ISSN 1070-3632, Russian Journal of General Chemistry, 2006, Vol. 76, No. 6, pp. 931–935. © Pleiades Publishing, Inc., 2006.
Original Russian Text © V.A. Pestunovich, N.F. Lazareva, A.I. Albanov, E.N. Buravtseva, L.E. Gusel'nikov, 2006, published in Zhurnal Obshchei Khimii, 2006, Vol. 76, No. 6, pp. 973–977.

Reactions of Alkoxy and Amino Derivatives of Silacyclobutane with Amino Alcohols

V. A. Pestunovich[a] †, N. F. Lazareva[a], A. I. Albanov[a], E. N. Buravtseva[b], and L. E. Gusel'nikov[b]

[a] *Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia*
[b] *Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, Russia*

Received November 10, 2005

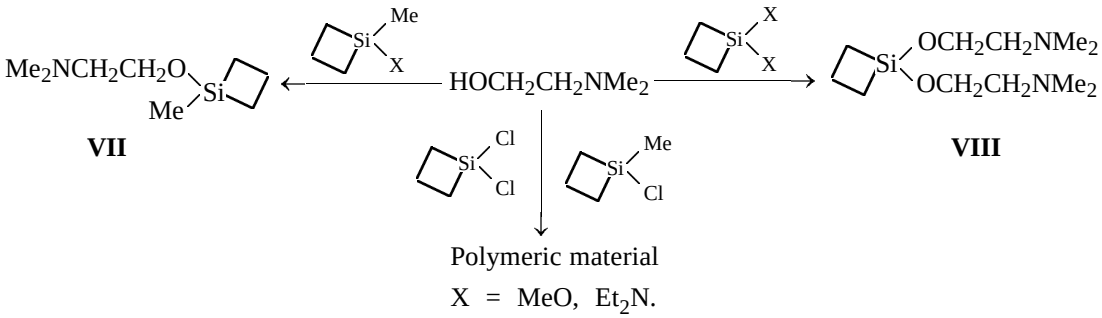
Abstract — 2-(*N*,*N*-Dimethylamino)ethanol readily replaces the MeO and Et_2N groups in 1-methoxy-1-methyl-, 1,1-dimethoxy-, 1-diethylamino-1-methyl- and 1,1-bis(diethylamino)-1-silacyclobutanes to form dimethylaminoethoxy derivatives. Triethanolamine and *N*,*N*-bis(2-hydroxyethyl)glycinamide split the silacyclobutane ring in 1,1-dimethoxy-1-silacyclobutane to form 1-propylsilathrane and 1-propyl-2-azasilathran-3-one, respectively.

DOI: 10.1134/S1070363206060132

Silacyclobutanes occupy a specific place in the chemistry of organosilicon compounds due to their ability to polymerize via ring opening [1, 2] and to generate sylenes via [2+2] cycloreversion [3, 4]. Moreover, they are interesting in that their silicon atom exhibits a stronger tendency for changing the coordination number than that in larger Si-containing rings or acyclic analogs. 1,1-Dimethyl-1-silacyclobutane reacts with the fluoride anion in the gas phase to form a five-coordinate silicon anion [5–7]. However, electroneutral silacyclobutane derivatives of five-coordinate silicon have not been described in the literature. Therefore, we considered it important to convert the silicon atom in silacyclobutane into the five-coordinate state by introducing effective chelating substituents to the molecule.

In this publication we describe the results of our research on reactions of 1-silacyclobutanes [1-chloro-1-methyl-1-silacyclobutane (**I**), 1,1-dichloro-1-silacyclobutane (**II**), 1-methoxy-1-methyl-1-silacyclobutane (**III**), 1,1-dimethoxy-1-silacyclobutane (**IV**), 1-diethylamino-1-methyl-1-silacyclobutane (**V**), and 1,1-bis(diethylamino)-1-silacyclobutane (**VI**)] with chelating agents, including 2-(*N*,*N*-dimethylamino)-ethanol, triethanolamine, and *N*,*N*-bis(2-hydroxyethyl)-glycinamide.

The reactions of 1-silacyclobutane derivatives with 2-(*N*,*N*-dimethylamino)ethanol resulted in formation of 1-methyl-1-[2-(*N*,*N*-dimethylamino)ethoxy]-1-silacyclobutane (**VII**) and bis[2-(*N*,*N*-dimethylamino)-ethoxy]-1-silacyclobutane (**VIII**):



VII **VIII**

These reactions were conducted under mild conditions in ether, chloroform, or methylene chloride with subsequent removal in a vacuum of the solvent and alcohol or amine formed. To purify the final products, the residue was reprecipitated several times from methylene chloride with pentane. Compounds **VII** and **VIII** are viscous liquids losing fluidity on

† Deceased.

Table 1. Reaction conditions in the reaction of compounds **I**–**VI** with 2-(*N*,*N*-dimethylamino)ethanol

Comp. no.	Solvent	Time, h	Temperature, °C	Product (yield, %)
I	Et_2O/Et_3N [a]	4	20	**VII** (traces)
I	Et_2O/Et_3N [a]	1	0	**VII** (5)
II	Et_2O/Et_3N [a]	1	20	**VIII** (0)
II	Et_2O/Et_3N [a]	1	0	**VIII** (traces)
III	CH_2Cl_2	8	20	**VII** (21)
III	CH_2Cl_2	24	20	**VII** (37)
III	CH_2Cl_2	36	0	**VII** (8)
IV	CH_2Cl_2	6	20	**VIII** (12)
IV	CH_2Cl_2	24	20	**VIII** (31)
IV	$CHCl_3$	24	20	**VIII** (39)
V	CH_2Cl_2	24	20	**VII** (43)
V	$CHCl_3$	24	20	**VII** (45)
VI	$CHCl_3$	24	20	**VIII** (38)
VI	$CHCl_3$	24	20	**VIII** (36)
VI	$CHCl_3$	48	20	**VIII** (41)

[a] Et_3N is HCl acceptor.

Table 2. ^1H, ^{13}C, ^{29}Si NMR spectral data for compounds **VII** and **VIII**, δ, ppm

Comp. no.	NMR spectrum	Me–Si	$(CH_2)_3$	NCH_2	OCH_2	NMe_2
VII [a]	^1H	0.28	1.19	2.48	3.82	2.26
	^{13}C	–2.15	12.28 ($CH_2CH_2CH_2$), 24.76 ($CH_2CH_2CH_2$)	57.24	58.17	47.42
VIII [b]	^1H	–	1.51	2.49	3.87	2.26
	^{13}C	–	11.78 ($CH_2CH_2CH_2$), 23.50 ($CH_2CH_2CH_2$)	57.95	58.86	46.98

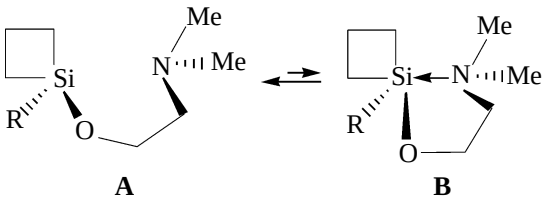
[a] ^{29}Si NMR spectrum, δ_{Si}, ppm: 15.7, 16.0 (–43°C). [b] ^{29}Si NMR spectrum, δ_{Si}, ppm: –18.1.

heating above 400°C (probably, due to polymerization). Table 1 shows the reaction conditions and yields. The reactions of compounds **I** and **II** with 2-(*N*,*N*-dimethylamino)ethanol even at low temperatures gave unidentified oligomers as major products, whereas compounds **VII** and **VIII** were found in trace amounts. We expected that at longer reaction times of compounds **III**–**VI** with 2-(*N*,*N*-dimethylamino)ethanol would provide higher yields of the target product. However, here, too, we observed nothing more than oligomer formation, due to cleavage of the silacyclobutane ring by the Si–C bond. The heterolytic Si–C bond cleavage under the action of nucleophilic or electrophilic reagents is a typical reaction of silacyclobutanes [1, 8]. The silacyclobutane ring opening is confirmed by the presence in the ^1H NMR spectra of the reaction mixtures of signals related to the propyl group (δ, ppm: 0.58–0.65, 0.92–0.98, 1.42–146).

The structure of compounds **VII** and **VIII** was studied by NMR spectroscopy (Table 2). It is seen that the OCH_2 and NCH_2 proton signals of the Si–OCH_2–CH_2–N group in compounds **VII** and **VIII** are downfield from the respective signals of open-chain aminoalkylsilanes. For example, the proton chemical shifts of the Si–OCH_2–CH_2–N fragment in $Me_3SiO\cdot CH_2CH_2NMe_2$ are 3.57 (OCH_2) and 2.33 ppm (CH_2N) and in $Me_2Si(OCH_2CH_2NMe_2)_2$, 3.70 and 2.37 ppm [9]. As noted in [9], acceptor substituents at the silicon atom in compounds of the $R_nSi(OCH_2CH_2\cdot NMe_2)_{4-n}$ series induce a downfield shift of proton signals of the ethanolamine fragment. Our results point to strong electron-acceptor properties of the strained silacyclobutane ring, in agreement with the fact that the Lewis acidity of the silicon atom in bis-[[(8-(dimethylamino)-1-naphthyl]-1-silacyclobutyl] ether is higher than in its linear analog, bis[[(8-(dimethylamino)-1-naphthyl]dimethylsilyl] ether [10]. We assumed that the silicon atom in the synthesized compounds is five-coordinate due to formation of an intramolecular N–Si coordination bond (structure **B**).

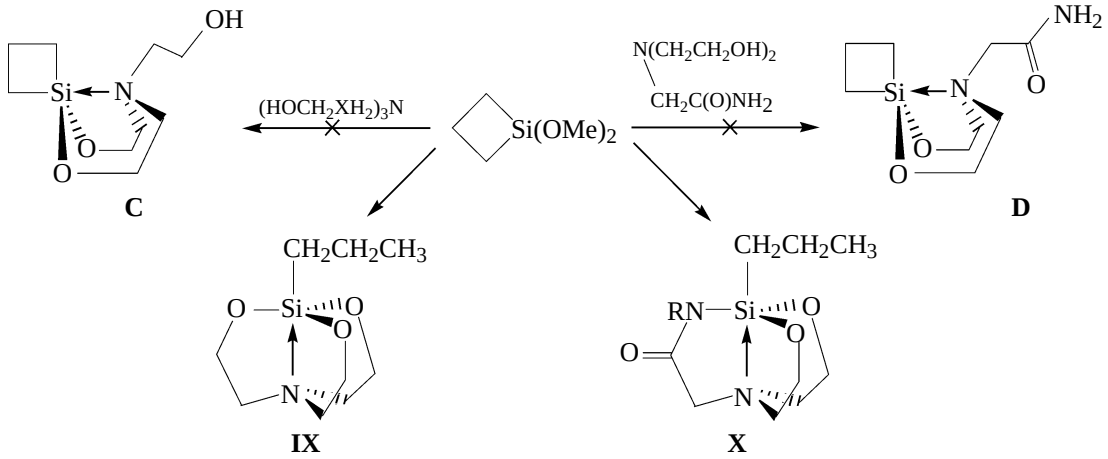
However, the ^{29}Si signal of compound **VIII** is

shifted upfield by 1 ppm only as compared with the model compound, 1,1-diethoxy-1-silacyclobutane, with a similar covalent surrounding (–17.1 ppm [11]). But this compound exerts a large ^{29}Si upfield shift as the temperature decreases: At –43°C the shift is 21.2 ppm, and at –65°C it is –24.5 ppm. Such an upfield ^{29}Si shift with decreasing temperature is typical of compounds with a five-coordinate silicon, unlike those with a four-coordinate silicon. This phenomenon was first discovered in silathranes, typical five-coordinate silicon compounds [12, 13]. Hence, in compound **VIII** we probably deal with a weak N–Si coordination interaction.



A **B**

We expected formation of compounds **C** and **D** in the reactions of 1,1-dimethoxysilacyclobutane with triethanolamine and bis(2-hydroxyethyl)glycinamide, respectively, but failed to isolate them. Actually, the reaction of 1,1-dimethoxy-1-silacyclobutane with triethanolamine results in cleavage of the silacyclobutane ring to form 1-propylsilathrane (**IX**).



C **D**

IX **X**

Already on mixing of equimolar amounts of the reagents we observed self-heating of the reaction mixture. The reaction occurred readily at room temperature both in the presence and in the absence of solvent. Physicochemical characteristics of compound **IX** are consistent with published data [14]. Bis(2-hydroxyethyl)glycinamide reacts with 1,1-dimethoxy-1-silacyclobutane much slower. As follows from ^{1}H NMR data, stirring at room temperature for 20 h leads to trace amounts of 1-propyl-2-azasilathran-3-one. Heating in chloroform yields 28% of 1-propyl-2-azasilathran-3-one (**X**). Its structure was confirmed by NMR and IR spectroscopy. The resulting spectral characteristics are close to those of 1-methyl-2-azasilathran-3-one we synthesized earlier [15].

It is not excluded that the key factor responsible for the cleavage of the four-membered silacyclobutane ring is the formation of an athrane cell structure stabilized by intramolecular N–Si coordination interaction. Compounds **C** and **D** can appear as intermediates. There are several examples to show that silathranes with an N–Si coordination bond are formed in preference to 5-aza-2,8-dioxa-1-silacyclooctane where such interaction is weaker. As known, diethoxy(methyl)(phenyl)- and (chloromethyl)diethoxy(methyl)silanes react with triethanolamine with Si–C bond cleavage and 1-methylsilathrane formation [16, 17]. The latter is also formed by the persilylation reaction of compounds of the R–R–Si$(OCH_2CH_2)_2 \cdot NCH_2CH_2OH$ series with methyltrimethoxysilane [18]. The most unexpected is Alk–N bond cleavage with 1-ethylsilathrane formation [19] in the reaction of ethyl[tris(2-chloroethoxy)]silane with *N*-alkyldiethanolamines.

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-75 instrument. The NMR spectra of compounds **VII**–**X**

(20% solutions in $CDCl_3$) were registered on a JEOL FX 90Q instrument with TMS as internal reference. Compounds **I**–**VI** were synthesized by the procedures described in [9, 11, 20]. Bis(2-hydroxyethyl)glycinamide was prepared by conventional procedures [21]. Commercial triethylamine, 2-(dimethylamino)ethanol, and triethanolamine were purified by distillation. Solvents were purified as described in [22]. All syntheses were performed under dry argon.

Reaction of 2-(dimethylamino)ethanol with compounds I and II. To a stirred solution of 0.005 mol of compound **I** or **II** in 20 ml of anhydrous ether, a mixture of equimolar amounts of Et_3N and 2-(dimethylamino)ethanol in 25 ml of anhydrous Et_2O was added dropwise. The required temperature (Table 1) was maintained by external cooling. Precipitate formation immediately began. After heat release was no longer observed, the reaction mixture was left to stand for some time. The precipitate was then filtered off and washed with anhydrous ether that was combined with the filtrate. Volatile reaction products were removed in a vacuum. The residues were viscous liquids. Their NMR spectra did not contain signals of the silacyclobutane ring, but contained broad signals indicating formation of polymeric substances.

Reaction of 2-(dimethylamino)ethanol with compounds III–VI. To a stirred solution of 0.005 mol of compound **III**–**VI** in 5 ml of anhydrous chloroform or methylene chloride, a solution of 0.005 or 0.01 mol, respectively, of 2-(dimethylamino)-ethanol was added dropwise maintaining a specified temperature, after which the reaction mixture was left to stand for some time (Table 1). The solvent and evolved methanol were removed under a water-pump vacuum, and the residue was dried under an oilpump vacuum at room temperature. Pure compounds were obtained after multiple reprecipitation with anhydrous pentane from CH_2Cl_2 (the purity was checked by ^1H NMR spectroscopy). The resulting oily substances were dried in a vacuum at room temperature to obtain almost colorless liquids. Compound **VII**. Found, %: C 55.12; H 10.87; N 8.12; Si 16.97. $C_8H_{19}NOSi$. Calculated, %: C 55.44; H 11.05; N 8.08; Si 16.20. Compound **VIII**. Found, %: C 53.81; H 10.69; N 11.49; Si 11.91. $C_{11}H_{26}N_2O_2Si$. Calculated, %: C 53.62; H 10.63; N 11.37; Si 11.40.

Reaction of triethanolamine with compound IV. 1,1-Dimethoxy-1-silacyclobutane, 0.65 g, was mixed with 0.74g of triethanolamine. On stirring the reaction mixture self-heated and homogenized. After 1 h the methanol that separated was removed in a vacuum, and the solid residue was dried. Sublimation on an oil bath (105–110°C, 1 mm Hg) gave 0.48 g (44%) of 1-propylsilathrane, mp 83.5°C. ^1H NMR spectrum, δ, ppm: 0.43 (CH_2Si), 0.92 (CH_3), 1.43 ($C–CH_2–C$), 2.78 (NCH_2), 3.76 (OCH_2). ^{29}Si NMR spectrum: δ_{Si} –64.95 ppm. Found, %: C 49.41; H 8.53; N 6.63; Si 12.37. $C_9H_{19}NO_3Si$. Calculated, %: C 49.74; H 8.81; N 6.44; Si 12.92.

Reaction of *N*,*N*-bis(2-hydroxyethyl)glycinamide with compound IV. 1,1-Dimethoxy-1-silacyclobutane, 0.65 g, was mixed with 0.81g of *N*,*N*-bis(2-hydroxyethyl)glycine in 15 ml of anhydrous chloroform. The mixture was refluxed with stirring and got homogeneous. After 10 h the methanol that separated and the solvent were removed in a vacuum, and the solid residue was dried. Recrystallization from a 1:1 $CHCl_3$–hexane mixture gave 0.32 g (28%) of 1-propyl-2-azasilathran-3-one, mp >92°C (decomp.). IR spectrum (mineral oil), cm^{-1}: 1685 (C=O), 1100 (Si–O), 3455 (NH). ^1H NMR spectrum, δ, ppm. 0.53 (CH_2Si), 0.93 ($CH_3–C$), 1.43 ($C–CH_2–C$), 2.91 and 3.04 (NCH_2, ^2J 12.4 Hz, ^3J 6.1 Hz); 3.34 ($CH_2C=O$), 3.80 t (OCH_2, ^3J 6.0 Hz), 4.82 (NH). ^{13}C NMR spectrum, δ_C, ppm: 8.12 ($Si–CH_2$), 14.82 ($C–CH_2–C$), 16.81($C–CH_3$), 54.67 (NCH_2), 57.12 ($CH_2C=O$), 58.05 (OCH_2), 173.72 (C=O). ^{29}Si NMR spectrum: δ_{Si} –68.2 ppm.

ACKNOWLEDGMENTS

The work was financially supported by INTAS (grant no. 05-51-4164).

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