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Abstract

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SILICACYCLOBUTANES

STRENGTH OF THE Si–C BOND OF THE SILICACYCLOBUTANE RING AND SYNTHESIS OF NEW SILICACYCLOBUTANE DERIVATIVES

The present work was carried out as a continuation of our studies in the field of silicacyclobutanes ([1]).

The aim of the work was: first, to study the strength of the Si–C bond of the ring toward the action of a number of agents and, thereby, to reveal reactions specific for the silicacyclobutane ring. Second, to clarify the possibilities for the synthesis of new silicacyclobutane derivatives by means of reactions of chlorine substitution in the compound

$$ClCH_3Si(CH_2CH_2CH_2)$$

(with retention of the silicacyclobutane ring).

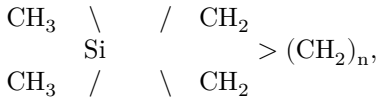
We investigated the strength of the silicacyclobutane ring using 1,1-dimethylsilicacyclobutane as an example, treating it with heptyl alcohol, acetic acid and acetic anhydride, hydrochloric acid and hydrogen chloride, water, and diethylamine.

The results of this part of the work are presented in Table 1. The reaction products obtained were identified by constants and by independent syntheses. From the data of Table 1 it is evident that the silicacyclobutane ring is active in reactions with acidic agents, alcohol, and water; moreover, in all these cases the transformation proceeds with cleavage of the Si–C bond of the ring according to the scheme

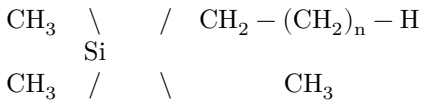
$$\begin{matrix} & & CH_2 & & \\ CH_3 & \backslash & & / & CH_2 \\ & Si & & & \\ CH_3 & / & & \backslash & CH_2 \end{matrix} \xrightarrow{HR} R-\underset{CH_3}{\overset{CH_3}{Si}}CH_2CH_2CH_2-H \qquad (1)$$

$$R = Cl, \quad O{-}C(=O){-}CH_3, \quad OC_7H_{15}\text{-n}, \quad OH$$

All these reactions are specific for the Si–C bond of the silicacyclobutane ring. They are not repeated for the subsequent members of the homologous series of 1,1-dimethylsilicacycloalkanes



where $n = 2$ and 3, nor for open-chain analogs of these heterocycles of the type



where n = 1-3. The reactions (1) indicated above, as well as the ease of thermal cleavage of the silicacyclobutane ring ([2]), attest to the exceptionally high reactivity of the Si–C bond in silicacyclobu-

Table 1

Chemical stability of 1,1-dimethylsilacyclobutane

Reagent	Ratio of silacyclobutane to reagent, mol	Reaction conditions	Reaction products and their yield
Hydrochloric acid (34%)	1 : 1	Stirring for 8 h (20°)	n-C_3H_7–$Si(CH_3)_2$–O–$Si(CH_3)_2$–C_3H_7-n (~15%)*
Same	1 : 3	Boiling for 8 h	Same (>80%)
HCl, gas	–	Bubbling through a solution in abs. pentane for 8 h (20°)	n-C_3H_7–$Si(CH_3)_2$–Cl (>60%)**
H_2O	1 : 10	Boiling for 8 h	n-C_3H_7–$Si(CH_3)_2$–OH (10%)***
n-$C_7H_{15}OH$	1 : 1	Boiling for 11 h	n-C_3H_7–$Si(CH_3)_2$–O–C_7H_{15}-n (58%)****
Glacial CH_3COOH	1 : 1	Heating in a sealed ampoule for 8 h (160–180°)	n-C_3H_7–$Si(CH_3)_2$–O–C(= O)–CH_3 (>65%)*****
$HN(C_2H_5)_2$	1 : 1	Boiling for 8 h	Starting materials were recovered

Reagent	Ratio of silacyclobutane to reagent, mol	Reaction conditions	Reaction products and their yield
Same	1 : 1	Heating in a sealed ampoule to 150°	Same

* b.p. 178-180°, n_D^{20} 1.4098, d_4^{20} 0.8024; literature data (*): b.p. 182°, n_D^{20} 1.4088.

** b.p. 110°, n_D^{20} 1.4133, d_4^{20} 0.8693; product obtained from n-C_3H_7Br and $(CH_3)_2SiCl_2$. b.p. 110°, n_D^{20} 1.4127, d_4^{20} 0.8706.

*** b.p. 126-128°, n_D^{20} 1.4128, d_4^{20} 0.8210.

**** b.p. 121-121.5°/38 mm Hg, n_D^{20} 1.4224, d_4^{20} 0.8082; product obtained from n-C_3H_7—$Si(CH_3)_2$—Cl and n-$C_7H_{15}OH$. b.p. 124-125°/40 mm Hg, n_D^{20} 1.4215, d_4^{20} 0.8081.

***** b.p. 148.5°, n_D^{20} 1.4070, d_4^{20} 0.8741; product obtained from n-C_3H_7—$Si(CH_3)_2$—Cl and CH_3—C(= O)—O—C(= O)—CH_3, b.p. 148.5°, n_D^{20} 1.4070, d_4^{20} 0.8779.

···tanes compared with the Si—C bond in other types of compounds: with alkenyl, aryl, and other radicals attached to silicon (3)*.

In the literature (1,4) there is little information on substitution reactions of functional groups present in the molecule of silacyclobutanes. Thus, it is known that 1-chloro-1-methylsilacyclobutane reacts with various reagents

* Unsubstituted hydrocarbon radicals are meant (not containing polar functional groups).

Grignard reagent, smoothly exchanging chlorine for a hydrocarbon radical. Under the action of alcoholic alkali, the hydride hydrogen of 1-hydro-1-methylsilacyclobutane is replaced by an ethoxyl group, but this reaction is accompanied by quantitative cleavage of the Si—C bond of the silacyclobutane ring.

We continued investigations in this direction and carried out a series of transformations of 1-chloro-1-methylsilacyclobutane, shown in scheme II.

Scheme II

[[chemical scheme: transformations of 1-chloro-1-methylsilacyclobutane]]

$$\text{ROH/pyridine/heptane} \rightarrow \text{1-alkoxy-1-methylsilacyclobutane} \quad \begin{cases} \text{for } R = C_7H_{15}\text{-}n : 82\%, \\ \text{for } R = OC_6H_5 : 61.1\% \end{cases} \quad \text{(II-a}$$

$$n\text{-}C_7H_{15}OH/\text{heptane} \rightarrow CH_3CH_2CH_2Si{-}(OC_7H_{15}\text{-}n)_2\ (>20\%) + \text{1-}n\text{-heptoxy-1-methylsilacyclobutane}\ (<$$

$$R_2NH \rightarrow \text{1-dialkylamino-1-methylsilacyclobutane} \quad \begin{cases} \text{for } R = C_4H_9\text{-}n : 58\%, \\ \text{for } R = C_2H_5 : 79\% \end{cases} \quad \text{(II-v)}$$

$$(CH_3CO)_2O \rightarrow \text{1-acetoxy-1-methylsilacyclobutane (48\%)} \quad \text{(II-g)}$$

Thus, reactions II-a, II-v, and II-g may serve as a method for obtaining representatives of previously unknown alkoxyl, acetoxyl, and amino derivatives of silacyclobutanes. It is interesting to note that the derivatives obtained show a stable exaltation of $MR_D(\sim +0.5)$, the same as in the series of silacyclobutane silicon hydrocarbons ([1]).

Experimental Part

1,1-Dimethylsilacyclobutane and 1-chloro-1-methylsilacyclobutane were obtained by the known method ([1]). Transformations of 1,1-dimethylsilacyclobutane are described in Table 1.

Alkoxy(aroxy)silacyclobutanes. a) To 15 g of 1-chloro-1-methylsilacyclobutane and 9.9 g of pyridine in 100 ml of *n*-hexane, 16.0 g of *n*-heptyl alcohol was added. After boiling for 2 hours, the mixture was filtered from pyridine hydrochloride and distilled in vacuo. 1-*n*-Heptoxy-1-methylsilacyclobutane was obtained (20.5 g, b.p. 86–89°/6.5 mm Hg).*

b) Similarly, from 12 g of 1-chloro-1-methylsilacyclobutane, 8 g of pyridine, and 10.8 g of phenol, 1-phenoxy-1-methylsilacyclobutane was obtained (13.5 g, b.p. 84–86°/5 mm Hg).

c) To a solution of 15 g of 1-chloro-1-methylsilacyclobutane in 50 ml of *n*-hexane, 21 g of *n*-heptyl alcohol was added. The mixture was boiled for 10 hours. As a result of distillation, 1-*n*-heptoxy-1-methylsilacyclobutane was isolated in a yield of $< 10\%$ (b.p. 76–81°/5 mm Hg, n_D^{20} 1.4390) and methylpropyl-di(*n*-heptoxy)silane in a yield of $> 20\%$ (b.p. 139.5–140°/2.5 mm Hg, n_D^{20} 1.4316, d_4^{20} 0.8500, MR_D calculated 96.62, found 96.52).

Found, %: Si 9.00; C 68.41; H 12.71
$C_{18}H_{40}SiO_2$. Calculated, %: Si 8.80; C 68.30; H 12.66

Aminosilacyclobutanes. a) To a solution of 43 g of diethylamine in 200 ml of *n*-hexane, a solution of 25 g of 1-chloro-1-methylsilacyclobutane in 100 ml of

n-hexane was added, after which the reaction mixture was boiled for 2 hours and then filtered from diethylamine hydrochloride. As a result of distillation in vacuo, 1-diethylamino-1-methylsilacyclobutane was obtained (25 g, b.p. 78–83°/40 mm Hg).

* The yields and constants of the silacyclobutane derivatives are given in Table 2.

b) Similarly, from 13 g of dibutylamine and 6 g of 1-chloro-1-methylsilacyclobutane, 1-dibutylamino-1-methylsilacyclobutane was obtained (6.2 g, b.p. 88-91°/2.5 mm Hg).

1-Acetoxy-1-methylsilacyclobutane. A mixture of 25 g of 1-chloro-1-methylsilacyclobutane and 20.4 g of acetic anhydride was heated

Table 2

Derivatives of silacyclobutanes

Product	B.p., °C	B.p., mm Hg	Yield, %	n_D^{20}	d_4^{20}	MR_D found	MR_D calculated*	Found, %	Calculated, %
1-Methyl-1-(*n*-heptyloxy)silacyclobutane	87,5–88	6,5	82	1,4412	0,8555	61,87	61,82	Si 14,27C 65,36H 11,91	Si 14,00C 66,00H 12,00
1-Methyl-1-phenoxysilacyclobutane	84–84,5	5	61	1,5139	0,9984	53,75	53,80	Si 15,64C 67,73H 7,97	Si 15,73C 67,41H 7,81
1-Diethylamino-1-methylsilacyclobutane	76–77	37	79	1,4518	0,8450	50,20	50,19	Si 17,65;18,19	Si 17,9
1-Dibutylamino-1-methylsilacyclobutane	90–91	2,5	58	1,4552	0,8455	68,51	68,71	Si 13,64N 6,72	Si 13,14N 6,5
1-Acetoxy-1-methylsilacyclobutane	62–63	30	48	1,4322	0,9679	38,67	38,66	Si 19,27C 49,95H 8,40	Si 19,47C 49,96H 8,38

* According to Warrick' s bond refractions (5), with a correction of +0.5 for the silacyclobutane ring (1).

for 10 hours at a temperature of 80–100°. As a result of distillation, acetyl chloride was isolated in 84% yield (b.p. 51–53°) and 1-acetoxy-1-methylsilacyclobutane (14 g, b.p. 61–66°/30 mm Hg).

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Note: Figure translations are in progress. See original paper for figures.