Carbofunctional silacyclobutanes
1. Synthesis of 1-(ω-hydroxyalkyl)silacyclobutanes

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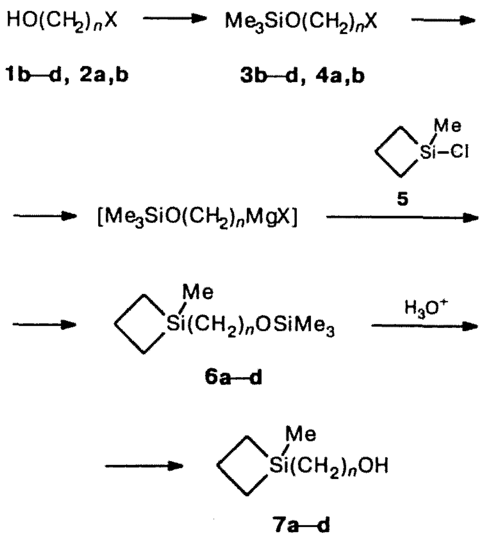
A four-step synthesis of 1-(ω-hydroxyalkyl)- and 1-(4-hydroxyphenyl)silacyclobutanes was carried out. The influence of the structure of the initial compounds and the reaction conditions on the ratio of the reaction products formed was studied. The stability of the silacyclobutane alcohols and the hydrolysis of their trimethylsilyl ethers were investigated.

Key words: carbofunctional silacyclobutanes, alcohols, trimethylsilyl ethers, synthesis.

Carbofunctional silacyclobutanes (CFS) are of considerable interest as monomers for the synthesis of heterochain organosilicon polymers that possess a set of valuable properties.[1,2] However, the CFS known to date are mainly aromatic derivatives with functional groups directly bound to an aromatic nucleus[2,3] (*i.e.*, with an sp^2-hybridized carbon atom). CFS with functional groups at the sp^3-hybridized carbon atom have not been investigated. In addition, among silacyclobutanes with aryl functional groups, halogen derivatives[4] and tertiary amines and derivatives with diphenyloxide group[5] are only known. CFS containing such classical functional groups as hydroxy group (alcoholic or phenolic), carboxy group (free or esterified), nitro, carbonyl, *etc.*, have not been described at all. At the same time, CFS containing alcoholic or halogen groups can serve as a basis for the synthesis of a series of CFS of other classes (carbonyl- and carboxyl-containing, *etc.*).

The present work begins a series of communications on CFS*; it is devoted to silylcyclobutanes containing alcoholic functional groups. We are the first to synthesize 1-(ω-hydroxyalkyl)- and 1-(4-hydroxyphenyl)silacyclobutanes (**7a—d** and **10**) (Schemes 1 and 2). The synthetic scheme starting from the corresponding haloalcohols involves four steps.

Scheme 1



X = Cl (**1**, **3**), Br (**2**, **4**) ; n = 3 (**a**), 4 (**b**), 5 (**c**), 6 (**d**)

The first step (trimethylsilylation with Me_3SiCl) is well known. Pyridine is usually used as the acceptor of HCl.[7] However, it turned out that it is much more convenient to employ dried urea, as recommended by Mironov *et al.*[8] This simplifies the reaction procedure, the isolation of the reaction products, and increases their yields practically up to the quantitative. The second step of the reaction, *i.e.*, the formation of Grignard reagents from haloalkoxy- (or -aryloxy)silanes (HAS), is complicated by the side reactions. On the one hand, the usual reaction of magnesium (in ether or THF) with β-, γ-, and δ-HAS does not afford stable organomagnesium compounds.[9] For example, the reaction of β-HAS with magnesium, regardless of the type of halogen (Cl, Br, or I) and solvent (Et_2O, Bu_2O, Pr^i_2O, or THF), leads to the elimination of ethylene (up to 60 %), as is the case with their ordinary carbon analogs (*e.g.*, $EtOCH_2CH_2Br$),[10] and to the formation of the products of cross-coupling (up to 30 %) in accordance with the radical nature of the reaction. The elimination of cyclopropane and the formation of products of cross-coupling (up to 15 %) are also observed in the case of γ-HAS. The reaction of δ-HAS (especially, of their bromoderivatives) proceeds as cross-coupling (~15 %), the yield of the Grignard reagent in this case being not

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* For preliminary communication, see Ref. 6.

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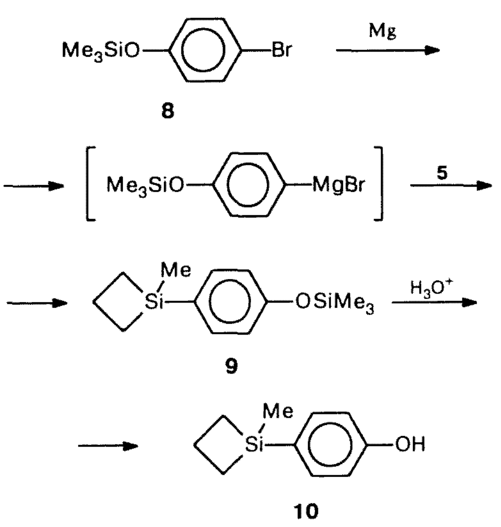
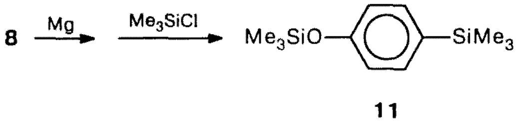
Scheme 2



Scheme 3

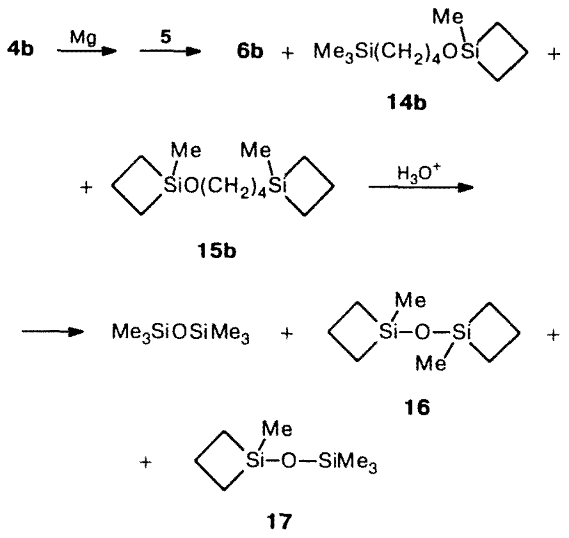


greater than 60 %. It should be noted that the highest yield of the organomagnesium compound (up to 75 %) is observed for the chloro-derivatives. On the other hand, the organomagnesium compounds formed should enter the intra- or intermolecular reaction at the SiOC center, regardless of the number of methylene groups between O and Mg atoms. Formally, in these reactions (intra- or intermolecular nucleophilic substitution at the silicon atom), the carbon atom of the nucleophile and the oxygen atom of the silyloxy group interchange (Speier rearrrangement).[11]

$$\mathrm{Me_3SiO(CH_2)}_n\mathrm{MgX} \longrightarrow \mathrm{Me_3Si(CH_2)}_n\mathrm{OMgX}$$

Such transformations have been observed in the reaction of ω-chloroalkoxy(trimethyl)silanes with lithium, sodium, and magnesium.[11]

Scheme 5



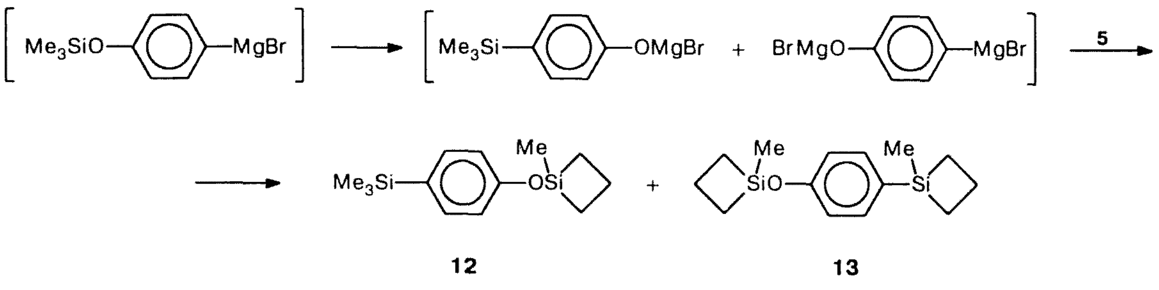
We have synthesized the silacyclobutane derivative of phenol (**10**) according to Scheme 2, which is similar to Scheme 1.

It is long believed that Speier rearrrangement is possible only for aliphatic compounds. In particular, no anomalies have been found[7] in the synthesis of trimethylsilyl *p*-trimethylsilylphenyl ether (**11**) according to Scheme 3.

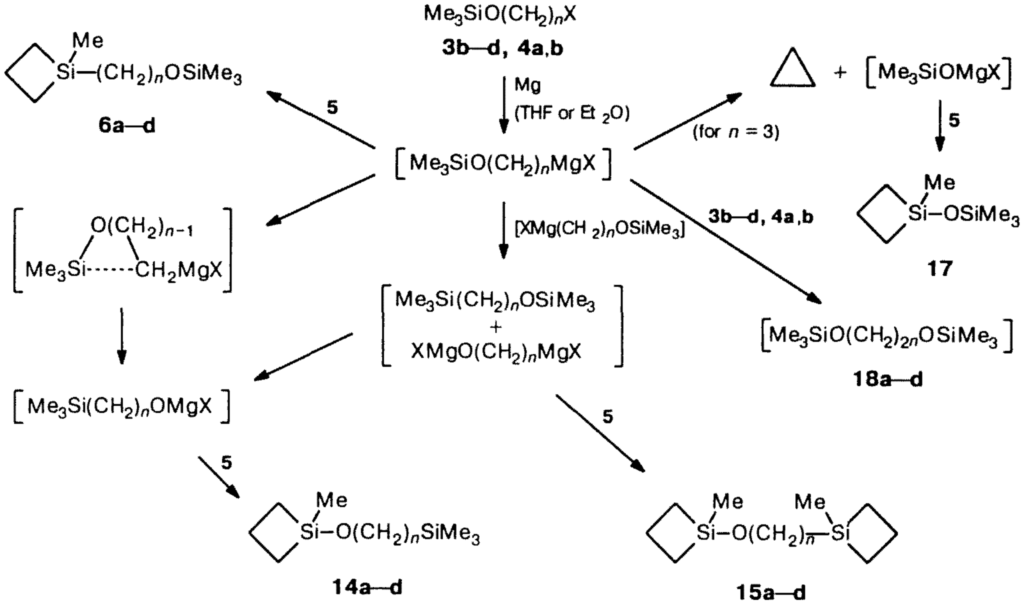
This may be explained by the fact that the reaction with trimethylchlorosilane in this case should result in the same compound no matter whether the rearrangement occurs or not. The rearrangement might be detected only if the reaction mixture is hydrolyzed before treatment with trimethylchlorosilane or if another chlorosilane is introduced into the reaction, *e.g.*, dimethylchlorosilane, ethylmethylchlorosilane, or, as in our case, chlorosilacyclobutane **5** (Scheme 4).

More recently, Mironov *et al.*[12] have established that Grignard reagents from silyl bromophenyl ethers also undergo Speier rearrangement. In a special experiment using compound **4b** as an example we have shown that if the reaction is carried out in the usual way (boiling ether or THF, 40—50 °C) and then quenched with water (Scheme 5), the liberated silanols produce hexamethyldisiloxane and disiloxanes **16** and **17** in a 2 : 8.5 : 3.5 ratio (determined using chromato-mass-spectrometry).

Scheme 4



Scheme 6



Taking into account the data available, we concluded that the real way of suppressing the abovementioned side processes is to prepare the Grignard reagents at a lowest possible temperature. We carried out the reactions of trimethyl(ω-bromoalkoxy)silanes with magnesium in THF at −20 °C (the chloro-derivatives react very slowly at a temperature below 0 °C); magnesium was chemically activated with dibromoethane.[13] In this case, the elimination reactions (for trimethyl(γ-bromopropoxy)silane) and cross-coupling (in all cases) are significantly suppressed, and the yield of the corresponding target ω-trimethylsilyloxyalkyl- (and -aryl)silacyclobutanes reaches 92 %. Nevertheless, the formation of the products of reaction of chlorosilacyclobutane **5** with the products of Speier rearrangement is observed in all cases even at −20 °C. Besides the target **6a—d** and **9**, compounds **12** (see Scheme 4), or **14a—d** (formed as the result of the reaction of chloride **5** with the products of intra- or intermolecular Speier rearrangement), and compound **13** (see Scheme 4) or **15a—d** with two silacyclobutane cycles (formed as the result of the reaction of chloride **5** only with the products of the intermolacular rearrangement) are also present in the reaction mixtures. The reaction mixture contains also the products of the elimination (siloxane **17**) and cross-coupling, $Me_3SiO(CH_2)_{2n}OSiMe_3$ (**18a—d**) and $Me_3SiOC_6H_4C_6H_4OSiMe_3$ (**19**). Scheme 6 generalizes the above data on the reactions of aliphatic HAS with magnesium and chlorosilacyclobutane **5**.

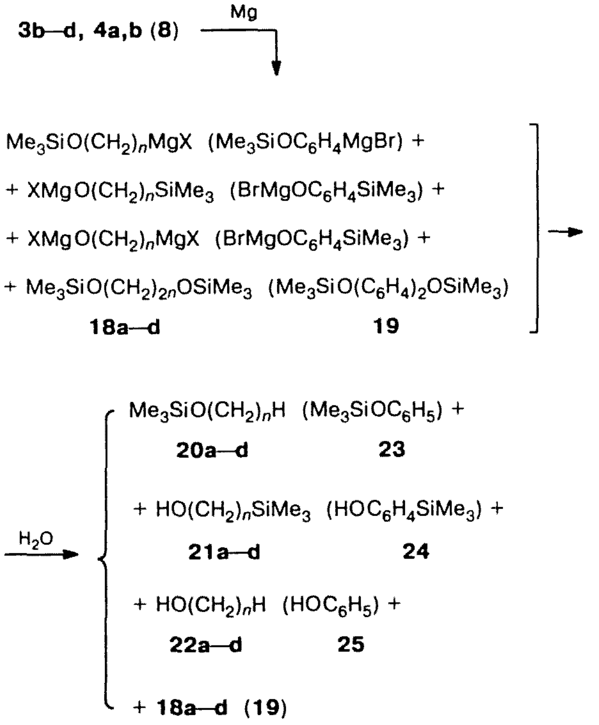
Table 1. The effect of conditions of the reaction of $Me_3SiO(CH_2)_nX$ (**3b—d**, **4a,b**) and $Me_3SiOC_6H_4$-*p*-Br (**8**) with magnesium and chlorosilacyclobutane **5** on the yield of the products

Compound	*T* /°C	Content of the final reaction product (Scheme 7) (%)				Yields of the products of the reaction of HAS with Mg and chlorosilacyclobutane 5 (%)							
						Consecutive procedure				One-pot procedure			
		20a—d; **23***	**21a—d**; **24***	**22a—d**; **25***	**18a—d**; **19***	**6a—d**; **9***	**12***; **14a—d**	**13***; **15a—d**	**18a—d**; **19***	**6a—d**; **9***	**12***; **14a—d**	**13***; **15a—d**	**18a—d**; **19***
4a	20	2.5	24.0	5.0	15.5								
4a	0	56.5	5.5	6.5	3.5	38.5	12.5	11.0	7.0	78.0	4.5	10.5	2.0
4a	−20	84.5	1.0	7.5	0.5	57.0	8.0	15.0	3.0	80.5	2.0	8.0	1.5
3b	20	62.0	18.0	2.0	3.5								
4b	20	54.0	28.5	3.0	14.0	40.0	26.0	22.0	9.0	52.5	12.0	16.0	10.0
4b	0	83.0	6.0	8.0	1.5	67.5	20.0	6.5	5.0	90.0	6.0	2.0	1.5
4b	−20	92.0	1.0	1.0	0.5	72.0	9.0	12.0	1.0	94.5	1.0	1.0	0.5
3c	0	90.0	5.0	3.0	1.0	70.0	12.5	8.5	3.0	92.5	1.5	2.0	0.5
3d	0	86.0	5.5	4.0	1.0	71.5	8.0	11.0	2.0	89.5	2.0	2.0	2.0
8	20	44.5	16.5	23.0	6.0	46.5	12.0	31.0	8.5	57.5	10.0	17.0	8.0
	0	82.0	2.5	8.0	1.5	73.0	5.5	9.0	4.5	86.0	2.0	5.5	2.0

* The starting HAS was **8**.

In order to estimate the influence of different factors (temperature, the character of halogen and the bridge between it and the silicon atom in HAS) on the contribution of the reactions proceeding in this system we determined the composition of the reaction mixture for the consecutive and one-pot reaction procedures (Table 1). In the consecutive procedure, we controlled the consumption of the initial HAS at the first step by GLC, and compound **5** was introduced into the reaction mixture after it had been completely depleted. The process was continued until the test of the reaction mixture for the presence of $Me_3SiO(CH_2)_nH$ (**20a—d**) or $HO(CH_2)_nH$ (**22a—d**) after quenching with an ethanol-water mixture was negative (this denoted that the reaction mixture did not contain compounds with C—Mg and C—OMg bonds). The results of the GLC analysis of the reaction solution after sedimentation of the precipitate are presented in Table 1. In the one-pot procedure, a mixture of the initial HAS and dibromoethane was added to a flask containing activated magnesium and chlorosilacyclobutane **5**. The temperature was kept constant until the decrease in the content of **5** was not observed. The results of the final GLC analysis are given in Table 1. For comparison, the data on the content of the products formed on hydrolysis of the reaction mixture with an ethanol-water mixture (Scheme 7, the derivatives of *p*-bromophenol are given in parentheses) are also included in Table 1.

Scheme 7



These data allow one to estimate the influence of the interaction of the C—Mg, C—OMg, and C—O—C fragments (it is known[14] that chlorosilanes can cleave THF at the C—O bond, especially in the presence of magnesium) on the composition of the products formed.

Examining the data of Table 1, we note first at all that the yields of the target products are much less and the yields of the products of side reactions are higher in the consecutive reaction (preparation of the corresponding Grignard reagent followed by addition of chlorosilane and their interaction at the same temperature) than those determined following quenching with a water-ethanol mixture. This may result from the activation of bimolecular reactions at the SiOC reaction center due to the interaction of the Si—Cl fragment with mixed associates of magnesium etherates and alcoholates. It should be noted that the formation in all cases of side products **15a—d** and **13** (with two silacyclobutane groups) itself indicates that Speier rearrangement proceeds as an intermolecular process (at least, to a very large extent). The data of Table 1 also show that a decrease in temperature to 0 °C and lower results in the most efficient retardation of the cross-coupling: the yields of coupling products decrease to 0.5—2 %. However, the remoteness of the halogen atom from the oxygen atom in HAS by more than three methylene groups has practically no effect on the yield of the target product. Some decrease in the formation of side products **14a—d** (in the case of the consecutive reaction) is noticed only as the number of methylene groups increases from four to six. This may probably be explained by the steric effect of the alkoxy fragment (it is known that the rate of the nucleophilic substitution of alkoxy groups at a silicon atom decreases with increase in their bulk).[15] The noticeably higher amount of product **13** with respect to product **12** in the case of HAS with an arylene bridge may also result from the steric effect of the phenoxy fragment (in the analysis following quenching with an ethanol-water mixture, $Me_3SiOC_6H_4SiMe_3$ is not completely transformed into product **24**, and the SiOAr group also does not react when a mixture of OMgX- and CMgX-containing compounds is treated with chlorosilane). Finally, unlike the consecutive procedure, the one-pot procedure provides the highest yields of the target products in all cases (for the first member of this series, a satisfactory yield of the γ-trimethylsilyloxypropyl derivative of silacyclobutane **6a** can only be obtained by the one-pot procedure). In addition, if the decrease in temperature from 20 to 0 °C increases the yield of target **6a—d** and **9** by ~30—40 %, further decrease in temperature to −20 °C results in only a ~5 % increase in the yield with substantial lengthening of the reaction time.

Thus, the nearly optimum conditions for the preparation of trimethylsiloxyalkyl (or -aryl)silacyclobutanes **6a—d** and **9** from HAS, magnesium, and compound **5** are the realization of the one-pot procedure in THF at ~0 °C.

The physicochemical constants and ^1H NMR and mass spectrometry data for the trimethylsiloxyalkyl (and aryl)silacyclobutane derivatives **6a—d** and **9** obtained

Table 2. Physicochemical properties of compounds **6a—d**, **9**, **13**, and **15a—d**

Compound	B.p./°C (p/Torr)	n_D^{20}	d_4^{20}	Mass spectrum, m/z (I_{rel} (%)) (the main ions)	^{1}H NMR (CCl_4), δ
6a	70—73 (3.0)	1.4442	0.8442	216 $[M]^+$ (0.01), 201 $[M-Me]^+$ (1.4), 188 $[M-C_2H_4]^+$ (34.1), 173 $[M-Me-C_2H_4]^+$ (34.7), 159 $[M-Me-(CH_2)_3]^+$ (59.1), 133 $[M-C_3H_5-(CH_2)_3]^+$ (100), 85 (15.7), 74 $[Me_2SiO]^+$ (17.0), 73 $[Me_3Si]^+$ (38), 43 (58)	0.15 (s, 9 H, OSiMe); 0.33 (s, 3 H, SiMe of the cycle); 0.63—1.22 (m, 2 H, $SiCH_2$; 4 H, α-CH_2 of the cycle); 1.32—2.3 (m, 2 H, CH_2C; 2 H, β-CH_2 of the cycle); 3.57 (t, 2 H, CH_2O)
6b	83.5—86 (1.5—2)	1.4467	0.8549	230 $[M]^+$ (0.7), 215 $[M-Me]^+$ (1.3), 202 $[M-C_2H_4]^+$ (4.2), 187 $[M-Me-C_2H_4]^+$ (9.7), 173 $[M-Me-(CH_2)_3]^+$ (18.9), 159 $[M-Me-(CH_2)_4]^+$ (57.3), 133 $[M-C_3H_5-(CH_2)_4]^+$ (50.1), 131 $[M-Me-C_2H_4-(CH_2)_4]^+$ (100), 74 $[Me_2SiO]^+$ (7.8), 73 $[Me_3Si]^+$ (65.6)	0.17 (s, 9 H, OSiMe); 0.35 (s, 3 H, SiMe of the cycle); 0.65—1.2 (m, 2 H, $SiCH_2$; 4 H, α-CH_2 of the cycle); 1.53 (m, 4 H, $SiCCH_2CH_2C$); 2.14 (m, 2 H, β-CH_2 of the cycle); 3.56 (t, 2 H, CH_2O)
6c	87.5—91 (1.0)	1.4495	0.8612	244 $[M]^+$ (0.35), 229 $[M-Me]^+$ (1.4), 201 $[M-Me-C_2H_4]^+$ (4.0), 159 $[M-Me-(CH_2)_5]^+$ (75.1), 133 $[M-C_3H_5-(CH_2)_5]^+$ (100), 131 $[M-Me-C_2H_4-(CH_2)_5]^+$ (91.1), 74 $[Me_2SiO]^+$ (18.0), 73 $[Me_3Si]^+$ (57.4)	0.18 (s, 9 H, OSiMe); 0.36 (s, 3 H, SiMe of the cycle); 0.70—1.23 (m, 2 H, $SiCH_2$; 4 H, α-CH_2 of the cycle); 1.33—1.74 (m, 6 H, $SiCCH_2CH_2CH_2C$); 2.16 (m, 2 H, β-CH_2 of the cycle); 3.61 (t, 2 H, CH_2O)
6d	102—104 (1.0)	1.4546	0.8705	258 $[M]^+$ (0.3), 243 $[M-Me]^+$ (0.07), 230 $[M-C_2H_4]^+$ (0.1), 215 $[M-Me-C_2H_4]^+$ (2.5), 159 $[M-Me-(CH_2)_6]^+$ (67.5), 133 $[M-C_3H_5-(CH_2)_6]^+$ (100), 131 $[M-Me-C_2H_4-(CH_2)_6]^+$ (76.0), 74 $[M_2SiO]^+$ (73.5), 73 $[Me_3Si]^+$ (70.7)	0.21 (s, 9 H, OSiMe); 0.39 (s, 3 H, SiMe of the cycle); 0.82—1.27 (m, 2 H, $SiCH_2$; 4 H, α-CH_2 of the cycle); 1.36—2.5 (m, 8 H, $SiC(CH_2)_4C$; 2 H, β-CH_2 of the cycle); 3.6 (t, 2 H, CH_2O)
9	83 (0.05—0.06)	1.5105	0.9650	250 $[M]^+$ (12.0), 235 $[M-Me]^+$ (7.5), 222 $[M-C_2H_4]^+$ (100), 207 $[M-C_2H_4-Me]^+$ (30.3), 179 $[M-C_2H_4-Me-C_2H_4]^+$ (27.1), 73 $[Me_3Si]^+$ (26.4). m*197.1 (250→222) $[M]^+-C_2H_4$, m*193.01 (222→207) $[M-C_2H_4]^+-Me$, m*154.8 (207→179) $[M-C_2H_4-Me]^+-C_2H_4$	0.23 (s, 9 H, OSiMe); 0.48 (s, 3 H, SiMe of the cycle); 1.17 (m, 4 H, α-CH_2 of the cycle); 2.12 (m, 2 H, β-CH_2 of the cycle); 6.53—7.46 (m, 4 H, *p*-phenylene)
15a	68—69 (1.0)	1.4596	0.8890	228 $[M]^{+\cdot}$ (0.01), 200 $[M-C_2H_4]^{+\cdot}$ (2.0), 185 $[M-C_2H_4-Me]^+$ (5.7), 172 $[M-C_2H_4-C_2H_4]^{+\cdot}$ (6.0), 159 $[M-C_2H_4-C_3H_5]^+$ (55.3), 145 $[M-C_3H_5-(CH_2)_3]^+$ (58.5), 143 $[M-Me-C_2H_4-(CH_2)_3]^+$ (88.7), 133 (8.3), 131 $[M-C_2H_4-C_3H_5-C_2H_4]^+$ (45.8), 117 $[M-C_2H_4-C_3H_5-(CH_2)_3]^+$ (50.2), 85 (36.8)	0.22 (s, 3 H, OSiMe); 0.4 (s, 3 H, SiMe); 0.77—2.5 (m, 2 H, $SiCH_2$; 8 H, α-CH_2 of the cycles; 2 H, $SiCCH_2CO$; 4 H, β-CH_2 of the cycles); 3.55 (t, 2 H, CH_2O)
15b	83—85.5 (1.0)	1.4646	0.8951	242 $[M]^{+\cdot}$ (0.01), 214 $[M-C_2H_4]^{+\cdot}$ (1.8), 199 $[M-C_2H_4-Me]^+$ (3.1), 186 $[M-C_2H_4-C_2H_4]^{+\cdot}$ (5.0), 159 $[M-C_2H_4-C_4H_7]^+$ (53.4), 145 $[M-C_3H_5-(CH_2)_4]^+$ (51), 143 $[M-Me-C_2H_4-(CH_2)_4]^+$ (71.2), 131 $[M-C_2H_4-C_2H_4-C_4H_7]^+$ (37.5), 117 $[M-C_2H_4-C_3H_5-(CH_2)_4]^+$ (33.2), 85 (35.0)	0.23 (s, 3 H, OSiMe); 0.42 (s, 3 H, SiMe); 0.69—2.53 (m, 2 H, $SiCH_2$; 8 H, α-CH_2 of the cycles; 4 H, $SiCCH_2CH_2CO$; 4 H, β-CH_2 of the cycles); 3.6 (t, 2 H, CH_2O)

Table 2. *(continued)*

Compound	B.p./°C (p/Torr)	n_D^{20}	d_4^{20}	Mass spectrum, m/z (I_{rel} (%)) (the main ions)	^{1}H NMR (CCl$_4$), δ
15c	102—105 (1.0)	1.4680	0.8972	256 $[M]^{+\cdot}$ (0.01), 228 $[M-C_2H_4]^{+\cdot}$ (1.5), 213 $[M-Me-C_2H_4]^+$ (3.0), 200 $[M-C_2H_4-C_2H_4]^{+\cdot}$ (4.8), 159 $[M-C_2H_4-C_5H_9]^+$ (57.2), 157 $[M-Me-(CH_2)_5]^+$ (8.0), 145 $[M-C_3H_5-(CH_2)_5]^+$ (87.8), 143 $[M-Me-C_2H_4-(CH_2)_5]^+$ (67.6), 131 $[M-C_2H_4-C_2H_4-C_5H_9]^+$ (30.1), 117 $[M-C_2H_4-C_3H_5-(CH_2)_5]^+$ (31.5), 85 (28.3), 43 (100)	0.21 (s, 3 H, OSiMe); 0.38 (s, 3 H, SiMe); 0.68—2.25 (m, 2 H, SiCH$_2$; 8 H, α-CH$_2$ of the cycles; 6 H, SiCCH$_2$CH$_2$CH$_2$CO;4 H, β-CH$_2$ of the cycles); 3.68 (t, 2 H, CH$_2$O)
15d	121—123 (1—1.5)	1.4701	0.8990	270 $[M]^{+\cdot}$ (0.01), 255 $[M-Me]^+$ (0.4), 242 $[M-C_2H_4]^{+\cdot}$ (1.0), 227 $[M-Me-C_2H_4]^+$ (3.5), 199 $[M-Me-C_2H_4-C_2H_4]^+$ (7.0), 171 $[M-Me-(CH_2)_6]^+$ (10.1), 159 $[M-C_2H_4-C_6H_{11}]^+$ (59.4), 145 $[M-C_3H_5-(CH_2)_6]^+$ (100), 143 $[M-Me-C_2H_4-(CH_2)_6]^+$ (54.7), 131 $[M-C_2H_4-C_2H_4-C_6H_{11}]^+$ (22.7), 117 $[M-C_3H_5-C_2H_4-(CH_2)_6]^+$ (34.3), 85 (32.3)	0.23 (s, 3 H, OSiMe); 0.41 (s, 3 H, SiMe); 0.73—2.61 (m, 2 H, SiCH$_2$; 8 H, α-CH$_2$ of the cycles; 8 H, SiC(CH$_2$)$_4$CO; 4 H, β-CH$_2$ of the cycles); 3.62 (t, 2 H, CH$_2$O)
13	92.5—93.5 (0.06)	1.5208	0.9873	262 $[M]^{+\cdot}$ (11.6), 234 $[M-C_2H_4]^{+\cdot}$ (100), 222 $[M-C_3H_4]^+$ (12.5), 221 $[M-C_3H_5]^+$ (12.2), 191 (12.5), 85 (6.2), 43 (12.5)	0.23 (s, 3 H, OSiMe); 0.49 (s, 3 H, SiMe); 0.88—1.4 (m, 8 H, α-CH$_2$ of the cycles); 1.87—2.39 (m, 4 H, β-CH$_2$ of the cycles); 6.55—7.50 (m, 4 H, *p*-phenylene)

and the silacyclobutoxyalkyl- (and -aryl)silacyclobutanes **15a—d** and **13** formed as side products are given in Table 2. The latter products were isolated by rectification (for all the cases) from the combined bottoms of several experiments.

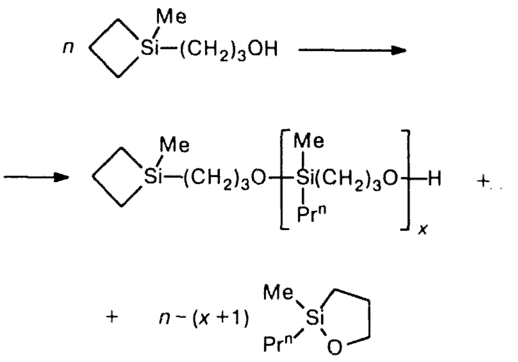
The ^{1}H NMR spectra of ω-trimethylsiloxyalkyl derivatives **6a—d** contain well-resolved singlet signals for the protons of the trimethylsilyl group and the methyl substituent at the heteroatom of the cycle (0.15—0.21 and 0.33—0.39 ppm, respectively). The spectra of all aliphatic derivatives with one (**6a—d**) and two (**15a—d**) cycles have well-defined triplets of protons of the methylene group linked to the oxygen atom (3.56—3.61 ppm). In monocyclic compounds **6a—d**, the signals for the protons of α-methylene groups of the cycle partially overlap the signals for a noncyclic methylene group linked to the silicon atom. The centers of multiplets of signals for the β-CH$_2$ group of the cycle lie within 2.14—2.16 ppm. For aromatic derivative **9**, the signals of all the types of protons are totally resolved. Some broading of the signals of protons for α- and β-CH$_2$ groups is observed in the ^{1}H NMR spectra of compounds **15a—d** and **13** with two silacyclobutane cycles, which results from the superposition of the signals of the corresponding protons of both cycles.

In the mass spectra of the compounds obtained, a molecular ion with intensity greater than 10 % is observed only for compounds with an arylene bridge (**9** and **13**), whereas for other compounds (**6a—d** and **15a—d**), the intensity of the molecular ion is very low. For **9** and **13**, the main ion in the spectrum arises from the elimination of ethylene, which is typical of silacyclobutanes.[16] The main fragmentation pathways in the mass spectra of the aliphatic derivatives involve elimination of the aliphatic bridge, which is accompanied by the formation of the siloxane bond. For example, in the spectra of compounds with tri- and tetramethylene bridges (**6a** and **6b**), the peaks with maximum intensity correspond to the ions formed on the elimination of ethylene molecule, methyl group, and the bridge (peaks with m/z 131). For compounds with penta- and hexamethylene bridges (**6c** and **6d**), these ions are formed as the result of elimination of the bridge and allyl radical (m/z 133). For the dicyclic structures with tri-, tetra-, and pentamethylene bridges (**15a—c**), the peaks with maximum intensities are assigned to the propyl radical (m/z 43), and for the structures with hexamethylene bridge (**6d**), to the ions corresponding to the elimination of the bridge and allyl radical (in this case, m/z 145), like for their trimethylsilyl analog. In this case, the intensity of the $[M-C_3H_5-(CH_2)_n]^+$ ion with m/z 145 increases monotonously from 58.5 % (n = 3) to 100 % (n = 6). An inverse dependence (the decrease in the intensity with the extension of the bridge) is observed for the ion with m/z 143 in the series of compounds with two silacyclobutane groups. The intensity of the ion with m/z 159 corresponding to the elimination of the methyl group and the aliphatic bridge ($[M-CH_3-(CH_2)_n]^+$) remains practically constant at different *n* for both series of compounds with one and two silacyclobutane cycles. The peak of medium intensity (from 10 to 39 %) with *m/z* 117 (corresponding probably to the $[Me(H)SiOSi(Me)=CH_2]^+$ fragment), which is present in the spectra of all the compounds of aliphatic series, results also from the rearrangement and elimination of the polymethylene bridge. Finely, the structure of the compound with the aromatic bridge and one silacyclobutane cycle (**9**) is confirmed by metastable transitions (see Table 2).

The structures of other compounds (**12** and **14a—d**, **19** and **18a—d**, **20a—d**, **21a—d**, **22a—d**, as well as **23**, **24**, and **25**) were determined by chromato mass-spectrometry. To identify the products of the cross-coupling (**18a—d**), the literature data[17,18] were used.

The final step of the Scheme 1, the removal of the silyl protection, is known to proceed without difficulty. We used conventional hydrolysis in an aqueous-ethereal system; the reaction was monitored by chromatography. The results, which are summarized in Table 3, allow one to estimate the relative rates of hydrolysis of silyl ethers **6a—d** and **9** from the time these compounds cannot be detected in the reaction mixture by GLC.

As one would expect,[19] the first member of the series of aliphatic 1-(ω-trimethylsiloxyalkyl)silacyclobutanes under consideration, compound **6a** with a trimethylene bridge, is most readily hydrolyzed. However, the observation that the far more rapid consumption of the initial **6a** is accompanied by the lowest yield of the corresponding alcohol (**7a**) as compared with the yields of the subsequent members of this series, suggests that compound **7a** formed is unstable. In fact, when the initial **6a** is no longer found in the reaction mixture, the content of alcohol **7a** continues to decrease, and the target product will be lost if some precautions are not taken. To obtain **7a** in largest yield, a higher dilution, lower temperature (0—2 °C), strict chromatographic control, and rapid separation (also with cooling) of aqueous and organic phases immediately after the reaction and in the subsequent operations should be used. A "quick" drying agent (*e.g.*, $MgSO_4$) should be applied (also with cooling), distillation should be carried out at the lowest possible pressure, product **7a** should be collected into a cooled flask, and the product obtained should be immediately characterized (a change in the integral intensities in the ^1H NMR spectra, as well as a change in the refraction index, are observed immediately after the first measurements). Possibly, the inter- and intramolecular cleavage of the Si—C bond in the silacyclobutane occurs in this case.*



Unstable **7a** should be stored at temperatures much lower than 0 °C (good results can be obtained with storage in Dewar flask with solid CO_2). Other silacyclobutane alcohols do not require special precautions in the synthesis and isolation.

The Speier rearrangement of 1-(ω-haloalkoxy)-silacyclobutanes, which, as we have found, is one of the side reactions decreasing the yield of the Grignard reagent, can serve as an alternative to the synthetic Scheme 1. The next communication is devoted to the application of this method for the synthesis of silacyclobutane alcohols.

The physicochemical constants and the ^1H NMR and mass spectral data for compounds **7a—d** and **10** obtained are presented in Table 4.

In the ^1H NMR spectra of alcohols **7a—d**, the chemical shifts of singlet signals for the protons of the SiMe methyl groups lie within 0.3—0.33 ppm, *i.e.*, they prac-

Table 3. Synthesis of silacyclobutane alcohols **7a—d** and **10** by hydrolysis of their trimethylsilyl ethers **6a—d** and **9**

Compound	Reaction time/h	*T*/°C	Yield of **7a—d** and **10** according to GLC (%)	Yield of isolated **7a—d** and **10** (%)
7a	1.25	20	15—17	8—11
	2.0	0—2	78—82	44—48
	2.75	0—2	85—90	55—62
7b	4.5	20	94—96	78—84
7c	4.25	20	92—97	77—81
7d	5.0	20	89—94	75—80
10	4.0	20	86—92	70—76

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* This reaction will be considered in detail in one of the subsequent communications.

Table 4. Physicochemical properties of silacyclobutane alcohols **7a—d** and **10**

Compound	B.p./°C (p/Torr)	n_D^{20}	d_4^{20}	Mass spectrum, m/z (I_{rel} (%)) (the main ions)	^{1}H NMR (CCl_4), δ
7a	39.5—41.5 (0.042—0.05)	1.4718	0.8910	144 $[M]^{+\cdot}$ (1.0), 129 $[M-Me]^+$ (4.2), 115 $[M-Et]^+$ (1.7), 101 $[M-C_2H_4-Me]^+$ (100), 74 $[Me_2SiO]^{+\cdot}$ (13.4), 73 $[M-C_2H_4-Me-C_2H_4]^+$ (48.7), 43 (12.6)	0.3 (s, 3 H, SiMe); 0.62—1.31 (m, 2 H, $SiCH_2$; 4 H, α-CH_2 of the cycle); 1.7 (m, 2 H, CCH_2C); 2.1 (m, 2 H, β-CH_2 of the cycle); 3.61 (t, 2 H, CH_2O); 4.21 (s, 1 H, OH)
7b	64.5—65 (1.0)	1.4728	0.9041	158 $[M]^{+\cdot}$ (3.2), 143 $[M-Me]^+$ (5.4), 129 $[M-Et]^+$ (0.85), 115 $[M-C_2H_4-Me]^+$ (100), 87 $[M-C_2H_4-Me-C_2H_4]^+$ (37.3), 74 $[Me_2SiO]^{+\cdot}$ (29.7), 73 (5.4), 43 (14.3)	0.32 (s, 3 H, SiMe); 0.62—1.21 (m, 2 H, $SiCH_2$; 4 H, α-CH_2 of the cycle); 1.56 (m, 4 H,CCH_2CH_2C); 2.12 (m, 2 H, β-CH_2 of the cycle);3.56 (t, 2 H, CH_2O); 4.09 (s, 1 H, OH)
7c	72—73 (2.0)	1.4761	0.9049	172 $[M]^{+\cdot}$ (0.9), 157 $[M-Me]^+$ (5.0), 143 $[M-Et]^+$ (1.05), 129 $[M-C_2H_4-Me]^+$ (100), 115 (9.1), 101 $[M-C_2H_4-Me-C_2H_4]^+$ (34.8), 61 (31.7), 43 (7.9)	0.33 (s, 3 H, SiMe); 0.66—1.88 (m, 2 H, $SiCH_2$; 4 H, α-CH_2 of the cycle; 6 H, $CCH_2CH_2CH_2C$); 2.12 (m, 2 H, β-CH_2 of the cycle); 3.58 (t, 2 H, CH_2O); 4.3 (s, 1 H, OH)
7d	86—88.5 (2.0)	1.4789	0.9069	186 $[M]^{+\cdot}$ (0.95), 171 $[M-Me]^+$ (4.8), 157 $[M-Et]^+$ (1.5), 143 $[M-C_2H_4-Me]^+$ (100), 115 $[M-C_2H_4-Me-C_2H_4]^+$ (38.5), 101 (7.1), 74 (6.1), 73 (8.8), 43 (8.5)	0.31 (s, 3 H, SiMe); 0.61—2.38 (m, 2 H, $SiCH_2$; 4 H, α-CH_2 of the cycle; 8 H, $C(CH_2)_4C$; 2 H, β-CH_2 of the cycle); 3.55 (t, 2 H, CH_2O);4.41 (s, 1 H, OH)
10	M.p./°C 95—99			178 $[M]^{+\cdot}$ (6.5), 163 $[M-Me]^+$ (1.5), 150 $[M-C_2H_4]^+$ (100), 137 $[M-C_3H_5]^+$ (12.3), 135 $[M-C_2H_4-Me]^+$ (30.2), 43 (9.5)	

tically do not depend on the number of methylene groups in the bridge. The differences in the chemical shifts of triplet signals for the protons of methylene groups linked to the oxygen atom are also rather small (3.55—3.61 ppm). The signals for the protons of the internal methylene groups of the $[SiC(CH_2)_{n-2}CO]$ bridge are superimposed on each other and partially on the signals of β-methylene groups of the cycle at 60 MHz, but at 300 MHz, the spectra of **7a** and **7b** (n = 3 and n = 4, respectively) are completely resolved. The values of the chemical shifts of protons of methylene groups of the bridges are close to those in the spectra of the corresponding trimethylsilyl analogs.[20,21]

The fragmentation of aliphatic alcohols **7a—d** under electron impact is identical for all the members of the series. The mass spectra are characterized by low-intense molecular ions (1—3 %) and by slightly more intense ions corresponding to the elimination of a methyl group (4—5 %). The ion corresponding to the elimination of ethylene, which is typical of ordinary nonfunctional silacyclobutane derivatives, is not manifested altogether in the spectra of these compounds, but the spectra contain a weak (not more than 2 %) $[M-Et]^+$ ion which sometimes appears in mass spectra of some silacyclobutanes.[22] The $[M-C_2H_4-Me]^+$ ion corresponding to the elimination of both ethylene and methyl group appears to be the main ion (with a maximum intensity) in the spectra of all aliphatic alcohols **7a—d**. Another ion typical of all the members of the series is the $[M-C_2H_4-Me-C_2H_4]^+$ ion, which is formed as a result of the elimination of two ethylene molecules and methyl radical (35—45 %). Thus, in the case of alcohols **7a—d**, the electron impact does not result in complete elimination of the polymethylene bridge as occurs in the case of their trimethylsilyl ethers, but two methylene groups and the second C_2H_4 molecule are eliminated from the each bridge (the easy elimination of the methyl group from $[M-C_2H_4]^+$ and $[M-2\ C_2H_4]^+$ ions is typical of 1-methyl-1-alkylsilacyclobutanes).[23] The mass spectrum of phenol derivative **10** contains a pronounced peak with maximal intensity of the molecular ion corresponding to the elimination of ethylene (m/z 163 $[M-C_2H_4]^+$) and a rather intense (more than 30 %) peak which results from the elimination of ethylene and methyl group.

Experimental

Mass spectra (EI) were obtained on LKB-2091 and Kratos MS-25 RF (70 eV) instruments. ^{1}H NMR spectra were recorded on Varian T-60 and Bruker MSL-300 instruments in CCl_4 with $SiMe_4$ as the internal standard. 1-Chloro-1-methylsilacyclobutane was obtained by the known procedure.[24] Commercial trimethylchlorosilane, α-halo-ω-hydroxyalkanes, and *p*-bromophenol were distilled before use. Ether, hexane, benzene, toluene, and THF were dried by usual methods.

Trimethylsilyl haloalkyl ethers (3b—d, 4a,b) and trimethylsilyl *p*-bromophenyl ether (8). Trimethylchlorosilane (1 equiv.) was added to a mixture of urea dried in a desiccator (1.1 equiv.) and ω-haloalkan-1-ol (1.05 equiv., without a solvent) or *p*-bromophenol (1.5—2 *M* solution in abs. benzene or toluene) with stirring and maintaining the temperatute below 40 °C. The mixture was stirred at 40—50 °C for 1.5 h, cooled, and the reaction products were separated by decantation or filtration. Distillation *in vacuo* afforded **1a—e** in 93, 95, 96, 91, and 92 % yields, respectively. Their constants are in good agreement with the literature data.[11]

1-Methyl-1-(ω-trimethylsiloxyalkyl)silacyclobutanes (6a—d) and 1-methyl-1-(4-trimethylsiloxyphenyl)silacyclobutane (9). General procedure. *A*. Consecutive procedure. A finely dispersed magnesium powder (1.0 g-at.) in abs. THF (350 mL) was activated with 1,2-dibromoethane (0.05 mol) in dry argon. After the reaction was completed, a solution of 1,2-dibromoethane (0.2 mol) and halide **3b—d**, **4a,b**, or **8** (0.7 mol) in THF (100 mL) was added over 6.5 h on cooling (usually at 0 °C and at −20 °C for trimethylene derivative **4a**). The mixture was then stirred on cooling until the complete consumption of the initial halide was established by GLC (usually for 2—4 h); if needed, the temperature was raised by 5° and the reaction was continued. A solution of 1-chloro-1-methylsilacyclobutane (**5**) (0.71 mol) in the same volume of THF was added over ~2.5 h on cooling. The mixture was stirred until the aliquot of the reaction mixture gave a negative result for the presence of Me_3SiORH or HORH after treatment with an ethanol-water mixture. Then abs. hexane (0.4 L) was added, the mixture was stirred, and the precipitate of magnesium halide was filtered off in dry atmosphere. The solvents and an excess of chloride **5** were removed, and the residue was distilled *in vacuo*.

***B*. One-pot procedure.** Powdered magnesium (1 g-at.) was activated with 1,2-dibromoethane (0.05 mol) in THF (450 mL) similarly to the procedure described above. The mixture was cooled to 0 °C and chloride **5** (0.71 mol) was added. Then a mixture of Me_3SiORX **3b—d**, **4a,b**, or **8** (0.7 mol) and 1,2-dibromoethane (0.2 mol) was added over 6.5 h on cooling and the mixture was stirred until the amount of chloride **5** in the reaction mixture (according to GLC data) ceased to decrease (usually for not less than 2 h). The temperature of the reaction mixture was raised to room temperature, then dry hexane (400 mL) was added, and the target products (**6a—d** and **9**) were isolated by the procedure described above (the yields and physicochemical constants are given in Table 2). **6a**. Found (%): C, 55.34; H, 11.31; Si, 26.16. $C_{10}H_{24}OSi_2$. Calculated (%): C, 55.48; H, 11.18; Si, 25.95. **6b**. Found (%): C, 57.49; H, 11.19; Si, 24.52. $C_{11}H_{26}OSi_2$. Calculated (%): C, 57.32; H, 11.37; Si, 24.37. **6c**. Found (%): C, 58.81; H, 11.29; Si, 23.30. $C_{12}H_{28}OSi_2$. Calculated (%): C, 58.94; H, 11.54; Si, 22.97. **6d**. Found (%): C, 60.44; H, 11.78; Si, 22.02. $C_{13}H_{30}OSi_2$. Calculated (%): C, 60.39; H, 11.70; Si, 21.72. **9**. Found (%): C, 62.38; H, 9.04; Si, 22.56. $C_{13}H_{22}OSi_2$. Calculated (%): C, 62.33; H, 8.85; Si, 22.42.

1-Methyl-1-[ω-(1-methylsilacyclobutoxy)alkyl]silacyclobutanes (15a—d) and 1-methyl-1-[4-(1-methylsilacyclobutoxy)phenyl]silacyclobutane (13) were isolated from the bottoms by rectification *in vacuo* (their physicochemical constants are given in Table 2). **15a**. Found (%): C, 57.97; H, 10.63; Si, 24.73. $C_{11}H_{24}OSi_2$. Calculated (%): C, 57.82; H, 10.59; Si, 24.58. **15b**. Found (%): C, 59.64; H, 12.02; Si, 23.28. $C_{12}H_{26}OSi_2$. Calculated (%): C, 59.43; H, 10.81; Si, 23.16. **15c**. Found (%): C, 61.12; H, 11.20; Si, 22.05. $C_{13}H_{28}OSi_2$. Calculated (%): C, 60.86; H, 11.00; Si, 21.90. **15d**. Found (%): C, 62.36; H, 11.40; Si, 20.98. $C_{14}H_{30}OSi_2$. Calculated (%): C, 62.15; H, 11.18; Si, 20.76. **13**. Found (%): C, 64.28; H, 8.74; Si, 21.61. $C_{14}H_{22}OSi_2$. Calculated (%): C, 64.06; H, 8.45; Si, 21.40.

Synthesis of silacyclobutane alcohols 7a—d and 10 by hydrolysis of their silyl ethers. General procedure. Silyl ether **6a—d** or **9** (0.05 mol) was added to a mixture of ether (50 mL or 150 mL for **6a**) and water (10 mL) (in the case of **6a**, the mixture was cooled with ice). The mixture was vigorously stirred, and the hydrolysis was monitored by GLC. After the reaction was completed, the organic layer was separated, the aqueous layer was extracted with ether (2×30 mL, or 2×60 mL for **7a**), and the combined layers were washed with water and dried with Na_2SO_4 (or $MgSO_4$). For the trimethylene derivative, cooled solvents (ether or water) were used, and the products were dried with the most effective drying agent (*e.g.*, $MgSO_4$) on cooling. Physicochemical constants for **7a—d** and **10** are given in Table 4. **7a**. Found (%): C, 58.54; H, 11.21; Si, 19.58. $C_7H_{16}OSi$. Calculated (%): C, 58.27; H, 11.18; Si, 19.46. **7b**. Found (%): C, 60.43; H, 11.61; Si, 18.06. $C_8H_{18}OSi$. Calculated (%): C, 60.69; H, 11.46; Si, 17.74. **7c**. Found (%): C, 62.89; H, 11.90; Si, 16.49. $C_9H_{20}OSi$. Calculated (%): C, 62.72; H, 11.70; Si, 16.30. **7d**. Found (%): C, 64.72; H, 11.81; Si, 15.33. $C_{10}H_{22}OSi$. Calculated (%): C, 64.45; H, 11.90; Si, 15.07. **10**. Found (%): C, 67.68; H, 8.14; Si, 16.02. $C_{10}H_{14}OSi$. Calculated (%): C, 67.36; H, 7.91; Si, 15.75.

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