SYNTHESIS AND REACTIONS OF 6-CHLORO-2,2,6-TRIMETHYL- AND 2,6-DICHLORO-2,6-DIMETHYL-1-OXA-2,6-DISILACYCLOHEXANES

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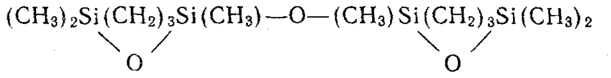
6-Chloro-2,2,6-trimethyl- and 2,6-dichloro-2,6-dimethyl-1-oxa-2,6-disilacyclohexanes have been synthesized. Their behavior in alcoholysis, amination, acetoxylation, and reduction reactions has been studied.

Cyclic organosilicon compounds are of great interest since they can be used for the synthesis of many organosilicon polymers.

The study of cyclic compounds containing functional groups on the silicon atoms and the study of the behavior of the latter and of the ring itself in various reactions (esterification, transesterification, amination, acetoxylation, reduction) was the subject of the present work.

We have previously obtained 6-chloro-2,2,6-trimethyl-1-oxa-2,6-disilacyclohexane (I) by heating $Cl_2(CH_3)Si(CH_2)_3Si(CH_3)_2Cl$ in acetone with the calculated amount of KOH in the presence of a small amount of water [1].

In the present work, compound I was obtained by independent synthesis involving the cleavage of



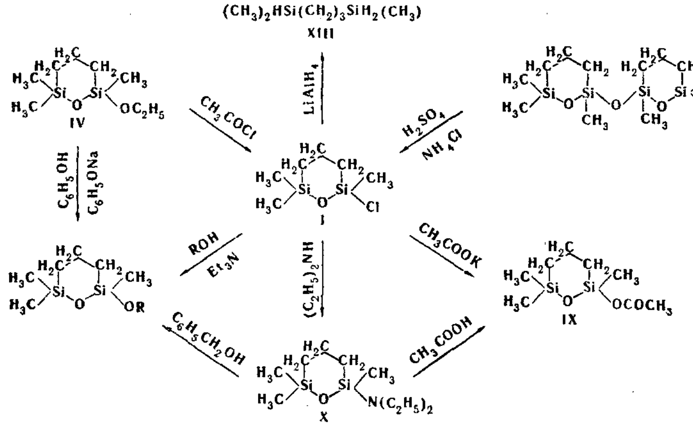
$$(CH_3)_2Si(CH_2)_3Si(CH_3)\text{—O—}(CH_3)Si(CH_2)_3Si(CH_3)_2$$

with concentrated H_2SO_4 and NH_4Cl and also by the reaction of 6-ethoxy-2,2,6-trimethyl-1-oxa-2,6-disilacyclohexane (IV) with acetyl chloride with yields of ~14 and ~70%, respectively. In the first case, a large amount of polymer was formed.

When I was esterified with alcohols (ethanol, propanol), the ring opened with the formation of polymeric products. It was impossible to isolate alkoxycyclosiloxanes, and only in the presence of an HCl acceptor—a mixture of triethylamine and urea—did esterification take place without the opening of the ring so that it was possible to isolate the alkoxytrimethyloxadisilacycloalkanes (**III–VIII**, **XI**) with yields of 60–80%. The ethoxy group in the ethoxytrimethyloxadisilacyclohexane obtained was transesterified with a phenoxy group in the presence of a catalyst—sodium phenoxide. The properties of the phenoxytrimethyloxadisilacyclohexane (**VIII**) obtained by transesterification and by the direct esterification of I were identical.

The reaction of I with diethylamine gave a ~60% yield of 6-diethylamino-2,2,6-trimethyl-2,6-disila-1-oxacyclohexane (**X**). The amino group in the aminotrimethyloxadisilacyclohexane was readily replaced by alkoxy and acetoxy groups without the cleavage of the Si—O—Si bond. Thus, the action of benzyl alcohol gave benzyloxytrimethyloxadisilacyclohexane and that of glacial acetic acid gave a ~90% yield of acetoxytrimethyloxadisilacyclohexane (**IX**), which was also obtained by independent synthesis from I and potassium acetate with a yield of ~60%.

When I was hydrogenated with $LiAlH_4$ in ether, with heating, not only the chlorine atom attached to the silicon but also the Si—O—Si bond was reduced, with the formation of $(CH_3)_2HSi(CH_2)_3Si(CH_3)H_2$ (**XIII**).



III $R=CH_3$; IV $R=C_2H_5$; V $R=C_3H_7$; VI $i\text{-}C_4H_9$; VII $i\text{-}C_5H_{11}$; VIII C_6H_5; XI $i\text{-}C_6H_5CH_2$

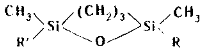
2,6-Dichloro-2,6-dimethyl-1-oxa-2,6-disilacyclohexane (II) was obtained by two methods:

1) hydrolysis of bis(methyldichlorosilyl)propane with the calculated amount of water in the presence of an HCl acceptor;

2) the reaction of a 2,6-dialkoxy-2,6-dimethyl-1-oxa-2,6-disilacyclohexane with acetyl chloride.

The yield of II from the hydrolysis of bis(methyldichlorosilyl)propane was low, in spite of the use of the calculated amounts of reactants; in addition to II a large amount of polymeric products was formed. The

Properties of the Carbocyclosiloxanes

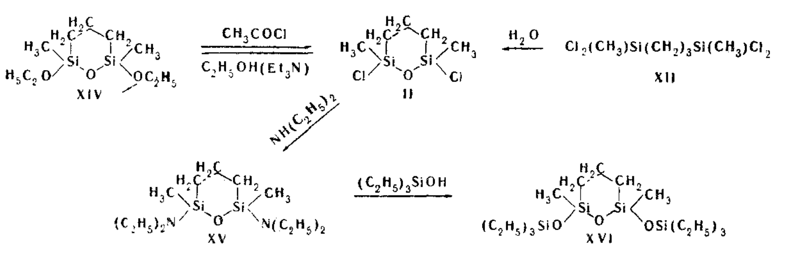


Compound	R	R′	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	MR_D		Mol. wt.		Found, %				Calculated, %				Yield, %
						found	calculated	found	calculated	C	H	Si	Cl (N)	C	H	Si	Cl (N)	
I	CH_3	Cl	50—52 (7)	1.4412	1.014	50.78	51.04	194	194.8	37.31	7.69	28.72	18.5 17.7	36.99	7.76	28.88	18.2	68
II	Cl	Cl	64—67 (7)	1.4592	1.1680	50.32	50.604	230	215	28.19	5.69	26.26	31.64	27.93	5.62	26.08	32.92	
III	CH_3	CH_3O	49—50 (10)	1.4254	0.9378	51.73	52.27	188	190	44.21	9.55	28.79	—	44.47	9.47	29.27	—	66
IV	CH_3	C_2H_5O	59—62 (10)	1.4264	0.9295	56.28	56.91	194	204	46.97	9.83	27.73	—	47.05	9.80	27.45	—	81.6
V	CH_3	n-C_3H_7O	71—73 (17)	1.4253	0.9177	61.20	61.56	199	218	49.40	9.38	24.98	—	49.54	10.09	25.68	—	56
VI	CH_3	i-C_4H_9O	86—87 (10)	1.4322	0.9178	65.72	66.21	232	232	51.66	10.36	23.78	—	51.72	10.34	24.13	—	60.5
VII	CH_3	i-$C_5H_{11}O$	94—99 (7)	1.4338	0.9125	70.29	70.85	233	242	53.36	10.73	22.68	—	53.61	10.57	22.78	—	67.5
VIII	CH_3	C_6H_5O	115—116 (7)	1.4888	1.0145	71.66	71.99	242	252	56.89	7.90	21.69	—	57.14	7.93	22.22	—	60.7
IX	CH_3	CH_3COO	76—80 (14)	1.4343	0.9922	57.02	56.94	228	218	43.9	8.40	24.69		44.03	8.25	25.68	—	a) 60.2 b) 91
X	CH_3	$(C_2H_5)_2N$	96—100 (7)	1.4438	0.9047	67.81	68.52	229	231	51.71	10.73	23.90	(7.05)	51.99	10.90	24.2	(6.05)	67
XI	CH_3	$C_6H_5CH_2O$	130—132 (10)	1.4848	1.008	75.76	76.68	256	266.4	58.4	8.48	21.26	—	58.59	8.33	21.09	—	64.5
XII	$Cl_2(CH_3)Si(CH_2)_3Si(CH_3)Cl_2$		132—136 (33)	1.4682	1.2104	62.03	61.22	—	—	23.95	4.67	21.00	52.38	22.23	4.45	20.74	52.48	86.5
XIII	$CH_3(H_2)Si(CH_2)_3Si(CH_3)_2H$		135—139	1.4286	0.7719	48.77	49.60	140	146.3	49.60	12.29	37.46	—	49.41	12.37	38.22	—	72.6

yield of II in its synthesis by the second method was almost quantitative.

Compound II readily hydrolyzes in the air. When it was esterified in the presence of triethylamine, there was no formation of a polymer and the reaction gave 2,6-diethoxy-2,6-dimethyl-1-oxa-2,6-disilacyclohexane (XIV) which we have obtained previously by the hydrolysis of bis(ethoxymethylchlorosilyl)propane [2].

The reaction of II with diethylamine led to the replacement of the chlorine by a diethylamino group with the formation of 2,6-bis(diethylamino)-2,6-dimethyl-1-oxa-2,6-disilacyclohexane (XV) together with a large amount of polymer. When the diamino derivative so obtained was heated with triethylsilanol, diethylamine was liberated and a quantitative yield was obtained of 2,6-dimethyl-2,6-bis(triethylsiloxy)-1-oxa-2,6-disilacyclohexane (XVI), which we have obtained previously [2] by the transesterification of 2,6-dialkoxy-2,6-dimethyl-1-oxa-2,6-disilacyclohexanes with triethylsilanol.

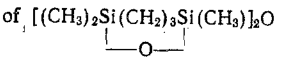


EXPERIMENTAL

2,6-Dichloro-2,6-dimethyl-1-oxa-2,6-disilacyclohexane (II). a) [3]. A mixture of 10 g (0.043 mole) of 2,6-diethoxy-2,6-dimethyl-1-oxa-2,6-disilacyclohexane and 16.8 g (0.214 mole) of CH_3COCl was left at room temperature for 4 days. After distillation, 3.4 g (92%) of ethyl acetate with bp 71–75° C, n_D^{20} 1.3780 and 7.0 g (77%) of II with bp 67–74° C (8 mm), n_D^{20} 1.4569 were obtained. After redistillation, bp 64–66° C (7 mm), n_D^{20} 1.4570, d_4^{20} 1.1655. Found, %: C 28.19, 28.27; H 5.69; 5.92; Si 26.26; 25.91; Cl 31.64; 31.49; MR_D 50.28; mol. wt. 230. Calculated for $C_5H_{12}OCl_2Si_2$, %; C 27.93; H 5.62; Si 26.08; Cl 32.92; MR_D 50.604; mol. wt. 215.2.

b) In drops, a mixture of 20.2 g (0.2 mole) of triethylamine, 1.8 g (0.1 mole) of water, and 50 ml of ether was added to a mixture of 12 g (0.2 mole) of urea, 27 g (0.1 mole) of bis(methyldichlorosilyl)propane and 50 ml of ether. The reaction mixture was heated for 3 hr and on the following day the precipitate was filtered off and the filtrate was distilled. This gave 2 g of II with bp 94–140° C (16 mm) and 15 g of polymeric still residue. After redistillation, the yield of II was 1.5 g, bp 90–91° C (15 mm), n_D^{20} 1.4592; d_4^{20} 1.1689; MR_D 50.32; Cl 33.2%.

6-Chloro-2,2,6-trimethyl-1-oxa-2,6-disilacyclohexane (I). a) A mixture of 9.8 g (0.048 mole) of 6-ethoxy-2,2,6-trimethyl-1-oxa-2,6-disilacyclohexane and 12 g (0.152 mole) of acetyl chloride was kept for 38 hr. Distillation yielded 6.4 g (68%) of I, bp 50–52° C (7 mm); n_D^{20} 1.4419.

b) Over 30 min at –35° C, 25.5 ml of concentrated H_2SO_4 was added to a mixture of 21 g (0.063 mole) of  $[(CH_3)_2\underbrace{Si(CH_2)_3Si}_{O}(CH_3)]_2O$ and 10 g (0.19 mole) of NH_4Cl. The reaction mixture was stirred for 2 hr (the temperature rising to that of the room) and the liquid was decanted from the solid matter and fractionated. The yield of I was 3 g (14.5%), bp 67–70° C (11 mm), n_D^{20} 1.4380. Found, %: Cl 17.67, 18.5. Calculated for $C_6H_{18}Si_2OCl$, %; Cl 18.2.

2,6-Diethoxy-2,6-dimethyl-1-oxa-2,6-disilacyclohexane (XIV). In drops, a solution of 4.5 g (0.021 mole) of II in 10 ml of ether was added to a mixture of 1.93 g (0.042 mole) of C_2H_5OH, 4.23 g (0.042 mole) of triethylamine, 0.021 mole of urea, and 20 ml of ether. The reaction mixture was heated for 1 hr and the precipitate was filtered off. From the filtrate was isolated 2.5 g of a substance with bp 97–100° C (33 mm), n_D^{20} 1.4250; d_4^{20} 0.9670. Found, %: Si 24.2; MR_D 62.00. Calculated for $C_9H_{22}Si_2O_3$, %: Si 23.96; MR_D 62.36.

Literature data [1]: bp 28–35° C (2 mm), n_D^{20} 1.4250; d_4^{20} 0.9655. Compounds III–VII were obtained similarly (see table).

2,2,6-Trimethyl-6-phenoxy-1-oxa-2,6-disilacyclohexane (VIII). a) Obtained from I and C_6H_5OH (see table).

b) A mixture of 5 g (0.0245 mole) of 6-ethoxy-2,2,6-trimethyl-1-oxa-2, 6-disilacyclohexane, 2. 31 g (0.0245 mole) of phenol, and 0.07 g of metallic sodium was heated with stirring for 4 hr. Ethyl alcohol with n_D^{20} 1.3673 distilled off 0.7 g; (62.4%). Distillation yielded 1.9 g of VIII with bp 134–134.5° C (16 mm), n_D^{20} 1.4810; d_4^{20} 1.0071; MR_D 71.20; calculated: MR_D 71.90.

6-Acetoxy-2,2,6-trimethyl-1-oxa-2,6-disilacyclohexane (IX). a) With stirring, 8 g (0.0413 mole) of I was added to 4.8 g (0.048 mole) of potassium acetate in 80 ml of benzene. The reaction mixture was boiled for 6 hr. The precipitate was filtered off. After the solvent had been driven off, 5.4 g (60.2%) of IX with bp 76–80° C (14 mm); n_D^{20} 1.4343; d_4^{20} 0.9922 was obtained. Found, %: C 44.70; H 8.09; Si 24.06; MR_D 57.02; mol. wt. 228. Calculated for $C_8H_{18}Si_2O_3$, %: C 44.03; H 8.25; Si 25.68%; MR_D 56.94; mol. wt. 218.

b) With stirring, 2.9 g (0.0126 mole) of 6-diethylamino-2,2,6-trimethyl-1-oxa-2,6-disilacyclohexane was added to 1.5 g (0.025 mole) of glacial acetic acid in 30 ml of petroleum ether and the resulting mixture was stirred at room temperature for 3.5 hr. The upper layer was separated off and, after the elimination of the solvent, distilled. The yield of IX was 2.31 g (91%), bp 79–85° C (10 mm); n_D^{20} 1.4316; d_4^{20} 0.9976. Found, %: C 43.90; H 8.40; Si 24.69; MR_D 56.61. Calculated for $C_8H_{18}Si_2O_3$, %: C 44.03; H 8.25; Si 25.68; MR_D 56.94.

6-Diethylamino-2,2,6-trimethyl-1-oxa-2,6-disilacyclohexane (X). With stirring, 10.2 g of I was added to 11.6 g (0.16 mole) of diethylamine in 80 ml of toluene. The mixture was stirred at the boil for 1 hr. The precipitate was filtered off. Distillation provided 7.5 g (62%) of X, bp 96–100° C (7 mm); n_D^{20} 1.4438; d_4^{20} 0.9047; MR_D 67.81; mol. wt. 229. Calculated: MR_D 68.52; mol. wt. 231.

2,6-Dimethyl-2,6-bis(triethylsiloxy)-1-oxa-2,6-disilacyclohexane (XVI). A mixture of 1.35 g (0.0047 mole) of 2,6-diethylamino-2,6-dimethyl-1-oxa-2,6-disilacyclohexane and 1.24 g (0.0094 mole) of $(C_2H_5)_3SiOH$ was heated for 2 hr and was then distilled. This gave 1.5 g (85%) of a substance with bp 168–173° C (8 mm); n_D^{20} 1.4433; d_4^{20} 0.9345; MR_D 115.50; mol. wt. 350. Calculated: MR_D 116.76; mol. wt. 406.9. Literature data [1]: bp 137–139° C (2 mm); n_D^{20} 1.4430; d_4^{20} 0.9340. Compound XI was obtained similarly (see table).

Bis(methyldichlorosilyl)propane (XII). A mixture of 155 g (1 mole) of allylmethyldichlorosilane, 2.4 g (1% by weight) of a 0.1 N solution of H_2PtCl_6 in isopropanol, and 20 g of methyldichlorosilane was heated to 60° C, as a result of which the temperature rose sharply to 115° C. At 115–100° C, 72 g of methyldichlorosilane was added dropwise. The reaction mixture was heated to 165° C for 1.5 hr and was distilled. The yield of XII was 187 g (86.5%). Bp 132–136° C (33 mm); n_D^{20} 1.4682; d_4^{20} 1.2104; MR_D 62.03. Calculated: MR_D 61.22.

Reduction of 6-chloro-2,2,6-trimethyl-1-oxa-2,6-disilacyclohexane. 6.4 g (0.033 mole) of I was added to 1.57 g (0.0413 mole) of $LiAlH_4$ in 60 ml of ether and the resulting mixture was stirred at 36° C for 1 hr. On the following day, the reaction mixture was decomposed with ice. The ethereal layer was separated off and the aqueous layer was extracted with ether. The ethereal extracts were dried over $CaCl_2$. Distillation yielded 2.5 g (72.6%) of **XIII** with bp 135–139° C; n_D^{20} 1.4286; d_4^{20} 0.7719; MR_D 48.77; mol. wt. 140. Calculated: MR_D 49.60; mol. wt. 146.3.

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