Carbofunctional silacyclobutanes
2.* Use of Speier rearrangement for the synthesis of silacyclobutanes with alcoholic functions

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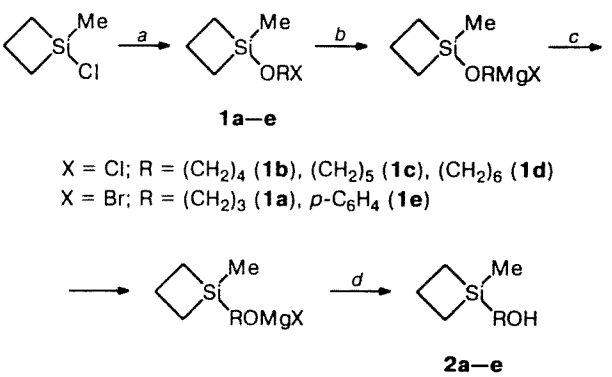
Speier rearrangement was used for the synthesis of 1-(ω-hydroxyalkyl)- and 1-(4-hydroxyphenyl)silacyclobutanes.

Key words: carbofunctional silacyclobutanes, alcohols, synthesis.

In a preceding commmunication[1] we have described the synthesis of 1-(ω-hydroxyalkyl)- and 1-(hydroxyaryl)silacyclobutanes by hydrolysis of their trimethylsilyl ethers, which in turn have been prepared from ω-trimethylsiloxyalkyl halides by the action of Grignard reagents on 1-methyl-1-chlorosilacyclobutane. In addition to the main reaction affording the target products, Grignard reagents underwent the so-called Speier rearrangement,[2] which involves nucleophilic attack on the SiOC group that decreased the yield of the desired products. It is established in the present work that the Grignard reagents prepared from 1-(ω-haloalkoxy)silacyclobutanes readily rearrange, which may serve as an alternative method for the synthesis of the corresponding silacyclobutane alcohols.[2] The scheme proposed involves the synthesis of haloalkoxy- or aryloxysilacyclobutanes (**1a—e**) (step *a*), preparation of the Grignard reagents from them (step *b*), rearragement (step *c*), and hydrolysis of the magnesium alcoholate formed (step *d*) to form silacyclobutane alcohols (**2a—e**) (Scheme 1).

Scheme 1



1a—e

X = Cl; R = $(CH_2)_4$ (**1b**), $(CH_2)_5$ (**1c**), $(CH_2)_6$ (**1d**)
X = Br; R = $(CH_2)_3$ (**1a**), *p*-C_6H_4 (**1e**)

2a—e

R = $(CH_2)_3$ (**2a**), $(CH_2)_4$ (**2b**), $(CH_2)_5$ (**2c**), $(CH_2)_6$ (**2d**), *p*-C_6H_4 (**2e**)

Halides **1a—e** that can be obtained in the first step in ~90 % yield are mobile liquids with a rather pleasant smell. Distillation at a sufficiently high vacuum at a lowest possible temperature is needed for their isolation, like in the case of other silacyclobutanes. The physicochemical constants and mass and ^1H NMR spectral data for compounds **1a—e** are given in Table 1.

The strongly coupled $[A]_4[B]_2$ spin system of protons of the cyclic methylene groups of compounds **1a—e** becomes even more complicated due to the presence of an electron-withdrawing substituent at the silicon atom, and the signals for the protons of the α- and β-CH_2 groups of the heterocycle in the ^1H NMR spectra of **1a—e** are somewhat drawn together, as is usually observed in silacyclobutanes with the Si—OC bond.[3] In the spectra of **1a—d**, these signals are partially superimposed with those for the internal CH_2 groups of the bridges. The triplet signals for the protons of the terminal CH_2 groups of the bridges (CH_2O and CH_2Cl for **1b—d** and CH_2O and CH_2Br for **1a**) are well resolved and their chemical shifts differ from each other by ~0.2 ppm on the average.

Mass spectra of silacyclobutanes **1a—e** are rather characteristic. Their distinguishing feature is the low intensity of peaks of the molecular ion and of ions corresponding to the elimination of the methyl group, one and two ethylene molecules, as well as the ethyl group. At the same time, the peaks corresponding to the $[M-C_2H_4-Me]^+$ ion formed on the elimination of ethylene and the methyl group have high intensities, and the main ions in the spectra are the $[M-C_2H_4-Et]^+$ ions formed on the elimination of the ethyl group and the ethylene molecule.

* For Part 1, see Ref. 1.

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Table 1. Physicochemical characteristics of 1-methyl-1-(ω-haloalkoxy)silacyclobutanes (**1a—d**) and 1-methyl-1-(*p*-bromophenoxy)silacyclobutane (**1e**)

Compound	R	X	Yield (%)	B.p./°C (*p*/Torr)	n_D^{20}	d_4^{20}	Mass spectrum, *m/z* (I_{rel} (%))	^{1}H NMR, δ
1a	$(CH_2)_3$	Br	88.5	80—82 (5.5—6)	1.4701	1.2074	222/224 $[M]^{+\cdot}$ (0.9/0.85), 207/209 $[M-Me]^+$ (1.1/1.05), 194/196 $[M-C_2H_4]^{+\cdot}$ (1.8/1.9), 193/195 $[M-Et]^+$ (1.3/1.3), 179/181 $[M-C_2H_4-Me]^+$ (46.2/45.8), 166/168 $[M-C_2H_4-C_2H_4]^{+\cdot}$ (10.5/10.1), 165/167 $[M-Et-C_2H_4]^+$ (100/41.2),122/124 (64/63.7)	0.36 (s, 3 H, SiMe); 0.89—2.26 (m, 4 H, α-CH_2 of the cycle; 2 H, 2 H, $OCCH_2CBr$; β-CH_2 of the cycle); 3.42 (t, 2 H,CH_2O); 3.6 (t, 2 H, CH_2Br)
1b	$(CH_2)_4$	Cl	94	84—87 (5—6)	1.4591	0.9857	192/194 $[M]^{+\cdot}$ (0.1/0.02), 177/179 $[M-Me]^+$ (1.1/0.26), 164/166 $[M-C_2H_4]^{+\cdot}$ (0.6/0.25), 163/165 $[M-Et]^+$ (0.65/0.4), 149/151 $[M-C_2H_4-Me]^+$ (27.5/10.4), 136/138 $[M-C_2H_4-C_2H_4]^{+\cdot}$ (13.3/4.4), 135/137 $[M-Et-C_2H_4]^+$ (100/35.8), 122 (34.7), 109 (42.8), 107 (21.4), 97 (14.7), 95 (46.9), 92/94 (61.2/25.4)	0.39 (s, 3 H, SiMe); 0.92—2.29 (m, 4 H, α-CH_2 of the cycle; 4 H, $OCCH_2CH_2CCl$; β-CH_2 of the cycle); 3.45 (t, 2 H, CH_2O); 3.68 (t, 2 H,CH_2Cl)
1c	$(CH_2)_5$	Cl	95	92—94 (5.5—6)	1.4626	0.9860	206/208 $[M]^{+\cdot}$ (0.2/0.08), 191/193 $[M-Me]^+$ (1.4/0.55), 178/180 $[M-C_2H_4]^{+\cdot}$ (0.75/0.35), 177/179 $[M-Et]^+$ (0.9/0.45), 163/165 $[M-C_2H_4-Me]^+$ (34.3/15.1), 150/152 $[M-2\ C_2H_4]^+$ (17.4/7.2), 149/151 $[M-Et-C_2H_4]^+$ (100/40.1), 136 (28.5), 123 (37.2), 121 (19.1), 111 (9.5), 109 (40.3), 106/108 (48.5/18.6), 100 (5.3), 92 (6.6)	0.37 (s, 3 H, SiMe), 0.89—2.28 (m, 4 H, α-CH_2 of the cycle; 6 H, $OCCH_2CH_2CH_2CCl$; 2 H, β-CH_2 of the cycle); 3.43 (t, 2 H, CH_2O); 3.7 (t, 2 H, CH_2Cl)
1d	$(CH_2)_6$	Cl	90	102—103.5 (6)	1.4674	0.9868	220/222 $[M]^{+\cdot}$ (0.25/0.08), 215/217 $[M-Me]^+$ (1.6/0.65), 192/194 $[M-C_2H_4]^{+\cdot}$ (0.95/0.45), 191/193 $[M-Et]^+$ (1.1/0.45), 177/179 $[M-C_2H_4-Me]^+$ (30.6/14.4), 164/166 $[M-C_2H_4-C_2H_4]^{+\cdot}$ (15.5/7.0), 165/167 $[M-Et-C_2H_4]^+$ (100/37.1), 150 (25.7), 137 (33.3), 135 (12.3), 125 (6.7), 123 (34.8), 120/122 (39.8/10.2), 100 (5.2), 92 (5.2)	0.38 (s, 3 H, SiMe); 0.9—2.27 (m, 4 H, α-CH_2 of the cycle; 8 H, $C(CH_2)_4CCl$; 2 H, β-CH_2 of the cycle); 3.44 (t, 2 H, CH_2O);3.68 (t, 2 H, CH_2Cl)
1e	*p*-C_6H_4	Br	89	65—66.5 (0.04)	1.5485	1.3472	256/258 $[M]^{+\cdot}$ (22.3/21.7), 228/230 $[M-C_2H_4]^{+\cdot}$ (31.8/30.6), 213/215 $[M-C_2H_4-Me]^+$ (19.4/20.2), 199/201 $[M-C_3H_6-Me]^+$ (7.2/7.2), 169/171 (7.2/7.0), 149 $[M-C_2H_4-Br]^+$ (100)	0.41 (s, 3 H, SiMe); 0.93—2.13 (m, 4 H, α-CH_2 of the cycle; 2 H, β-CH_2 of the cycle); 6.53 и 6.66 (d, 2 H, *ortho*-); 7.08 и 7.21 (d, 2 H, *meta*-)

Haloalkoxy- and -phenoxysilacyclobutanes **1a—e** form Grignard reagents according to the regularities previously found by us[1] for their trimethylsilyl analogs. Since the nature of a halogen is not essential for Speier rearrangement (step *c*), the initial halogen derivatives were chosen so as to minimize the side processes and taking into account that bromides are more reactive. For example, we used bromides **1a** and **1e** since the reaction with **1a** may be carried out at a lower temperature (in order to prevent elimination of cyclopropane) and aryl bromides are known to be more reactive in the reaction with magnesium as compared with chlorides. The choice of chloro-derivatives **1b—d** is explained by the fact that these compounds may be safely heated in the preparation of Grignard reagents since chloro-derivatives are less susceptible to cross-coupling.

For all the cases, except for compound **1a**, the third step, *i.e.*, the rearrangement itself, was carried out following the preparation of a Grignard reagent by refluxing in THF.

Finally, the last step of the scheme (hydrolysis) was carried out on cooling and in a weakly acidic medium since high temperature and acidity favor silacyclobutane ring opening. The yields of silacyclobutane alcohols **2a—e** are 72—92 %, which is higher than those in their synthesis *via* trimethylsilyl haloalkyl ethers (44—84 %).[1] It is particularly noteworthy that the rearrangement allows one to increase the yield of 1-(3-hydroxypropyl)silacyclobutane **2a**.

The structure of the alcohols obtained is confirmed by mass and ^{1}H NMR spectral data; their physicochemical constants practically coincide with those for the compounds obtained *via* trimethylsilyl haloalkyl ethers.[1]

Experimental

Mass spectra were obtained on LKB-2091 and Kratos MS-25 RF (70 eV) instruments. ^{1}H NMR spectra were recorded on a Varian T-60 instrument in CCl_4 with $SiMe_4$ as the internal standard. **1-Chloro-1-methylsilacyclobutane** was obtained by the known procedure.[4] Commercial ω-haloalkanols and *p*-bromophenol were distilled before use. Solvents were dried by usual methods. Dibromoethane was dried with $MgSO_4$ and distilled.

1-Methyl-1-(ω-haloalkoxy)silacyclobutanes (1a—d) and 1-methyl-1-(*p*-bromophenoxy)silacyclobutane (1e). General procedure. 1-Chloro-1methylsilacyclobutane (0.92 equiv.) was added to a mixture of urea dried in a desiccator (1 equiv.) and ω-haloalkanol (or a solution of *p*-bromophenol in abs. benzene or toluene) (0.9 equiv.) with stirring and at a temperature not higher than 40 °C. The mixture was stirred at 50 °C for 4 h and then cooled. The liquid phase was decanted and distilled *in vacuo*. The yields and physicochemical characteristics of halides **1a—e** are given in Table 1.

1a. Found (%): C, 37.86; H, 6.61; Br, 35.57; Si, 12.81. $C_7H_{15}BrOSi$. Calculated (%): C, 37.67; H, 6.77; Br, 35.84; Si, 12.58. **1b**. Found (%): C, 50.12; H, 9.03; Cl, 18.20; Si, 14.77. $C_8H_{17}ClOSi$. Calculated (%): C, 49.83; H, 8.89; Cl, 18.41; Si, 14.57. **1c**. Found (%): C, 52.32; H, 9.38; Cl, 17.01; Si, 13.77. $C_9H_{19}ClOSi$. Calculated (%): C, 52.26; H, 9.26; Cl, 17.16; Si, 13.58. **1d**. Found (%): C, 54.51; H, 9.70; Cl, 16.22; Si, 12.97. $C_{10}H_{21}ClOSi$. Calculated (%): C, 54.38; H, 9.58; Cl, 16.07; Si, 12.72. **1e**. Found (%): C, 46.87; H, 5.21; Br, 30.78; Si, 11.19. $C_{10}H_{13}BrOSi$. Calculated (%): C, 46.68; H, 5.09; Br, 31.09; Si, 10.92.

Synthesis of silacyclobutane alcohols. 1. ***A.*** Magnesium (0.4 g-at.) was activated in THF (100 mL) by the addition of dibromoethane (1 mL), then a solution of ω-chloroalkoxy (**1b—d**) or *p*-bromophenoxy (**1e**) derivative of silacyclobutane (0.2 mol) and dibromoethane (0.05 mol) in THF (50 mL) was added over 4—4.5 h at 15—20 °C, and the mixture was refluxed for 5—6 h.

B. Dibromoethane (1 mL) was added to powdered magnesium (0.4 g-at.) in THF (100 mL) in dry argon. After the activation, the mixture was cooled to −20 to −25 °C, and a solution of 1-(γ-bromopropoxy)-1-methylsilacyclobutane (0.2 mol) and dibromoethane (0.1 mol) in THF (50 mL) was added over 5.5 h, and the mixture was stirred for 1 h. The temperature was raised to −10 to −15 °C and the mixture was stirred for 96 h. Then the mixture was allowed to warm to room temperature, kept for 24 h, and refluxed for 3 h.

2. The reaction mixture obtained as described above was cooled with ice-water and hydrolyzed with water and then with 2 % HCl (pH ≈ 5—6). Pentane or hexane was added, and the organic phase was washed with cooled water to neutral reaction. The solution was quickly dried with $MgSO_4$, the solvent was distilled off *in vacuo*, and the residue was distilled. The following compounds were obtained: 1-(3-hydroxypropyl)-1-methylsilacyclobutane **2a**, yield 72 %, b.p. 42—43 °C/0.053 Torr, n_D^{20} 1.4723; 1-(4-hydroxybutyl)-1-methylsilacyclobutane **2b**, yield 89 %, b.p. 65.5—66 °C/~1 Torr, n_D^{20} 1.4734; 1-(5-hydroxypentyl)-1-methylsilacyclobutane **2c**, yield 92.5 %, b.p. 72—73.5 °C/~2 Torr, n_D^{20} 1.4764; 1-(6-hydroxyhexyl)-1-methylsilacyclobutane **2d**, yield 90 %, b.p. 89.5—90 °C/~2 Torr, n_D^{20} 1.4786; 1-(4-hydroxyphenyl)-1-methylsilacyclobutane **2e**, yield 91 %, m.p. 97—102 °C.

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