

## METALLOCANES OF GROUP 14 ELEMENTS. 1. DERIVATIVES OF SILICON AND GERMANIUM. (REVIEW)

A. A. Selina, S. S. Karlov, and G. S. Zaitseva

*Results on the synthesis of silocanes and germocanes, eight-membered heterocycles with the general formula  $D(CH_2CH_2Z)_2MX_kY_n$  are analyzed and classified. The chemical behavior of these compounds and the characteristics of the element–nitrogen transannular bond are studied.*

**Keywords:** germanium, germocanes, silicon, silocanes, hypervalent interaction.

Metallocanes include eight-membered heterocyclic compounds with the general formula  $D(CH_2CH_2Z)_2MX_kY_n$  ( $k, n = 0-2$ ), in which transannular interaction is possible between the atom of the metal (metalloid) M and the heteroatom D containing an unshared electron pair. Such derivatives are known for a large number of elements (M = B, Si, Ge, Sn, Pb, As, Sb, Bi, transition metals). Among the compounds formed by the atoms of nontransition elements the metallocanes of group 14 (mainly derivatives of silicon and germanium) have been investigated most.

In the present article the currently available data on the synthesis and reactivity of silocanes and germocanes and on the physicochemical investigation of the compounds are reviewed. The review includes data on compounds in which the central group 14 atom forms four covalent bonds and is capable of forming one or two additional intramolecular hypervalent interactions. A major contribution to the development of the chemistry of these derivatives was made by several research groups led by E. Lukevics, M. Voronkov, V. Mironov, V. D'yakov, A. Tzschach and K. Jurkschat, J. Corey, M. Gilen, R. Holmes, and M. Dräger. It is also necessary to mention a recent review on the metallocanes of heavy elements of groups 14 and 15 [1].

### 1. SILOCANES

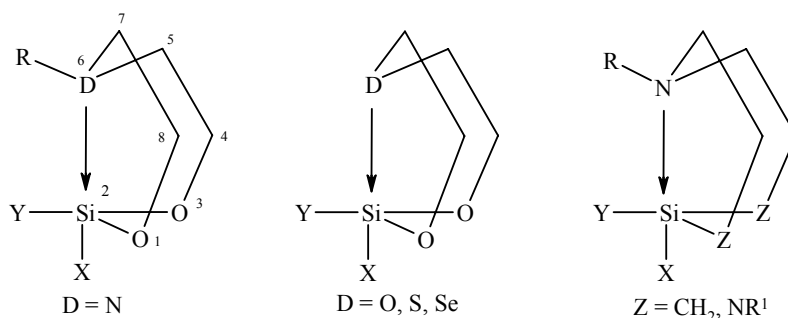
Cyclic organosilicon derivatives of the ocane type are a well studied group of compounds. At the present time representatives containing nitrogen, oxygen, sulfur, and selenium atoms as electron-pair donors (D) are known.

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\* Dedicated to Prof. E. Lukevics on his 70th birthday.

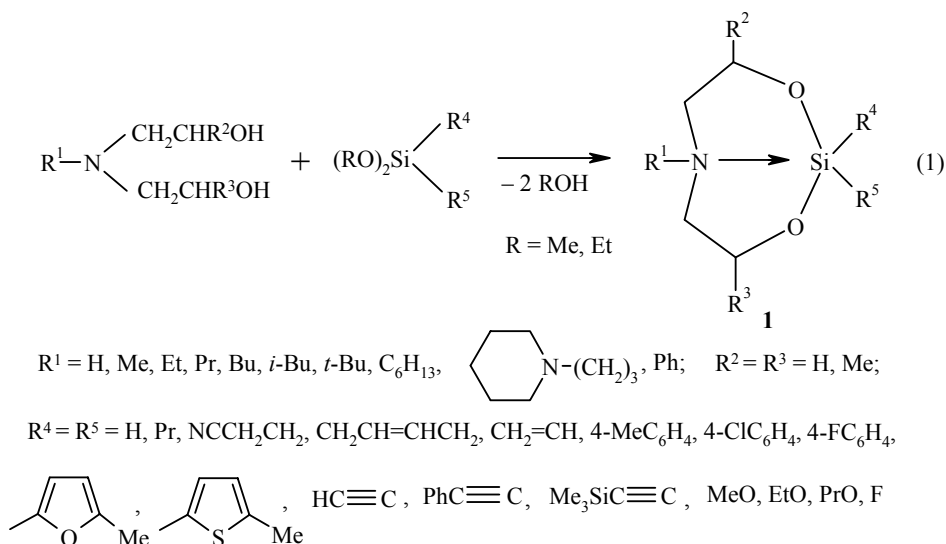
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## 1.1. Methods for the Production of Silocanes

**1.1.1. Reaction of Dialkanolamines with Dialkoxysilanes.** The classical method for the synthesis of cyclic organosilicon ethers of dialkanolamines is the reaction of an amino alcohol with a diorganodialkoxysilane. Historically this method became the first method for the production of such compounds [2-4] and was subsequently used widely in the synthesis of a large number of functionally substituted silocanes [5-16].



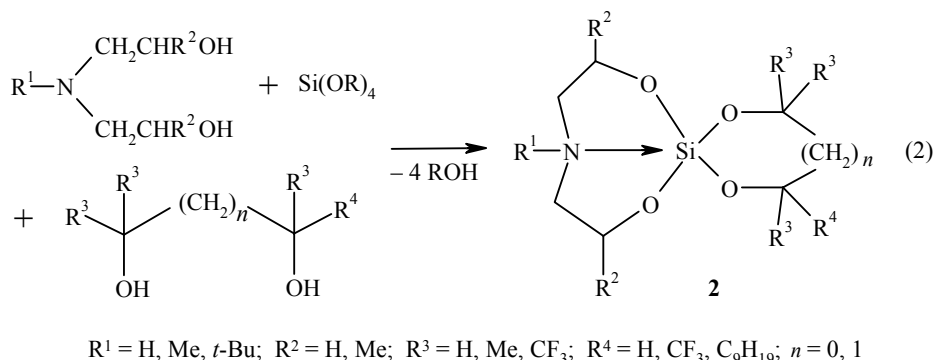
Dimethoxysilanes react more quickly than the diethoxy derivatives [7]. The yields of compounds **1** vary within wide limits between 29 and 95%, depending on the nature of the substituents  $R^1, R^4,$  and  $R^5$ . A decrease in the yields as a result of the formation of polymeric compounds was observed when  $HN(CH_2CH_2OH)_2$  was used [4, 8, 12, 17].

As a rule reaction (1) is carried out by heating an equimolar mixture of the reagents in the presence of an alkaline catalyst with simultaneous distillation of the alcohol that is formed. The process may be catalyzed by the diethanolamine itself [7], and in a number of cases the presence of the catalyst is not therefore essential. The presence of a substituent more electronegative than alkyl at the silicon atom facilitates transalkoxylation and does not require the presence of a catalyst [6, 9, 16, 18].

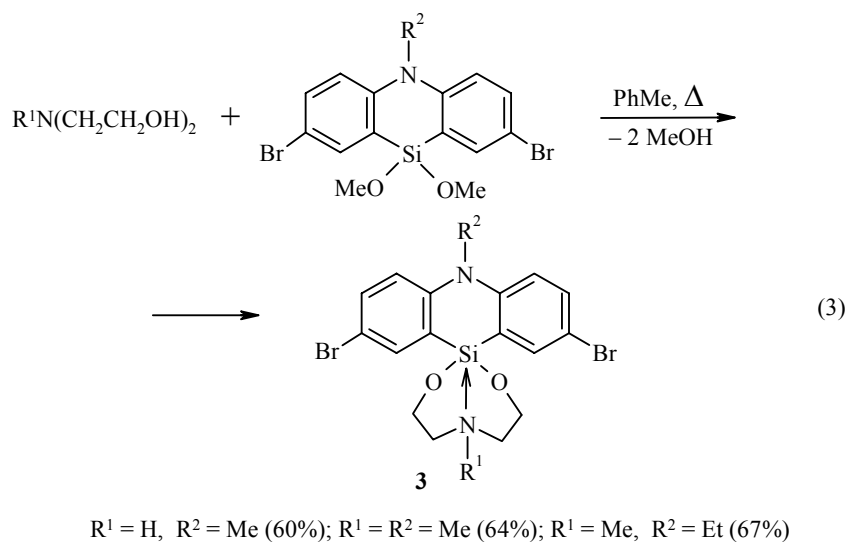
The use of trialkoxyarylsilanes  $ArSi(OR)_3$  leads to the production of silocanes containing an alkoxy group at the silicon atom. In this case too the reaction is conducted in the absence of a catalyst since otherwise the formation of polymeric compounds is observed [7, 9, 12, 13]. A tendency to form polymers is observed in

the reaction of equimolar amounts of dialkanolamine and tetraalkoxysilane. Only by careful realization of the reaction is it possible to isolate the monomeric silocanes with yields of 28-51% alongside the polymeric products [7]. The use of dimethoxyphenylsilane  $\text{Ph}(\text{H})\text{Si}(\text{OMe})_2$  and *N*-methyldiethanolamine methiodides in reaction (1) does not lead to the formation of the corresponding cyclic derivatives [7].

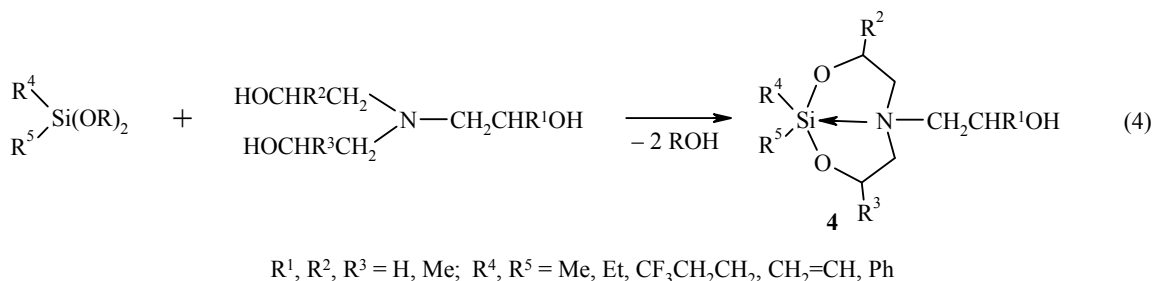
Mixed spirocyclic silicate esters of dialkanolamines **2** are produced with yields of 29-67% by the direct reaction of equimolar amounts of amino alcohol, alkanediol, and tetraalkoxysilane by heating with or without the presence of catalytic amounts of  $\text{MeONa}$  [19-22].



The spirocyclic silocanes **3**, in which the silicon atom is included in the rigid heterocyclic structure of 2,8-dibromo-5,10-dihydrophenazasilin, are formed when the reagents are boiled in toluene [17].



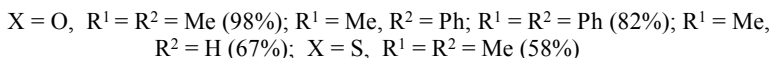
When tris(2-hydroxyalkyl)amines were used in the transesterification of dialkoxydiorganosilanes a series of silocanes **4** containing a 2-hydroxyalkyl group at the nitrogen atom were obtained [7, 13, 18, 23-26].



The transesterification of dialkyl- and alkyl(vinyl)dialkoxysilanes only occurs in the presence of an alkaline catalyst [23]. The possibility of obtaining 6-(2-hydroxyethyl)-1,3-dioxo-2,2-diphenyl-6-aza-2-silacyclooctane (**4**) ( $R^1 = R^2 = R^3 = H$ ,  $R^4 = R^5 = Ph$ ) with a yield of 12% under standard conditions was mentioned in [7, 13], but the authors did not give the experimental conditions. A preparative method was later described for the production of 2-phenyl-2-organosilocanes of type **4** ( $R^4, R^5 = Me, Et, Ph$ ;  $R^1 = R^2 = R^3 = H$ ) in dioxane in the presence of alkaline catalysts [25].

At the same time it was noted that under more rigorous conditions the S-C<sub>Ar</sub> bond is broken, and 1-organosilatrane are formed [18, 23, 27]. Analogous cleavage of the silicon-carbon bond was observed in the case of the reaction of (2-cyanoethyl)methyldiethoxysilane with triethanolamine in the presence of EtONa [24]. Removal of the chloromethyl group from chloromethyl(methyl)diethoxysilane takes place even more readily [18, 23, 25]. The intermediate products are high-molecular compounds, which decompose when heated above 150°C with the formation of 1-methylsilatrane and methyl chloride [23].

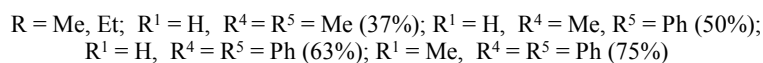
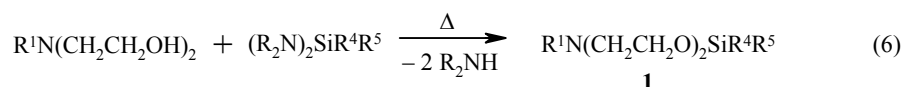
Transesterification is a convenient method for the synthesis not only of nitrogen-containing 1,3,6,2-dioxasilocanes but also of their oxygen and sulfur analogs (reaction 5, yield for  $R^1 = Me$ ,  $R^2 = Ph$ , not given in the literature source) [4, 13, 28, 29].



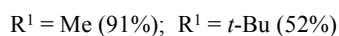
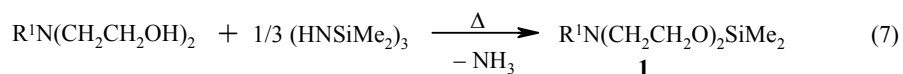
The synthesis was realized by heating with [4, 28] or without [29] the presence of an alkaline catalyst. It should be noted that it is possible to obtain hydride-substituted 1,3,6,2-trioxasilocane by the reaction of diethylene glycol with Me(H)Si(OEt)<sub>2</sub> [29]. Attempts to obtain an analogous derivative by the reaction of dialkanolamine with dimethoxyphenylsilane were unsuccessful [7].

In the literature there are fragmentary data on representatives of selenium-containing silocanes Se(CH<sub>2</sub>CHMeO)<sub>2</sub>SiR<sup>1</sup>R<sup>2</sup>, synthesized using transalkoxylation [30].

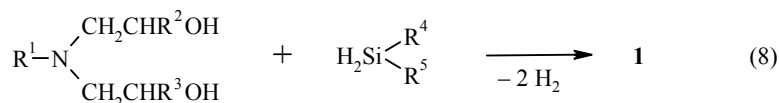
**1.1.2. Reaction of Dialkanolamines with Bis(dialkylamino)silanes.** An alternative approach to the production of cyclic silyl ethers of dialkanolamines is the reaction of amino alcohols with bis(dialkylamino)silanes (heat, 10-15 h) [7, 15, 31].



The use of bis(dimethylamino)silanes gives high yields of the cyclization products [7]. As initial silane for the synthesis of 2,2-dimethylsilocanes **1** ( $R^4 = R^5 = Me$ ) it was proposed to use hexamethylcyclotrisilazan [7, 32], which is less volatile and therefore more convenient to use than (Me<sub>2</sub>N)<sub>2</sub>SiMe<sub>2</sub>.



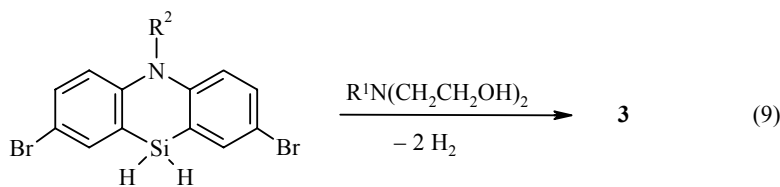
**1.1.3. Reaction of Dialkanolamines with Dihydrosilanes.** Apart from dialkoxy- and diaminosilanes phenyl-substituted hydrosilanes can also be used as starting reagents for the synthesis of 1,3-dioxa-6-aza-2-silacyclooctanes [7, 17, 29, 33]. When they are mixed with dialkanolamines at room temperature the vigorous release of hydrogen is observed, and the corresponding silocanes are formed.



R<sup>1</sup> = Me, R<sup>2</sup> = R<sup>3</sup> = H, R<sup>4</sup> = R<sup>5</sup> = Ph (87%) [7];  
 R<sup>1</sup> = Me, R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H, R<sup>5</sup> = Ph (24%) [7], (64%) [29];  
 R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = Me, R<sup>4</sup> = H, R<sup>5</sup> = Ph (33%) [7], (24%) [29];  
 R<sup>1</sup> = Et, R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H, R<sup>5</sup> = Ph (32%) [7];  
 R<sup>1</sup> = Ph, R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H, R<sup>5</sup> = Ph (18%) [7], (70%) [33]

With H<sub>3</sub>SiPh it is possible to obtain derivatives containing a hydride substituent at the silicon atom. In this case, however, the yield of the required silacyclooctanes is reduced. In the production of the N-phenyl-substituted silocane the yield is increased significantly if the synthesis is conducted in the presence of H<sub>2</sub>PtCl<sub>6</sub> [33].

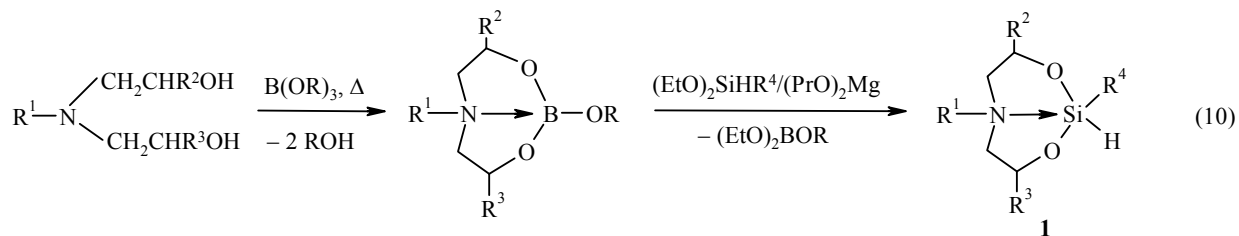
The possibility of using this method for the synthesis of spirocyclic silocanes of type **3** was studied in [17].



R<sup>1</sup> = R<sup>2</sup> = Me (25%); R<sup>1</sup> = Me, R<sup>2</sup> = Et (29%, in the presence of (Ph<sub>3</sub>P)<sub>3</sub>RhCl)

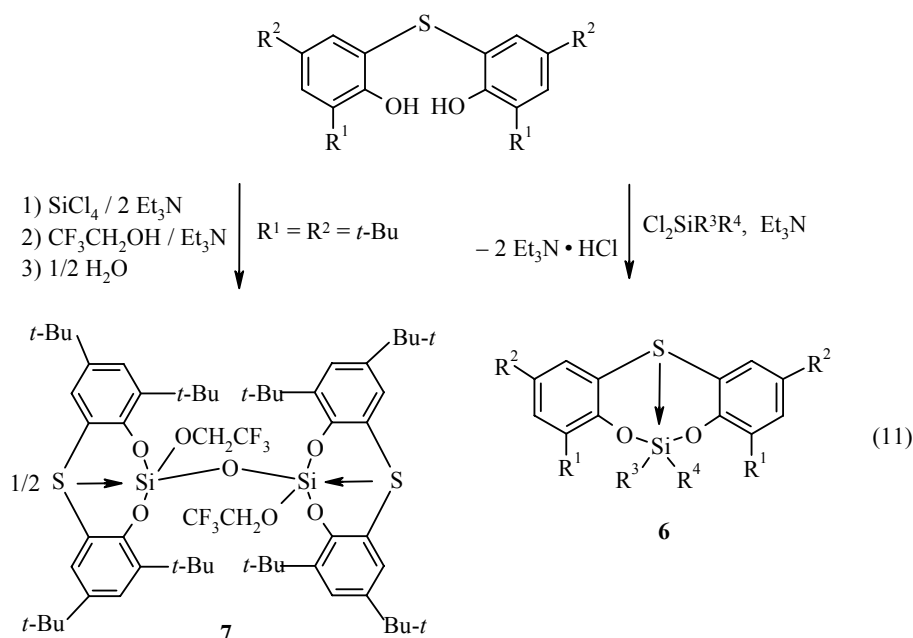
As in the case of phenylsilane, the formation of polymers leads to low yields of the desired compounds, while the addition of a catalyst based on Rh(I) only leads to an insignificant increase in the amount of the isolated silocane. It is better to use transalkoxylation (3) for the synthesis of compounds of type **3**.

A two-stage method of synthesis, involving treatment of the dialkylamine with trialkyl borate followed by reaction of the obtained 2-alkoxyboroxane with alkyldiethoxysilane, was proposed as a convenient approach to 2-alkyl-2-hydrosilocanes of type **1** [29, 33].



R = Me, Et, *i*-Am; R<sup>1</sup> = R<sup>4</sup> = Me, R<sup>2</sup> = R<sup>3</sup> = H (27%); R<sup>1</sup> = Me, R<sup>2</sup> = R<sup>3</sup> = H, R<sup>4</sup> = Et (45%); R<sup>1</sup> = Et, R<sup>2</sup> = R<sup>3</sup> = H, R<sup>4</sup> = Me (26%); R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = Me, R<sup>4</sup> = Me (34%)

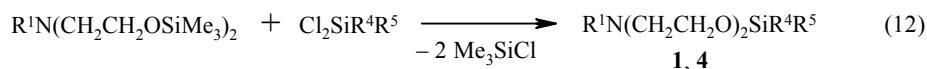
**1.1.4. Reaction of Bis(*ortho*-phenols) with Dichlorosilanes.** A series of sulfur-containing dibenzosilocanes **6** were obtained by the reaction of dichlorosilanes with the corresponding diols. The reaction mixture was kept at 25-55°C, and triethylamine was used to combine with the hydrogen chloride that formed [34-37].



$R^1 = R^2 = t\text{-Bu}$ ,  $R^3 = \text{H}$ ,  $R^4 = \text{Me}$  (56%);  $R^1 = R^2 = t\text{-Bu}$ ,  $R^3 = \text{H}$ ,  $R^4 = \text{Ph}$  (41%);  
 $R^1 = R^2 = t\text{-Bu}$ ,  $R^3 = \text{Me}$ ,  $R^4 = \text{Ph}$ ;  $R^1 = R^2 = t\text{-Bu}$ ,  $R^3 = R^4 = \text{Ph}$ ;  
 $R^1 = R^2 = t\text{-Bu}$ ,  $R^3 + R^4 = -(\text{CH}_2)_4-$  (89%);  $R^1 = t\text{-Bu}$ ,  $R^2 = R^3 = R^4 = \text{Ph}$  (70%);  
 $R^1 = t\text{-Bu}$ ,  $R^2 = \text{Me}$ ,  $R^3 = \text{Ph}$ ,  $R^4 = \text{Vin}$  (90%);  $R^1 = R^2 = R^3 = R^4 = \text{Me}$  (63%);  
 $R^1 = R^2 = \text{Me}$ ,  $R^3 = R^4 = \text{Ph}$  (95%)

The isolation of the 2,2-dichloro-substituted silocane **6** ( $R^3 = R^4 = \text{Cl}$ ) in the reaction with silicon tetrachloride was prevented by the occurrence of hydrolytic processes. At the same time treatment of the reaction mixture *in situ* with one equivalent of 2,2,2-trifluoroethanol followed by hydrolysis led to the formation of the cyclic disiloxane **7** [36].

**1.1.5. Reaction of Bis(trimethylsilyl) Ethers of Dialkanolamines with Dichlorosilanes, Dialkoxysilanes, and Diacetoxysilanes.** In addition to amino alcohols, it is possible to use their trimethylsilyl derivatives for the synthesis of 1,3-dioxo-6-aza-2-silacyclooctanes. A series of silocanes of types **1** and **4** were obtained by heating the bis(trimethylsilyl) ethers of diethanolamines and also triethanolamines with dichlorosilane [7, 38].

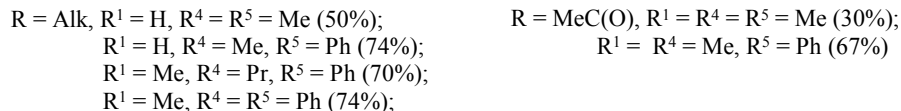
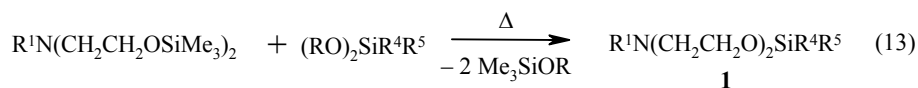


$R^1 = \text{H}$ ,  $R^4 = \text{Me}$ ,  $R^5 = \text{Ph}$  (25%);  $R^1 = \text{H}$ ,  $R^4 = \text{Cl}$ ,  $R^5 = \text{Ph}$  (100%);  
 $R^1 = R^4 = \text{Me}$ ,  $R^5 = \text{Vin}$  (60%);  $R^1 = R^5 = \text{Ph}$ ,  $R^4 = \text{Cl}$  (100%);  
 $R^1 = R^4 = \text{Me}$ ,  $R^5 = \text{Ph}$  (57%);  $R^1 = \text{Me}_3\text{SiOCH}_2\text{CH}_2$ ,  $R^4 = R^5 = \text{Me}$  (88%);  
 $R^1 = \text{H}$ ,  $R^4 = R^5 = \text{Ph}$  (49%);  $R^1 = \text{Me}_3\text{SiOCH}_2\text{CH}_2$ ,  $R^4 = \text{Me}$ ,  $R^5 = \text{Vin}$  (88%)

Compared with transalkoxylation, the yields are as a rule low and amount on the average to 50-60%. The decrease of the yields is due to the formation of a certain amount of polymeric compounds.

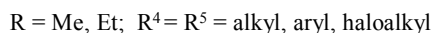
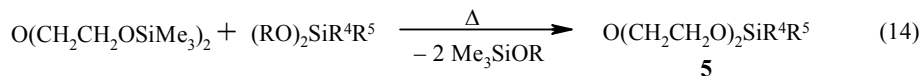
The method gives the best results in the case of phenyltrichlorosilane, since it makes possible to obtain 2-chloro-substituted silocanes with almost quantitative yields. The reaction of tris(2-trimethylsilyloxyethyl)-amine with phenyl-substituted silanes leads to the formation of silatranes [38].

Preparative methods for the production of 1,3-dioxo-6-aza-2-silacyclooctanes **1** are provided by the reactions of the silyl ethers of dialkanolamines with dialkoxy- and diacetoxysilanes [7].



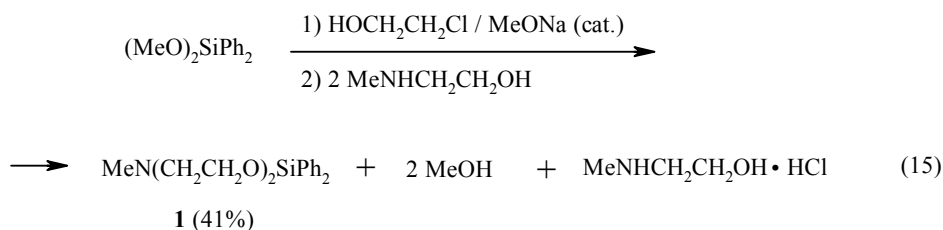
The reaction with dialkoxysilanes requires the presence of an alkaline catalyst, and the process takes place rather more slowly compared both with transesterification by the free dialkanolamines and with the above-mentioned reaction of silylated amino alcohols with dichlorosilanes. This method is of value for the synthesis of functionally substituted silocanes in the case where transalkoxylation cannot be used on account of side processes involving the hydroxyl groups of the amino alcohols. Diacetoxysilanes react readily according to Eq. (13) without a catalyst.

Like the reaction described above, the transsilylation of the bis(trimethylsilyl) ether of diethylene glycol with dialkoxysilanes was proposed for the synthesis of 1,3,6-trioxa-2-silacyclooctanes [30].

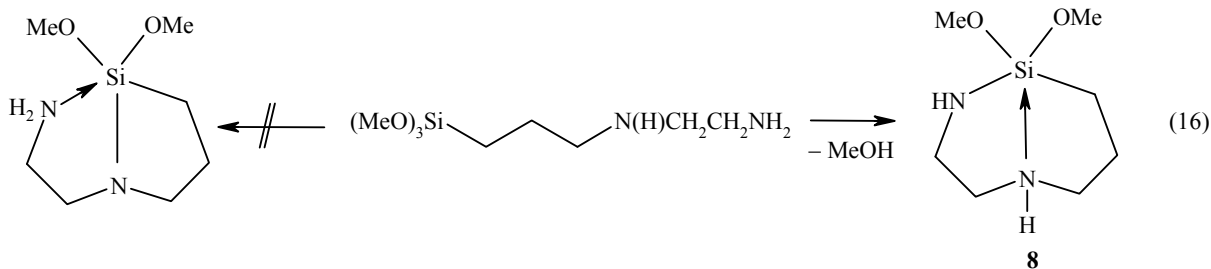


This method leads to high yields of the cyclization products. It should be noted that 2-chloromethyl-1,3,6-trioxasilocane can be obtained by reaction (14) given that its nitrogen-containing analog could not be synthesized by any of the known methods.

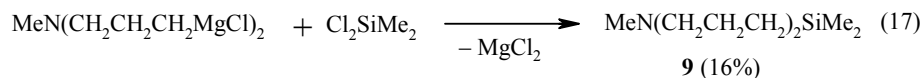
**1.1.6. Other Methods.** Silacyclooctane **1** (R<sup>1</sup> = Me, R<sup>2</sup> = R<sup>3</sup> = H, R<sup>4</sup> = R<sup>5</sup> = Ph) was obtained by a two-stage synthesis according to Eq. (15). At the first stage the dimethoxysilane reacts with the ethylene chlorohydrin in the presence of the sodium alkoxide with the formation of the 2-(chloroethoxy) derivative. Further treatment of the reaction mixture with N-methylethanolamine gives a moderate yield of the cyclization product [7].



1,6-Diaza-2-silacyclooctane (**8**) is formed when the corresponding acyclic derivative is heated [Eq. (16)]. Its structure was established by X-ray crystallographic analysis [39].



In the reaction of the organomagnesium derivative of bis(3-chloropropyl)amine with dimethyldichlorosilane the nitrogen-containing dicarbasilocane **9** was isolated. In spite of the high dilution the reaction was accompanied by the formation of a significant amount of oligomeric compounds [40].



## 1.2. Investigation of Silocanes by Physicochemical Methods\*

The initial interest in silocanes arose from the possibility of their practical use as catalysts for the vulcanization of polyester resins [2, 3]. Recent developments in the chemistry of hypervalent compounds of silicon have forced investigators to pay greater attention to the question of the presence of transannular bonding in the molecules of silocanes and its strength in comparison with the close structural analogs silatranes.

It is necessary to note that 2,2-diaryl, 2,2-dialkoxy, 2-aryl-2-halo, and 2-aryl-2-hydro derivatives of silacyclooctanes and also all N-phenyl-substituted silocanes are crystalline substances, but the larger part of the alkyl derivatives are high-boiling liquids. For this reason methods that make it possible to judge the structure of silocanes in the liquid phase and in solution, such as NMR spectroscopy, IR spectroscopy, and dipole moment determination, have been widely used in addition to X-ray crystallographic analysis. In addition, the structural characteristics of the compounds in the gas phase have been investigated by mass spectrometry. Greatest attention was paid to the question of the presence of transannular interaction in the molecule and also to the factors determining the strength of this interaction.

In contrast to the silatranes, the eight-membered ring of silocanes has the possibility of conformational isomerism, and the stability of one or the other conformer is determined to a considerable degree by the strength of the intramolecular bonding. Thus, study of the conformational equilibria also lay at the focus of investigations into compounds of the silocane class.\*<sup>2</sup>

**1.2.1. X-Ray Crystallographic Analysis.** The initial view that there was no transannular Si←N interaction in the molecules of silacyclooctanes [15] was disproved in 1974, when the first structural data for these compounds were published [41-43]. It was found that in the solid phase the Si←N distances are comparable with those in silatranes, for which at that time the presence of transannular bonding was considered to have proved both by physicochemical methods and by reactivity data [15].

At present the structures of 22 1,3-dioxa-2-silacyclooctanes have been investigated by X-ray crystallographic analysis. Fourteen of them contain a nitrogen atom as potential donor [10, 17, 20-22, 39, 41-44], seven contain a sulfur atom, and only in one of the investigated compounds is the potential electron donor an oxygen atom [28].

The most significant geometric parameters of the crystalline 1,3-dioxa-6-aza-2-silacyclooctanes are presented in Table 1. As seen from the presented data, the Si←N distance varies in the range of 1.99-3.20 Å. The shortest Si←N distances were found in the derivatives **2a-d** containing a cyclic ether group with strong

\* For chromatographic investigations of silocanes, see: V. D. Shatz, V. A. Belikov, I. P. Urtane, G. I. Zelchan, and E. Lukevics, *J. Chromatogr.*, **237**, 57 (1982). V. A. Belikov, V. D. Shatz, and E. Lukevics, *J. Chromatogr.*, **388**, 161 (1987) (Editor's Note).

\*<sup>2</sup> The conformational characteristics of silocanes are examined in: E. L. Kupche and E. Lukevics, *Conformational Characteristics of Elementocanes – Eight-Membered Heterocycles with 1,5-Transannular Interaction* [in Russian], Part II, Institute of Organic Synthesis, LatvSSR Akad. Sci, Riga (1986), 64 pp. (Editor's note).



TABLE 1. The Key Structural Characteristics of 1,3-Dioxo-6-aza-2-silacyclooctanes

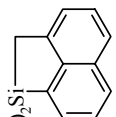
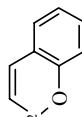
1	Compound 2	l, Å			Angle, deg. N-Si-X <sub>alk</sub>	ΔSi	ΔN	Conf.	Ref.
		Si←N	Si→X <sub>alk</sub> /Si-X <sub>alk</sub>	Si-O					
<b>2a</b>	HN(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> Si[-OC(CF <sub>3</sub> ) <sub>2</sub> C(CF <sub>3</sub> ) <sub>2</sub> O-] HN(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> Si[-OCH <sub>2</sub> CH <sub>2</sub> O-]	1.99(1)	1.732(8)	1.656	175.6(4)	0.09	0.42	BC	[44]
		2.004(3)	1.710(2)	1.665(3)	178.3(1)	0.10	—	—	[21]
<b>2b</b>	MeN(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> Si[-OC(CF <sub>3</sub> ) <sub>2</sub> C(CF <sub>3</sub> ) <sub>2</sub> O-]	2.032(7)	1.683(3)	1.667(2)	176.4(3)	0.09	0.45	BC	[20]
<b>2c</b>	MeN(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> Si[-OC(CF <sub>3</sub> ) <sub>2</sub> C(CF <sub>3</sub> ) <sub>2</sub> O-]	2.247(5)	1.731(6)	1.640(6)	174.1(2)	0.22	0.45	—	[22]
<b>2d</b>	MeN(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> Si[-OCMe <sub>2</sub> CH <sub>2</sub> CMe <sub>2</sub> O-]	1.690(5)	1.671(4)	1.643(4)	—	—	—	—	[43]
<b>10a</b>	MeN(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> Si- 	1.651(4)	1.901(7)	1.646(5)	—	0.16	—	—	
		2.263(6)	1.881(7)	1.658(5)	—	—	—	—	
<b>10b</b>	MeN(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> - 	2.297(6)	1.698(4)	1.636(6)	—	—	—	—	[42]
			1.851(6)	1.643(5)	—	—	—	—	

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10
<b>3a</b>	 <chem>CCN(CCOC)OCC1=CC=C(C=C1)N(C)Si1(C)OCN(CCOC)O1</chem>	2.968	1.87(1) 1.80(2)	1.65(1) 1.62(1)	170	—	—	BC	[17]
<b>3b</b>	 <chem>CCN(CCOC)OCC1=CC=C(C=C1)N(CC)Si1(C)OCN(CCOC)O1</chem>	2.986	1.848(8) 1.856(9)	1.637(6) 1.616(6)	170	—	—	BC	[17]
<b>1a</b>	 <chem>CCN(CCOC)OCC1=CC=C(C=C1)N(C2=CC=CC=C2)Si1(C)OCN(CCOC)O1C2=CC=CC=C2</chem>	2.301	1.901(6) 1.886(7)	1.644(5) 1.659(5)	174.0(3)	—	—	BB	[41]
<b>1b</b>	 <chem>CCN(CCOC)OCC1=CC=C(C=C1)N(C2=CC=CC=C2)Si1(C)OCN(CCOC)O1C2=CC=CC=C2</chem>	2.68(1)	1.88(1) 1.85(1)	1.62(1) 1.64(1)	170(1)	0.38	0.38	BB	[10]
<b>1c</b>	 <chem>CCN(CCOC)OCC1=CC=C(C=C1)N(C2=CC=CC=C2)Si1(C)OCN(CCOC)O1C2=CC=CC=C2</chem>	3.08(1)	1.87(1) 1.86(1)	1.63(1) 1.65(1)	164(1)	0.48	0.16	CC	[10]
<b>1d</b>	 <chem>CCN(CCOC)OCC1=CC=C(C=C1)N(C2=CC=CC=C2)Si1(C)OCN(CCOC)O1C2=CC=CC=C2</chem>	3.16(2)	1.95(3) 1.95(3)	1.63(2) 1.66(2)	167(1)	0.49	0.42	—	[10]
<b>1e</b>	 <chem>CCN(CCOC)OCC1=CC=C(C=C1)N(C)Si1(C)OCN(CCOC)O1C1=CC=C(C=C1)</chem>	3.19(1)	1.85(1) 1.83(1)	1.63(1) 1.63(1)	166(1)	0.50	0.12	CC	[10]

electron-withdrawing characteristics at the silicon atom. In compounds **2a-c** the coordination of the silicon atom is close to the ideal trigonal bipyramid, while the axial positions are occupied by the nitrogen atom and the fourth oxygen atom.

On the whole all the S–O bonds in these derivatives are significantly elongated in comparison with the analogous bonds in the related spirocyclic compound with a tetracoordinated silicon atom (OCMe<sub>2</sub>CMe<sub>2</sub>O)<sub>2</sub>Si [1.625(3) Å] [21]. A substantial difference is also observed between the lengths of the Si–O bonds. The axial Si–O bond is significantly longer than the equatorial bonds at the silicon. Here the equatorial Si–O bond in the dioxasilacyclopentane fragment is somewhat longer (by ~0.05 Å) than for the equatorial Si–O bonds of the eight-membered ocane ring, which can probably be explained by stronger strain in the five-membered ring [21, 44]. In the change to the less strained six-membered ring in compound **2d** the difference in the lengths of the equatorial S–O practically disappears (~0.01 Å).

The presence of the methyl group bulkier than hydrogen at the nitrogen atom only leads to small elongation of the transannular Si←N bond in compound **2c** (by 0.03 Å) compared with that in the molecule of **2a**. At the same time the presence of the methyl group instead of a hydrogen atom at the nitrogen atom and the six-membered spirocycle instead of the five-membered spirocycle at the silicon atom leads to an increase of 0.25 Å in the Si←N distance in compound **2d** compared with **2b** and also to greater distortion of the coordination of the silicon atom from trigonal-bipyramidal in **2d**.

All three five-membered heterocycles in compounds **2a-c** are nonplanar. The five-membered rings containing the dative Si←N bond have the *envelope* form with projection from the plane of the carbon atoms at the  $\alpha$ -position to the nitrogen atom.

Decrease of the number of oxygen atoms at the silicon to three and two in the spirocyclic compounds **10b** and **10a** leads to some increase in the lengths of the transannular Si←N bond to 2.263(6) in **10a** and 2.297(6) Å in **10b**.

The effect of electronic and steric factors on the geometric characteristics of the silocane molecules can be traced most clearly during examination of the series of derivatives **1a-e**. Compounds **1a,b,d** with two phenyl groups at the silicon atom differ in the nature of the substituents at the nitrogen atom. X-ray crystallographic investigation showed that the interatomic silicon–nitrogen distance and also the  $\Delta$ Si value for the projection of the silicon atom from the plane of the equatorial substituents increase in the order H < Me < *t*-Bu, i.e., the coordination environment of the silicon atom changes from trigonal-bipyramidal to tetrahedral. Such changes do not correspond to the increase in the donor capacity of the substituents, but they do agree with the increase in their steric volume. Consequently, in the silocanes **1** with alkyl groups at the nitrogen atom the steric effects of the substituents predominate over the electronic effects and thus have a determining effect on the strength of transannular Si←N interaction in the molecule. In compound **1d** with the bulky *tert*-butyl substituent interaction between the silicon and nitrogen atoms is absent [10].

The action of the electronic factors shows up in the case of the silocanes **1c,e**, in which the nitrogen atom is bonded to the phenyl substituent. In these compounds the unshared pair of the nitrogen atom is involved in *p*– $\pi$  interaction with the  $\pi$ -system of the phenyl ring, as a result of which the transannular Si←N bond is not formed [10]. In spite of the absence of intramolecular interaction in these derivatives one of the substituents at the silicon atom occupies a pseudoaxial position.

The degree of transannular interaction of the nitrogen and silicon atoms in the silacyclooctanes determines to a significant degree the ability of the eight-membered heterocycle to adopt one or the other conformation. As a rule the molecules with a relatively short Si←N distance in the solid phase exist in the *boat–boat* (**1a,b**) or *boat–chair* (**2a,c**) conformation, whereas in the absence of intramolecular coordination the characteristic form of the molecule becomes the *chair–chair* conformation (**1c, e**) with the silicon and nitrogen atoms most widely separated in space [10, 44].

Compounds **3a,b** are formally structural analogs of 6-methyl-2,2-diphenylsilocane (**1b**). In spite of the fact that the eight-membered ocane ring in both cases has the identical *boat–chair* conformation the interatomic silicon–nitrogen distances in the derivatives **3a,b** are substantially longer ( $\Delta = 0.29, 0.31$  Å) than in compound

**1b**. This is due to the steric requirements of the tricyclic phenazasilin fragment and, in particular, the rigid fixation of the phenyl rings in relation to each other. The strictly defined orientation of the substituents at the silicon atom, in contrast to compound **1b**, does not permit approach of the nitrogen atom and the silicon center, and this is the reason for the absence of clearly defined Si←N interaction in molecules of type **3** [17].

It is necessary to mention certain correlations between the geometry characteristics obtained from analysis of the X-ray crystallographic data for the molecules of 1,3-dioxa-6-aza-2-silacyclooctanes. The relation between the silicon–nitrogen distance and the displacement  $\Delta\text{Si}$  of the silicon atom from the plane formed by the three equatorial substituents was obtained from data for 12 compounds and is described by the following equation:

$$\Delta\text{Si} = 0.332d(\text{Si}\leftarrow\text{N}) - 0.549 \quad (r = 0.990) \quad [44].$$

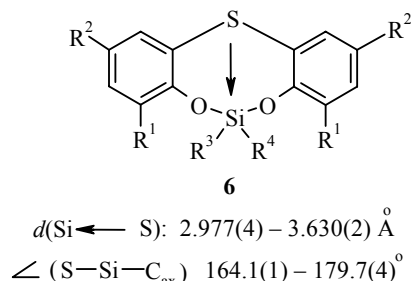
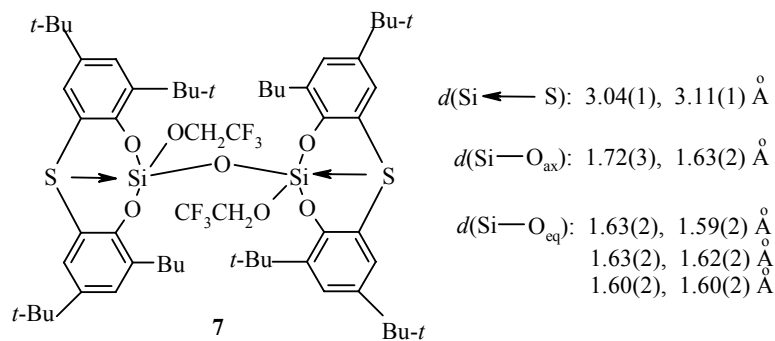
The proportionality coefficient in this equation is smaller than that obtained for the molecules of silatranes, i.e., the  $\Delta\text{Si}$  value in the silocanes increases to a lesser degree with increase in the interatomic Si←N distance. This indicates a greater contribution from steric factors acting on the interatomic Si←N distance in the molecules of silocanes compared with silatranes [44].

For a large number of compounds with a pentacoordinated silicon atom containing a nitrogen atom as donor of electron density, including silocanes, a linear relation was found between the N–Si–X<sub>eq</sub> angle and the Si←N distance:

$$\text{N–Si–X}_{\text{eq}} = 120.9 - 17.4d(\text{Si}\leftarrow\text{N}) \quad (r = 0.99) \quad [21].$$

Yet another compound with an intramolecular Si←N bond, the structure of which has been studied by X-ray crystallographic analysis, is 2,2-dimethoxy-1,6-diaza-2-silacyclooctane, HN(CH<sub>2</sub>CH<sub>2</sub>NH)(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Si(OMe)<sub>2</sub> (**8**) [39]. The compound has a bicyclic structure with a pentacoordinated silicon atom. The Si←N distance [2.126(1) Å] is close to the lower limit of the range of values observed in compounds of the silocane type. The fairly strong transannular interaction is due to the presence of the  $\sigma$ -electron-withdrawing methoxy groups at the silicon atom and the hydrogen atom at the nitrogen not creating steric hindrances.

A series of compounds **6a–f** and **7**, in which the eight-membered ring contains a sulfur atom capable of acting as a donor of electron density, have been studied by X-ray crystallographic analysis [34–36]. Analysis of the structural data showed the existence of transannular Si←S interaction of various strengths (2.98–3.63 Å, sum of the van der Waals radii of the Si and S atoms 3.90 Å) in these derivatives. The observed Si←N bond lengths correspond to approximately 35–55% shift of the coordination environment of the silicon from tetrahedral to trigonal bipyramid. In the formed trigonal bipyramid the sulfur atom occupies the axial position.



- 6 a** R<sup>1</sup> = R<sup>2</sup> = *t*-Bu, R<sup>3</sup> = H, R<sup>4</sup> = Ph; **b** R<sup>1</sup> = R<sup>2</sup> = *t*-Bu, R<sup>3</sup> = Me, R<sup>4</sup> = Ph; **c** R<sup>1</sup> = R<sup>2</sup> = *t*-Bu, R<sup>3</sup> = R<sup>4</sup> = Ph; **d** R<sup>1</sup> = *t*-Bu, R<sup>2</sup> = Me, R<sup>3</sup> = Ph, R<sup>4</sup> = Vin; **e** R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = Me; **f** R<sup>1</sup> = R<sup>2</sup> = Me, R<sup>3</sup> = R<sup>4</sup> = Ph

As a result of the greater +I effect of the *tert*-butyl substituents the introduction of *tert*-butyl substituents into the *o*-phenylene fragments in place of the methyl groups leads to an increase in the donor capacity of the sulfur atom, resulting in increased interaction between the sulfur and silicon atoms.

With the comparatively strong transannular Si←O interaction the eight-membered silocane ring of the molecule adopts a symmetrical or somewhat distorted *boat–boat* conformation. In the case of the derivative **6f**, for which the longest Si←S distance [3.630(2) Å] among the investigated series of compounds was found, the conformation of the eight-membered ring is described as *boat–chair*.

In the molecule of the only structurally characterized 1,3,6-trioxa-2-silacyclooctane O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>SiPh<sub>2</sub> **5a** only slight distortion of the tetrahedral coordination of the silicon atom toward the trigonal bipyramid is observed, and the oxygen atom at position 6 of the ocane ring occupies the axial position [28]. The Si←O distance amounts to 2.976(5) Å, which is ~0.5 Å less than the sum of the van der Waals radii of the silicon and oxygen atoms (3.50 Å) [45]. The eight-membered ring in the molecule of **5a** has a distorted *crown* conformation. It can be seen that the Si←O interaction is considerably weaker than the Si←N interaction in structurally similar silocanes. This is consistent with the greater donor capacity of the nitrogen atom compared with the oxygen atom.

**1.2.2. NMR Spectroscopy.** The <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si, and <sup>15</sup>N NMR spectra for 1,3-dioxa-6-aza-2-silacyclooctanes with various substituents at the nitrogen and silicon atoms have been studied well. The largest contribution to systematic investigation of the spectral characteristics with a view to determining the effect of the nature of the substituents in the molecule on the strength of the Si←N interaction and also on the conformational transformations in solution has been made by the group of E. Lukevics, as reflected in the number of publications [9, 11, 12, 44, 46, 47]. The effect of the nature of the solvent on the position of the resonance signals of the <sup>29</sup>Si and <sup>15</sup>N nuclei [48] and, in addition, the possibility of using solid-phase <sup>29</sup>Si NMR spectroscopy to assess the intramolecular interactions in the cyclic silicon ethers of alkanolamines in the crystalline state [49] were studied in detail.

For compounds of the R<sup>1</sup>N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>SiR<sup>4</sup>R<sup>5</sup> type **1** the signals for the methylene protons of the eight-membered heterocycle can appear in the form of triplets, corresponding to the degenerate AA'XX' spin system, or as multiplets forming an ABXY system. The form of the signals is determined by the conformational mobility of the ring at the given temperature, which in turn depends on the strength of the transannular Si←N bonding. In the case of silocanes of the HOCHR<sup>1</sup>CH<sub>2</sub>N(CH<sub>2</sub>CHR<sup>2</sup>O)(CH<sub>2</sub>CHR<sup>3</sup>O)SiR<sup>4</sup>R<sup>5</sup> type **4** (R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> ≠ H) the proton spectra are significantly complicated. The reasons for the complication are both the conformational nonuniformity of the molecules in the solution and the formation of diastereomeric forms. A detailed examination of these questions was presented in [26, 44].

The chemical shifts of the protons of the NCH<sub>2</sub> groups of the silocane ring only undergo a very small downfield shift in relation to the signals of the initial diethanolamine [11, 12, 44]. This indicates an insignificant degree of "quaternization" of the nitrogen atom and partial transfer of charge along the S←N bond in the molecules of the silocanes. The downfield shift increases with increase in the electron-withdrawing characteristics of the substituents at the silicon atom as also in the case of the NH derivatives. The existence of bonding is also demonstrated by the geminal nonequivalence of the protons of the NCH<sub>2</sub> groups observed in the compounds with two different substituents at the silicon atom [12, 44].

As a rule, for derivatives containing an aromatic substituent at the silicon atom the resonance signal for the alkyl group at the nitrogen atom is shifted significantly upfield (~0.8 ppm) in comparison with the initial amino alcohol as a result of the effect of the ring currents of the aryl substituents [11, 12, 44, 48, 50]. With decrease in temperature the signals for the methyl protons at the nitrogen atom undergo a further upfield shift. An analogous shift of the signals is observed for the *ortho*-protons of the phenyl groups at the silicon. Such temperature changes in the position of the signals in the <sup>1</sup>H NMR spectra are regarded as direct evidence for the existence of the *chair–chair – boat–boat* conformational equilibrium of the silocane molecules in the solution [11, 12]. It was established that increase in the electron-donating capacity of the substituents at the silicon and

also increase in the size of the substituent at the nitrogen atom lead to a shift of the equilibrium toward the *chair-chair* conformation, which is characterized by the absence of Si←N interaction. If the temperature of the solution is reduced the fraction of the *boat-boat* conformation with the Si←N bond is increased [11].

In the  $^{13}\text{C}$  NMR spectra the presence of the Si←N bond shows up as an upfield shift of the resonance signals for the carbon atoms attached to the nitrogen atom in relation to the N-substituted diethanolamines [12, 44, 46]. This corresponds to partial transition of the nitrogen to the quaternized state, and the degree of Si←N interaction decreases appreciably in the order  $\text{NMe} > \text{N-}t\text{-Bu} > \text{NPh}$  [44, 46]. The carbon atoms at the *para* positions of the phenyl groups at the silicon and the  $\alpha$ -carbon atoms of the SiMe groups also show a change of the chemical shifts in relation to those observed in the model compounds (the methiodides of silocanes, characterized by the absence of intramolecular interaction) [44, 46].

During study of the chemical shifts of the  $^{13}\text{C}$  nuclei of the furyl fragments in 2-ethoxy-2-(2-furyl)- and 2,2-di(2-furyl)-substituted silocanes it was found that the accepting characteristics of the silocane substituent  $-\text{Si}(\text{OCH}_2\text{CH}_2)_2\text{NMe}$  are somewhat higher than for the silatrane group  $-\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$  but weaker than in the case of the triethoxysilyl substituent  $-\text{Si}(\text{OEt})_3$ . This is consistent with the additional donating influence of intramolecular Si←N interaction in silocanes, which is however weaker than in silatranes [9].

The resonance of the  $^{29}\text{Si}$  nuclei in the silocane derivatives is observed in the upfield region compared with the corresponding diethoxysilanes [5, 11, 44, 46, 50]. It was demonstrated that such a shift is due directly to change in the coordination number of the silicon atom [11] and provides unequivocal evidence for the presence of transannular Si←N interaction in the silocanes in solution. The  $\Delta\delta^{29}\text{Si}$  shift decreases with increase in the volume of the substituent at the nitrogen atom, indicating weakening of the interaction [11, 44, 46]. Thus, the effect of the steric factors in the substituents at the nitrogen on the strength of transannular Si←N bonding, established by X-ray crystallographic analysis for the solid phase [10], is also present in the solution.

As a result of study of the temperature changes in the  $^{29}\text{Si}$  NMR spectra of silocanes in various solvents [48] it was established that increase in the polarity of the solvent leads to strengthening of the Si←N bond. Increase in the basicity of the solvent (for the NH derivatives) and also decrease in temperature also lead to strengthening of this bond.

For silicones with two different substituents at the silicon atom splitting of the  $^{29}\text{Si}$  signals with decrease of temperature is observed [47], indicating the presence of two conformers in the solution. A dissociative mechanism was proposed for the exchange between the conformers with different equatorial-axial arrangement of the substituents [11, 44]. It should be noted that the sterically strained equatorial position in the trigonal bipyramid corresponds to the less favorable axial orientation of the substituent in the eight-membered heterocycle. This conflict of "conformational tendencies," which substantially affects the position of the conformational equilibrium, was studied in detail in the work of E. Lukevics and his coworkers [47].

During investigation of the  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectra for 1,3,6-trioxa-2-silacyclooctanes  $\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{SiR}^4\text{R}^5$  **5** ( $\text{R}^4, \text{R}^5 = \text{Me, Pr, Ph, OMe}$ ) it was found that the chemical shifts hardly differ at all from those observed in the corresponding diethoxysilanes [51].\* Low-temperature experiments made it possible to establish an inversion barrier for the eight-membered ring ( $\Delta G_c \sim 8$  kcal/mol), which was lower than in the nitrogen-containing silocanes ( $\Delta G_c \sim 12$  kcal/mol) [11]. On the basis of the obtained results it was concluded that transannular Si←O interaction is absent in the investigated series of compounds or it has purely electrostatic character.

During the investigation of silocanes using  $^{15}\text{N}$  NMR spectroscopy it was established that in most cases the resonance signals of the nitrogen are observed in the upfield region compared with the corresponding diethanolamines [44, 46, 52]. The shift of the  $^{15}\text{N}$  resonance  $\Delta\delta$  is determined by two factors: 1) the degree of transfer of charge along the Si←N bond; 2) the steric repulsion of the  $\text{SiR}^4\text{R}^5$  and  $\text{NR}^1$  groups. Increase in the

\* For the  $^{29}\text{Si}$  NMR spectra of compounds **5** and their S-analog, see also: E. Kupce and E. Lukevics, in: *Isotopes in the Physical and Biomedical Science* (E. Buncel and J. R. Jencks, Eds.), Elsevier Science Publishers, Amsterdam (1991), Vol. 2, p. 213 (Editor's note).

degree of charge transfer gives rise to a downfield shift of the signal  $\delta^{15}\text{N}$ , whereas the steric effects lead to upfield displacement of the chemical shifts of the nitrogen. Thus, the shift of the signal in relation to the initial amino alcohols observed in silocanes is due largely to steric interactions of the N- and Si-substituents, while the comparatively small values of  $\Delta\delta^{15}\text{N}$  [(-0.2)-(-11.7) ppm] are due to the opposite effect of the steric and electronic effects in the transition of the molecule to the bicyclic conformation [44, 52]. It should be noted that the position of the signal for the nitrogen atom in spirocyclic silocanes of type **2**, in the molecules of which the shortest Si←N bond was found, is shifted downfield, although by a small amount. For the methiodides **11** the downfield shift in relation to the dialkanolamines is  $\Delta\delta^{15}\text{N} = \sim 25$  ppm.

Evidence for the existence of transannular Si←N interaction in silocanes is provided by the obtained relation between the  $\delta^{15}\text{N}$  chemical shifts and the Taft induction constants of the substituents at the silicon atom. The corresponding correlations are presented in [44, 46]. It should be noted that a similar relationship between  $\delta^{15}\text{N}$  and  $\Sigma\sigma^*(\text{R}^4\text{R}^5)$  is not observed in the series of N-methylsilocane methiodides, where the Si←N bond is impossible.

For the N-methyl derivatives the shift of the resonance signal of the silicon in relation to the diethoxysilanes  $\Delta\delta^{29}\text{Si}$  is related linearly to the difference  $\Delta\delta^{15}\text{N}$ :

$$\Delta\delta^{29}\text{Si} = (-28.3 \pm 11.0) + (-1.85 \pm 1.0)\Delta\delta^{15}\text{N} \quad (r = 0.958)$$

The value of the slope in this equation indicates that the resonance of the  $^{29}\text{Si}$  nucleus in the N-methylsilocanes is more sensitive to the interaction of the nitrogen and silicon atoms than the  $^{15}\text{N}$  resonance [46].

The dependence of the signals in the  $^{15}\text{N}$  NMR spectra on temperature and the nature of the solvent is similar to that examined above for the chemical shifts of the silicon nuclei. The screening of the nitrogen increases with increase of temperature and with decrease of the solvent polarity [48].

The  $^{29}\text{Si}$ - $^{15}\text{N}$  spin-spin coupling constants through the Si←N coordination bond depend in a complex manner on the nature of the substituents at the nitrogen and silicon atoms. The  $^1J(^{29}\text{Si}-^{15}\text{N})$  values lie in the range between 0 and 10 Hz. For the spirocyclic N-methylsilocanes a linear correlation was obtained between the free energy of activation for cleavage of the Si←N bond and the spin-spin coupling constants between the nitrogen and silicon nuclei forming this bond:

$$\Delta G_c^\ddagger = 51.5 + 5.11^1J(^{29}\text{Si}-^{15}\text{N}) \quad (r = 0.999)$$

At the same time it was shown that, in contrast to covalent Si-N bonds, the  $^1J(^{29}\text{Si}-^{15}\text{N})$  values for the Si←N coordination bonds can increase with decrease in the electronegativity of the substituents at the silicon. Consequently, analysis of the observed values of the  $^{29}\text{Si}$ - $^{15}\text{N}$  spin-spin coupling constants in the case of transannular Si←N interaction in silocanes requires a degree of caution [44, 53].\*

Silocanes of the  $\text{X}(\text{CH}_2\text{CH}_2\text{O})_2\text{SiMe}_2$  type (X = RN, O, S) were investigated by  $^{17}\text{O}$  NMR spectroscopy [51, 54]. The derivatives for which preferential existence in the *crown* conformation in solution was established show a downfield shift of the  $^{17}\text{O}$  resonance signals by 7-10 ppm in relation to the compounds having the preferred *chair-boat* conformation in solution. The observed relationships were explained on the basis of the idea of the existence of an anomeric effect in the molecules of the silocanes.

**1.2.3. Dipole Moments.** The values of the dipole moments can provide an important test for transannular interaction in the molecules of silacyclooctanes in solution. The dipole moments ( $\mu$ ) for ten silocanes of the  $\text{R}^1\text{N}(\text{CH}_2\text{CH}_2\text{O})_2\text{SiR}^4\text{R}^5$  type **1** were measured in benzene solutions [12, 15] and in the liquid

\* For the  $^{29}\text{Si}$ - $^{15}\text{N}$  spin-spin coupling constants in silocanes, see also: E. L. Kupce and E. Lukevics, *Usp. Khim.*, **58**, 1777 (1998) (Editor's note).

phase [8]. In the case of the NH- and N-alkyl-substituted derivatives containing methyl, methoxy, and phenyl groups at the silicon atom the obtained values lie in the range of 2.52-3.63 D, whereas for N-phenyl-2,2-dimethylsilocane  $\mu = 1.44$  D.

The experimental values were compared with the calculated values for the *boat-boat* conformation with and without the Si←N bond and also the *chair-chair* [8] or *crown* [12, 15] conformations. It was suggested on the basis of the obtained results that, with the exception of the N-phenyl derivatives, the molecules of the silocanes in the liquid state and in solution are in a conformational equilibrium [8, 12], where the extreme forms can be regarded as the *boat-boat* conformation, characterized by the steric proximity of the Si and N atoms and the possible formation of the Si←N donor-acceptor bond, and the *chair-chair* conformation, in which transannular interaction is impossible.

The difference between the dipole moments for the investigated silocanes calculated with and without dative S←N interaction amounts to  $\sim 2.0$  D. This corresponds to the transfer of charge  $0.18 \bar{e}$ , whereas the analogous value in the corresponding derivatives of triethanolamine (silatranes) is  $0.20 \bar{e}$  [12].

Thus, it was concluded on the basis of the investigations of the dipole moments that a transannular Si←N donor-acceptor bond exists in silocanes containing aromatic substituents at the silicon atom and alkyl substituents or hydrogen at the nitrogen atom. In the opinion of the authors [8, 15] this interaction is much weaker than that in silatranes.

**1.2.4. Mass Spectrometry.** To confirm the hypothesis about the presence of transannular interaction in the molecules of silocanes an investigation was undertaken into the dissociation of a series of derivatives of the  $R^1N(CH_2CHR^2O)_2SiR^4R^5$  type **1** under electron impact [5, 13, 14, 44, 55, 56].

The mass spectra of the compounds with  $R^4, R^5 = Me, OMe, Ph$  are characterized by low intensity for the molecular ion, although the last compound is stabilized a little by the presence of the phenyl and also the N-(trimethylsilyl)carboxamidomethyl substituent at the nitrogen atom [13, 55]. Two main parallel directions of primary fragmentation in the silocanes were identified.

The *first* direction (the so-called silatrane type of fragmentation) includes removal of the  $R^4$  or  $R^5$  radical (more vigorously for the phenyl) with the formation of ions in which the donor-acceptor bond between the nitrogen and silicon atoms is retained, being converted into a covalent bond.

The *second* direction (the amine type of fragmentation) is the  $\alpha$ -cleavage typical of amines in the presence of an alkyl substituent at the nitrogen atom. The Si←N bond is absent in the obtained fragment.

The obtained primary fragment ions then eliminate the molecules of oxiranes or aldehydes. In silocanes with strong Si←N interaction the unshared pair of the nitrogen atom is not very accessible for electron impact during ionization, and therefore the first fragmentation path clearly prevails in such compounds. In accordance with this a method for qualitative comparison of the degree of donor-acceptor interaction in a series of compounds of the same type on the basis of analysis of mass-spectrometric data for silocanes **1** with a spirocyclic silicon atom ( $R^4 + R^5 = -CH_2CH=CHCH_2-$ ) was proposed in [14].

During investigation of the mass-spectral dissociation of the spirocyclic derivatives **1** ( $R^4 + R^5 = -CH_2CH=CHCH_2-$ ) [14] and **2** [19, 44] preferred dissociation of the smaller ring was discovered, indicating stabilization of the eight-membered nitrogen-containing ring on account, probably, of the Si←N coordination bond.

The mass spectra of 1,3,6-trioxa-2-silacyclooctanes **5** ( $X = O, R^1, R^2 = Me, Ph$ ) are characterized by the low intensity or absence of the molecular ion. The initial fragment ions are formed by ejection of the radical from the silicon atom, and the  $H_2O, H_2CO,$  and  $CH_2CH_2O$  molecules are then eliminated. In comparison with 1,3-dioxa-6-aza-2-silacyclooctanes the mass spectra of the oxygen analogs are characterized by a reduced fraction of primary fragment ions in the total current. This indicates relative destabilization of these ions by virtue of the absence of the Si←N donor-acceptor bond in the molecules of compound **5** ( $X = O$ ) [13].

The  $[M^+ - H]$  ions and the protonated form of the respective dialkanolamine  $[R^1(H)N(CH_2CHR^2OH)(CH_2CHR^3OH)]^+$  appear in the mass spectra of silocanes of type **1** ( $R^1 = Me, t-Bu, Ph, R^2, R^3 = H, Me, R^4 = R^5 = Me, Ph, p-tolyl$ ) obtained by fast-atom bombardment (FAB) [57]. On the whole the

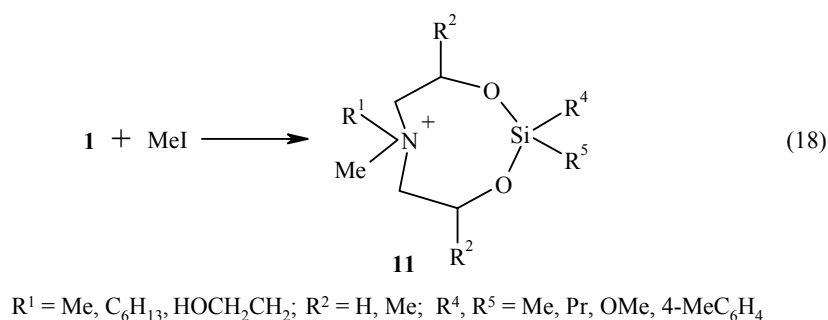


fragmentation paths retain the features observed above during examination of the dissociation of silocanes under electron impact. Thus, both methods make it possible to reach analogous conclusions about the weakening of the Si←N donor–acceptor interaction in the presence of a bulky *tert*-butyl or electron-withdrawing phenyl substituent at the nitrogen atom both in the gas phase and in the condensed phase.

Mass spectrometry has been used in a number of papers [17, 37, 39, 40] to confirm the structure of the obtained derivatives of silacyclooctanes.

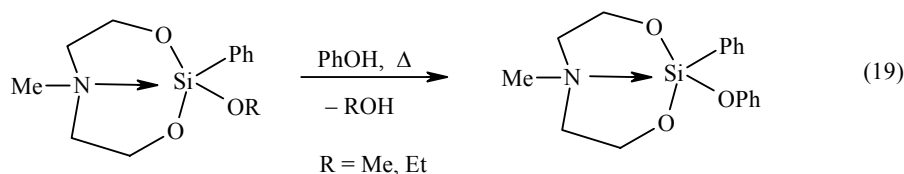
### 1.3. Reactivity of Silocanes

**1.3.1. Reaction with Methyl Iodide.** Unlike silatranes, the silocanes **1** containing alkyl substituents at the nitrogen atom enter into reaction with methyl iodide, forming the corresponding methiodides **11** [7, 15], which are crystalline substances with melting points above 150°C.

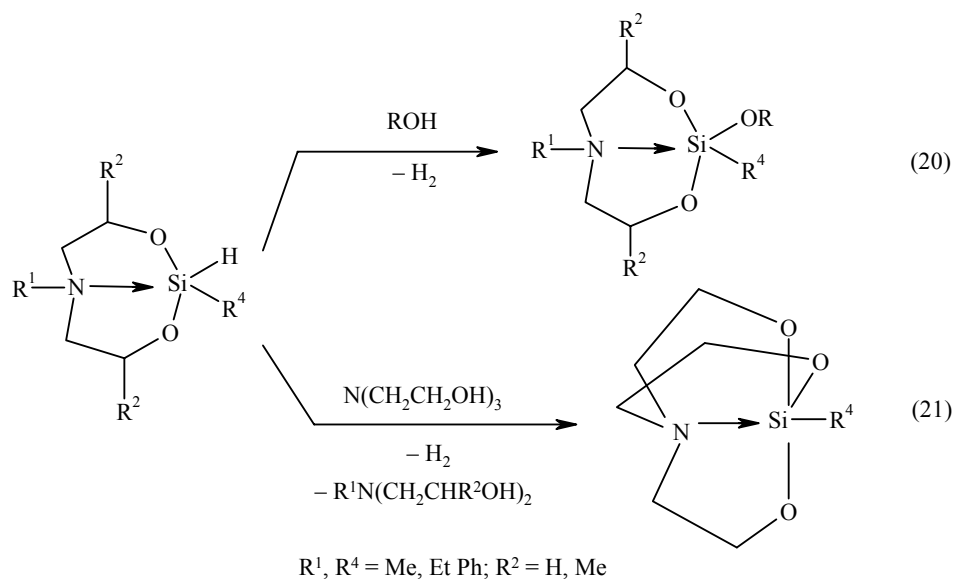


The ease of the process depends substantially on the strength of transannular bonding in the molecule. In the series of N-methylsilocanes the reaction rate decreases appreciably with increase in the Si←N interaction. Silocanes with a bulky *tert*-butyl group and also the N-phenyl derivatives are inert toward methyl iodide both at room temperature and with heating [7].

**1.3.2. Change of Substituent at the Silicon Atom.** Replacement of the alkoxy substituent by a phenoxy group in 2-alkoxy-2-phenylsilocanes by heating with phenol in the presence of sodium alcoholate with simultaneous distillation of the alcohol that forms can provide a good method for the production of the 2-aryloxy derivatives of silacyclooctanes [7, 12].

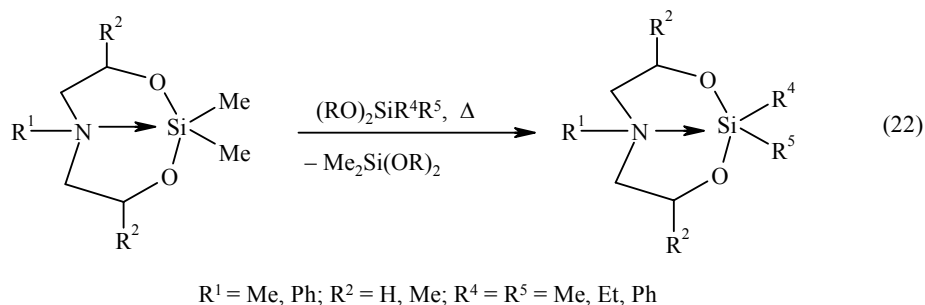


When heated with alcohols the silocanes with a hydride substituent at the silicon are transformed into the corresponding 2-alkoxy-2-organo derivatives. Treatment of the same compounds with triethanolamine leads to the formation of 1-alkyl- or 1-phenylsilatranes [33].



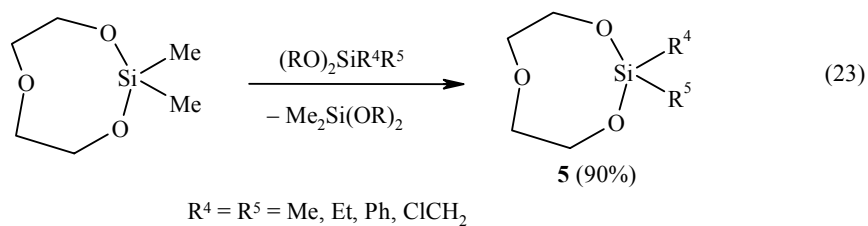
The reaction with triphenylchloromethane, characteristic of 1-hydrosilatrane, does not occur in the case of 2-hydro-2-phenyl-substituted silocanes **1** [33].

**1.3.3. Transsilylation.** In reaction with the heavier diorganodialkoxysilanes the simplest silocanes, such as the 2,2-dimethyl derivatives, undergo recyclization. The reaction can be used as a method for the synthesis of higher silacyclooctanes of type **1** [5, 58, 59].

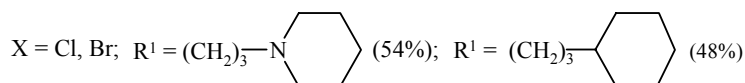
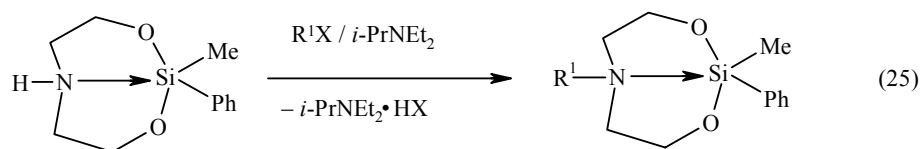
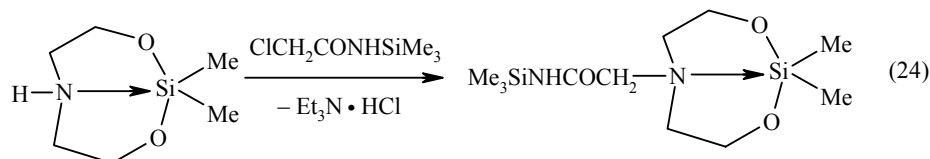


As a rule, the reaction takes place under harsh conditions at high temperature (200-250°C) and in the presence of Lewis acids (AlCl<sub>3</sub>, ZnCl<sub>2</sub>). Nevertheless the yields of the products are fairly high (34-96%). Replacement of the dialkoxysilanes by dichlorosilanes leads to a decrease of the yields to 27-38% as a result of the formation of polymeric side products [5].

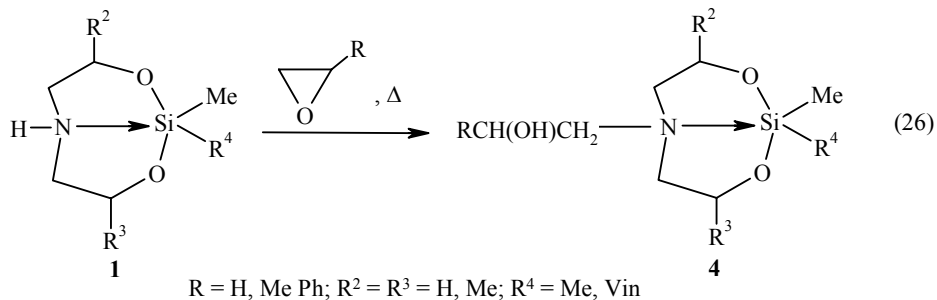
The analogous "transsilylation-recyclization" reaction can be used for the production of the higher homologs of 1,3,6-trioxa-2-silacyclooctanes **5** [30].



**1.3.4. Reactions of NH-Silocanes at the Nitrogen Atom.** In silocanes of the  $R^4R^4Si(OCH_2CH_2)_2NH$  type **1** the nitrogen atom is readily available and can enter into reactions characteristic of secondary amines. Thus, silocanes unsubstituted at the nitrogen atom react with alkyl halides [8] and their derivatives [55] in the presence of a hydrogen halide acceptor.



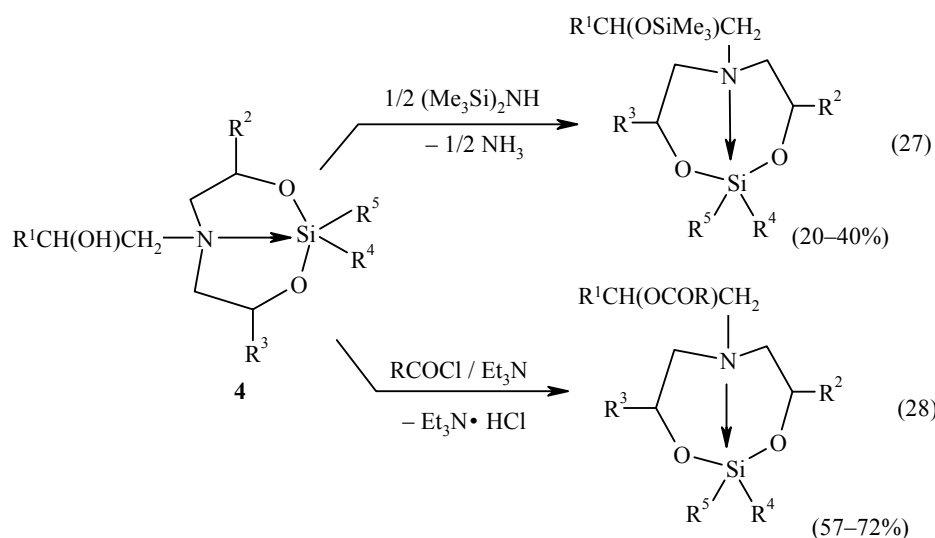
NH-Containing silocanes open the ring of oxiranes on heating, leading to the formation of the corresponding N-(2-hydroxyalkyl)silocanes with yields of 40-80% [26].



Reactions of  $R^4R^5Si(OCH_2CH_2)_2NH$  (**1**) with diethyl phosphite in the presence of triethylamine [60] and also with trimethylsilyl N,N-diethylcarbamate [61] have also been described.

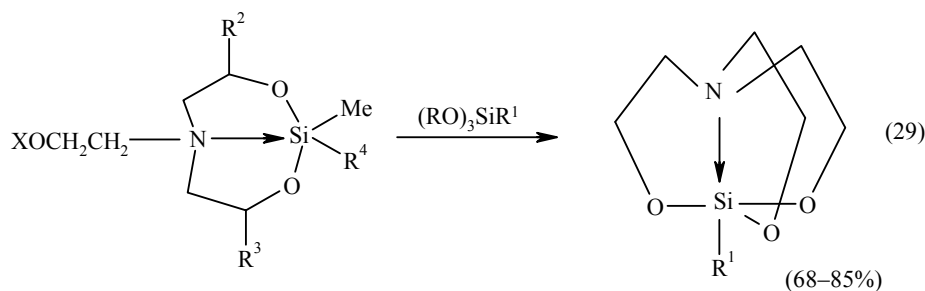
**1.3.5. Reactions of Silocanes Containing a 2-Hydroxyalkyl or 2-Trimethylsilyloxyalkyl Substituent at the Nitrogen Atom.** The chemical transformations of silocanes of type **4** containing a 2-hydroxyalkyl or 2-(trimethylsilyl)alkyl substituent at the nitrogen atom were studied in [23, 38]. When heated with  $\text{HN}(\text{SiMe}_3)_2$  the 2-hydroxyalkyl derivatives form the corresponding trimethylsilyl ethers (27). In a number of cases the reaction is conducted in the presence of catalytic amounts of sulfuric acid. As a rule the yield does not exceed 40%.

The esterification of N-(2-hydroxyalkyl)-substituted silocanes with carboxylic acid chlorides in the presence of triethylamine as hydrogen chloride acceptor takes place fairly smoothly. The esters of the silocanes were isolated with good yields [18, 23].



R = Me, Et, CH<sub>2</sub>Ph, Ph; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> = H, Me; R<sup>4</sup>, R<sup>5</sup> = Me, Et, CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>, Vin, Ph

The reaction of the N-(2-hydroxyethyl) derivatives of silocanes and also their trimethylsilyl ethers with alkyltrialkylsilylanes in the presence of alkaline catalysts leads to the formation of the corresponding silatranes [38].

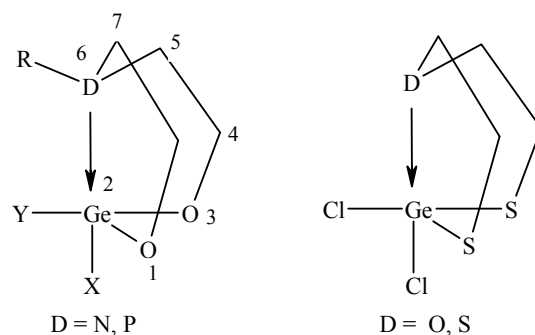


R = Me, Et; R<sup>1</sup> = Me, Et; R<sup>4</sup> = Me, Vin, Ph, Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>; X = H, SiMe<sub>3</sub>

The formation of high yields of silatranes is also observed during the action of catalytic amounts of alkali on trimethylsilyl ethers containing a phenyl substituent at the silicon atom. The process is accompanied by the elimination of trimethylsilylbenzene [38].

## 2. GERMOCANES

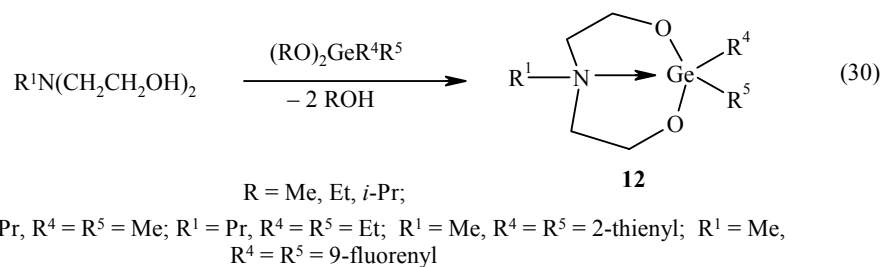
The cyclic ocane derivatives of germanium type (germocanes) are a much less studied class of compound than the silocanes. At the present time 1,3-dioxa-6-aza- and 1,3-dioxa-6-phospha-2-germacyclooctanes and 6-oxa-1,3-dithia- and 1,3,6-trithia-2-germacyclooctanes are known.



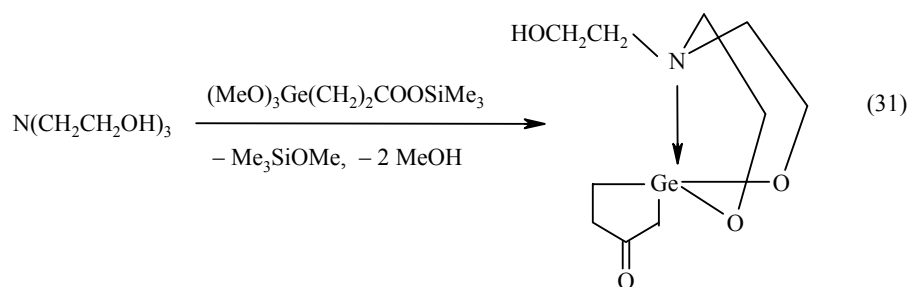
## 2.1. Methods for the Production of Germocanes

The most studied approach to the synthesis of 1,3-dioxa-6-azagermacyclooctanes is the reaction of dialkanolamines with various germanium-containing compounds. In contrast to siloxane chemistry, methods based in the use of the silyl ethers of dialkanolamines have been developed to a significantly lesser degree. This approach was first used for the synthesis of germocanes by E. Lukevics' group as far back as 1984. However, it has only been developed recently in so far as it proved extremely useful for the synthesis of 2,2-dihalo derivatives, which are the most attractive representatives of this group of compounds.

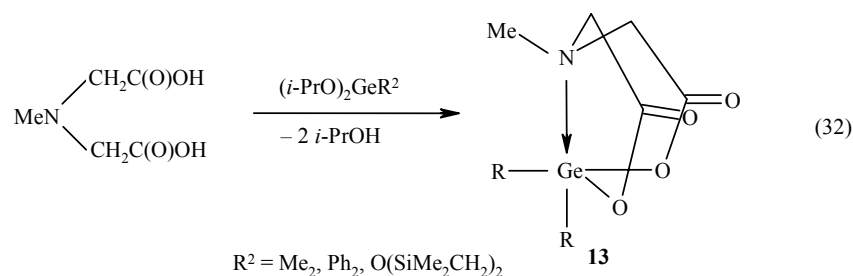
**2.1.1. Reaction of Dialkanolamines with Alkoxygermanes.** With dialkoxydiorganogermanes transalkoxylation leads smoothly to the corresponding germocanes with yields of 55-75% [16, 56, 62].



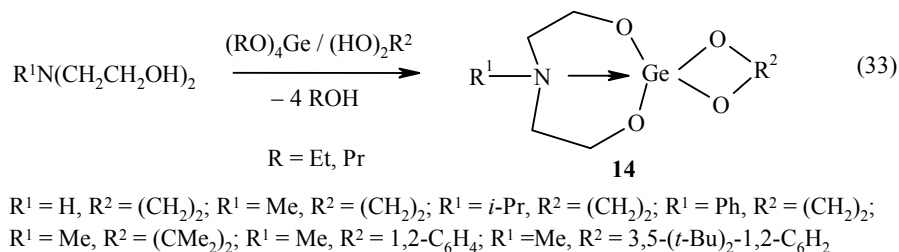
An unexpected result was obtained during the reaction of triethanolamine with trimethylsilyl 3-(trimethoxygermyl)propionate [63]. The reaction of these compounds is accompanied by ejection of the trimethylsilyl group and closure of the germolactone ring, leading to the formation of a spirocyclic germocane (31).



The use of N-methyliminodiacetic acid in reaction with diorganodialkoxygermanes leads to the formation of carbonyl-substituted germocanes [64].

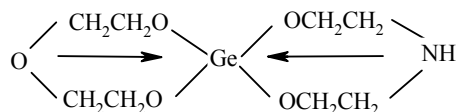


A large set of spirocyclic germocanes were obtained during the treatment of germanium tetraalkoxides with diethanolamine in the presence of such bidentate ligands as glycols [65, 66]

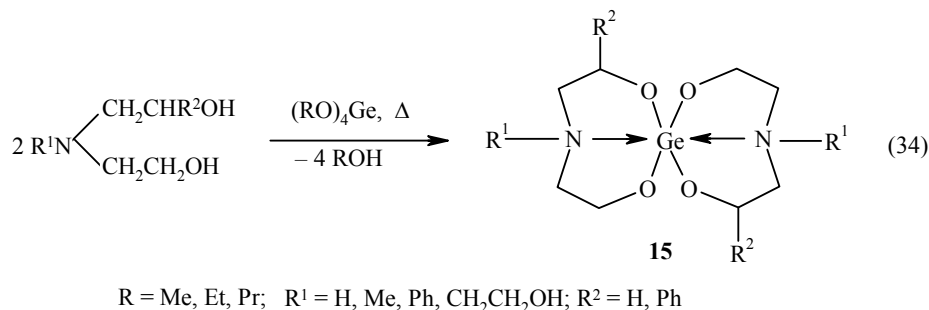


The authors point out the selectivity of the reactions, i.e., the formation of only mixed spirocycles. This is explained by stabilization of the eight-membered germocane fragment and the molecule as a whole on account of the formation of additional transannular  $\text{Ge} \leftarrow \text{N}$  interaction, promoted by the high electronegativity of the cyclic substituent at the germanium atom [65].

Use of the bidentate ligand diethylene glycol in a similar reaction led to the formation of a derivative in which the presence of a hexacoordinated germanium atom was assumed [65].



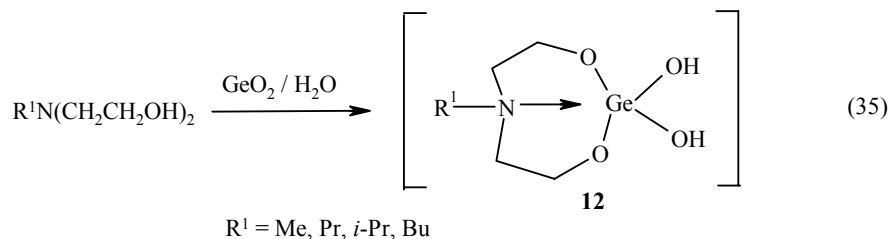
An attempt to produce dialkoxygermocane by the transalkoxylation of equimolar amounts of tetraalkoxygermanium and diethanolamine was unsuccessful [67]. It was found that the reaction of tetraalkoxygermanes with dialkanol- and triethanolamines in a ratio of 1:2 led to the corresponding bisgermocanes [65, 67, 68].



The NH derivative obtained in this way is a high-molecular polymer capable of depolymerization in the gas phase. The N-methyl- and N-phenylbisgermocanes **15** were synthesized with yields of 44-100%. The extreme instability of the bisgermocanes **15** ( $\text{R}^1 = \text{Me, Ph}$ ) toward atmospheric moisture was noted [65, 68].

**2.1.2. Reaction of Dialkanolamines with Germanium Oxides.** The reaction of trialkanolamines with germanium dioxide in the presence of water was used successfully for the production of 1-hydroxygermatranes [69]. The possibility of using a similar approach in the synthesis of germocanes was studied in [65, 66, 70-72].

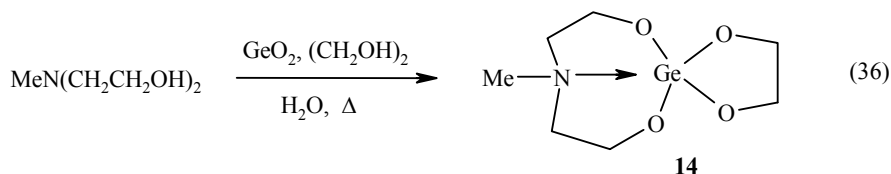
It was found that the addition of water to a suspension of germanium dioxide in diethanolamines leads to an exothermic reaction and to dissolution of the  $\text{GeO}_2$ . By analogy with the results obtained earlier for trialkanolamines the authors had expected the formation of the corresponding 2,2-dihydroxygermocanes [72].



However, it was suggested on the basis of data on the reactivity of the synthesized substances that the reaction of  $\text{GeO}_2$  with diethanolamines leads to complex compounds of orthogermanic acid with the corresponding amino alcohols [72].

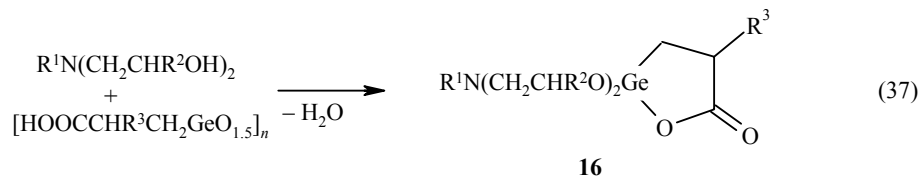
Later, in [70, 71], the chemical shifts for the protons of the  $\text{NCH}_2$  and  $\text{OCH}_2$  groups in the  $^1\text{H}$  NMR spectra of the similarly obtained NH- and N-methyl-2,2-dihydroxygermocanes were published. The same investigators noted the existence of a substantial equilibrium between the 2,2-dihydroxygermocanes and the products from their self-condensation with the elimination of water [70] (see below).

By a modification of the method, involving the addition of ethylene glycol to the reaction mixture, it was possible to obtain the previously mentioned 9-methyl-1,4,6,12-tetraoxa-9-aza-5-germaspiro[4.7]dodecane [66].



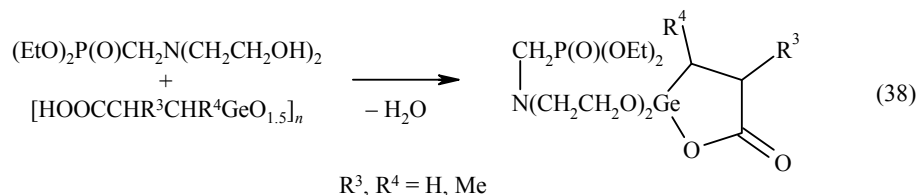
There is also information about the possibility of obtaining compounds containing ethyl, isopropyl, butyl, and phenyl substituents at the nitrogen atom by this method [66]. If diethanolamine unsubstituted at the nitrogen and ethylene glycol are used as ligands, it is not possible to separate the required compound from the  $[\text{HN}(\text{CH}_2\text{CH}_2\text{O})_2]_2\text{Ge}$  impurity. Realization of the reaction in the presence of pinacone leads to the isolation of the corresponding spirogermocane with a very low yield (5%) [65].

A method involving treatment of germasesquioxanes with di- and trialkanolamines was used successfully in [63]. by using (2-carboxyalkyl)germasesquioxanes the authors obtained a series of new spirocyclic germocanes with a lactone ring.

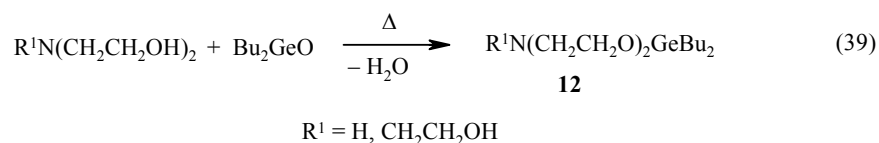


$\text{R}^1 = \text{H, Me, Pr, } i\text{-Pr, Bu, CH}_2\text{CH}_2\text{OH, CH}_2\text{CHMeOH, CH}_2\text{COOH; R}^2, \text{R}^3 = \text{H, Me}$

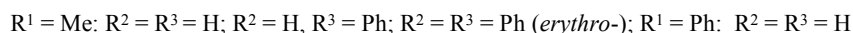
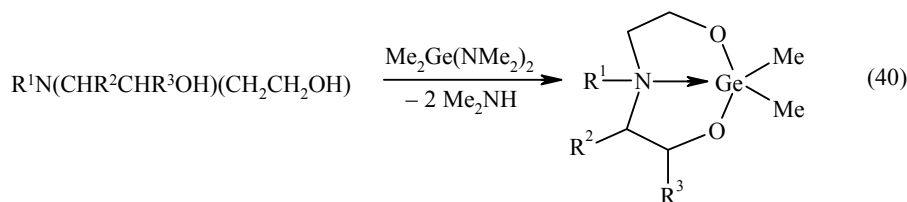
Later, the first germocanes containing a phosphonyl group in the substituent at the nitrogen atom were obtained [73].



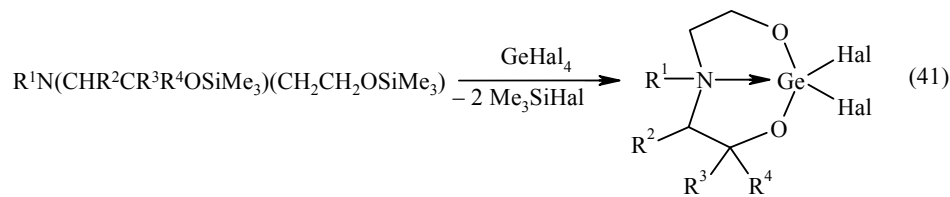
2,2-Dialkylgermocanes were first obtained in 1966 by the reaction of dibutylgermanium oxide with di- and triethanolamines [74], but the method was not developed further.



**2.1.3. Reaction of Dialkanolamines with Bis(dimethylamino)germanes.** Germocanes with methyl groups at the germanium atom were obtained with almost quantitative yields by the reaction of  $\text{Me}_2\text{Ge}(\text{NMe}_2)_2$  with various dialkanolamines [16, 75].

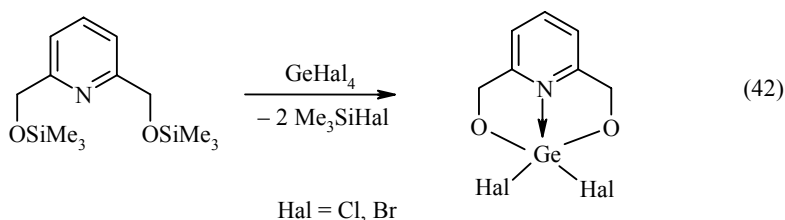


**2.1.4. Reaction of Trimethylsilyl Ethers of Dialkanolamines with Halogermanes.** The method of formation of the germocane fragment based on the reaction of the silyl ethers of dialkanolamines with dihalogermanes was first described in work by E. Lukevics and coworkers [76]. 2,2-Dichloro-6-methyl- and 2,2-dichloro-6-isopropylgermocanes were isolated with almost quantitative yields. Later Zaitseva and coworkers were able to develop this approach; it was used to prepare a large number of 2,2-dichloro- and 2,2-dibromogermocanes containing various types of substituents both at the nitrogen atom and in the ocane ring [16, 75]. The reactions take place on heating and lead to the required compounds with yields of 12-87%, and the yields of the dibromogermocanes are as a rule lower than the yields of the corresponding dichloro derivatives.

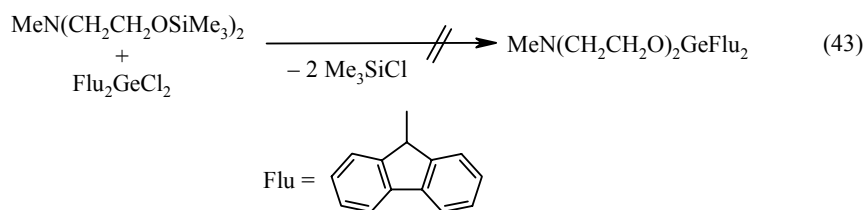




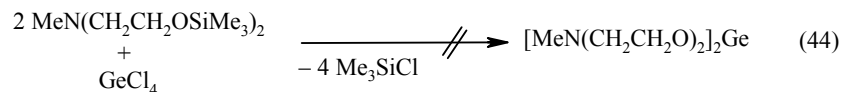
Analogs of germocanes containing the 2,6-bis(hydroxymethyl)pyridine fragment (a ligand sterically more rigid than dialkanolamines) in their structure were synthesized similarly [77].



The given method of generating the ocane ring only gives positive results for the synthesis of compounds containing accepting substituents at the germanium atom [16].

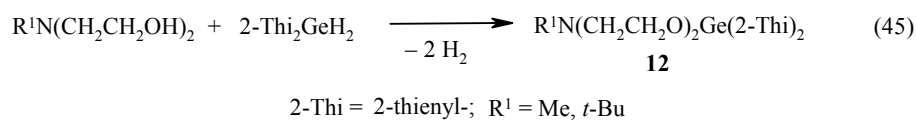


It was also impossible to synthesize the spirocyclic bisgermocane expected in the reaction of  $\text{GeCl}_4$  with two equivalents of bis(trimethylsilyl) ether by this method [68].

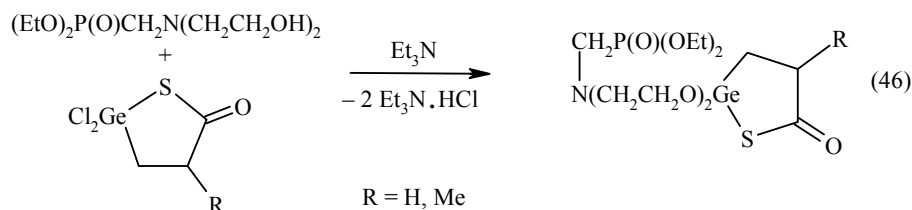


**2.1.5. Other Methods.** Apart from the already discussed method the possibility of using other methods for the production of compounds with a germocane structure was also demonstrated for isolated examples.

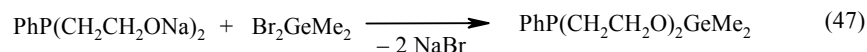
Thus, E. Lukevics and coworkers found [62] that dihydrogermanes can be used successfully as the initial germanium-containing compounds for the synthesis of germocanes.



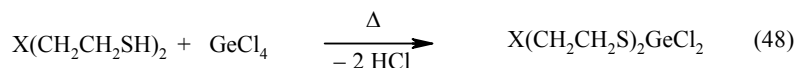
The reaction of a heterocyclic dichlorogermane with diethyl  $\text{N,N}$ -bis(2-hydroxyethyl)aminomethylphosphonate in the presence of triethylamine led to the formation of spirogermocanes according to the equation presented below [78].



A germocane containing a phosphorus atom in the eight-membered ring was obtained by the reaction of the disodium derivative of P-phenyldiethanolphosphine with dimethyldibromogermane [78]. The instability of this compound is stressed.



The reaction of germanium tetrachloride with an equimolar amount of bis(2-mercaptoethyl) sulfide or bis(2-mercaptoethyl) ether leads to 1,3,6-trithia- and 6-oxa-1,3-dithia-2-germacyclooctanes respectively. The reaction is carried out with boiling until the release of hydrogen chloride has stopped [79].



17

X = S (78%), O (59%)

## 2.2. Investigation of Germocanes by Physicochemical Methods

**2.2.1. X-ray Crystallographic Analysis.** The existence of intramolecular Ge←N coordination interaction in 6-aza-1,3-germacyclooctanes was demonstrated most convincingly by investigation of these compounds by X-ray crystallographic analysis. At the present time structural data have been obtained for a fairly significant number of germocanes [16, 62, 66, 68, 71, 75, 80-85] (see Table 2). It should be noted that there is a substantially larger diversity compared with the silocanes both in the steric and in the electronic characteristics of the substituents located at various "points" in the molecules of the investigated compounds. The latter makes it possible to form a more complete idea of what effect the nature of the substituent at the nitrogen and germanium atoms and also in the ring has on the strength of the transannular Ge←N interaction and also on the geometry of the molecule as a whole.

Analysis of the data in Table 2 shows that there is transannular Ge←N bonding (2.080-2.286 Å) in all the investigated 1,3-dioxa-6-aza-2-germacyclooctanes containing at least one electron-withdrawing substituent (oxygen, halogen) at the germanium atom. On account of the presence of transannular Ge←N bonding the germanium atom is pentacoordinated, while its coordination environment represents a distorted trigonal bipyramid. In all the germocanes **12a-e**, **14a,b**, and **16a,c**, as in the studied silicon analogs (silocanes), the nitrogen atom occupies the axial position, opposite one of the substituents X<sub>ax</sub> at the germanium. The two oxygen atoms and the second substituent X<sub>eq</sub> at the germanium atom lie in the equatorial plane. It should be noted that when X<sub>ax</sub> ≠ X<sub>eq</sub> the more electronegative substituent always occupies the axial position [80, 84]. The germanium atom is displaced from the equatorial plane by 0.02-0.17 Å toward the axial substituent X<sub>ax</sub>. The small values of ΔGe (0.02-0.10 Å), characteristic of spirocyclic germocanes with a lactone ring and of the 2,2-dihalo derivatives, correspond to only small distortion of the trigonal bipyramid and indicate the presence of strong Ge←N interaction.

In spite of the possibility of interaction between the unshared pair of the nitrogen atom and the aromatic system of the benzene ring in compounds **12c,d**, the length of the Ge←N bond in the germocanes PhN(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>GeX<sub>2</sub> (X = Cl, Br) hardly differs at all from that in MeN(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>GeBr<sub>2</sub> **12b**. At the same time, as mentioned above (section 1.2.1), the analogous replacement of the methyl group by phenyl in the series of silocanes leads to a significant increase of the Si←N distance in PhN(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>SiPh<sub>2</sub> [3.08(1) Å] compared with the value in MeN(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>SiPh<sub>2</sub> [2.68(1) Å] [10]. The reasons for such different behavior in the silicon and germanium derivatives of the ocane series may be: 1) The smaller radius of the silicon compared with the

TABLE 2. The Key Structural Characteristics of Germocanes

	Compound	I, Å			Angle, D-Ge-X <sub>ax</sub> , deg	ΔGe	Ref.
		Ge←D	Ge-X <sub>ax</sub>	Ge-X <sub>eq</sub>			
<b>14a</b>	MeN(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> Ge[-OCPh <sub>2</sub> C(O)O-]	2.080(3)	1.870(2)	1.77(2)	178.0(1)	—	[80]
<b>12a</b>	HN(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> Ge(OH) <sub>2</sub>	2.123(4)	1.793(3)	1.762(4)	177.9(2)	0.17	[71]
<b>16a</b>	HOCH <sub>2</sub> CH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> Ge[-CH <sub>2</sub> CH <sub>2</sub> C(O)O-]	2.143(6)	1.916(6)	1.958(8)	170.5(3)	0.03	[81, 84]
<b>14b</b>	MeN(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> Ge[-OCH <sub>2</sub> CH <sub>2</sub> O-]	2.159(7)	1.808(6)	1.795(6)	178.7(3)	0.13	[66, 82]
<b>16b</b>	BuN(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> Ge[-CH <sub>2</sub> CH <sub>2</sub> C(O)O-]	2.16(1)	1.895(8)	1.93(1)	171.0(4)	0.02	[83]
<b>12b</b>	MeN(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> GeBr <sub>2</sub>	2.166(5)	2.415(1)	2.322(1)	170.3(1)	0.06	[75]
<b>12c</b>	PhN(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> GeCl <sub>2</sub>	2.202(2)	2.218(1)	2.166(1)	171.8(1)	0.10	[86]
<b>12d</b>	PhN(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> GeBr <sub>2</sub>	2.202(4)	2.385(1)	2.320(1)	170.9(1)	0.09	[16]
<b>12e</b>	<i>erythro</i> -MeN(CH <sub>2</sub> CH <sub>2</sub> O)(CHPhCHPhO)GeBr <sub>2</sub>	2.217(2)	2.379(1)	2.328(1)	169.1(1)	0.10	[16]
<b>16c</b>	(MeO) <sub>2</sub> P(O)CH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> Ge[-CH <sub>2</sub> CHMeC(O)O-]	2.286	1.889	—	171.4	0.05	[85]
<b>12f</b>	MeN(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> Ge(2-thienyl) <sub>2</sub>	2.446(8)	1.954(9)	1.912(11)	162.1(4)	—	[62]
<b>12g</b>	MeN(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> Ge(9-fluorenyl) <sub>2</sub>	2.739(1)	1.994(2)	1.982(1)	168.3(1)	0.35	[16]
<b>12h</b>	PhN(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> GeMe <sub>2</sub>	3.182(1)	1.926(2)	1.925(2)	165.4(1)	0.55	[16]
<b>17a</b>	O(CH <sub>2</sub> CH <sub>2</sub> S) <sub>2</sub> GeCl <sub>2</sub>	2.36(1)	2.212(4)	2.179(4)	172.8(3)	—	[87]
		2.39(1)	2.204(4)	2.131(6)	169.3(3)	—	
<b>17b</b>	S(CH <sub>2</sub> CH <sub>2</sub> S) <sub>2</sub> GeCl <sub>2</sub>	3.005	2.208	2.149	182.2	—	[88]

radius of germanium; 2) the greater susceptibility of the  $\text{GeX}_2$  group ( $\text{X} = \text{Cl}, \text{Br}$ ) to the formation of the transannular bond compared with  $\text{SiPh}_2$  in view of the stronger electron-accepting character and at the same time the smaller steric hindrances created by the halogen atoms compared with the phenyl substituents.

The transition from the dibromogermocane **12b** to the derivatives **12f** with two weakly accepting but at the same time fairly bulky 2-thienyl substituents and **12g** with two electron-donating and bulky fluorenyl groups is accompanied by a significant increase in the  $\text{Ge}\leftarrow\text{N}$  distance [ $\Delta = 0.280(9)$  and  $0.573(5)$  Å respectively]. In the opinion of the authors [16, 62] these compounds have only a weak  $\text{Ge}\leftarrow\text{N}$  bond, which is particularly weak in the case of the difluorenyl derivative.

The  $\text{Ge}\leftarrow\text{N}$  interaction is absent in the germocane **12h**, containing an electron-withdrawing phenyl group at the nitrogen atom and two donating methyl groups at the germanium atom. The  $\text{Ge}\cdots\text{N}$  distance amounts to 3.182(1) Å, while the coordination polyhedron of the germanium atom is a slightly distorted tetrahedron. The nitrogen atom lies almost in the plane formed by its substituents [16].

In the germocanes **12a-e**, which have a significant degree of transannular  $\text{Ge}\leftarrow\text{N}$  bonding and have identical substituents  $\text{X}_{\text{ax}}$  and  $\text{X}_{\text{eq}}$  at the germanium atom, the axial  $\text{Ge}-\text{X}_{\text{ax}}$  bonds are appreciably longer than the equatorial  $\text{Ge}-\text{X}_{\text{eq}}$  bonds, which is consistent with the concepts of hypervalent interaction theory. As the  $\text{Ge}\leftarrow\text{N}$  interaction becomes weaker in compounds **12f-h** the difference in the  $\text{Ge}-\text{X}_{\text{ax}}$  and  $\text{Ge}-\text{X}_{\text{eq}}$  distances is practically levelled out. The difference between  $\text{Ge}-\text{X}_{\text{ax}}$  and  $\text{Ge}-\text{X}_{\text{eq}}$  is also small in the spirocyclic diolate **14b**, but this is due to the significant strain of the five-membered  $-\text{Ge}-\text{O}-\text{C}-\text{C}-\text{O}-$  ring. The tendencies found in the currently studied 1,3-dioxa-6-aza-2-germacyclooctanes are similar to those for the silocanes examined above.

As a result of the formation of the additional intramolecular dative  $\text{Ge}\leftarrow\text{N}$  bond the eight-membered ring is separated into two five-membered heterocycles  $\text{Ge}-\text{O}-\text{C}-\text{C}-\text{N}$ , which are in the *envelope* conformation. In most cases the carbon atom at the  $\alpha$  position to the nitrogen projects from the plane of the remaining ring atoms by approximately 0.5-0.6 Å, forming the *flap* of the *envelope*. Exceptions are the germocane **12e** with two phenyl groups in the ring and the germocane **12h** with methyl substituents at the germanium, in which transannular  $\text{Ge}\leftarrow\text{N}$  is absent. In these compounds the  $\text{C}(\beta)$  atom has the greatest deviation from the plane of the  $\text{Ge}-\text{O}-\text{C}-\text{C}-\text{N}$  rings [16].

The eight-membered heterocycle of 1,3,6,2-trithiagermocane  $\text{S}(\text{CH}_2\text{CH}_2\text{S})_2\text{GeCl}_2$  (**17b**) in the solid phase exists in two enantiomeric forms of the *boat-chair* conformation [88]. The oxygen-containing analog  $\text{O}(\text{CH}_2\text{CH}_2\text{S})_2\text{GeCl}_2$  (**17a**) crystallizes in the *chair-chair* conformation. The crystals contain two independent molecules, which are not however enantiomers on account of the presence of a plane of symmetry passing through the O, Ge, Cl, and Cl atoms [87]. The  $\text{Ge}\leftarrow\text{S}$  (3.005 Å) and  $\text{Ge}\leftarrow\text{O}$  [2.36(1), 2.39(1) Å] interatomic distances and also the trigonal-bipyramidal environment of the germanium atom make it possible to assign these compounds to derivatives with fairly strong intramolecular  $\text{Ge}\leftarrow\text{S}$  and  $\text{Ge}\leftarrow\text{O}$  coordination. It should be noted that the  $\text{Ge}-\text{Cl}$  bonds in the germocanes **17a,b** have almost identical length, and in both cases the  $\text{Ge}-\text{Cl}_{\text{ax}}$  bond is appreciably longer than  $\text{Ge}-\text{Cl}_{\text{eq}}$ .

The length of the  $\text{Ge}\leftarrow\text{N}$  bonds in the spirocyclic bisocane **15a** [2.307(2) Å] is close to the upper limit of the range of values found for the germocanes **12a-e**, **14a,b**, and **16a-c** examined above (2.080-2.286 Å). This makes it possible to propose the formation of two fairly strong transannular  $\text{Ge}\leftarrow\text{N}$  interactions in this compound. The coordination environment of the germanium atom has the geometry of a distorted octahedron, where the nitrogen atoms of the two ligands are in the *cis* orientation to each other [ $\text{N}-\text{Ge}-\text{N}$  angle  $105.05(9)^\circ$ ]. The lengths of the  $\text{Ge}-\text{O}$  bonds in the molecule of **15a** [1.821(1)-1.834(1) Å] are noticeably greater than the analogous values in  $\text{Ge}(\text{O}-i\text{-Pr})_4$  [1.745(1) Å] with a tetracoordinated germanium atom and also in the germocane  $\text{MeN}(\text{CH}_2\text{CH}_2\text{O})_2\text{Ge}(-\text{OCH}_2\text{CH}_2\text{O}-)$  (**16b**) [1.776(6)-1.808(6) Å], where the germanium atom is pentacoordinated. Such elongation is explained by additional donation of electron density straight from the two nitrogen atoms to the germanium center. It should be noted that the  $\text{Ge}-\text{O}$  bond in compound **15a**, which is in the *trans* position to the nitrogen atom, hardly differs at all from the other  $\text{Ge}-\text{O}$  bonds [ $\Delta = 0.013(1)$  Å].

TABLE 3. The Key Structural Characteristics of Bisgermcanes

	Compound	<i>I</i> , Å			Angle, deg.		Ref.
		Ge←D	Ge-X*	D-Ge-X	X-Ge-X*		
<b>15a</b>	[MeN(CH <sub>2</sub> CH <sub>2</sub> O)(CH <sub>2</sub> CHPhO)] <sub>2</sub> Ge	2.307(2)	1.821(1); 1.834(1)	<i>trans</i> -170.44(6)	<i>trans</i> -154.67(9)	[68]	
<b>15b</b> <sup>*2</sup>	[PhN(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> Ge	3.016(2); 2.795(2)	1.744(2)-1.761(2)	<i>cis</i> - 80.26(6); 81.79(6); 84.40(6)	<i>cis</i> - 92.25(9); 93.99(6); 103.56(6)	[68]	
<b>19a</b>	[S(CH <sub>2</sub> CH <sub>2</sub> S) <sub>2</sub> ] <sub>2</sub> Ge	3.055(2); 2.779(2)	1.749(2)-1.761(2)	<i>trans</i> - 172.23(7); 165.37(7)	99.90(8)-122.40(8)	[89]	
<b>19b</b> <sup>*2</sup>	[O(CH <sub>2</sub> CH <sub>2</sub> S) <sub>2</sub> ] <sub>2</sub> Ge	3.237(3); 3.453(3); 2.914(3); 3.040(3)	2.210(3)-2.236(3)	—	97.0(1)-118.5(1)	[89]	
		2.946(3); 2.955(3)	2.217(1)-2.218(1)	—	96.32(5)-115.53(5)	[89]	
			2.216(1)-2.222(3)		96.11(5)-116.32(5)		

\* The range of values is indicated for **15b** and **19a,b**.

<sup>\*2</sup> Two independent molecules.

In contrast to the germocanes **12b,d**, for which replacement of the methyl group at the nitrogen atom by phenyl does not have an appreciable effect on the strength of the transannular Ge←N bonding, analogous replacement in the case of the bisgermocanes **15a,b** leads to loss of the additional coordination by the germanium atom. The closest environment of the germanium atom in compound **15b** represents a distorted tetrahedron, formed by the four covalently bonded oxygen atoms. All the Ge–O bonds [1.744(2)–1.761(2) Å] are shorter than in the derivative **15a** and close to the values in Ge(O-*i*-Pr)<sub>4</sub> [1.745(1) Å], which once again confirms the absence of significant donation of electron density from the PhN group to the germanium.

The eight-membered Ge–O–C–C–N–C–C–O heterocycles in the molecule of **15a** adopt the *chair-boat* conformation, while those in **15b** adopt the *crown* conformation that is characteristic of the case of weak **12f** or absent **12h** transannular Ge←N interaction.

The sulfur-containing bisgermocanes **19a** and **19b** have similar structures with close values for the bond lengths and angles. In both compounds the coordination polyhedron of the germanium atom represents a distorted tetrahedron. The authors [89] explain the fairly noticeable deviation of the geometry from tetrahedral by the presence of interaction between the germanium atom and the atoms of the potential donors of electron density (S, O). At the same time the Ge←O [2.914(3)–3.040(3) Å] and Ge←S [3.237(3), 3.453(3) Å] distances in these bisocanes substantially exceed the corresponding values found in dichlorogermocanes **17a** [2.36(1), 2.39(1) Å] and **17b** (3.005 Å). The latter makes it possible to state that, if they exist at all, only very weak secondary Ge←O and Ge←S interactions are present in the molecules of compounds **19a** and **19b**, and these compounds must be regarded rather as derivatives of tetracoordinated germanium.

On the whole analysis of the X-ray crystallographic data obtained at the present time indicates that the strength of Ge←N interaction in the germocanes D(CH<sub>2</sub>CH<sub>2</sub>Z)<sub>2</sub>Ge(X)Y (Z = O, S; D = RN, O, S) is highly sensitive, primarily, to the nature of the substituents at the germanium atom and only then to the nature of the substituents at the nitrogen atom in the case where D = RN and also in the case of bisgermocanes. By varying the substituents at these positions of the molecule it is possible to obtain germocanes with strong or weak transannular Ge–N interaction and also without such interaction.

**2.2.2. NMR spectroscopy.** The structure of nitrogen-containing germocanes in solution was studied by <sup>1</sup>H, <sup>13</sup>C, and <sup>73</sup>Ge NMR spectroscopy. In contrast to silocanes, the investigations of their germanium analogs were not so systematic in nature, and only recently obtained data [16, 68, 75] make it possible to reach certain conclusions about the effect of the characteristics of the substituents on the structure of the molecules and on the strength of transannular Ge←N interaction in the liquid phase.

Germocanes not containing substituents at the carbon atoms of the ocane skeleton can be divided into two groups according to the outward appearance of the resonance signals in the <sup>1</sup>H NMR spectrum [16, 75]. The first group includes such compounds as N-phenyl-substituted germocanes PhN(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>GeX<sub>2</sub> **12c** (X = Cl) and **12d** (X = Br), 2,2-dimethylgermocanes R<sup>1</sup>N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>GeMe<sub>2</sub> **12h** (R<sup>1</sup> = Ph) and **12i** (R<sup>1</sup> = Me), and germocanes containing bulky substituents at the Ge atom such as MeN(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>GeFlu<sub>2</sub> (**12g**) and MeN(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>Ge(2-thienyl)<sub>2</sub> (**12f**). They are characterized by the presence of two triplets for the NCH<sub>2</sub>CH<sub>2</sub>O groups, forming a degenerate AA'XX' system. Spectra of such a type demonstrate the slackness of the ocane skeleton of the compounds in solution. The second group contains halo-substituted germocanes MeN(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>GeX<sub>2</sub> **12j** (X = Cl); **12b** (X = Br) and MeN(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>Ge(X)OR (X = Cl, Br; R = Me, Ment, CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>), in which the protons of the NCH<sub>2</sub>CH<sub>2</sub>O groups form an ABXY system and appear in the spectrum as a set of three multiplets (two for NCH<sub>2</sub> and one for OCH<sub>2</sub>). This makes it possible to conclude that the processes of intramolecular dynamics (the conformational transitions of the eight-membered ring, Berry pseudorotation) are inhibited at room temperature and that these compounds exist in solution in the form of one "frozen" conformation. The derivatives MeN(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>Ge(OR)<sub>2</sub> (R = Me, Ment) with two alkoxy substituents at the germanium atom occupy an intermediate position between the two indicated groups. Their spectra contain one triplet for the protons of the OCH<sub>2</sub> groups and one or two multiplets for the protons of the

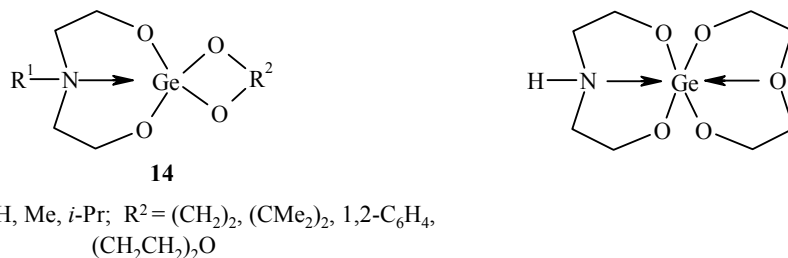
NCH<sub>2</sub> groups, corresponding to the formation of an AA'XY system by the protons of the ocane skeleton. The spectra of the spirocyclic germocanes **14**, containing a 1,2-diol residue at the germanium atom, have similar form [65, 66].

Thus, it is possible to judge the presence or absence of conformational transitions in the solution from the outward appearance of the <sup>1</sup>H NMR spectra of the unsubstituted germocanes. However, these data do not make it possible to reach an unambiguous conclusion about the strength of the transannular Ge←N interaction [16]. The introduction of substituents at the carbon atoms leads to nonequivalence in all the protons of the ocane ring in the germocanes MeN(CH<sub>2</sub>CH<sub>2</sub>O)(CHR<sup>2</sup>CR<sup>3</sup>R<sup>4</sup>O)GeX<sub>2</sub> (X = Br, Me; R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> = H, Ph) and, consequently, to complications in the <sup>1</sup>H NMR spectra.

The centers of the signals for the protons of the NCH<sub>2</sub>, NCHPh, and NMe groups in the spectra of the dihalo derivatives MeN(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>GeX<sub>2</sub> (X = Cl, Br) and MeN(CH<sub>2</sub>CH<sub>2</sub>O)(CHR<sup>2</sup>CHPhO)GeBr<sub>2</sub> (R<sup>2</sup> = H, Ph) are shifted downfield in comparison both with the initial amino alcohols and with the corresponding dimethyl-substituted MeN(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>GeMe<sub>2</sub> and MeN(CH<sub>2</sub>CH<sub>2</sub>O)(CHR<sub>2</sub>CHPhO)GeMe<sub>2</sub> (R<sup>2</sup> = H, Ph). This means that the 2,2-dihalogermocanes in solution have stronger Ge←N coordination than the corresponding 2,2-dimethyl derivatives [16]. However, such an approach to determination of the strength of intramolecular Ge←N interaction in solution has certain limitations. As already mentioned in section 1.2.2, if the substituents at the germanium atom contain aromatic fragments the effect of the ring currents in the latter leads to a significant upfield δ<sup>1</sup>H shift of the protons lying close in space [as, for example, for the compound MeN(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>GeFlu<sub>2</sub> with fluorenyl substituents].

An attempt to use the NOE to establish the structural features of germocanes in solution was made in [16, 75] for a series of 2,2-dimethyl derivatives. The presence of a strong NOE between the protons of the N–Me and the protons of the Ge–Me groups was detected for the germocane MeN(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>GeMe<sub>2</sub> (**12i**). This indicates the existence of a transannular Ge←N bond for this compound in solution. A similar experiment for the compound MeN(CH<sub>2</sub>CH<sub>2</sub>O)(CH<sub>2</sub>CHPhO)GeMe<sub>2</sub> (**12k**) showed the presence of weak Ge←N interaction. The absence of the NOE between the protons of the phenyl ring of the N–Ph group and the protons of Ge–Me makes it possible to suppose that the compound Ph(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>GeMe<sub>2</sub> **12h** exists in solution predominantly in the *crown* conformation analogous with that found for the solid phase.

A series of germocanes of type **14** were investigated by <sup>73</sup>Ge NMR spectroscopy [90].\* The increase in the screening of the germanium atom in the investigated derivatives compared with the model compound (tetraethoxygermane) confirms that the intramolecular Ge←N bond found in the solid phase by X-ray crystallographic analysis is also present in solutions of these germocanes.

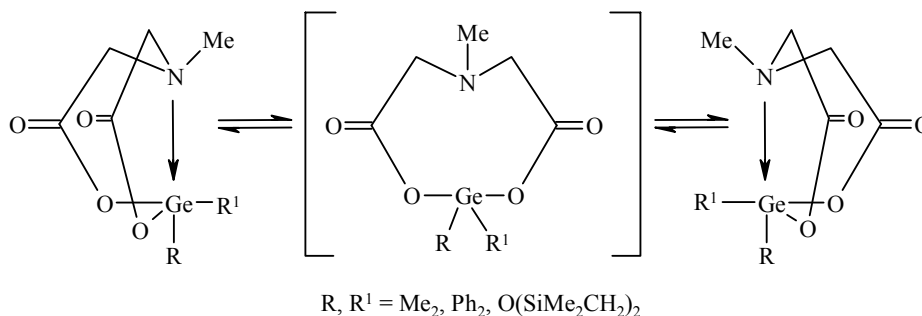


The existence of donor–acceptor Ge←N interaction in the solutions is further indicated by the temperature dependence of the width of the resonance signal; the width of the lines increases with decrease of temperature.

\* For the <sup>73</sup>Ge NMR spectra of germocanes, see also: E. Kupce and E. Lukevics, *Izv. Akad. Nauk LatvSSR. Ser. Khim.*, 498 (1989) (Editor's note).

Substitution of a hydrogen atom at the nitrogen atom by methyl or isopropyl does not have an appreciable effect on the  $^{73}\text{Ge}$  chemical shift. A more substantial upfield shift of the resonance in relation to  $\text{Ge}(\text{OEt})_4$  compared with the other germocanes was observed for the ethylene glycol derivative, making it possible to assume that the germanium atom in this compound is hexacoordinated.

During investigation of germocanes containing carbonyl groups in the ring by  $^1\text{H}$  NMR spectroscopy a scheme with mutual exchange of the substituents at the germanium atom between the axial and equatorial positions in the trigonal bipyramid was proposed. The supposed process includes cleavage of the  $\text{Ge}\leftarrow\text{N}$  bond and inversion at the nitrogen atom [64].



The activation energy of this process amounts to 19.1-21.3 kcal/mol, which significantly exceeds the barrier to inversion in normal 7-9-membered nitrogen-containing organic rings (6-7 kcal/mol) and indicates the presence of additional transannular  $\text{Ge}\leftarrow\text{N}$  interaction in the molecule.

A detailed investigation of the temperature dependence of the  $^1\text{H}$  NMR spectra of thiagermocanes  $\text{X}(\text{CH}_2\text{CH}_2\text{S})_2\text{GeCl}_2$  **17a** ( $\text{X} = \text{O}$ ) and **17b** ( $\text{X} = \text{S}$ ) was presented in [79]. The resonance signals of the  $\text{XCH}_2\text{CH}_2\text{S}$  protons form an AA'BB' system, which remains unchanged over a wide range of temperatures (-30 to +60°C for **17a** and -2- to +120°C for **17b**). Gradual broadening and coalescence of the multiplets into two broad signals are observed at temperatures below -30°C for compound **17a** and below -20°C for **17b**. At -60°C the signals for the protons of the germocane **17a** begin to split again into individual lines of the ABCD spin system expected in this case.

The presence of the AA'BB' system in the spectra indicates that the molecules of  $\text{X}(\text{CH}_2\text{CH}_2\text{S})_2\text{GeCl}_2$  in solution at room temperature exist simultaneously in three conformations, i.e., the achiral *boat-boat* and *chair-chair* forms and the chiral *chair-boat* form, each of which is characterized by the presence of transannular  $\text{Ge}\leftarrow\text{X}$  interaction. The dynamic equilibrium between the conformers is realized by means of rapid (on the NMR time scale) two-barrier transitions. The two symmetrical energy barriers between the three equilibrium conformations for compounds **17a** and **17b** are close and amount to ~10 kcal/mol.

In the  $^1\text{H}$  NMR spectra of the spirocyclic bisgermocanes  $[\text{R}^1\text{N}(\text{CH}_2\text{CH}_2\text{O})_2]_2\text{Ge}$  **15b** ( $\text{R}^1 = \text{Ph}$ ) and **15c** ( $\text{R}^1 = \text{Me}$ ) and  $[\text{X}(\text{CH}_2\text{CH}_2\text{S})_2]_2\text{Ge}$  **19a** ( $\text{X} = \text{S}$ ) and **19b** ( $\text{X} = \text{O}$ ) the signals for the methylene protons of the ocane skeleton appear in the form of two triplets of an AA'XX' system. The resonance signals for the protons of the MeN and NCH<sub>2</sub> groups of compound **15c** and also of the phenyl-substituted compound  $[\text{MeN}(\text{CH}_2\text{CH}_2\text{O})(\text{CH}_2\text{CHPhO})]_2\text{Ge}$  (**15a**) are shifted downfield in relation to the values for the corresponding dialkanolamines, whereas such a shift of the signals for the protons of the NCH<sub>2</sub> groups is not observed in the case of the bisgermocane **15b**. This is probably explained by the presence in the solution of transannular  $\text{Ge}\leftarrow\text{N}$  bonding in the molecules of **15a,c** and by the significantly weaker (or absent) interaction between the nitrogen and germanium atoms in the derivative **15b**. Thus, the tendencies found for compounds **15a** and **15b** in the solid phase by X-ray crystallographic analysis do remain in the solution.

With the set of data obtained during investigation of germocanes by X-ray crystallographic analysis in the solid phase and by NMR spectroscopy in solution it is possible to formulate the following relationships for the dependence of the change in the strength of transannular  $\text{Ge}\leftarrow\text{N}$  interaction on the nature of the substituents

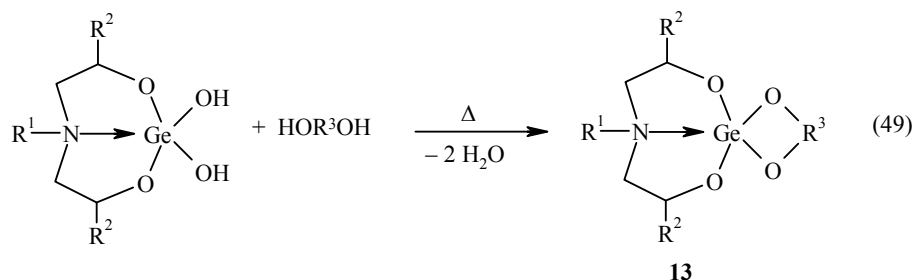


at various positions of the ocane ring. A determining role is played by the nature of the substituents at the germanium atom. Groups with clearly defined electron-withdrawing characteristics (halogens, oxygen-containing substituents) give rise to strong Ge←N interaction, and the nature of the substituents here at the nitrogen and carbon atoms in this case does not have an appreciable effect on the strength of the bond. On the whole the introduction of donating substituents (e.g., methyl or fluorenyl groups) at the germanium atom reduces the degree of Ge←N bonding. The decrease in the bonding is accompanied by a significant increase in the effect of the nature of the N- and C-substituents at the nitrogen atom, and bulky substituents at the carbon atoms (e.g., phenyl groups) lead to weakening of the transannular interaction.

**2.2.3. Mass Spectrometry.** The structure of germocanes in the gas phase was investigated by mass spectrometry in [56, 76]. By analyzing the fragmentation under electron impact the authors were able to conclude that there was no transannular Ge←N interaction in germocanes  $R^1N(CH_2CH_2O)_2GeR^2$  ( $R = Cl, Me, Et, R^1 = Me, i\text{-}Pr, Pr$ ) in the gas phase. Mass spectrometric investigation of these compounds was also undertaken in some papers devoted to spirocyclic germocanes and also to oxygen-containing and sulfur-containing germocanes, and a mass spectrometric investigation of the compounds was also conducted [63, 65, 68, 79, 91].

### 2.3. Reactivity of Germocanes

The chemical properties of germocanes have been studied little and mainly for the case of the reaction of 2,2-dihydroxygermocanes with various bidentate ligands. Spirocyclic germocanes were obtained as a result of these reactions [70, 80, 91].

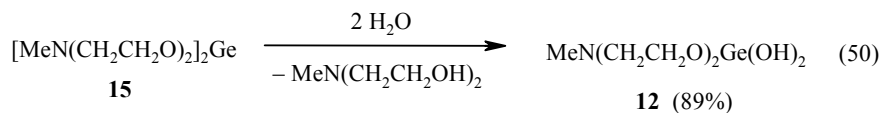


$R^1 = H, Me, n\text{-}Bu; R^2 = H, Me; R^3 = (CH_2)_2, 1,2\text{-}c\text{-}C_6H_{10}, CH_2C(O), CHMeC(O), CHPhC(O), CMe_2C(O), CPh_2C(O), (O)CC(O), 2,6\text{-}((O)C)_2C_5H_3N, (CHR^2CH_2)_2NH$

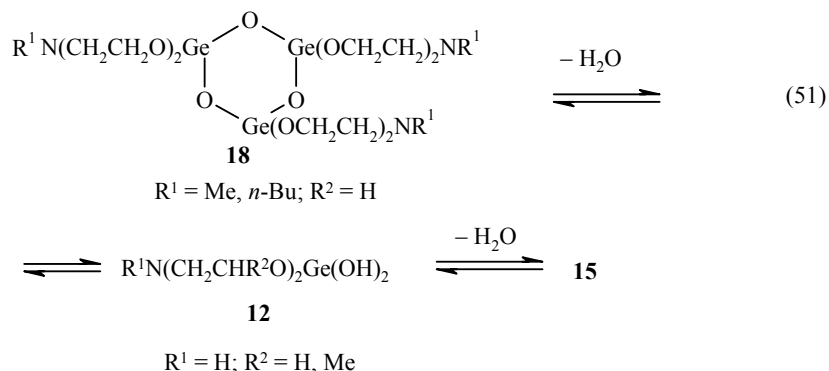
It was noted that the reactions are accelerated by ligands with acidic characteristics [80].

The obtained compounds were solids poorly soluble in most organic solvents but soluble in polar solvents such as methanol and water. For spirogermocanes produced by the reaction of dihydroxygermocanes with  $\alpha$ -hydroxy acids it was established that the Ge–O bonds are hydrolyzed in two days in aqueous solutions with the formation of the initial dihydroxygermocanes (NMR spectroscopy) [91].

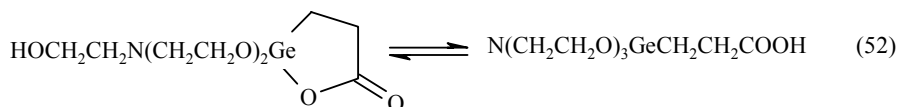
The controlled hydrolysis of the spirocyclic bisgermocane **15** ( $R^1 = Me, R^2 = H$ ) was studied in [68]. The reaction takes place under mild conditions and gives a high yield of the 2,2-dihydroxy derivative **12**.



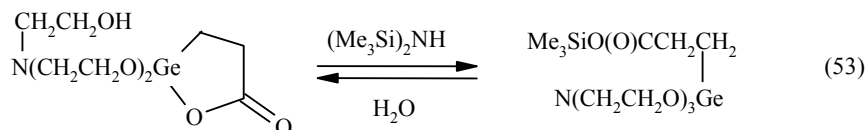
At elevated temperature and during prolonged storage dihydroxygermocanes are susceptible to the elimination of water, and the structure of the self-condensation products depends on the substituent at the nitrogen atom [70]. The addition of water to compounds **15** and **18** leads again to the initial 2,2-dihydroxy derivatives.



The tautomeric germocane–germatrane transition has been studied in a fair amount of detail [63, 81]. It was established by <sup>1</sup>H NMR spectroscopy that the spirocyclic germocane containing a lactone fragment in DMSO-d<sub>6</sub> solution changes reversibly into 1-(2-carboxyethyl)germatrane, and the transannular Ge←N interaction is preserved as a result of this transformation.

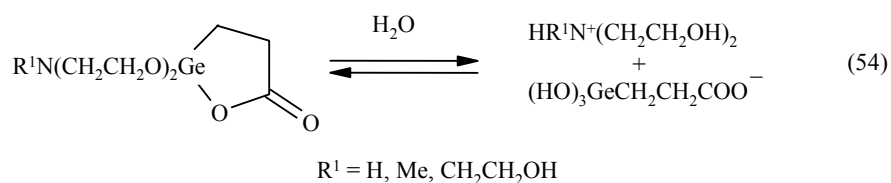


In DMSO-d<sub>6</sub> solution at room temperature both forms (germocane and germatrane) exist. The rate of exchange between the two tautomers increases with increase of temperature. The equilibrium can be shifted toward the germatrane by chemically bonding the proton of the carboxyl group [63]. It was noted that the reaction is reversible in the presence of traces of water.

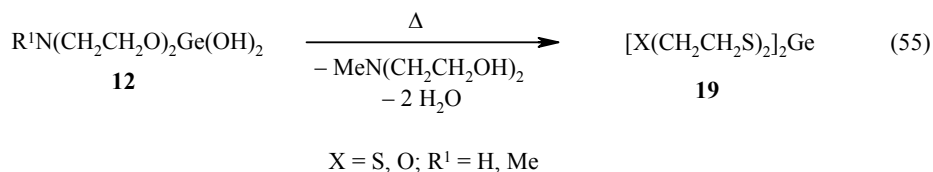


The possibility of germocane–germatrane rearrangement was also considered for another spirogermocane HOOCCH<sub>2</sub>N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>Ge(–CH<sub>2</sub>CH<sub>2</sub>COO–), containing a CH<sub>2</sub>COOH group at the nitrogen atom [63]. Individual signals corresponding to the germocane and germatrane tautomeric forms are not observed in the <sup>1</sup>H and <sup>13</sup>C NMR spectra of this compound in DMSO-d<sub>6</sub>. The authors attribute this fact to the high rate of exchange between these structures even at room temperature.

Spirogermocanes with a lactone ring are hydrolyzed at the Ge–O bonds of both the lactone and the germocane fragment [63]. The reversibility of this process was demonstrated for three compounds by <sup>1</sup>H NMR and IR spectroscopy.

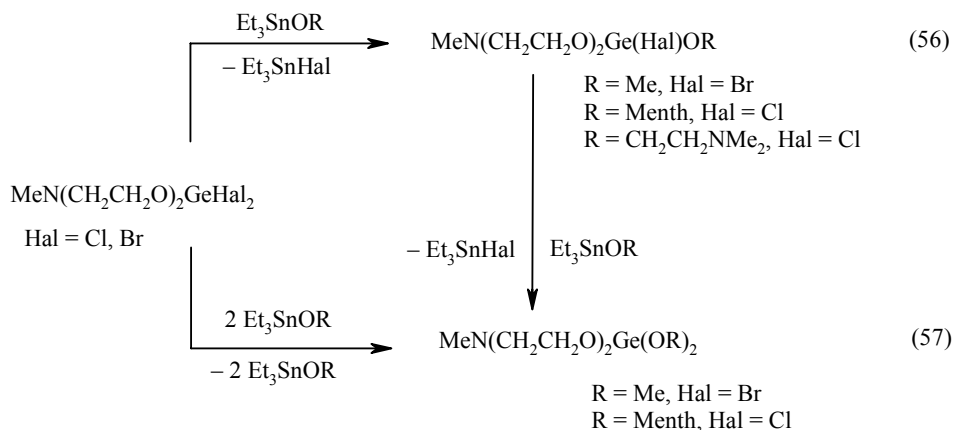


Ligand exchange reactions were studied for the case of dihydroxygermocanes. Treatment of the 2,2-dihydroxy derivatives with two equivalents of  $\text{S}(\text{CH}_2\text{CH}_2\text{SH})_2$  or  $\text{O}(\text{CH}_2\text{CH}_2\text{SH})_2$  gave the thio analogs of bisgermocanes **19** [89].



The authors suggest that the intermediates of the reaction are mixed complexes  $\text{R}^1\text{N}(\text{CH}_2\text{CH}_2\text{O})_2\text{Ge}(\text{SCH}_2\text{CH}_2)_2\text{X}$ , which could not, however, be isolated in individual form.

An investigation into the reactivity of the 2,2-dihalogermocanes that are most promising from the standpoint of the synthesis of new functionally substituted derivatives of the germocane series was started recently [16]. It was established that reaction with an equimolar amount of triethylalkoxystannane leads to selective substitution of one of the halogen atoms by an alkoxy group (56). Subsequent treatment of the obtained alkoxyhalogermocanes with a second equivalent of  $\text{Et}_3\text{SnOR}$  or reaction of the initial dihalo derivatives with two equivalents of  $\text{Et}_3\text{SnOR}$  also led smoothly to the corresponding dialkoxygermocanes (57).



2,2-Dihalo-6-methylgermocanes have also been investigated in reactions with lithium reagents. In the reaction of dibromogermocane with two equivalents of  $\text{PhC}\equiv\text{CLi}$  the only reaction product, containing a phenylethynyl group, was  $(\text{PhC}\equiv\text{C})_4\text{Ge}$  [16, 92]. The treatment of dichlorogermocane with fluorenyllithium led to the corresponding difluorenyl derivative but with an insignificant yield [16]. The reaction of dihalogen derivatives with organolithium reagents cannot therefore be used as a method for the synthesis of new compounds of the germocane series. This is an important difference between germocanes and their tricyclic analogs (germatranes), for which the successful use of lithium reagents was recently described [69].

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