Synthesis of organosiloxanes with reactive groups at silicon atoms

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The heterofunctional condensation of (dihydroxy)organodisiloxanes and -trisiloxanes with vinyl(hydro)organodichlorosilanes was studied with the purpose of preparing α,ω-dichloroorganosiloxanes with reactive Si—H and Si—CH=CH$_2$ groups. During the isolation, 1,9-dichloro-1,9-dihydropentamethyloctasiloxane disproportionates with the elimination of (dichloro)methylsilane to form heptamethylcyclotetrasiloxane. A series of cyclotetra-, cyclohexa-, and cyclooctasiloxanes with Si—H and Si—CH=CH$_2$ groups was obtained by the condensation of α,ω-dihydroxyorganosiloxanes with α,ω-(dichloro)divinyl(dihydro)organosiloxanes.

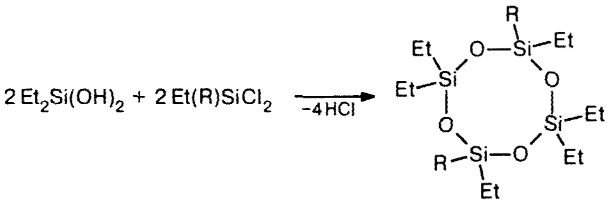
Key words: α,ω-dichlorodivinyl(dihydro)organosiloxanes, divinyl(dihydro)organocyclosiloxanes, heterofunctional condensation, IR, ^{1}H, and ^{29}Si NMR spectra.

In silicon chemistry, heterofunctional condensation (HFC) is widely used to prepare organosiloxanes with functional groups.[1—3]

The aim of the present study is the synthesis of new organosiloxanes with four or more silicon atoms containing reactive vinyl or hydride groups, for subsequent preparation of cyclolinear polymers.

It has been shown previously[2] that organocyclotetrasiloxanes with reactive groups at a definite position can be synthesized by HFC of (dihydroxy)organosilanes with dialkyldichlorosilanes in one stage. In the present work, 1,5-dihydro(divinyl)hexaethylcyclotetrasiloxanes (**1** and **2**) are prepared by the condensation of diethyldihydroxysilane with (dichloro)ethylsilane (DCES) and (dichloro)(ethyl)vinylsilane in the presence of an acceptor of HCl (Scheme 1).

Scheme 1

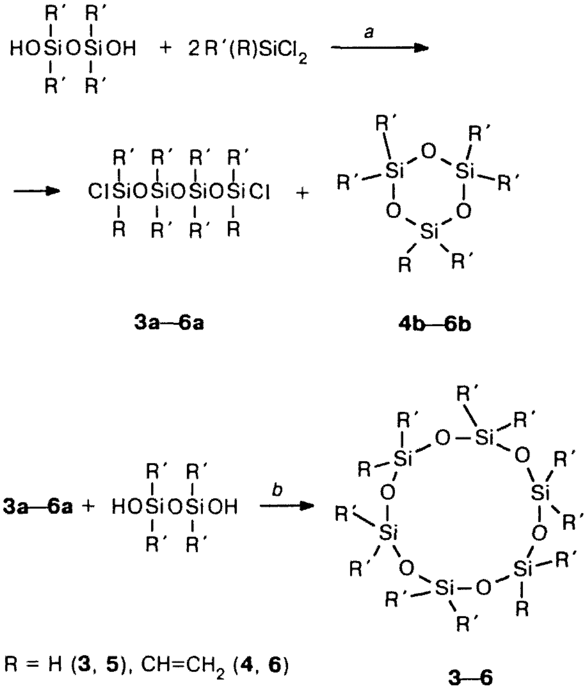


R = H (**1**), CH=CH$_2$ (**2**)

The yields of chromatographically pure **1** and **2** were 34 and 42 %, respectively. (Pentaethyl)vinylcyclotrisiloxane (17 %) and unidentified mixed cyclopenta- and cyclohexasiloxanes were the side-products. In the reaction with DCES, a series of mixed higher cyclosiloxanes is formed instead of pentaethylcyclotrisiloxane.

Organocyclohexasiloxanes were synthesized by a multistep HFC. At the first stage, (dihydroxy)organosiloxane reacts with an excess of (dichloro)organosilane affording α,ω-(dichloro)octaorganotetrasiloxanes (**3a—6a**), which react with (dihydroxy)organodisiloxane at the second stage giving organohexacyclosiloxanes (**3—6**) (Scheme 2).

Scheme 2



R = H (**3**, **5**), CH=CH$_2$ (**4**, **6**)
R′ = Me (**3**, **4**), Et (**5**, **6**)

[†] Deceased.

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The reaction of 1,3-(dihydroxy)tetramethyldisiloxane (DTMDS) and a twofold excess of (dichloro)(methyl)vinylsilane (DCMVS) or (dichloro)(methyl)silane (DCMS) was carried out in diethyl ether at 0—5 °C in the presence of aniline as the HCl acceptor. GLC analysis of the reaction mixture demonstrated that in the case of DCMVS, (pentamethyl)vinylcyclotrisiloxane **4b** (yield 10—15 %) and three unidentified compounds, the total yield of which did not exceed 10—15 %, are formed along with **4a** (70—80 %). In the reaction with DCMS, the corresponding organocyclotrisiloxane is not formed. Compounds **3a** and **4a** were isolated by vacuum distillation in 76 and 43 % yields, respectively.

The condensation of 1,3-(dihydroxy)tetraethyldisiloxane (DTEDS) with DCES and (dichloro)(ethyl)vinylsilane (DCEVS) was carried out analogously. The reaction with DCES affords mainly 1,7-(dichloro)-(1,7-dihydro)hexaethyltetrasiloxane (**5a**) and pentaethylcyclotrisiloxane (**5b**) (yields 76 and 24 %, respectively, GLC analysis). In the reaction with DCEVS, (pentaethyl)vinylcyclotrisiloxane (**6b**) (yield up to 87 %) and 1,7-dichloro-(1,7-divinyl)hexaethyltetrasiloxane (**6a**) (yield 13 %) are formed. At a molar ratio of (dihydroxy)organodisiloxane and DCES equal to 1 : 16, the cyclization is slightly suppressed, which increases the yield of **6a** from 13 to 30 %.

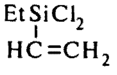
It is known that nonpolar solvents favor the formation of linear siloxanes in the reaction of hydrolytic condensation of (dichloro)organosilanes. In addition, as was shown in our studies, the concentration of the starting compounds and the nature of an acceptor influence the synthesis of the linear (dichloro)siloxanes in HFC. As can be seen from the data presented in Table 1, with an increase in the bulk of the substituent at the silicon atom (replacement of H by the $CH_2{=}CH$ group) the yield of (dichloro)organosiloxane **6a** decreases sharply due to the formation of cyclotrisiloxane. The cyclization could be suppressed (to 8 %) by using pyridine as the HCl acceptor. Physicochemical properties of α,ω-(dichloro)divinyl(dihydro)siloxanes are listed in Table 2.

Cyclohexasiloxanes with the Si—H and $Si{-}CH{=}CH_2$ groups were prepared by the reaction of **3a—6a** with the corresponding 1,3-(dihydroxy)tetraalkyldisiloxanes (see Scheme 2). The reaction was performed in diethyl ether at the stoichiometric ratio of the components using pyridine as the HCl acceptor. After rectification, chromatographically pure organocyclohexasiloxanes containing the $CH_2{=}CH$- or H-substituents at the Si atom were isolated (Table 3).

Organooctasiloxanes with the $Si{-}CH{=}CH_2$ or Si—H groups were synthesized according to Scheme 3.

At the first stage, the interaction of 1,5-(dihydroxy)hexamethyltrisiloxane (DHMTS) with $Me(CH_2{=}CH)SiCl_2$ and $Me(H)SiCl_2$ resulted in organocyclotetrasiloxane, *i.e.*, the cyclization product in addition to two major products, *viz.*, 1,9-dichloro-1,9-divinyloctamethylpentasiloxane (**7a**) and 1,9-dichloro-1,9-dihydrooctamethylpentasiloxane (**8a**), respectively. The conditions of reaction *a* leading to α,ω-dichloropentasiloxanes (see Scheme 3) were optimized in the reaction with $Me(CH_2{=}CH)SiCl_2$, because the conditions of reaction *a* presented in Scheme 2 gave unsatisfactory results. The reaction conditions and ratios between the cyclic and linear products are given in Table 4. As can be seen from these data, the optimal conditions for the preparation of **7a** include the use of toluene as the solvent and aniline as the acceptor. Dihydro derivative (**8a**) could not be isolated in an amount sufficient for subsequent reactions, although according to GLC data, its yield reached 80 %. It was found that during the isolation of compound **8a** at the stage of removal of the solvent, it disproportionates with the elimination of DCMS and the formation of organocyclotetrasiloxane (Scheme 4).

Table 1. Effect of conditions of HFC on the ratio of the cyclic and linear organosiloxanes

Organo(dichloro)-silane (X)	Molar ratio DTEDS : X	C*/mol L^{-1}	Solvent	Acceptor of HCl	GLC yield (%)	
					5b or **6b**	**5a** or **6a**
$EtHSiCl_2$	1 : 4	$\frac{0.4}{0.83}$	Et_2O	Aniline	24	76
 $EtSi(CH{=}CH_2)Cl_2$	1 : 4	$\frac{0.4}{0.83}$	The same	The same	87	13
The same	1 : 16	$\frac{0.4}{0.83}$	» »	» »	64	30
» »	1 : 6	$\frac{0.4}{0.83}$	Toluene	» »	87	13
» »	1 : 4	$\frac{0.4}{0.83}$	The same	Pyridine	24	76
» »	1 : 4	$\frac{0.6}{1.65}$	» »	The same	8	92

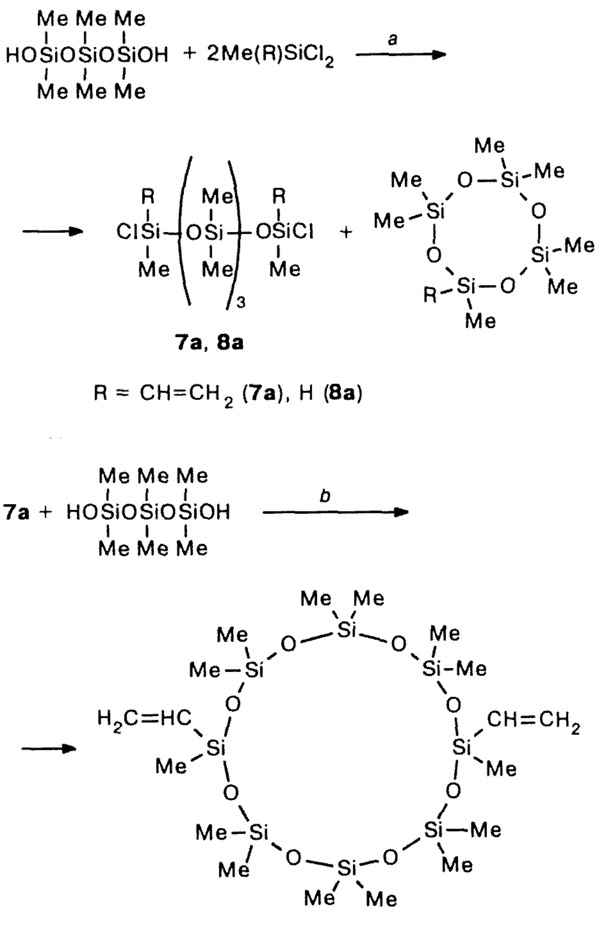
* C for DTEDS are given in the numerator and those for X are given in the denominator.

Table 2. Characteristics of α,ω-chloroorganosiloxanes **3a**—**8a**

Compound	B.p./°C (*p*/Torr)	Yield (%)	NMR, δ				
			^{1}H			^{29}Si	
			R'Si(1)	R'Si(2)	RSi	Si(1)	Si(2)
3a	90—95 (20)	60	0.56	0.16	5.28		
4a	90—94 (15)	43	0.5	0.16	5.9—6.1 m		
5a	146—152 (4)	76	0.72 m; 1.0 m		5.25	−13.415	−17.584
6a	120 (1)	66	0.65 m; 1.1 m		5.8—6.0 (m, Et)	−10.805	−18.785
7a	109—112 (1)	62	0.53	0.18; 0.14 (Si(3))	5.9—6.1 m		
8a*	98—101 (1)	—	0.60	0.25; 0.15 (Si(3))	5.25	−14.697	−17.499

* A signal at δ −20.224 (Si(3)) was also observed.

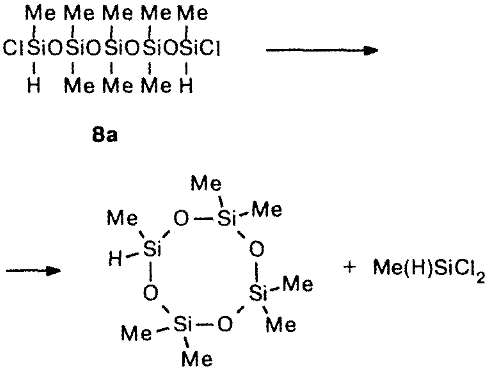
Scheme 3



R = CH=CH$_2$ (**7a**), H (**8a**)

7

Scheme 4



Experimental results on the synthesis of α,ω-(dichloro)siloxanes of different size and with different substituents demonstrate that the reactions are accompanied by undesired cyclization, which can be suppressed by selecting the solvent, the acceptor, and the concentration of the reagents. If the cyclization is thermodynamically favorable, diethyl ether is the undesirable solvent (see Tables 1 and 4); even an increase in the ratio of (dihydroxy) the derivative to dichlorosilane (1 : 10, 1 : 16) does not result in a significant decrease in the percentage of organocyclosiloxanes in the reaction mixture, *i.e.*, the reagent ratio is not critical. The experimental results on the study of reaction *a* in Scheme 2 (see Table 1) demonstrate that it is the acceptor that has a substantial effect in this case: the use of pyridine instead of aniline increases the yield of dichloroorganotetrasiloxanes.

Toluene also appeared to be the solvent of choice for reaction *a* presented in Scheme 3, and aniline was the

Table 3. Characteristics of organocyclosiloxanes **1—7**

Compound	Yield (%)	B.p./°C (p/Torr)	n_D^{25}	NMR, δ				
				^{1}H			^{29}Si	
				R'Si(1)	R'Si(2)	RSi	Si(1)	Si(2)
1	34	95—98 (2)	1.4230	0.62 q; 1.07 t		4.72	−33.65	−16.92; −17.13
2	42	85—89 (1)	1.4379	0.60 m; 1.06 m		6.05 m	−34.51; −34.47	−18.87
3	59	66—68 (1)	1.3971	0.14; 0.15	0.096; 0.099; 0.106; 0.109	4.68		
4	64	83—85 (1—2)	1.4128	0.157; 0.150	0.082; 0.085	5.75 m		
5	53	175—178 (1)	1.4341	0.6 q; 1.0 t		4.65	−37.90; −37.85	−21.64
6	49	180—182 (1)	1.4443	0.45 q; 0.85 t		5.85 m	−37.42	−22.28
7	31	119—122 (2)	1.4139	0.23; 0.25	0.12	5.95 m	−36.49	−22.21; −22.59 (Si(3))

most efficient acceptor of HCl. Unfortunately, it is difficult to reveal the general regularities for the synthesis of α,ω-(dichloro)organosiloxanes.

1,9-Divinyltetradecamethylcyclooctasiloxane (**7**) was synthesized by reaction *b* (see Scheme 3). The reaction was carried out in diethyl ether at three different concentrations of **7a** and 1,5-(dihydroxy)hexamethyltrisiloxane: 1.0, 0.5, and 0.1 mol L^{-1}. In a dilute solution, the reaction did not go to completion; according to GLC data, the unchanged dichloroorganosiloxane was present in the reaction mixture; at a concentration of the reagents of 1 mol L^{-1}, the reaction proceeded faster, but more than 75 % of the reaction mixture represented nonvolative material. At a concentration of 0.5 mol L^{-1}, the yield of **7** was 31 % and *ca.* 50 % was a nonvolatile residue.

Compounds **1—7** and **3a—8a** were identified on the basis of elemental analysis, ^{1}H and ^{29}Si NMR, and IR spectral data. Analysis of the IR spectra of the cyclic compounds obtained has demonstrated that ν_{as} SiOSi for cyclotetra- and cyclohexasiloxanes were observed in the 1077—1080 cm^{-1} region regardless of substituents, and at 1053 cm^{-1} for cyclooctasiloxane. The absorption bands of Si—H and Si—CH=CH$_2$ occur at the 2150—2160 (Si—H) region and at 1410 (C=C), 1600 (C=C), 3030 (CH=CH$_2$) cm^{-1}, regardless of substituents R' and the ring size. The chemical shifts in the ^{1}H and ^{29}Si NMR spectra of the compounds obtained are presented in Tables 2 and 3. The structure of organocyclosiloxanes **1—7** is confirmed by ^{1}H and ^{29}Si NMR spectroscopy (see Table 3). In the ^{29}Si NMR spectrum of compound **1**, three signals are observed: one signal belongs to the HEtSi group and two signals of equal intensity correspond to the SiEt$_2$ group, which indicates that compound **1** exists as a mixture of *cis*- and *trans*-isomers in a 1 : 1 ratio. For compound **2**, three signals are also observed: one for SiEt$_2$ and two signals of equal intensity for EtCH$_2$=CHSi that also corresponds to the ratio of *cis*- and *trans*-isomers of 1 : 1. An analogous pattern is observed for compound **5**. The isomeric ratios for compounds **6** and **7** could not be determined by NMR spectra because the splitting of the corresponding signals for the ^{29}Si nuclei was not registered.

Experimental

The ^{1}H and ^{29}Si NMR spectra (200.13 and 39.76 MHz, respectively) were recorded with a Bruker WP-200SY spectrometer (CCl$_4$ + C$_6$D$_6$ was used as the solvent). The ^{29}Si NMR spectra were recorded using pulse, Overhauser-free proton decoupling (period 25—30 s). Chromatographic analysis was performed with an LKhM-80 instrument, column 3 m × 3 mm, stationary phase SE-30 on Chromaton. Helium was used as the carrier gas at a rate of 30 mL min^{-1}. A katharometer was used as the detector, injector temperature 270 °C, column temperature program from 50 to 300 °C.

The results of the search for optimal conditions of the reactions are given in Tables 2 and 4. The acceptor was introduced simultaneously with a solution of the (dihydroxy) derivative. In the chromatographic analysis, only peaks of organocyclosiloxane and α,ω-(dichloro)organosiloxane were taken into account, their total area taken as 100 %.

Diethyl(dihydroxy)silane was obtained as reported in Ref. 4, and 1,3-(dihydroxy)tetraethyldisiloxane and 1,5-(dihydroxy)hexamethyltrisiloxane were prepared as described previously in Ref. 1.

1,3,3,5,7,7-Hexaethylcyclotetrasiloxane (1). Solutions of diethyl(dihydroxy)silane (18.0 g, 0.15 mol) in Et$_2$O (350 mL) and DCES (19.35 g, 0.15 mol) in Et$_2$O (350 mL) were added simultaneously from two dropping funnels to a solution of pyridine (24.55 g, 0.31 mol) in Et$_2$O (100 mL) at 0—5 °C. The mixture was stirred at *ca.* 20 °C for 24 h and filtered.

Table 4. Effect of conditions of HFC on the ratio of the cyclic and linear siloxanes (molar ratio DHMTS : (dichloro)silane = 1 : 6)

Chlorosilane (X)	C^*/mol L^{-1}	Solvent	Acceptor of HCl	GLC yield (%)	
				Cyclosiloxane	**7a** or **8a**
$MeSiCl_2CH=CH_2$	0.34 0.86	Et_2O Et_2O	Aniline	92	8
	**0.34 0.86	Et_2O Et_2O	Aniline	95	5
	0.34 0.96	Et_2O Et_2O	Pyridine	90	3
	0.34 1.50	Et_2O Toluene	Aniline	77	23
	0.34 12.00	Et_2O Toluene	Aniline	73	27
	0.34 ***	Et_2O —	Aniline	71	29
	0.34 12.00	Et_2O Et_2O	Aniline	59	41
	0.34 12.00	Toluene Toluene	Aniline	19	81
	0.34 12.00	Toluene Toluene	Pyridine	42	58
$MeHSiCl_2$	0.34 12.00	Et_2O Et_2O	Aniline	95	5
	0.34 12.00	Toluene Toluene	Pyridine	55	45
	0.34 12.00	Toluene Toluene	Aniline	20	80
	0.60 12.00	Toluene Toluene	Et_3N	90	10
	0.60 1.65	Toluene Toluene	Et_3N	45	55

* The data for DHMTS are given in the numerator and those for X are given in the denominator.
** The ratio of reagents is 1 : 10. *** Without a solvent.

After removal of the solvent *in vacuo*, the residue was fractionated *in vacuo* (p = 1 Torr). The product was further purified by fractionation on a column with metal packing. Compound **1** (19.1 g, 34 %) was prepared; b.p. 95—98 °C/2 Torr. Found (%): C, 35.59; H, 7.85; Si, 32.00. $C_{12}H_{32}O_4Si_4$. Calculated (%): C, 35.61; H, 7.91; Si, 31.88.

1,3,3,5,7,7-Hexaethyl-1,5-divinylcyclotetrasiloxane (2). Solutions of diethyl(dihydroxy)silane (9.5 g, 0.079 mol) in Et_2O (200 mL) and DCEVS (12.23 g, 0.079 mol) in Et_2O (200 mL) were added to a solution of pyridine (13.10 g, 0.166 mol) in Et_2O (100 mL) at 0—5 °C. The reaction was performed as in the preparation of **1**. Compound **2** (6.7 g, 42 %) was prepared; b.p. 85—89 °C/1 Torr. Found (%): C, 47.32; H, 7.49; Si, 28.01. $C_{16}H_{36}O_4Si_4$. Calculated (%): C, 47.48; H, 7.42; Si, 27.78.

1,7-Dichloro-1,3,3,5,5,7-hexamethyltetrasiloxane (3a). A solution of DTMDS (33.2 g, 0.2 mol) and aniline (37.2 g, 0.4 mol) in Et_2O (300 mL) was added to a solution of DCMS (92 g, 0.8 mol) in Et_2O (400 mL) at 0 °C in a flow of Ar. The mixture was stirred at *ca.* 20 °C for 24 h and filtered in a flow of Ar; Et_2O was removed together with an excess of DCMS, and the residue was fractionated. The fraction with b.p. 90—95 °C/20 Torr was collected to give compound **3a** (30.6 g, 60 %). Found (%): C, 21.56; H, 6.21; Si, 35.01; Cl, 20.99. $C_6H_{20}Cl_2O_3Si_4$. Calculated (%): C, 22.26; H, 6.18; Si, 34.75; Cl, 21.96.

1,7-Dichloro-1,3,3,5,5,7-hexamethyl-1,7-divinyltetrasiloxane (4a). A solution of DTMDS (16.6 g, 0.1 mol) and aniline (18.6 g, 0.2 mol) in 150 mL Et_2O was added to a solution of DCMVS (56.42 g, 0.4 mol) in Et_2O (200 mL) at 0 °C. The reaction mixture was treated as described for the preparation of **3a**. In the fractional distillation, the fraction with b.p. 90—94 °C/15 Torr was collected giving compound **4a** (16.2 g, 43 %). Found (%): C, 31.56; H, 6.40; Si, 29.01; Cl, 19.31. $C_{10}H_{24}Cl_2O_3Si_4$. Calculated (%): C, 31.96; H, 6.39; Si, 29.93; Cl, 18.92.

1,7-Dichloro-1,3,3,5,5,7-hexaethyltetrasiloxane (5a). A solution of DTEDS (11.2 g, 0.05 mol) and aniline (9.61 g, 0.103 mol) in Et_2O (120 mL) was added to a solution of DCES (32.6 g, 0.256 mol) in Et_2O (300 mL) at 0—5 °C. Then the reaction was carried out as described for the preparation of **3a**. In the fractional distillation, the fraction with b.p.

146—152 °C/4 Torr was collected yielding compound **5a** (14.5 g, 76 %). Found (%): C, 35.22; H, 7.65; Si, 27.00; Cl, 17.01. $C_{12}H_{32}Cl_2O_3Si_4$. Calculated (%): C, 35.35; H, 7.85; Si, 27.58; Cl, 17.43.

1,7-Dichloro-1,3,3,5,5,7-hexaethyl-1,7-divinyltetrasiloxane (6a). A solution of DTEDS (10.3 g, 0.046 mol) and pyridine (7.68 g, 0.0973 mol) in toluene (75 mL) was added to a solution of DCEVS (28.75 g, 0.185 mol) in dry toluene (116 mL) at 0 °C. The reaction mixture was stirred for 6 h and filtered; toluene and the excess of DCEVS were removed at atmospheric pressure, and the residue was fractionated *in vacuo*. The fraction with b.p. 120 °C/1 Torr was collected giving compound **6a** (14.0 g, 66 %). Found (%): C, 41.01; H, 8.12; Si, 30.98; Cl, 14.96. $C_{16}H_{36}Cl_2O_3Si_4$. Calculated (%): C, 41.62; H, 8.24; Si, 31.21; Cl, 15.38.

1,9-Dichloro-1,3,3,5,5,7,7,9-octamethyl-1,9-divinylpentasiloxane (7a). A solution of DHMTS (14.1 g, 0.058 mol) and aniline (11.81 g, 0.1275 mol) in toluene (170 mL) was added to a solution of DCMVS (49.0 g, 0.348 mol) in toluene (28.4 mL) at 0 °C. The mixture was stirred at *ca.* 20 °C for 24 h, then treated as described for preparation of **6a**. The residue was fractionated *in vacuo* and the fraction with b.p. 109—112 °C/1 Torr was collected giving compound **7a** (16.1 g, 62 %) Found (%): C, 32.13; H, 7.16; Si, 30.93; Cl, 14.98. $C_{12}H_{30}Cl_2O_4Si_5$. Calculated (%): C, 31.90; H, 7.09; Si, 31.11; Cl, 14.01.

1,3,3,5,5,7,9,9,11,11-Decamethylcyclohexasiloxane (3). Solutions of **3a** (24.4 g, 0.074 mol) in Et_2O (300 mL) and DTMDS (12.3 g, 0.074 mol) in Et_2O (300 mL) were added simultaneously to a solution of pyridine (12.85 g, 0.163 mol) in Et_2O (100 mL) cooled to 0—5 °C. The mixture was stirred at *ca.* 20 °C for 48 h and filtered, the solvent was removed, and the residue was fractionated *in vacuo*. In the fractional distillation, the fraction with b.p. 66—68 °C/1 Torr was collected giving compound **3** (18.1 g, 59 %). Compound **3** was purified additionally using a rectification column with metal packing. Found (%): C, 28.90; H, 7.79; Si, 40.10. $C_{10}H_{32}O_6Si_6$. Calculated (%): C, 28.90; H, 7.68; Si, 40.46.

1,3,3,5,5,7,9,9,11,11-Decamethyl-1,7-divinylcyclohexasiloxane (4). Compound **4** (64 %) was prepared as described above for compound **3**: b.p. 83—85 °C/1 Torr. Found (%): C, 35.28; H, 7.62; Si, 36.08. $C_{14}H_{36}O_6Si_6$. Calculated (%): C, 35.85; H, 7.68; Si, 35.97.

1,3,3,5,5,7,9,9,11,11-Decaethylcyclohexasiloxane (5) was prepared as described for **3**, starting from **5a** (14.2 g, 38.5 mmol) in Et_2O (140 mL) and DTEDS (7.74 g, 38.5 mmol) in Et_2O (140 mL) in the presence of pyridine (6.24 g, 79 mmol) in Et_2O (60 mL) yielding 11.0 g (53 %), b.p. 175—178 °C/1 Torr. Found (%): C, 43.17; H, 9.35; Si, 30.95. $C_{20}H_{52}O_6Si_6$. Calculated (%): C, 43.12; H, 9.34; Si, 30.28.

1,3,3,5,5,7,9,9,11,11-Decaethyl-1,7-divinylcyclohexasiloxane (6). Solutions of DTEDS (6.63, g, 29.8 mmol) in Et_2O (130 mL) and **6a** (13.7 g, 29.8 mmol) in Et_2O (130 mL) were added to a solution of pyridine (4.4 g, 62.5 mmol) in Et_2O (50 mL); the reaction was carried out as described above for compound **3**. Compound **6** (8.9 g, 49 %) was prepared with b.p. 180—182 °C/1 Torr. Found (%): C, 47.65; H, 9.35; Si, 27.79. $C_{24}H_{56}O_6Si_6$. Calculated (%): C, 47.33; H, 9.20; Si, 27.33.

1,3,3,5,5,7,7,9,11,11,13,13,15,15-Tetradecamethyl-1,9-divinylcyclooctasiloxane (7). A solution of DHMTS (11.5 g, 47.8 mmol) in Et_2O (100 mL) and **7a** (21.5 g, 47.8 mmol) was added to a solution of pyridine (8.0 g, 10.1 mmol) in Et_2O (50 mL). Compound **7** (9.2 g, 31 %) was prepared as described for **3**, b.p. 119—122 °C/1 Torr. Found (%): C, 34.98; H, 8.71; Si, 36.25. $C_{18}H_{48}O_8Si_8$. Calculated (%): C, 34.69; H, 8.67; Si, 36.09.

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