UDC 546.287

RESEARCHES ON ALKOXYSILANES

XVII. Cyclic Ethers from Dialkylsilanediols*

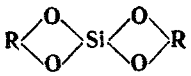
M. G. Voronkov and Yu. P. Romadan

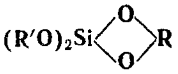
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 2, No. 6, pp. 879–891, 1966

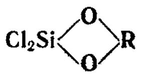
Reaction of 1,2-, 1,3-, 1,4-, 1,5-, and 1,6-glycols, and of catechol, pentaerythritol, and glycerol with dialkyldichlorosilanes (in the presence of tertiary amines) dialkyldialkoxysilanes, or polydialkylsiloxanes gives 30 ethers of dialkylsilanediols containing 5, 6, 7, 8, 9, and 10-membered rings (16 being new). Among them are 8-membered ring ethers containing along with Si, O, and C, N or S, and 6-membered ring ethers containing NH_2, NO_2, and OH groups. 2-Sila-1,3-dioxolanes are obtained only when formation of the 1,3,6,8-tetraoxa-2,7-disilacyclodecane ring is hindered or prevented by the presence of one or two substituents on each carbon atom with two substituents on the silicon. 2,2-Dialkyl-1,3-dioxa-2-silacyclanes, which contain 8 and 9-membered rings, can be obtained only by thermal depolymerization of originally formed polymeric ethers of the type $[-O(CH_2)_nOSiR_2-]_m$. Many of the monomeric cyclic ethers prepared dimerize or polymerize on keeping.

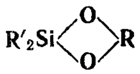
For a long time numerous attempts to prepare monomeric cyclic organosilicon ethers from bifunctional alcohols or phenols, by reacting $SiCl_4$ with glycols [2, 3], catechol [4, 5], ethylene dinitrite [6], or transetherification of tetraalkoxysilanes with glycols [7–10], have been unsuccessful. Moreover, these compounds were not found when glycols were reacted with alkylchloro- and alkylalkoxysilanes [11–17].

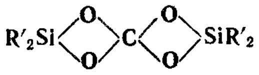
The first type I spirocyclic ether from orthosilicic acid was described by Kipping in a paper [18] which completed his prolonged experimental research on organic compounds of silicon. Subsequently, a number of papers appeared describing [19-58] silicon-containing cyclic ethers of various structures:


I 18–30

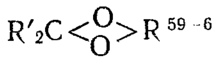

II 20, 26, 27, 30–32


III 26, 27, 33–35

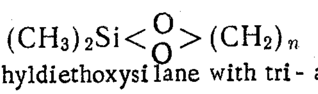

IV 3, 21–24, 29, 36–57


V 21, 23, 24, 41, 58

where R is a divalent organic group, and R' a monovalent one.

The present paper describes** organosilicon analogs of cyclic ketals  $R'_2C<\substack{O\\O}>R^{59-68}$ which are cyclic ethers of dialkylsilanediols of type IV with R' = Me, Et, or Ph.

One of us previously showed [22–24], that type IV cyclic ethers of dialkylsilandiols with 6, 7, 8, and 9-membered rings, as well as type I spirocyclic ethers derived from orthosilicic acid and containing two 6-membered rings, could be obtained by reacting the appropriate glycols with dialkyldiacetoxysilanes or tetraacetoxysilanes. Subsequently, a study was made of the reaction of dialkylidiacetoxysilanes with polyfunctional alcohols [41].

Type IV compounds  $(CH_3)_2Si<\substack{O\\O}>(CH_2)_n$ with n = 3 or 4 were first synthesized as early as 1947 [36] by transetherification of dimethyldiethoxysilane with tri- and tetramethyleneglycols in the presence of 1% p-toluenesulfonic acid as catalyst*** (yields not given). It was not possible, the authors found, to prepare these ethers by reacting the appropriate glycols with dimethyldichlorosilanes (cf. [3], however).

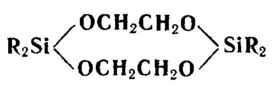
---

* For Part XVI see [1].

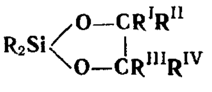
** Data were previously published in 1958 [22].

*** The analogous derivatives of di- and triethyleneglycol were prepared in the same way.

Reaction of dimethyldiacetoxysilane [22, 24, 69], dimethyldiethoxysilane, or dimethyldichlorosilane [36, 53] with ethylene glycol was always found to give 2, 2, 7, 7-tetramethyl-1, 3, 6, 8-tetraoxa-2, 7 disilacyclodecane (VI, R = Me), and not the expected 2, 2-dimethyl-2-sila-1, 3-dioxalene* (VII, R = Me, R^I, R^{II}, R^{III}, R^{IV} = H):



VI



VII

Compounds with a 1-sila, 1, 3-dioxolane ring could not be obtained by other researchers [30] who studied the reaction of ethylene glycol with dicyclohexoxy- and diphenoxydichlorosilane (in the latter case VI with R = C_6H_5O was obtained).

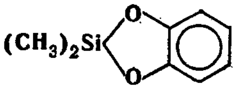
However, at present, some type I compounds with the 2-sila-1, 3-dioxolane ring are already known:

$[R = (C_6H_5)_2\overset{|}{C}-\overset{|}{C}(C_6H_5)_2{}^{18}$, $(CH_3)_2\overset{|}{C}-\overset{|}{C}(CH_3)_2$ and $C_6H_{11}\overset{|}{C}H-H\overset{|}{C}C_6H_{11}{}^{19}]$,

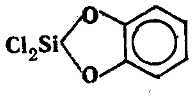
II $[R = (CH_3)_2\overset{|}{C}-\overset{|}{C}(CH_3)_2{}^{22}]$ and IV $[R = (CH_3)_2\overset{|}{C}-\overset{|}{C}(CH_3)_2{}^{23, 46, 57}$,

$CH_3(C_2H_5)\overset{|}{C}-\overset{|}{C}(C_2H_5)CH_3{}^{56}$ and $H_2\overset{|}{C}-\overset{|}{C}(CH_3)_2{}^{23}]$.

2, 2-Dimethyl-2-sila-1, 3-benzodioxol (VIII), obtained by the reaction of dimethyldichlorosilane with catechol, or better, with its lead salt [37, 38, 53, 55], and 2, 2-dichloro-2-sila-1, 3 benzodioxol (VIIIa) [33, 34], are described:

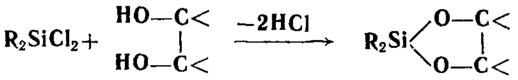


VIII



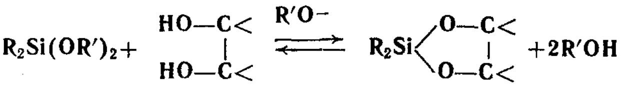
VIIIa

We found it of interest to determine experimentally the structural factors affecting formation of 2, 2-dialkyl-2-sila-1, 3-dioxolanes (VII). We attempted to synthesize these compounds by reacting aliphatic 1, 2-glycols with dialkyldichlorosilanes (in the presence of tertiary amines):



$$R_2SiCl_2 + \begin{matrix} HO-C< \\ | \\ HO-C< \end{matrix} \xrightarrow{-2HCl} R_2Si\begin{matrix} O-C< \\ | \\ O-C< \end{matrix} \quad (1)$$

or dialkyldialkoxysilanes



$$R_2Si(OR')_2 + \begin{matrix} HO-C< \\ | \\ HO-C< \end{matrix} \overset{R'O^-}{\rightleftarrows} R_2Si\begin{matrix} O-C< \\ | \\ O-C< \end{matrix} + 2R'OH \quad (2)$$

to ascertain the effects of substituents at the carbon and silicon atoms on the courses of reactions 1 and 2, whether they promoted formation of 2-sila-1, 3 dioxolanes (VII), or of their type VI dimers.

Investigation of the reaction of dialkyldichlorosilanes with 1, 2 glycols in the presence of tertiary amines (dimethylaniline, triethylamine, or pyridine) showed that with ethylene and propylene glycol, reaction results in formation of type VI dimeric compounds (R = Me, Et, Ph). Similar dimeric compounds are also obtained by reacting methyl-di-n-butoxysilane with ethylene and propylene glycols. Reaction of diethyldimethoxysilane with ethylene glycol in the presence of the sodium derivative of the latter as catalyst, also gave a 10-membered ring compound (VI, R = Et). However in the case of a glycol with only one hydroxyl at a tertiary carbon atom, the product is the correspondingly substituted 2, 2-dimethyl-2-sila-1, 3-dioxolane (VII). We obtained type VII compounds by reacting dimethyldibutoxysilane with 2-methylpropane-1, 2-diol R^I, R^{III} = CH_3; R^{III}, R^{IV} = H) and with 2, 3-dimethylbutane-2-3-diol (R^I, R^{II}, R^{III}, R^{IV} = CH_3). The reaction of dimethyl-, diethyl-, and diphenyldichlorosilane with the di-secondary glycol butane-2, 3-diol also gives 2, 2-dialkyl-2-sila-1, 3-dioxolanes (VII). However here these compounds, even immediately after vacuum-distillation, dimerize considerably (e. g., to 50%), this being complete after two days (Table 2). On

---

* This paper uses the oxa-aza (a)-nomenclature [70].

Table 1

Cyclic Ethers from Dialkylsilanediols

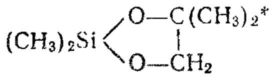
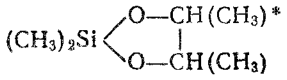
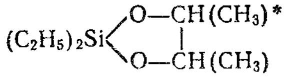
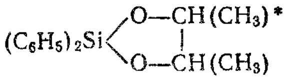
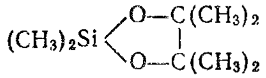
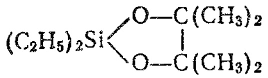
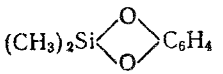
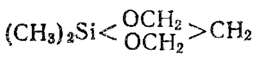
Compound	Bp, °C (pressure, mm)	n_D^{20}	M		C, %		H, %		Si, %		Yield, %, method of preparation
			Found	Calculated	Found	Calculated	Found	calculated	Found	Calculated	
1	2	3	4	5	6	7	8	9	10	11	12
	127 (762)	1.4285	143.9 150.0	146.27	49.29 49.38	49.27	9.71 9.77	9.65	18.93 18.90	19.20	62 (1)
	61.5—62.5 (63)	1.4272	211.5 284.8	146.26 (292.52)		49.27		9.65	19.05 18.98	19.20	44 (2)
	172—173 (758)	1.4412	288.7 346.3	174.32 (348.63)		55.12		10.41	16.23 16.02	16.11	81 (1)
	171—174 (6.5)		414.7 530.5	270.40 (540.81)	69.89 69.77	71.07	6.48 6.82	6.71	10.36 10.27	10.39	72 (1)
	152 (760)	1.4220	175.1 177.3	174.32	55.27 55.36	55.12	10.40 10.48	10.41	16.10 16.21	16.11	60 (1) 68 (2)
	194—196 (760)	1.4350	204.2 205.0	202.37	60.01 59.74	59.35	10.82 10.84	10.95	13.20 13.29	13.87	30 (1)
 (VIII)	71 (3); 211 (754)	1.5325***	167.0 169.6	166.26	57.55 57.52	57.30	6.16 6.31	6.06	16.46 16.55	16.29	50 (1) 69 (2)
	122 (763)	1.4130	136.6 138.7	132.24	45.26 45.14	45.41	9.05 9.27	9.15	21.00 20.90	21.24	65 (1); 74 (6) 71 (3)

Table 1 (cont.)

1	2	3	4	5	6	7	8	9	10	11	12
$(CH_3)_2Si<\begin{matrix}OCH\\OCH_2\end{matrix}\overset{CH_3*}{>}CH_2$	39 (7) 119—121 (758)	1.4107	148.3 149.2	146.27	49.06 49.01	49.27	9.82 9.87	9.65	18.91 19.00	19.20	62 (3) 79 (6)
$(CH_3)_2Si<\begin{matrix}OCH_2\\OCH_2\end{matrix}>C(CH_3)_2$	144—145 (762)	1.4272		160.29		52.45		10.06	17.31 16.98	17.52	75 (3)
$(CH_3)_2Si<\begin{matrix}OCH_2\\OCH_2\end{matrix}>C(NO_2)CH_3*$	109—110 (12)			191.26		37.78		6.85	14.09 14.42	14.68	78 (3)
$(CH_3)_2Si<\begin{matrix}OCH_2\\OCH_2\end{matrix}>C(NH_2)CH_3*$	67—69 (9)			161.28		44.68		9,38	17.63 17.51	17.41	73 (3)
$(CH_3)_2Si<\begin{matrix}OCH_2\\OCH_2\end{matrix}>CHOH$	147 (18)	1.4554		148.24	40.78 41.00	40.51	8.00 8.25	8.16	18.60 18.53	18.95	63 (4)*****
$(C_2H_5)_2Si<\begin{matrix}OCH_2\\OCH_2\end{matrix}>C(CH_3)_2$	46 (5)	1.4333	185.4 184.1	188.38	57.64 57.74	57.40	10.82 10.95	10.70	14.79 14.65	14.91	54 (1)
$(CH_3)_2Si\left\langle\begin{matrix}OCH_2CH_2\\ \vert\\ OCH_2CH_2\end{matrix}\right.$	142—144 (758)	1.4220	145.0 143.8	146.27	49.40 49.48	49.27	9.60 9.55	9.65	19.07 19.31	19.20	79 (3) 79 (6)
$(CH_3)_2Si\left\langle\begin{matrix}OCH(CH_3)CH_2*\\ \vert\\ O—CH_2—CH_2\end{matrix}\right.$	145 (746)	1.4258	162.7 163.1	160.29	52.82 52.91	52.75	10.11 10.17	10.06	17.47 17.39	17.52	75 (3)
$(C_2H_5)_2Si\left\langle\begin{matrix}OCH_2CH_2*\\ \vert\\ OCH_2CH_2\end{matrix}\right.$	189 (758)	1.4371	169.5 170.9	174.32	54.92 54.84	55.12	10.31 10.23	10.41	15.93 15.80	16.11	60 (1) 60 (3)
$(CH_3)_2Si<\begin{matrix}OCH_2CH_2\\OCH_2CH_2\end{matrix}>CH_2$	163,5 (764)	1.4330	162.0 163.1	160.29	52.60 52.49	52.75	10.04 10.01	10.06	17.31 17.44	17.52	67 (3)
$(CH_3)_2Si<\begin{matrix}OCH_2CH_2\\OCH_2CH_2\end{matrix}>NH*$	93—94 (30)	1.4547		161.28	44.54 44.39	44.68	9.47 9.53	9.37	17.21 17.29	17.41	80 (5)
$(CH_3)_2Si<\begin{matrix}OCH_2CH_2\\OCH_2CH_2\end{matrix}>NC_2H_5*$	200 (755) 77—78 (10)	1.4496	193.7 195.0	189.34	50.55 50.42	50.75	10.00 10.28	10.12	14.89 14.98	14.84	86 (5)

Table 1 (cont.)

1	2	3	4	5	6	7	8	9	10	11	12
$(CH_3)_2Si<\substack{OCH_2CH_2\\OCH_2CH_2}>S$*	204.5 (756) 102—103 (26)	1.4858	184.3 186.9	178.33	40.63 40.71	40.41	7.80 7.76	7.92	15.61 15.83	15.75	58 (5)
$(CH_3)_2Si<\substack{OCH_2CH_2\\OCH_2CH_2}>O$	166.5 (761) 89—90 (54)	1.4338	150.2 159.0	162.27	44.49 44.30	44.41	8.65 8.54	8.70	17.22 17.08	17.31	98 (5)
$(CH_3)_2Si\begin{matrix}\diagup OCH_2CH_2CH_2\\ \quad\quad\quad\quad\quad\vert\\ \diagdown OCH_2CH_2CH_2\end{matrix}$	183.5 (764) 52 (4)	1.4398	171.7 170.5	174.32	55.24 55.33	55.12	10.38 10.33	10.41	16.08 16.27	16.11	48 (3)
$(CH_3)_2Si<\substack{OCH_2CH_2O\\OCH_2CH_2O}>Si(CH_3)_2$	181 (770) 84—86 (10)	1.4379****	238.2 239.1	236.42		40.64		9.14	23.61 23.50	23.75	62 (2)
$(C_2H_5)_2Si<\substack{OCH_2CH_2O\\OCH_2CH_2O}>Si(C_2H_5)_2$*	204.5 (762)	1.4481	281.1 284.7	292.53	49.20 48.86	49.27	9.89 9.82	9.65	19.05 18.92	19.20	60 (1) 73 (2)
$(C_6H_5)_2Si<\substack{OCH_2CH_2O\\OCH_2CH_2O}>Si(C_6H_5)_2$*	210—215 (10)			484.70	69.13 68.85	69.38	6.00 6.08	5.82	11.26 11.68	11.59	71 (1)
$(CH_3)_2Si<\substack{OCH(CH_3)CH_2O\\OCH_2(CH_3)CHO}>Si(CH_3)_2$	160 (765)	1.4323	270.4 273.0	264.48	45.52 45.61	45.41	9.26 9.34	9.15	21.03 20.90	21.24	81 (1)
$(C_2H_5)_2Si<\substack{OCH(CH_3)CH_2O\\OCH_2(CH_3)CHO}>Si(C_2H_5)_2$*	178—179	1.4430	329.6 326.8	160.29 (320.58)		52.45		10.06	17.37 17.29	17.52	85 (1)
$(C_6H_5)_2Si<\substack{OCH(CH_3)CH_2O\\OCH_2(CH_3)CHO}>Si(C_6H_5)_2$*	186—188 (6)		508.3 506.7	256.38 (512.76)		71.07		6.71	10.36 10.27	10.39	69 (1)
$(CH_3)_2Si<\substack{OCH_2\\OCH_2}>C<\substack{CH_2O\\CH_2O}>Si(CH_3)_2$	244—245 (751)		249.5 250.2	248.44	43.37 43.29	43.51	8.04 7.99	8.11	22.27 22.39	22.61	91 (2)

---

*New compound.

**Molecular weight of dimer in brackets.

***Supercooled mp 75° C.

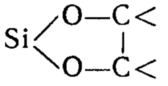
****Supercooled mp 56°.

*****$AlCl_3$ catalyst.

repeated distillation, the dimers formed depolymerize, dimerizing again on keeping.

Yields of the compounds prepared, their physical constants, analyses, and experimental molecular weights are given in Table 1.

The failure of all attempts to synthesize type VII monomers without substituents at the ring carbon atoms, or with only one substituent, is to be ascribed to the strain in the 2-sila-1,3-dioxolane ring, due to the atomic radius of the silicon atom being greater than that of carbon. Formation of an unstrained 5 membered ring

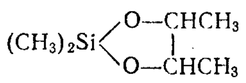
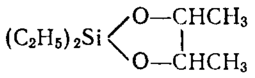
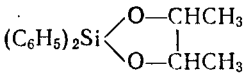
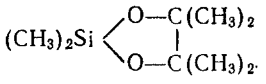


$\mathrm{Si}\begin{smallmatrix}\mathrm{O-C<}\\ |\\ \mathrm{O-C<}\end{smallmatrix}$

requires decrease in the usual tetrahedral valence angles of C—C—O, C—O—Si or O—Si—O, i.e., ring compression. According to the Thorpe-Ingold hypothesis [72], such compression takes place when there are gem substituents at the carbon and silicon atoms in the 5-membered ring formed. In contrast to this, 1,3-dioxolane and its 2 monosubstituted derivatives, with their unstrained rings, are very readily formed, and are amply described in the literature [59–63, 71], while 2,2-dialkyl-1,3-dioxolanes are formed with difficulty.

Table 2

Changes in Molecular Weights and Refractive Indices of 4,5-Dimethyl 2,2-diorganyl-2-sila-1,3-dioxolanes

Cyclic ether	M calculated	M found		n_D^{20}	
		Immediately after distilling	After keeping*	Immediately after distilling	After keeping*
 $(CH_3)_2Si\begin{smallmatrix}O-CHCH_3\\ |\\ O-CHCH_3\end{smallmatrix}$	146.26	211.5	284.8(3) 278.2(4)	1.4272	1.4317(20)
 $(C_2H_5)_2Si\begin{smallmatrix}O-CHCH_3\\ |\\ O-CHCH_3\end{smallmatrix}$	174.31	288.7	346.3(2)	1.4412	1.4449(15)
 $(C_6H_5)_2Si\begin{smallmatrix}O-CHCH_3\\ |\\ O-CHCH_3\end{smallmatrix}$	270.40	414.7	530.5(3)		
 $(CH_3)_2Si\begin{smallmatrix}O-C(CH_3)_2\\ |\\ O-C(CH_3)_2\end{smallmatrix}$	174.32	175.1	177.3(3)	1.4220	1.4223(60)

---

* Number of days for which kept given in brackets.

Study of Briegleb-Stuart molecular models confirms the strain in the 2-sila-1,3-dioxolane ring, and shows that monomers containing this ring can be obtained when formation of the 1,3,6,8-tetraoxa-2,7-disilacyclodecane (VI) ring is hindered or impossible because of the presence of one or two substituents at each carbon atom with two substituents at the silicon atom.

Thus all 1,2-glycols of the type $HOCH_2CH_2OH$ and $HOCH_2CHROH$ react with dialkyldichloro- or dialkyldialkoxysilanes to give only dimers, containing the 10-membered heterocyclic ring (VI). But glycols of the type HOCHRCHROH, $HOCHRCR_2OH$ and $HOCR_2CR_2OH$ give more or less stable monomers, containing 5-membered heterocyclic ring.

In all cases formation of dimeric cyclic ethers is to be expected from monomers of the type $RSiHX_2$, and this is confirmed by the results in the literature [46].

All cyclic ethers of type IV dialkylsilanediols, with six or more atoms in the heterocyclic ring, have an unstrained configuration, and can readily be obtained monomeric. We consider that the most convenient method of synthesizing them is transetherification of dialkyldialkoxysilanes with 1,3-, 1,4-, 1,5-, and 1,6-glycols, the equation being

$$R_2Si\begin{smallmatrix}OR'\\ OR'\end{smallmatrix} + \begin{smallmatrix}HO\\ HO\end{smallmatrix}(CH_2)_n \overset{R'O^-}{\rightleftharpoons} R_2Si\begin{smallmatrix}O\\ O\end{smallmatrix}(CH_2)_n + 2R'OH, \qquad (3)$$

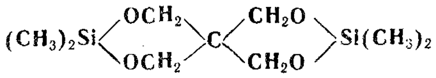
where n ≥ 3.

The best catalysts for this reaction are the sodium or potassium alkoxides or glycolates. The previously recommended acid catalysts (p-toluenesulfonic acid, camphorsulfonic acid, or amberlite [18, 41]) are less effective, and in a number of cases (penta- and hexamethylene glycols, etc.) do not enable the corresponding monomeric cyclic ethers to be obtained.

To synthesize cyclic ethers of dimethylsilanediol, it is preferable to use dimethyldi-n-butoxysilane, and not dimethyldiethoxysilane, as described in the literature [18, 41], since the latter partly disappears from the reaction zone as an azeotrope, boiling point, 77°C, n_D^{20} 1.3663, with the ethanol formed by transetherification, the azeotrope's content of the latter being 81%.

We obtained a number of cyclic ethers of dimethylsilanediol containing 6, 7, 8, and 9-membered rings (Table 1) in good yields by reacting dimethyldi-n butoxysilane with 1,3-, 1,4-, 1,5-, and 1,6-glycols.

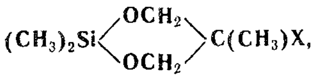
Dimethyldi-n-butoxysilane reacted smoothly with catechol to give 2,2-dimethyl-2-sila-1,3 benzodioxol (VIII), and it reacted with pentaerythritol to give 3,3,9,9-tetramethyl 3,9-disila-2,4 8,10-tetraoxa [5,5]-spirocycloundecane (IX):



$$(\mathrm{CH_3})_2\mathrm{Si}\begin{matrix}\diagup\mathrm{OCH_2}\diagdown\\ \diagdown\mathrm{OCH_2}\diagup\end{matrix}\mathrm{C}\begin{matrix}\diagup\mathrm{CH_2O}\diagdown\\ \diagdown\mathrm{CH_2O}\diagup\end{matrix}\mathrm{Si(CH_3)_2}$$

IX

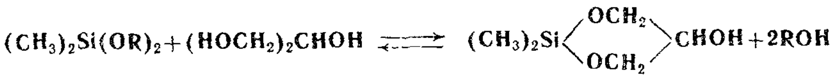
Transesterification of dimethyldiethoxysilane with 2-methyl-2-amino-propane 1,3-diol and 2 methyl-2-nitropropane 1,3-diol gave hitherto unknown crystalline cyclic ethers of dimethylsilanediol with a 6-membered heterocyclic ring linked to a functional group:



$$(\mathrm{CH_3})_2\mathrm{Si}\begin{matrix}\diagup\mathrm{OCH_2}\diagdown\\ \diagdown\mathrm{OCH_2}\diagup\end{matrix}\mathrm{C(CH_3)X},$$

where X = NH_2 (X) or NO_2 (XI).

We investigated the transetherification of dimethyl-n-butoxysilane with glycerol, with a view to obtaining 2,2-dimethyl-5-hydroxy-2-sila-1,3-dioxane (XII) according to the equation

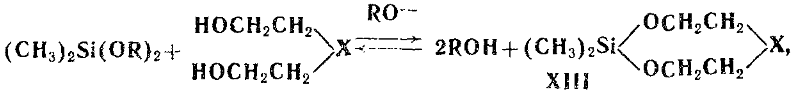


$$(\mathrm{CH_3})_2\mathrm{Si(OR)_2}+(\mathrm{HOCH_2})_2\mathrm{CHOH} \rightleftarrows (\mathrm{CH_3})_2\mathrm{Si}\begin{matrix}\diagup\mathrm{OCH_2}\diagdown\\ \diagdown\mathrm{OCH_2}\diagup\end{matrix}\mathrm{CHOH}+2\mathrm{ROH} \qquad (4)$$

XII

However, the two compounds did not react together in the presence of sodium glycerolate. It was possible to bring about reaction with an acid catalyst ($AlCl_3$, p-toluenesulfonic acid), and to obtain a 63% yield of XII which polymerizes very readily.

Transetherification of dimethyldi n-butoxysilane was also effected with thiodiglycol, diethanolamine, N-ethyldiethanolamine, and diethylene glycol, in the presence of alkaline catalyst, the equation for the reaction being

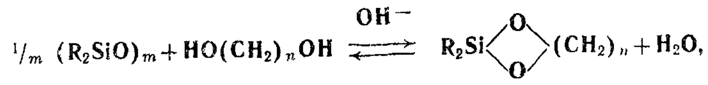


$$(\mathrm{CH_3})_2\mathrm{Si(OR)_2}+\begin{matrix}\mathrm{HOCH_2CH_2}\diagdown\\ \mathrm{HOCH_2CH_2}\diagup\end{matrix}\mathrm{X}\overset{\mathrm{RO^-}}{\rightleftarrows} 2\mathrm{ROH}+\underset{\mathrm{XIII}}{(\mathrm{CH_3})_2\mathrm{Si}}\begin{matrix}\diagup\mathrm{OCH_2CH_2}\diagdown\\ \diagdown\mathrm{OCH_2CH_2}\diagup\end{matrix}\mathrm{X}, \qquad (5)$$

where X = S, NH, NEt, O; R = n-C_4H_9. In that way, good yields of new heterocyclic compounds with oxygen and silicon also sulfur or nitrogen, in addition to carbon atoms in the ring, are obtained for the first time (Table 1).

It should be mentioned that, unlike the transetherification of dimethyldi-n-butoxysilane with N ethyldiethanolamine (XIII, X = NEt) the similar reaction with diethanolamine gives a much lower yield, and the resultant 2,2-dimethyl 1,3-dioxa 2-sila-6-azacyclooctane (XIII, X = NH) is characterized by poor stability, and it decomposes merely on keeping, or when distilled under ordinary pressure.

It was shown for the first time that 2,2-dialkyl-1,3-dioxa-2-silacyclanes can be synthesized by splitting cyclic or linear polydialkylsiloxanes with glycols in the presence of alkaline catalysts, the reaction being



$$^1/_m\ (\mathrm{R_2SiO})_m+\mathrm{HO(CH_2)}_n\mathrm{OH} \overset{\mathrm{OH^-}}{\rightleftarrows} \mathrm{R_2Si}\begin{matrix}\diagup\mathrm{O}\diagdown\\ \diagdown\mathrm{O}\diagup\end{matrix}(\mathrm{CH_2})_n+\mathrm{H_2O}, \qquad (6)$$

where $m \geq 3$; $n \geq 2$.

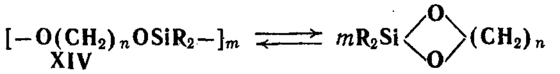
The reaction is effected by continuously distilling off from the reaction mixture the water formed as an azeotrope, the conditions used being those previously described by one of us [21, 73, 75] for scission of organosiloxanes by alcohols. Thus, for example, reaction of octamethylcyclotetrasiloxane with butane-1,4 diol gives a 79% yield of 2,2 dimethyl-1,3-dioxa-2-silacycloheptane.

It should be mentioned that all methods of synthesis of 2,2-dialkyl-1,3-dioxa 2-silacyclanes, nominally formed by a bimolecular reaction, give, along with these monomers, polymeric products formed by the polymolecular reaction

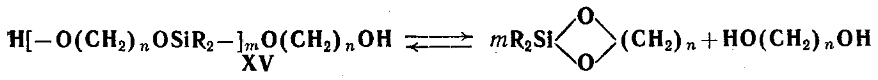
$$mR_2SiX_2 + mHO(CH_2)_nOH \longrightarrow \underset{\text{XIV}}{[-O(CH_2)_nOSiR_2-]_m} + 2mHX \qquad (7)$$

$$mR_2SiX_2 + (m+1)HO(CH_2)_nOH \longrightarrow \underset{\text{XV}}{H[-O(CH_2)_nOSiR_2-]_mO(CH_2)_nOH} + 2mHX \qquad (7a)$$

2,2-Dialkyl-1,3-dioxa-2 silacyclanes with m = 1 are the main products of reaction 7 only with γ-, β-, mono- and di-tertiary, and di-secondary α-glycols, i.e., when n = 4, 3, and sometimes 2. As has been stated, most other α-glycols give cyclic ethers XIV with m = 2. Glycols with $n \geq 5$ form practically entirely high-molecular compounds ($m > 2$).* Only subsequent thermal depolymerization of these polymers, catalyzed by bases and evidently inhibited by acids, makes it possible to obtain monomeric 2,2-dialkyl-1,3-dioxa-2-silacyclanes:



$$\underset{\text{XIV}}{[-O(CH_2)_nOSiR_2-]_m} \rightleftarrows mR_2Si\langle O_2 \rangle(CH_2)_n \qquad (8)$$



$$\underset{\text{XV}}{H[-O(CH_2)_nOSiR_2-]_mO(CH_2)_nOH} \rightleftarrows mR_2Si\langle O_2 \rangle(CH_2)_n + HO(CH_2)_nOH \qquad (8a)$$

For precisely that reason, the transetherification of dialkyldialkoxysilanes with glycols must be carried out in the presence of alkaline catalysts, not acid ones, since the latter do not facilitate depolymerization of the polymers formed. Therein lies the explanation of unsuccessful attempts [36, 42] to synthesize a number of cyclic ethers of dialkylsilanediols in the presence of acid catalysts.

The above reaction is an example of rearrangement of Si—O—C bonds according to the equation**

$$>\!Si-O-C\!< + >\!\overset{*}{Si}-O-\overset{*}{C}\!< \rightleftarrows >\!Si-O-\overset{*}{C}\!< + >\!\overset{*}{Si}-O-C\!<, \qquad (9)$$

previously described in the literature for the case of alkoxysilanes [21, 73]. The equilibrium nature of this rearrangement is indicated by monomeric 1,3-dioxa-2-silacyclanes dimerizing or polymerizing on keeping.

Experimental

Preparation and purification of the starting dimethyl-n-butoxysilane, dimethyldiethoxysilane [75], diethyldimethoxysilane [74], dimethyldichlorosilane [76], and octamethylcyclotetrasiloxane [75, 73], have previously been described.

Dimethylaniline, triethylamine, and pyridine were dried over KOH and distilled immediately before use.

Purification methods and physical constants for most of the glycols are given in a paper by one of us [71]. The properties of the other glycols, catechol, glycerol, and pentaerythritol, which were purified similarly by distillation or recrystallization, are given in Table 3.

Synthetic Methods

Reaction of glycols with dimethyldichlorosilane (I). This was carried out in a 250 ml 2-necked round-bottomed flask, fitted with reflux condenser, $CaCl_2$ guard tube, dropping funnel, and mechanical stirrer. A solution of 0.5 mole of the appropriate glycol in 50 ml dry ether and 1 mole of the appropriate tertiary amine were put in the flask, the mixture cooled and stirred, and a solution of the dialkyldichlorosilane in 50 ml ether added dropwise. The reaction mixture slowly heated up and a precipitate of amine hydrochloride formed. Then the mixture was stirred and heated for 6 hr on a water-bath, the precipitate of amine hydrochloride filtered off, after which followed extraction with

---

*Along with other workers, [41] we have found it impossible to isolate type XV monomers with m = 1 and 2.

** The mechanism of this reaction is analogous to that given by one of us for rearrangement of Si—O—C and Si—O—Si bonds [21, 73].

ether. The solvent was distilled off from the bulked ether extracts, and the residue distilled under ordinary or reduced pressure.

Reaction of glycols with dimethyl-n butoxysilane, dimethyldiethoxysilane, and diethyldimethoxysilane (2,3,5). A flask was fitted with a 25 cm rod-and-disc fractionating column and into it added 0.21–0.25 mole of the appropriate glycol, in which 0.05–0.1 g Na was dissolved and 0.2 mole dialkyldialkoxysilane. The reaction mixture was boiled slowly until the theoretical quantity of the corresponding alcohol had distilled over, and then the residue was distilled (preferably under vacuum). In a number of cases the residue was polymer, and distillation involved thermal depolymerization. A second distillation at ordinary or reduced pressure gave the pure cyclic ether.

Table 3

Properties of Starting Glycols

Compound	Bp, °C (5 mm)	Mp, °C	n_D^{20}
$CH_2(CH_2CH_2OH)_2$	126		1.4500
$O(CH_2CH_2OH)_2$	112	−10.4	1.4472
$S(CH_2CH_2OH)_2$	149		1.5203
$HN(CH_2CH_2OH)_2$	141	28	1.47
$C_2H_5N(CH_2CH_2OH)_2$	121	—	1.4665
$HOCH(CH_2OH)_2$	155	—	1.4743
$HO(CH_2)_6OH$	124	42.5	—
$C(CH_2OH)_4$	—	260.5	—
$1,2\text{-}(HO)_2C_6H_4$	—	105	—
$HOCH_2C(NH_2)(CH_3)CH_2OH$	—	109—111	—
$HOCH_2C(NO_2)(CH_3)CH_2OH$	—	147—149	—

Reaction of glycols with polydialkylsiloxanes (6). A flask was fitted with a ground-in condenser and a water-separating trap, and charged with 0.2 mole of the appropriate glycol, 0.05 mole polydialkylsiloxane, 0.1–0.2 g powdered KOH, and 100 ml benzene or toluene. The reaction mixture was boiled until water ceased to separate in the trap, then the solvent distilled off and the residue distilled, first of all at ordinary pressure, and then under vacuum over Na metal.

Table 1 gives the physical constants and molecular weights of all compounds synthesized, as found immediately after preparation.

The above methods of preparing cyclic ethers of dialkylsilanediols are illustrated below with some examples.

Reaction of dimethyldichlorosilane with 2,3-dimethylbutane 2,3-diol. 5.2 g (0.4 mole) dimethyldichlorosilane in 50 ml ether was added dropwise to a mixture of 6.4 g (0.42 mole) anhydrous pinacol, 9.9 g (0.82 mole) dimethylaniline, and 50 ml dry ether. After heating for 5 hr on a water-bath, the precipitate of dimethylaniline hydrochloride was filtered off, and extraction with ether performed. The ether was distilled off from the bulked ether extracts, and the residue fractionally distilled. Yield of 2,2,4,4,5,5-hexamethyl-2-sila-1,3-dioxolane bp 148°–151°C, n_D^{20} 1.4216, 10.6 g (61%). Table 1 gives its properties after a second distillation.

Transetherification of diethyldimethoxysilane with ethylene glycol. Slow distillation of a mixture of 13.0 g (0.21 mole) ethylene glycol and 29.6 g (0.2 mole) diethyldimethoxysilane in which 0.1 g Na had been dissolved, gave 12.1 g (94%) MeOH bp 64°–65°C. Fractional distillation of the residue gave 21.9 g (75%) tetraethyl-1,3,6,8-tetraoxa-2,7-disilacyclodecane, bp 203°–205°C, whose constants after a second distillation are given in Table 1.

Reaction of dimethyldi-n-butoxysilane with thiodiglycol. 40.9 g (0.2 mole) dimethyldi-n-butoxysilane was added to a solution of 0.05 g Na in 28.1 g (0.23 mole) thiodiglycol. Distillation of the reaction mixture gave 27.5 g (93%) n-BuOH bp 117–119° C. Further vacuum-distillation of the residue (distillation at ordinary pressure led to a decomposition) gave 20.7 g (58%) 2,2-dimethyl-1,3-dioxa-6-thia-2-silacyclooctane, bp 86°–92°C (10 mm); Table 1 gives its physical constants after a second distillation.

Reaction of octamethylcyclotetrasiloxane with butane-1,4-diol. A mixture of 15.3 g (0.05 mole) octamethylcyclotetrasiloxane, 17.6 g (0.2 mole) butane-1,4-diol, 0.2 powdered KOH, and 100 ml benzene, was vigorously boiled under a reflux condenser with a water trap, so that the water formed in the reaction was continuously removed as its azeotrope with benzene (3.4 ml water separated, i.e., 94%). Fractional distillation of the reaction products gave 23.2 g (79%) 2,2-dimethyl-1,3-dioxa-2-silacycloheptane, bp 132°–145°C. After redistilling over Na it had 142°–144° C, n_D^{20} 1.4222.

REFERENCES

1. M. G. Voronkov and S. M. Rabkina, ZhOKh, **31**, 1259, 1961.
2. F. Taurke, Ber., 38, 1661, 1905.
3. H. W. Kohlschütter and G. Jackel, Z. Anorg. Chem., **271**, 185, 1953.
4. A. Rosenheim and O. Sorge, Ber., 53, 932, 1920.
5. Yu. N. Vol'nov and B. N Dolgov, ZhOKh, 10, 556, 1940.
6. W. Bolzani, German Patent no. 459738, 1928; C. **11**, 1716, 1928.
7. L. Knorr and H. Weyland, German Patent no. 285285, 1915; C., **11**, 373, 1915.
8. L. Holzapfel, Koll. Z., **100**, 380, 1942.
9. D. F. Peppard, W. G. Brown, and W. C. Johnston, J. Am. Chem. Soc., **68**, 73, 1946.
10. Farbenfabriken Bayer, A-G., British Patent no. 712845, 1954; Siemens-Schuckert-Werke, British Patent no. 717408. A-G, C.A., 49, 2780, 1955.
11. W. E. Hanford, U.S. Patent no. 2386793, 1945; C. A., **40**, 604, 1946.
12. W. E. Hanford, U.S. Patent no. 2441066, 1948; C. A., **42**, 5268, 1948.
13. D. X. Klein and D. E. Kvalnes, U.S. Patent no. 2476307, 1949; C.A., 44, 167, 1950.
14. K. Jost, German Patent no. 803079, 1951; C. A., **45**, 5453, 1951.
15. M. J. Hunter and L. A. Rauner, U. S. Patent no. 2584351, 1952; C. A., **46**, 4851, 1952; British Patent no. 663599, 1951; C. A., **47**, 8415, 1953; German Patent no. 841362, 1952; C. A., **51**, 760, 1957.
16. M. C. Brooks and R. H. Evart, U. S. Patent no. 2680124, 1954; C. A., **49**, 9324, 1955; U. S. Patent no. 2715135, 1955; C. A., **50**, 2198, 1956.
17. K. W. Krantz, U.S. Patent no. 2887467, 1959; C. A., **53**, 16586, 1959.
18. F. S. Kipping and J. T. Abrams, J. Chem. Soc., 81, 1944.
19. W. Hahn, Makromol. Chem., **11**, 51, 1953.
20. W. Hahn, Makromol. Chem., **11**, 64, 1952.
21. M. G. Voronkov, Heterolysis of the Siloxane Bond [in Russian], Moscow, 1961.
22. M. G. Voronkov, V. P. Davydova, and B. N. Dolgov, Izv. AN SSSR, OKhN, 698, 1958.
23. V. P. Davydova, M. G. Voronkov, and B. N. Dolgov, Khimiya i prakticheskoe primenie kremneorganisch--kikh soedinenii, **1**, 204, 1958.
24. V. P. Davydova, Acyloxysilanes and Their Reaction with Organic Compounds Containing the Hydroxyl Group [in Russian], Master's Thesis, LGU, Leningrad, 1958.
25. J. J. Zuckerman, J. Chem. Soc., 873, 1962; J. J. Zuckerman, Ph. D. Thesis, Cambridge University, England, 1962.
26. R. Schwarz and W. Kuchen, Z. anorg. allg. Chem., **279**, 84, 1955.
27. A.-G. Siemens-Schuckertwerke, British Patent no. 798163, 1958; C. A., **53**, 5205, 1959.
28. R. Müller and L. Heinrich, Ber., **94**, 2225, 1961.
29. R. M. Ismail, Z. Naturforsch, **19**b, 873, 1964.
30. M. Staudinger and W. Hahn, Makromol. Chem., **11**, 24, 1953; Federal German Republic Patent no. 929189, 1955; RZhKh, 72803, 1956.
31. A.-G. Siemens-Schuckertwerke, German Patent no. 1057129, 1959; C.A., 55, 7364, 1961.
32. A.-G. Siemens-Schuckertwerke, German Patent no. 1053518, 1959; C. A., **55**, 13384, 1961.
33. Yu. N. Vol'nov, ZhOKh, **17**, 1428, 1947.
34. R. Schwarz and W. Kuchen, Z. anorg Chem., **266**, 185, 1951.
35. A.-G. Siemens-Schuckertwerte, German Patent no. 1032747, 1958; C. A., **54**, 2148, 1960.
36. R. H. Krieble and C. A. Burkhard, J. Am. Chem. Soc., **69**, 2689, 1947.
37. S. D. Radosavlević, M. S. Jačovič, and M. D. Dragojević, Glasn. Khem. Drush., **20**, 273, 1955.
38. M. S. Jačovič, Z. anorg. Chem., **288**, 324, 1956.
39. Midland Silicones Ltd., British Patent no. 749958, 1956; C.A., **50**, 19123, 1956.
40. J. L. Speier and L. M. Schorr, U.S. Patent no. 2811542, 1957; C. A., **52**, 2450, 1958.
41. V. P. Davydova and M. G. Voronkov, ZhOKh, 28, 1879, 1958.
42. M. M. Sprung, J. Org. Chem., **23**, 58, 1958.
43. F. A. Henglein and H. Gräser, Makromol. Chem., **26**, 236, 1958.
44. W. C. May, U.S. Patent no. 2833658, 1958; C. A., **52**, 21227, 1958.
45. Imperial Chemical Industries, French Patent no. 1161094, 1958; C. 7001, 1960.
46. R. A. Hall, British Patent no. 791169, 1958; C.A., **52**, 16199, 1958.
47. R. Calas and P. Nicou, C. r., **249**, 1011, 1959.
48. R. Egli, Über Polyalkikieselsaureester, Promotionsarbeit, Zürich, 1959.
49. N. Spassky, C. r., **251**, 2371, 1960.
50. P. L. De Benneville and M. J. Hurtwitz, U.S. Patent no. 2876209, 1959; C.A., **53**, 12321, 1959.
51. J. Jack, British Patent no. 857153, 1960; C. A., **55**, 18684, 1961.

52. A. B. Finestone, U. S. Patent no. 2953545, 1960; C. A., **55**, 4045, 1961.
53. M. Wieber and M. Schmidt, Ang. Chem., **75**, 1116, 1963.
54. M. Wieber and M. Schmidt, J. Organometal Chem., **1**, 93, 1963.
55. H. J. Emeleus and J. J. Zuckerman, J. Organometal. Chem., **1**, 328, 1964.
56. R. M. Ismail and Z. Naturforsch, **18b**, 1124, 1963.
57. R. Hall and N. New, British Patent no. 800554, 1958; C. A., **55**, 12728, 1959.
58. L. W. Breed, W. J. Haggerty, and J. Harvey, J. Org. Chem., **25**, 1804, 1960.
59. J. Boeseken and P. H. Hermans, Rec. trav. chim., **40**, 525, 1921; **41**, 3758, 1922; **42**, 1104, 1923.
60. L. Smith and J. Lindberg, Ber., **64**, 505, 1931.
61. R. Dworzak and K. Herrman, Mon., **52**, 87, 1929.
62. R. Dworzak and T. Lasch, Mon., **51**, 59, 1928.
63. G. F. Hennion, J. Am. Chem. Soc., **58**, 1658, 1936; **60**, 1717, 1938.
64. E. J. Salmi and V. Ranniko, Ber., **72**, 600, 1939.
65. C. K. Ikeda, R. A. Braun, and B. E. Soreson, J. Org. Chem., **29**, 286, 1964.
66. C. F. Wilcox and D. L. Nealy, J. Org. Chem., **28**, 3446, 1963.
67. L. L. Sims, U. S. Patent no. 3113156, 1963; RZhKh, **11H**, 19, 1965.
68. P. Trotter, U. S. Patent no. 3113154, 1963; RZhKh, **11H**, 20, 1965.
69. K. A. Andrianov, A. A. Zhdanov, and A. A. Bogdanova, ZhOKh, **27**, 2073, 1957.
70. M. G. Voronkov and B. N. Dolgov, Uch. zap LGU, **155**, no. 11, 80, 1952; khimiya i prakticheskoe primennie kremneorganicheskikh soedinenii, Leningrad, no. 5, 1958.
71. M. G. Voronkov and E. S. Titlinova, ZhOKh, **24**, 613, 1954; Author's certificate 101559, 1959.
72. N. A. Domnin, Structure of Cyclic Compounds in the Light of Strain Theory [in Russian], Leningrad, ONTI, 164, 1936; E. L. Eliel amd M. S. Newman, Steric Effects in Organic Chemistry, New York, John Wiley and Sons, 1956.
73. M. G. Voronkov, ZhOKh, 29, 907, 1959; Khimiya i prakticheskoe primenenie kremneorganicheskikh soedinenii, 1, **229**, 1958.
74. M. G. Voronkov and V. N. Zgonnik, ZhOKh, **27**, 1476, 1957.
75. M. G. Voronkov and Z. I. Shabarov, ZhOKh, **29**, 1528, 1959.
76. M. G. Voronkov and B. N. Dolgov, ZhOKh, **24**, 1082, 1954.

12 February 1965

Institute or Organic Synthesis
AS Latvian SSR, Riga