisilacyclooctanes form three configurational isomers (Fig. 1). So, the first problem in using these substances for stereochemical investigation was the definite assignment of the signals observed in the chromatograms and spectra to the configurational isomers. *cis,trans*-Isomers **B** can be formed in two enantiomers. Thus, the statistical weight of formation is two times that of the other isomers, and its signals in the mixtures of configurational isomers must have a two-fold intensity of the two other signals. The assignment of **A** and **C** signals is more complicated. We found two sources of information. First, we used the rule of Pelletier and Harrod [12], which says that in all cases the signals of the *trans,trans*-isomer show the highest low field shift (Table 1) [1]. The second source of information is the ratio of the isomers in the equilibrium mixture. All the *cis*-isomers should be sterically more hindered than the *cis,trans*-isomer, and the *trans,trans*-derivative should have the lowest sterical hindrance. Indeed, the signals of the three isomers differ in their intensity very clearly from the values which should be expected from the statistical ratio of 25:50:25 [1]. Table 2 shows that the assignments obtained by the difference method are the same as taken with the Harrod rule. The only exceptions from the difference rule are formed by hydrogen compounds **6**, **14**, and **27**. Because the hydrogen

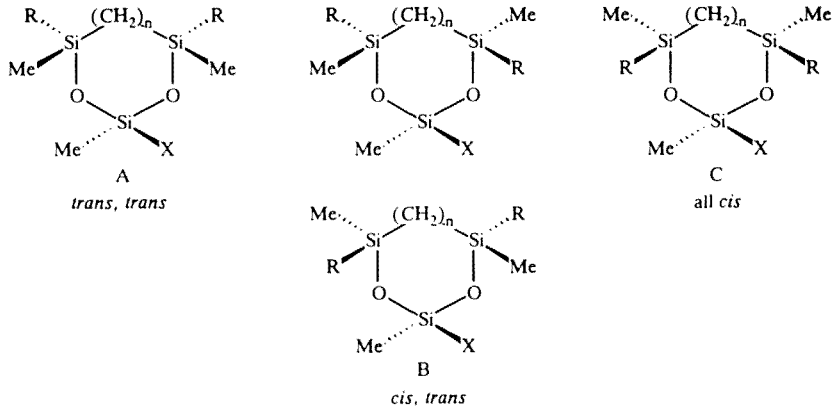


Fig. 1

atom is smaller than the methyl group, in these compounds the all *cis*-isomers are present in the mixture in a percentage higher than the statistically expected one.

2.3. Steric Course of Substitution Reactions

The reactions of hydrogen substituted dioxatrisilacycloheptanes **6** and **14** and dioxatrisilacyclooctane **27** with chlorine or bromine in carbon tetrachloride were monitored by gas chromatography. To prevent the cycles from cleavage by hydrochloric acid, pyridine was added as an HCl acceptor. Always the *trans,trans*-isomers showed the highest reactivity and all the *cis*-isomers, the lowest one (Table 3). So, also these reactions should have a retention stereochemistry. But in all cases the percentage of the configurational isomers of the chloroderivatives in the reaction mixture is not in agreement with the percentage of the isomers of the starting hydrogen compounds. We could show that the compositions of the chloroderivatives given in Table 2 are the result of isomerization processes caused by pyridine added to the reaction mixtures. So, the values for the chloroderivatives **7**, **15**, and **28** given in Table 2 represent the thermodynamically determined equilibrium states and not the outcome of kinetically determined reactions. The chloroderivatives further reacted with alcohols in the presence of amines. The reaction mixtures were analyzed by ^{1}H NMR spectroscopy and gas chromatography. Only the reaction of **7** with methanol and isopropyl alcohol and the reaction of **15** with methanol could be studied kinetically. The relative reactivities once more point to a retention stereochemistry. The reactions of **15** with isopropyl alcohol and tert-butanol could not be followed kinetically because the nucleophilic substitution reactions were superimposed by isomerization reactions. But the percentage of the configurational isomers in the reaction mixtures clearly suggest retention of the configuration also in these cases. We assume the ring strain relief via an axial-equatorial arrangement of the silacycles in the pentacoordinated trigonal-bipyramidal intermediates of the nucleophilic substitution reactions to be the reason for the unusual retention stereochemistry [1, 2].

Comparing the relative reactivities of the configurational isomers of dioxatrisilacycloheptanes and dioxatrisilacyclooctanes with those of cyclotrisiloxanes [1] it becomes evident that the differences are smaller for the derivatives of the larger ring systems. Obviously, a higher degree of conformational freedom diminishes the differences in sterical strain.

3. EXPERIMENTAL

3.1. Methods

3.1.1. Gas chromatography

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

3.1.2. ^{1}H NMR and ^{13}C NMR spectra

^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker AC 200 P spectrometer at 200.13 MHz and 50.323 MHz, respectively. The chemical shifts are given in ppm and referred to TMS.

3.1.3. ^{29}Si NMR spectra

^{29}Si NMR measurements ($CDCl_3$ solutions or pure substances with external lock) were run on a Bruker MSL spectrometer at 59.627 MHz applying the inverse gate decoupling technique with a repetition time of 5 sec and a 30° flip angle. The spectra were recorded with 0.2 Hz/point.

3.2. Materials

3.2.1. Solvents and reagents

All solvents were dried by standard methods prior to use. 1-Chloro-1,3,3,3-tetramethyldisiloxane (**1**), 1-chloro-1,3,3,3-tetramethyl-1-vinyldisiloxane (**2**) and 1,1-dichloro-1,3,3,3-tetramethyldisiloxane (**19**) were synthesized by equilibration of the respective chlorosilanes with hexamethyldisiloxane [equations (1), (2), and (17)] [5, 6]. Chloromethylphenylsilane (**9**), chloromethylphenylvinylsilane (**10**), and allylchloromethylphenylsilane (**23**) were made from dichloromethylsilane, dichloromethylvinylsilane or allyldichloromethylsilane, respectively, and phenylmagnesiumbromide according to the literature methods [equations (9), (10), and (21)] [7, 8].

3.2.2. Preparations

2,5-Dichloro-2,5-bis(trimethylsiloxy)-2,5-disilahexane (3). A solution of 200 μl of H_2PtCl_6 in isopropyl alcohol was added to a mixture of 16.85 g (0.1 mol) **1** and 194.5 g (1 mol) **2**. The reaction solution was heated to 80°C. After the reaction started, as indicated by a temperature increase and decoloration of the catalyst, another 151.65 g (0.9 mol) **1** were added dropwise by stirring.

Yield: 196 g (54%); bp 133°C/27 mbar; d_4^{25} 0.993 g cm^{-3}; hydrolyzable chlorine found: 19.15%. Calculated, %: 19.5; ^{29}Si ($CDCl_3$): δ 12.27 (Me_3Si); 4.14 ($MeClSiCH_2$); ^{13}C ($CDCl_3$): δ 11.16 (CH_2); 1.87 (CH_3); 1.66 ($Si(CH_3)_3$).

2,5-Dimethyl-2,5-bis(trimethylsiloxy)-1-oxa-2,5-disilacyclopentane (4) and 2, 5-Dihydroxy-2, 5-bis(trimethylsiloxy)-2,5-disilahexane (5). A solution of 73 g (0.2 mole) **3** in 200 ml diethyl ether was added dropwise to a vigorously stirred sus-pension 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_2SO_4. After evaporation of diethyl ether the residue was distilled under reduced pressure.

4, Yield: 23 g (37%); bp 40°C/0.27 mbar; ^{29}Si ($CDCl_3$): δ 8.46; 8.36 (Me_3Si); −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 ($Si(CH_3)_3$).

5, Yield: 24 g (37%); bp 90°C/0.27 mbar; ^{29}Si ($CDCl_3$): δ 7.30; 7.40 (Me_3Si); −12.20 ($Me(OH)SiCH_2$).

2,5-Dihydroxy-2,5-bis(trimethylsiloxy)-2,5-disilahexane (5). Aqueous NaOH (0.5 ml, 0.1 N) was added to a stirred solution of 7.1 g (23 mmol) **4** in 5 ml 1,4-dioxane. The obtained mixture was distilled under reduced pressure.

2,4,7-Trimethyl-4,7-bis(trimethylsiloxy)-1,3-dioxa-2,4,7-trisilacycloheptane (6). 32.7 g (0.1 mol) **5** 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 hr. 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%); bp 50°C/0.13 mbar; d_4^{25} 0.90 g cm^{-3}; ^{29}Si (C_6D_6 ext.): δ 8.09; 7.98; 7.84 (Me_3Si); −17.92; −17.99; −18.07; −18.10 ($MeSiCH_2$); −31.83; −31.98; −32.25 (MeSiH).

2-Chloro-2,4,7-trimethyl-4,7-bis(trimethylsiloxy)-1,3-dioxa-2,4,7-trisilacycloheptane (7). A solution of 1.14 g (16 mmol) chlorine in carbon tetrachloride was added dropwise to a stirred solution of 6 g (16 mmol) **6** 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.

Bp 65°C/0.065 mbar; ^{29}Si ($CDCl_3$): δ 8.84; 8.75; 8.61 (Me_3Si); −16.94; −16.99; −18.34; −18.48 ($MeSiCH_2$); −39.80; −40.06 (MeSiCl).

2-Isopropoxy-2,4,7-trimethyl-4,7-bis(trimethylsiloxy)-1,3-dioxa-2,4,7-trisilacycloheptane (8). 8 was obtained by reacting **7** with stoichiometric amounts of isopropyl alcohol and base during the measurements of the relative reactivities of isomers.

^{29}Si ($CDCl_3$): δ 7.94; 7.68; 7.79; 7.76 (Me_3Si); −19.20; −19.32; −19.85; −20.05 ($MeSiCH_2$); −55.56; −55.67; −56.50 (MeSiOPr-*i*). ^{1}H ($CDCl_3$): δ −0.1−0.05 (m, Si($\underline{CH_3}$)3, $CH_2Si\underline{CH_3}$, $(CH_3)_2CHOSi\underline{CH_3}$); 0.5-0.6 (m, CH_2); 1.0-1.1 (3d, $SiOCH(\underline{CH_3})_2$); 3.8-4.2 (m, $SiO\underline{CH}(CH_3)_2$).

2,5-Dichloro-2,5-diphenyl-2,5-disilahexane (11) [9]. Compound **11** was synthesized in the same way as compound **3**, using 156.45 g (1 mol) **9** and 182.45 g (1 mol) **10**.

Yield: 271.5 g (80%); bp 170°C/0.665 mbar; hydrolyzable chlorine found: 19.6%. Calculated, %: 20.89; ^{29}Si ($CDCl_3$): δ 22.02 ($MePhClSiCH_2$).

2,5-Dimethyl-2,5-diphenyl-1-oxa-2,5-disilacyclopentane (12) [10, 11]. 20 g (59 mmol) **11** 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 (118 mmol) 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%); bp 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_6H_5).

2,5-Dihydroxy-2,5-diphenyl-2,5-disilahexane (13). Aqueous NaOH (0.5 ml, 0.1 N) was added to a stirred solution of 6.5 g (23 mmol) **12** in 5 m 11,4-dioxane. *meso*-**13** crystallized on leaving at ambient temperature for 48 h.

Yield: 3.2 g (46%); mp 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-diphenyl-1,3-dioxa-2,4,7-trisilacyclo-heptane (14). 4 g (13 mmol) **13** and 1.5 g (13 mmol) dichloromethylsilane, each in 20 ml diethyl ether were reacted in the same way as above described for the preparation of **6**.

Yield: 0.67 g (15%); bp 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*-isomers 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, $PhSi\underline{CH_3}$); 0.25-0.3 (m, 3H, $HSi\underline{CH_3}$); 4.9 (m, 1H, SiH); 7.3-7.7 (m, 10H, C_6H_5).

2-Methoxy-2,4,7-trimethyl-4,7-diphenyl-1,3-dioxa-2,4,7-tri-silacycloheptane (16). 16 was obtained by reacting **15** with stoichiometric amounts of methanol and bases during the measurements of the relative reactivities of isomers.

^{29}Si ($CDCl_3$): δ 1.50; 1.27; 1.24 ($MePhSiCH_2$); −50.43; −50.62; −50.99 (MeSiOMe); ^{1}H ($CDCl_3$): δ 0.2-0.25 (3s, 3H, $CH_3OSi\underline{CH_3}$); 0.3-0.4 (4s, 6H, $PhSi\underline{CH_3}$); 1.0-1.1 (m, 4H, CH_2); 3.4-3.6 (3s, 3H, OCH_3); 7.3-7.7 (m, 10H, C_6H_5).

2-Isopropoxy-2,4,7-trimethyl-4,7-diphenyl-1,3-dioxa-2,4,7-trisilacycloheptane (17). 17 was analogously obtained starting from **15** and isopropyl alcohol.

^{29}Si ($CDCl_3$): δ 0.93; 0.89; 0.82 ($MePhSiCH_2$); −53.39; −53.44; −53.69 (MeSiOPr-*i*); ^{1}H ($CDCl_3$): δ 0.2 (3s, 3H, $(CH_3)_2CHOSi\underline{CH_3}$); 0.3-0.4 (4s, 6H, $PhSi\underline{CH_3}$); 1.0-1.1 (m, 4H, CH_2); 1.1-1.3 (3d, 6H, $SiOCH(\underline{CH_3})_2$); 3.9-4.4 (m, 1H, $SiO\underline{CH}(CH_3)_2$); 7.3-7.7 (m, 10H, C_6H_5).

2-*tert*-Butoxy-2,4,7-trimethyl-4,7-diphenyl-1,3-dioxa-2,4,7-trisilacycloheptane (18). 18 was analogously prepared starting from **15** and *tert*-butyl alcohol.

^{29}Si ($CDCl_3$): δ 0.64; 0.52; 0.43 ($MePhSiCH_2$); −57.61; −57.68; −57.81 (MeSiOBu-t). ^{1}H ($CDCl_3$): δ 0.2-0.4 (7s, 9H, $(CH_3)_3COSi\underline{CH_3}$, $PhSi\underline{CH_3}$); 0.9-1.1 (m, 4H, CH_2); 1.2-1.4 (3s, 9H, $SiOC(\underline{CH_3})_3$); 7.3-7.7 (m, 10H, C_6H_5).

1-Allyl-1-chloro-1,3,3,3-tetramethyldisiloxane (20). 100 ml of a 2-molar solution of allylmagnesiumchloride in tetrahydrofurane were slowly added to a solution of 40.6 g (0.2 mol) **19** in 300 ml tetrahydrofurane by vigorous stirring in a N_2-atmosphere. After the end of the exothermic phase of the reaction the mixture was reflux boiled for two additional hours. The precipitated magnesium chloride was filtered off by suction. The solvent was evaporated and the residue distilled under vacuum.

Yield: 14.6 g (35%); bp 78°C/60 mbar; d_4^{25} 0.941 g·cm^{-3}; hydrolyzable chlorine found: 16.8%; Calculated, %: 17.0; ^{1}H ($CDCl_3$): δ 5.6-5.9 (m, 1 H, CH=); 4.8-5.0 (m, 2H, CH_2=); 1.5-1.6 (d, 2H, Si—CH_2); 0.1 (s, 12H, $SiCH_3$).

2,6-Dichloro-2,6-bis(trimethylsiloxy)-2,6-disilaheptane (21). 21 was prepared in the same way as **3** using 16.85 g (0.1 mol) **1** and 20.9 g (0.1 mol) **20**.

Yield: 20.4 g (54%); bp 137°C/15 mbar; d_4^{25} 0.955 g·cm^{-3}, hydrolyzable chlorine found: 17.45%. Calculated, %: 18.78; ^{29}Si ($CDCl_3$ ext.): δ 11.92 (Me_3Si); 3.03 (Cl_2SiCH_2).

2,6-Dimethyl-2,6-bis(trimethylsiloxy)-1-oxa-2,6-disilacyclohexane (22). 22 was analogously prepared as **13** using 38 g (0.1 mol) **21**.

Yield: 17.4 g (54%); bp 43°C/0.134 mbar; ^{1}H ($CDCl_3$): δ 1.6-1.8 (m, 2H, CH_2); 0.5-0.6 (t, 4H, CH_2); 0.0-0.2 (2×2s, 24H, CH_3, $Si(CH_3)_3$); ^{13}C ($CDCl_3$): δ −0.032; −0.130 (CH_3); 1.88 ($SiOCH_3$); 16.98; 17.05 (CH_2); 0.62 ($SiCH_3$); 17.15; 17.69 ($SiCH_2CH_2$, $SiCH_2CH_2$); ^{29}Si ($CDCl_3$): δ 7.92 (Me_3Si); −16.68; −17.39 ($MeSiCH_2$).

2,6-Dichloro-2,6-dimethyl-2,6-diphenyl-2,6-disilaheptane (24). 24 was prepared by hydrosilylation of 19.1 g (0.1 mol) **23** with 15.6 g (0.1 mol) **9**, using the same procedure as described above for the preparation of **3**.

Yield: 23 g (65%); bp 164°C/0.5 mbar; d_4^{25} 1.152 g cm^{-3}; hydrolyzable chlorine found: 19.08. Calculated, %: 19.87; ^{1}H ($CDCl_3$): δ 7.4-7.8 (m, 10H, C_6H_5); 1.6-1.8 (m, 2H, CH_2); 1.1-1.4 (m, 4H, CH_2); 0.7 (2s, 6H, $Si(CH_3)_3$); ^{13}C ($CDCl_3$): δ 0.4 (CH_3); 17.0 (CH_2); 21.6 (CH_2); 128.1; 130.3; 133.3 (C_6H_5).

2,6-Dimethyl-2,6-diphenyl-1-oxa-2,6-disilacyclohexane (25) [12]. 51.25 g (0.1 mol) **24** in 200 ml diethyl ether and 1.8 g (0.1 mol) water in 200 ml 1,4-dioxane were added dropwise and simultaneously to a stirred solution of 15.82 g (0.2 mol) pyridine in 400 ml diethyl ether. The solution was stirred for another 2 h. The precipitated pyridine hydrochloride was filtered off. The solvents were evaporated and the residue was distilled under reduced pressure.

Yield: 32.9 g (78%); bp 116-118°C/0.134 mbar; ^{1}H ($CDCl_3$): δ 0.3-0.4 (2s, 6H, CH_3); 0.75-1.05 (m, 4H, $SiCH_2$); 1.8-2.1 (m, 2H, $SiCH_2\underline{CH_2}$); 7.3-7.7 (m, 10H, C_6H_5); ^{13}C ($CDCl_3$): δ −0.02; −0.133 (CH_3); 16.25; 16.35; 17.68; 17.86 (CH_2); 127.7; 127.8; 129.4; 129.41; 133.09; 133.18; 138.72; 139.03 (C_6H_5); ^{29}Si ($CDCl_3$): δ 3.06 (*cis*); 3.01 (*trans*) ($PhMeSiCH_2$); (C_6D_6 ext.) 2.31; 2.39.

2,4,8-Trimethyl-4,8-diphenyl-1,3-dioxa-2,4,8-trisilacyclo-octane (27). A mixture of 0.95 g (16.3 mmol) potassium hydroxide dissolved in 5 ml ethyl alcohol was added to 5 g (16.8 mmol) **25** in 20 ml *n*-hexane under argon atmosphere. The mixture was stirred for 1.5 hr. The azeotrope ethyl alcohol-*n*-hexane was distilled off. Then the reaction mixture was reflux boiled for 1 hr. The remaining *n*-hexane was evaporated under vacuum. The residue was dissolved in 100 ml diethyl ether and cyclized with 1.93 g (16.8 mmol) dichloromethylsilane. Potassium chloride was filtered off under suction. The solvents were evaporated and the residue distilled under vacuum.

Yield: 13% (GC, contaminated with some **26**); bp 140°C/1.3·10^{-4} mbar (bulb tube furnace); ^{29}Si ($CDCl_3$): δ 2.22; 2.20 ($MePhSiCH_2$); −29.50; −29.99; −30.42 (MeSiH).

REFERENCES

1. K. Rühlmann, S. Jähnichen, U. Scheim, D. Scheller, and F. Keidel, J. Organomet. Chem., **505**, 29 (1995).
2. R. Gewald, K. Rühlmann, U. Scheim, and A. Porzel, J. Organomet. Chem., **377**, 9 (1989).
3. R. Gewald, U. Scheim, R. Lang, K. Rühlmann, and R. Lehnert, J. Organomet. Chem., **446**, 79 (1993).
4. R. J. P. Corriu, Ch. Guerin, and J. J. E. Moreau, Top. Stereochem., **15**, 43 (1984).
5. S. Nitzsche, H. Triem, M. Wick, and K.-H. Wegehaupt, D-AS I 279 019 (04.01.1967); Chem. Abstr., **70**, 37912v (1969).
6. L. Engelbrecht and G. Sonnek, Plaste und Kautschuk., **30**, 362 (1983).
7. Pat. 622970 (10.05.1949) Brit., A. J. Barry, Chem. Abstr., **44**, 658i (1950).
8. J. W. Curry, J. Am. Chem. Soc., **78**, 1686 (1956).
9. W. A. Piccoli, G. G. Haberland, and R. L. Merker, J. Am. Chem. Soc., **82**, 1883 (1960).
10. J. Nagy, E. Gergö, K. A. Andrianov, L. M. Volkova, and N. V. Delazari, J. Organomet. Chem., **67**, 19 (1974).
11. A. Kunai, E. Toyoda, T. Kawakami, and M. Ishikawa, Organomet., **11**, 2899 (1992).
12. B. Suryanarayanan, B. W. Peace, and K. G. Mayhan, J. Polym. Sci., **12**, 1109 (1974).
13. E. Pelletier and J. F. Harrod, Organomet., **3**, 1070 (1984).