

## NEW SILICON-CONTAINING HETEROCYCLIC RINGS DERIVED FROM 1, 3-BIS(METHYLDICHLOROSILYL)PROPANE

K. A. Andrianov, L. M. Volkova, N. V. Delazari, L. I. Sosnovskaya, and N. A. Chumaevskii

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Reaction of 1,3-bis(methyldichlorosilyl)propane with alcohols gives (methylalkoxychlorosilyl)propanes. Hydrolysis of the latter with the calculated amount of water in the presence of a HCl acceptor gives 2,6-dimethyl-2,6-dialkoxy-1-oxa-2,6-disilacyclohexanes. Hydrolysis of 1,3-bis(methyl-dichlorosilyl)propane and 1,3-bis(methylalkoxychlorosilyl)propane gives a tricyclic carbocyclosiloxane. A study is made of the reactions of 2,6-dimethyl-2,6-dialkoxy-1-oxa-2,6-disilacyclohexane with alcohols, triethylsilanol, triethylchlorosilane, and  $C_6H_5MgBr$ .

1,3-Bis(methylalkoxychlorosilyl)propanes (I) are of potential interest for preparing carbocyclosiloxanes and polymers based on the latter. The present paper describes the synthesis of I, and reactions involved in their conversion to carbocyclosiloxanes.

When 1,3-bis(dichloromethylsilyl)propane (III) reacts with alcohols in a mole ratio 1:2, the course of the reaction of replacement of chlorine atoms by alkoxy groups greatly depends on the nature of the alcohol taken. The yield of I decreases as chain length increases. 1,3-Bis(methylphenoxychlorosilyl)propane and 1,3-bis(methylbenzyloxychlorosilyl)propane are formed only in the presence of a HCl acceptor, urea. When the reaction is run with a III:ROH mole ratio of 1:1, the monoalkoxy derivatives II are always accompanied by considerable amounts of the dialkoxy ones (I):

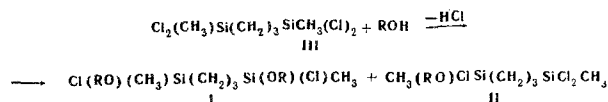
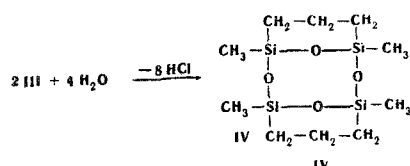


Table 1 on p. 350 gives the properties of the I and II compounds obtained.

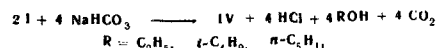
When investigating the hydrolysis of 1,3-bis(methyldichlorosilyl)propane (III) in neutral medium, formation of polymers was expected on hydrolysis of a tetrafunctional monomer. Instead there is quite unexpected formation of a crystalline compound IV, in 87.5% yield, melting point 101°-102°, and boiling point 135°-140° C (30 mm). Change in solution pH during hydrolysis of III affects only the yield of IV. Thus hydrolysis in acid and alkaline solution give, respectively, a 45% and a 60.5% yield of IV. Investigation of the properties of IV showed that the equation for the reaction is:



and the main product is the tricyclic carbocyclosiloxane IV, stable in air. Its properties are given in

Table 2. The figure (p. 351) shows the IR spectra.

Reaction of I with sodium bicarbonate in ether at room temperature gives mainly IV.



However, if the reaction with  $\text{NaHCO}_3$  is run in ether solution in the presence of  $\text{Na}_2\text{SO}_4$  at 5°-10° C, alkoxy group hydrolysis is partly suppressed, and along with IV there is formed, in 10% yield, 2,6-dimethyl-2,6-dialkoxy-1-oxa-2,6-disilacyclohexanes (V). If hydrolysis of I is run in ether using the calculated amount of water plus triethylamine alone or admixed with urea, the main product is V, which is formed in 50% yield:

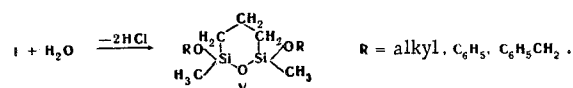


Table 3 gives the properties of the V compounds prepared.

Investigation of the IR absorption spectra of V showed that they were alike, particularly in the region of Si—O—Si and Si—O—C vibrations. As an example, we give the IR absorption spectrum (in the 850-1350  $\text{cm}^{-1}$  region) of a V where  $R = n\text{-}C_5H_{11}$ .

In assigning the Si—O—Si and C—O—Si vibrations, papers [1, 2] were utilized.

Spectra of exactly the same character as that shown in the Fig. are observed for all V compounds. An almost similar picture is also found for V when  $R = \text{Et}_3\text{Si}$ . Table 3 gives Si—O—Si and Si—O—C vibration frequencies.

The IR spectra of the V compounds where  $R = C_6H_5$  and  $i\text{-}C_3H_7$  do not show Si—O—C vibration bands with the usual  $\sim 1100 \text{ cm}^{-1}$  frequency. This is because in the spectra of  $(\text{CH}_3)_3\text{SiOC}_3\text{H}_7$ -i and  $(\text{CH}_3)_3\text{SiOC}_6\text{H}_5$ , the C—O—Si vibration frequency is, respectively, 1040 and 1260  $\text{cm}^{-1}$ .

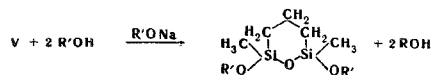
The table shows that there is practically no interaction between Si—O—Si and Si—O—C vibrations, and this is indicated by the frequencies of these vibrations being independent of the nature of R, as well as agreement with the frequencies of the vibrations of Si—O—Si and Si—O—C of compounds containing those groups [1, 2]. Furthermore the constancy of the frequencies of the Si—O—Si and Si—O—C vibrations in V indicates the lack of any effect of R on these vibrations in the C—O—Si—O—Si—O—C chain.

Study of the reactivity of the alkoxy group of V in reactions with alcohols, triethylsilanols, trialkyl-

Table 1  
1-(Methyldichlorosilyl)-2-(methylalkoxychlorosilyl)propanes (II)  
and 1, 3-Bis(methylalkoxychlorosilyl)propanes (I)

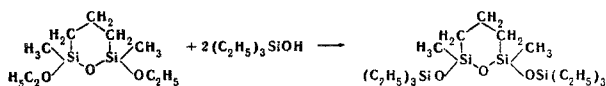
R	Bp, °C (pressure, mm)	$n_D^{20}$	$d_4^{20}$	$MR_D$		Found, %		Calculated, %		Yield, %
				Found	Calcu- lated	Si	Cl	Si	Cl	
<b>II</b>										
C <sub>2</sub> H <sub>5</sub>	139—141 (35)	1.4500	1.1193	67.60	67.10	20.04 20.20	37.9 37.4	20.4	38.1	71.5
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	140—144 (7)	1.4530	1.073	81.05	81.04	17.50 16.90	33.10 33.0	17.44	33.07	32.6
<i>i</i> -C <sub>5</sub> H <sub>11</sub>	138—140 (8)	1.4525	1.073	81.02	81.04	17.25 17.30	33.6 33.6	17.44	33.07	39.0
<b>I</b>										
CH <sub>3</sub>	98—103 (7)	1.4431	1.0890	63.58	63.63	21.60 21.50	28.01 28.06	21.44	27.15	95
C <sub>2</sub> H <sub>5</sub>	145—147 (35)	1.4380	1.0415	72.95	72.98	19.49 19.83	24.51 24.70	19.42	24.50	80.7
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	118—127 (7)	1.4340	1.0030	82.49	82.27	17.90 18.41	22.0 22.30	17.46	22.06	47.2
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	155—158 (7)	1.4440	1.005	91.26	91.57	16.1 16.3	20.4 20.2	16.25	20.6	46.1
<i>i</i> -C <sub>4</sub> H <sub>9</sub>	110.1—113 (1)	1.4400	0.9917	91.75	91.57	16.24 16.44	20.01 20.0	16.25	20.6	67.6
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	172—177 (7)	1.4465	0.9913	100.60	100.86	15.6 15.25	19.8 19.4	15.02	18.98	32.0
<i>i</i> -C <sub>5</sub> H <sub>11</sub>	165—173 (9)	1.4470	0.9844	100.90	100.86	14.78 15.00	19.1 19.5	15.02	18.98	56.0
C <sub>6</sub> H <sub>5</sub>	185—195 (2)	1.5295	1.150	103.20	103.12	13.43 13.90	18.65 18.77	14.33	18.41	36.4
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	236—242 (8)	1.5231	1.1235	112.50	112.42	13.26 13.08	15.99 16.03	13.57	17.15	49.6

chlorosilanes, and the Grignard reagent, showed that the OR groups readily undergo transesterification in the presence of minute amounts of sodium alkoxide.

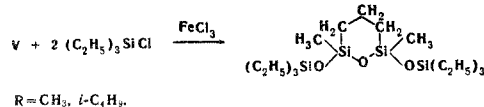


No considerable amounts of polymer and linear compounds were found to be formed in any of the reactions with alcohols.

In the reaction of 2,6-dimethyl-2,6-diisopropoxy-1-oxa-2,6-disilacyclohexane with benzyl alcohol, transesterification took place without addition of a catalyst. Thus, mono- and dibenzylloxycarbocyclosiloxane were isolated. The structures of the transesterification products are proved by the identities of their physical constants with those of the compounds obtained by hydrolyzing I. The ethoxyl groups in 2,6-dimethyl-2,6-diethoxy-1-oxa-2,6-disilacyclohexane are easily replaced, in the presence of sodium silanolate by triethylsiloxy groups, to give 2,6-dimethyl-2,6-di(triethylsiloxy)-1-oxa-2,6-disilacyclohexane in 70.5% yield:

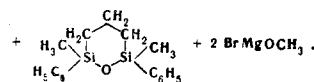
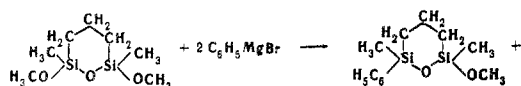


This compound is obtained in yields up to 9% by reacting V with  $(\text{C}_2\text{H}_5)_3\text{SiCl}$  in the presence of 0.1%  $\text{FeCl}_3$ :

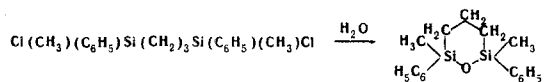


The analogous reaction of V with R = Me or  $\text{C}_4\text{H}_9$ , with trimethylchlorosilane or trimethylacetoxysilane in the presence of  $\text{FeCl}_3$  does not take place.

Treatment of V with the Grignard reagent gives replacement of the alkoxy group by phenyl. The reaction takes place stepwise. 2,6-Dimethyl-2-methoxy-6-phenyl-1-oxa-2,6-disilacyclohexane and 2,6-dimethyl-2,6-diphenyl-1-oxa-2,6-disilacyclohexane were isolated:



The structure of 2,6-dimethyl-2,6-diphenyl-1-oxa-2,6-disilacyclohexane was shown from its preparation by hydrolysis of 1,3-bis(methylphenylchlorosilyl)propane:



Hydrolysis of unsymmetrical 1,3-bis(dimethylphenylchlorosilyl)propane led to the isolation of a bicyclic compound:

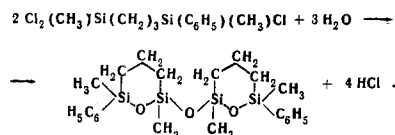


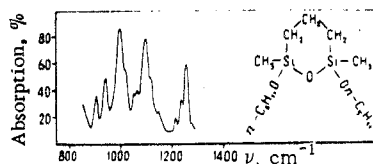
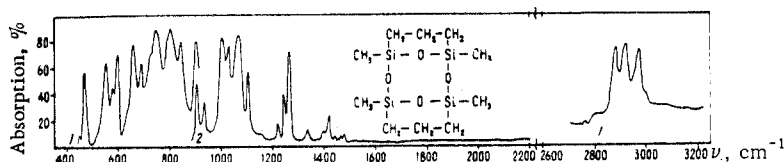
Table 2 gives the properties of the compounds prepared.

EXPERIMENTAL

**1,3-Bis(methylethoxychlorosilyl)propane.** A 3-necked flask, fitted with stirrer, reflux condenser, dropping funnel, and thermometer, was charged with 39.0 g (0.145 mole) III, which was stirred, and over a period of 20 min, 46.07 g (0.29 mole) EtOH added dropwise. The mixture was kept at 110° C for 2 hr, with stirring. Fractionation gave 33.86 g (80.7%) 1,3-bis(methylethoxychlorosilyl)propane, bp 145°–147° C (35 mm);  $n_D^{20}$  1.4380;  $d_4^{20}$  1.0415. Found: C 36.92; 36.72; H 7.55; 7.44; Si 19.49; 19.89; Cl 24.51; 24.71%;  $M_R$  72.95. Calculated for  $\text{C}_9\text{H}_{22}\text{Si}_2\text{O}_2\text{Cl}_2$ : C 37.4; H 7.67; Si 19.42; Cl 24.50%;  $M_R$  72.98.

The other I and II compounds (Table 1) were obtained similarly, apart from the compound with R =  $\text{C}_6\text{H}_5\text{CH}_2$ .

**1,3-Bis(methylbenzyloxychlorosilyl)propane.** A flask, fitted as above, was charged with 27 g (0.1 mole) III, 12.1 g (0.2 mole) urea, and 50 ml toluene, the mixture stirred, and 21.6 g (0.2 mole) benzyl alcohol added. The mixture was held at 80° C and



IR absorption spectra of IV and 2,6-dimethyl-2,6-di-n-amyloxy-1-oxa-2,6-disilacyclohexane: 1) Compound tabletted with KBr; 2)  $\text{CCl}_4$  solution, any concentration.

Table 2  
Heterocyclic Compounds Prepared from 1, 3-Bis(methylalkoxychlorosilyl)propane

Compound	Bp, °C (pressure, mm)	$n_D^{20}$	$d_4^{20}$	M		MR <sub>D</sub>		Found, %			Calculated, %			Yield, %
				Found	Calculated	Found	Calculated	C	H	Si	C	H	Si	
	135-140 (30) T. n.l. 101-102°	—	—	310; 318 342; 330	320.4	—	—	37.43 37.39	7.52 7.52	34.55 34.82	37.41	7.55	35.04	87.5
	90-93 (1)	1.4825	1.022	300	310.46	86.66	86.72	58.73 58.91	8.42 8.38	17.15 17.26	58.04	8.423	18.08	32
	142.5-143 (1) 135-137 (1)	1.5445 1.5495	1.050 1.0503	293 293	298.44	90.92 90.32	91.74	67.36 68.0	7.37 7.24	18.91 18.78	68.45	7.44	18.8	31.1
	92-95 (1)	1.5130	1.044	240	252.38	72.66	71.94	60.40	7.78	18.08	57.1	7.932	22.23	16.8
	222-228 (2)	1.5222	1.070	420	458	130.7	131.52	57.65 57.82	7.43 7.44	23.93 23.97	57.64	7.42	24.45	—

Table 3  
2, 6-Dimethyl-2, 6-dialkoxy-1-oxa-2, 6-disilacyclohexane (V)

R	Bp, °C (pressure, mm)	$n_D^{20}$	$d_4^{20}$	M		MR <sub>b</sub>		Found, %			Calculated, %			Yield, %	$\nu_{Si-O-Si}$ cm <sup>-1</sup>	$\nu_{Si-O-C}$ cm <sup>-1</sup>
				Found	Calcu- lated	Found	Calcu- lated	C	H	Si	C	H	Si			
CH <sub>3</sub>	59-61 (7)	1.4250	1.001	200.0 190.0	206.4	52.72	52.86	41.31 41.41	8.69 8.85	27.03 27.10	40.75	8.82	27.18	57.6	998	1096
C <sub>2</sub> H <sub>5</sub>	28-36 (2)	1.4250	0.9655	212.0 204.0	234.5	62.13	62.36	46.31 46.27	9.29 9.09	23.89 23.93	46.11	9.47	23.96	51.7	993	1093
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	51-54 (1)	1.4240	0.9371	242.0 228.94	262.37	71.47	71.65	49.18 49.43	9.86 9.85	21.83 21.48	50.43	9.988	21.38	39.8	998	1040
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	122-127 (4)	1.4345	0.9477	264.0 261.0	290.2	79.82	80.95	52.88 52.48	10.27 10.24	19.67 19.87	53.79	10.34	19.33	38.6	998	1098
<i>i</i> -C <sub>4</sub> H <sub>9</sub>	68-69 (1)	1.4300	0.9286	261.7 253.4	290.2	80.74	80.95	53.80	10.54	19.34	53.74	10.34	19.33	49.5	1000	1096
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	91-93 (1)	1.4380	0.9346	—	318.6	89.50	90.24	56.20 56.07	10.80 10.73	18.03 17.99	56.55	10.76	17.50	38.5	998	1097
<i>i</i> -C <sub>5</sub> H <sub>11</sub>	97-98 (1)	1.4360	0.9306	—	318.6	89.50	90.24	56.13 56.41	10.67 10.73	17.92 18.05	56.55	10.76	17.60†	43.1	998	1097
C <sub>6</sub> H <sub>5</sub>	138-141 (1)	1.5285	1.100	268.0 260.9	330	92.58	92.50	62.03 62.04	6.85 6.95	16.190 16.170	61.78	6.711	16.98	42.0	998	1265
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	173-176 (1)	1.5220	1.083	336.8 321.0	358.46	101.1	101.96	62.98 63.22	7.38 7.32	15.95 15.80	63.64	7.29†	15.65	74.5	997	1096
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Si	137-139 (2)	1.4430	0.9340	390.0 368.0	406.9	115.4	116.76	50.51 50.57	10.50 10.43	27.39 27.90	50.18	10.40	27.62	70.5	996	1080

stirred for 1 hr 30 min. Distillation then gave 20.5 g (49.6%) 1, 3-bis(methylbenzyloxysilyl)propane, bp 236°–242° C (8 mm);  $n_D^{20}$  1.5231;  $d_4^{20}$  1.1235. Found: Si 13.26; 13.08; Cl 16.99; 16.03%;  $MR_D$  112.50. Calculated for  $C_{19}H_{26}Si_2O_2Cl_2$ : Si 13.57; Cl 17.15%;  $MR_D$  112.42.

**Conversion of III to IV.** A flask fitted as described above, but without a thermometer, was charged with 43 g (0.508 mole)  $NaHCO_3$ , 6 g (0.042 mole)  $Na_2SO_4$ , and 125 ml ether. The whole was stirred, and over a period of 30 min a solution of 34.4 g (0.127 mole) III in 35 ml ether added. Vigorous evolution of  $CO_2$  was observed. Then the mixture was heated and stirred for an hour. The solid was filtered off, mass 48 g. It was then washed with ether. On evaporating the ether filtrate, crystals separated. Cooling gave a further quantity of crystals. Successive cooling and filtering gave 17.8 g (87.5%) IV, mp 98°–101° C. The crystalline IV could readily be distilled. Distillation of 2.1 g gave 1.9 g compound bp 135°–140° C (30 mm); mp 101°–102° C. Found: C 37.43; 37.39; H 7.52; 7.52; Si 34.55; 34.82%; M 318; 310 (in benzene) 342; 330 (Rast). Calculated for  $C_{10}H_{24}Si_4O_4$ : C 37.47; H 7.55; Si 35.04%; M 320.4.

**2, 6-Dimethyl-2, 6-diethoxy-1-oxa-2, 6-disilacyclohexane.** A 3-necked flask, fitted as in the preceding experiment, was charged with a solution of 13.3 g (0.046 mole) 1, 3-bis(methylethoxysilyl)propane in 28 ml ether, then 9.20 g (0.092 mole) triethylamine and 0.828 g (0.046 mole) water in 28 ml ether added over 20 min, with stirring (formation of triethylamine hydrochloride observed), 50 ml ether was added to give better stirring of the precipitate, the mixture was heated for 1 hr and then filtered. The solid was washed with ether. Distillation of the filtrate gave 5.54 g (51.7%) 2, 6-dimethyl-2, 6-diethoxy-1-oxa-2, 6-disilacyclohexane, bp 115°–130° C;  $n_D^{20}$  1.4249;  $d_4^{20}$  0.9655. Repeated distillation gave 3.22 g pure compound bp 32°–34° C (2 mm);  $n_D^{20}$  1.4250;  $d_4^{20}$  0.9655. Found: Si 23.89; 23.93%; H 9.29; 9.09; C 46.31; 46.27%;  $MR_D$  63.13. Calculated for  $C_9H_{22}Si_2O_3$ : C 46.11; H 9.47; Si 23.96%;  $MR_D$  62.36.

**2, 6-Dimethyl-2, 6-dimethoxy-1-oxa-2, 6-disilacyclohexane.** A mixture of 22.46 g (0.865 mole) 1, 3-bis(methylmethoxysilyl)propane, 10.5 g (0.173 mole) urea, 1.56 g (0.0865 mole) water, and 30 ml ether was stirred and heated for 40 min. A further 60 ml ether was added as precipitate formed. The mixture was stirred and heated for 2 hr. Distillation gave 10.26 g 2, 6-dimethyl-2, 6-dimethoxy-1-oxa-2, 6-disilacyclohexane, bp 59°–61° (7 mm);  $n_D^{20}$  1.4250;  $d_4^{20}$  1.001. Found: C 41.31; 41.41; H 8.69; 8.85; Si 27.03; 27.10%;  $MR$  52.86. Calculated for  $C_7H_{18}Si_2O_3$ : C 40.75; H 8.82; Si 27.18%;  $MR_D$  52.72.

**2, 6-Dimethyl-2, 6-bis(triethylsiloxy)-1-oxa-2, 6-disilacyclohexane.** A flask was fitted with stirrer, condenser set for downward distillation, and thermometer, and charged with 4.67 g (0.02 mole) 2, 6-dimethyl-2, 6-diethoxy-1-oxa-2, 6-disilacyclohexane, 5.30 g (0.04 mole) triethylsilanol, and 0.10 g Na. The mixture was held at 150° C for 4 hr, with stirring.

Distillation then gave 4.68 g (70.5%) 2, 6-dimethyl-2, 6-bis(triethylsiloxy)-1-oxa-2, 6-disilacyclohexane, bp 105°–127° (1 mm);  $n_D^{20}$  1.4425;  $d_4^{20}$  0.9346. After repeated distillation it had bp 137°–139° C (2 mm);  $n_D^{20}$  1.4430;  $d_4^{20}$  0.9346. Found: C 50.51; 50.57; H 10.50; 10.43; Si 27.39; 27.90%;  $MR_D$  115.4. Calculated for  $C_{17}H_{42}Si_4O_3$ : C 50.18; H 10.40; Si 27.62%;  $MR_D$  116.76.

**Reaction of phenylmagnesium bromide with 2, 6-dimethyl-2, 6-dimethoxy-1-oxa-2, 6-disilacyclohexane.** A solution of 8.77 g (0.0425 mole) 2, 6-dimethyl-2, 6-dimethoxy-1-oxa-2, 6-disilacyclohexane in 80 ml ether was dropped slowly into a heated solution, in 100 ml ether, of the Grignard reagent prepared from 2.07 g (0.085 mole) Mg and 13.55 g (0.085 mole) bromobenzene. The mixture was then heated for 2 hr 30 min, and stirred vigorously. Distillation of the filtrate gave: 1) 1.78 g (16.8%) 2, 6-dimethyl-2-methoxy-6-phenyl-1-oxa-2, 6-disilacyclohexane bp 92°–95° (1 mm);  $n_D^{20}$  1.5130;  $d_4^{20}$  1.044. Found: C 60.40; H 7.78; Si 18.68%;  $MR_D$  72.66. Calculated for  $C_{12}H_{20}Si_2O_2$ : C 57.1; H 9.32; Si 22.23%;  $MR_D$  71.93; 2) 3.94 g (31.1%) 2, 6-dimethyl-2, 6-diphenyl-1-oxa-2, 6-disilacyclohexane, bp 142.5°–143° C (1 mm);  $n_D^{20}$  1.5445;  $d_4^{20}$  1.050. Found: C 67.36; H 7.37; Si 18.91%;  $MR_D$  90.92. Calculated for  $C_{17}H_{22}Si_2O$ : C 68.45; H 7.44; Si 18.8%;  $MR_D$  91.74.

**2, 6-Dimethyl-2, 6-diphenyl-1-oxa-2, 6-disilacyclohexane.** A flask with a stirrer, reflux condenser, thermometer, and dropping funnel, was charged with 21.5 g KOH, 70 ml water, and 70 ml ether, the mixture cooled to +5° C, and at that temperature a solution of 54.3 g (0.154 mole)  $CH_3(C_6H_5)ClSiCH_2CH_2CH_2SiCH_3(C_6H_5)Cl$  in 200 ml ether dropped in. Then the mixture was stirred for 1 hr, the ether layer separated off, washed with water till neutral, dried, and vacuum-distilled, to give 26 g of the desired product, bp 134°–137° (1 mm);  $n_D^{20}$  1.5495;  $d_4^{20}$  1.0509. Found: C 68.00; 67.91; H 7.04; 7.24; Si 18.80; 18.78%;  $MR_D$  90.32. Calculated for  $C_{17}H_{22}Si_2O$ : C 68.45; H 7.38; Si 18.71%;  $MR_D$  91.74.

**2, 6-Dimethyl-2, 6-di-n-amyloxy-1-oxa-2, 6-disilacyclohexane.** a) A mixture of 14.66 g (0.039 mole) 1, 3-bis(methyl-n-amyloxysilyl)propane, 4.73 g (0.078 mole) urea, 0.702 g (0.039 mole) water, and 50 ml ether, was heated and stirred for 40 min. After cooling to room temperature, a solution of 7.88 g (0.078 mole)  $Et_3N$  in 50 ml ether was added, and the whole heated for 2 hr. Fractional distillation gave 4.79 g (38.5%) 2, 6-dimethyl-2, 6-di-n-amyloxy-1-oxa-2, 6-disilacyclohexane, bp 138°–144° C (7 mm). After repeated distillation it had bp 91°–93° C (1 mm);  $n_D^{20}$  1.4380;  $d_4^{20}$  0.9346. Found: C 56.20; 56.07; H 10.80; 10.73; Si 18.00; 17.99%.  $MR_D$  89.50. Calculated for  $C_{15}H_{34}Si_2O_3$ : C 56.55; H 10.76; Si 17.60%;  $MR_D$  90.24.

b) 4.60 g (0.022 mole) 2, 6-dimethyl-2, 6-dimethoxy-1-oxa-2, 6-disilacyclohexane, 3.88 g (0.044 mole) n-AmOH, and 0.16 g Na were heated and stirred together for 4 hr at 120°–160° C, the MeOH being distilled off (1.6 ml;  $n_D^{20}$  1.3350). Distillation

of the residue in the flask gave 2.68 g 2, 6-dimethyl-2, 6-di-n-amyloxy-1-oxa-2, 6-disilacyclohexane, bp  $105^{\circ}$ - $107^{\circ}$  (2 mm);  $n_D^{20}$  1.4378;  $d_4^{20}$  0.9311.

**Reaction of 2, 6-dimethyl-2, 6-diisopropoxy-1-oxa-2, 6-disilacyclohexane with benzyl alcohol.** 3.85 g (0.0139 mole) 2, 6-dimethyl-2, 6-diisopropoxy-1-oxa-2, 6-disilacyclohexane and 3.36 g (0.031 mole)  $C_6H_5CH_2OH$  were heated together for 5 hr, and 1 ml i-PrOH distilled off. Distillation of residue in the flask gave: 1) 1.08 g material  $90^{\circ}$ - $93^{\circ}C$  (1 mm);  $n_D^{20}$  1.4825;  $d_4^{20}$  1.022. Found: C 58.73; 58.91; H 8.42; 8.38; Si 17.15; 17.26%;  $MR_D$  86.66. Calculated for  $C_{15}H_{26}Si_2O_3$ : C 58.04; H 8.42; Si 18.08%;  $MR_D$  86.724; 2) 1.43 g dibenzyloxydimethyldisilacyclohexane bp  $140^{\circ}$ - $142^{\circ}C$  (0.5 mm);  $n_D^{20}$  1.5120;  $d_4^{20}$  1.072. Found: C 62.67; H 7.49; Si 16.16%;  $MR_D$  100.3. Calculated for  $C_{19}H_{26}Si_2O_3$ : C 63.64; H 7.296; Si 15.65%;  $MR_D$  101.79.

**2, 6-Dimethyl-2, 6-dibenzyloxy-1-oxa-2, 6-disilacyclohexane.** Hydrolysis of 16.41 g (0.0398 mole)

1, 3-bis(methylbenzyloxychlorosilyl)propane with 0.7 g water (0.0398 mole), in the presence of 4.8 g (0.0796 mole) urea, and 8.06 g (0.0796 mole)  $Et_3N$  in 50 ml ether gave 9 g 2, 6-dimethyl-2, 6-dibenzyloxy-1-oxa-2, 6-disilacyclohexane bp  $173^{\circ}$ - $176^{\circ}C$  (1 mm)  $n_D^{20}$  1.5220;  $d_4^{20}$  1.083. Found: C 62.98; 63.22; H 7.38; 7.32; Si 15.95; 15.80%;  $MR_D$  101.1. Calculated for  $C_{19}H_{26}Si_2O_3$ : C 63.66; H 7.29; Si 15.65%;  $MR_D$  101.7.

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AS USSR, Moscow