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Silylated Derivatives of Azasilacyclopentanes

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Abstract—Catalytic intramolecular cyclization of 3-aminopropylalkoxysilanes and 3-aminopropylalkoxydisiloxanes in the presence of hexamethyldisilazane has been studied; structure and reactivity of the formed azasilacyclopentanes have been investigated. In particular, the prepared cyclic azasilanes were studied by ^{1}H, ^{29}Si, and ^{13}C NMR spectroscopy. Possibility of catalytic co-condensation of the compounds containing methoxy and trimethylsiloxy groups with preservation of azasilacyclopentane structure has been demonstrated. Depending on temperature and the reactants ratio, the interaction of 3-aminopropylmethyldimethoxysilane with hexamethyldisilazane can yield 1-(trimethylsilyl)-2-methyl-2-methoxy-1-aza-2-silacyclopentane or the polymer bearing azasilacyclopentane fragments in the main chain.

Keywords: azasilacyclopentane, polymer, hexamethyldisilazane, siloxane

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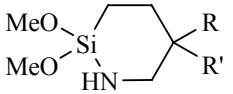
Development of procedures to prepare azasilacyclopentanes and azasilacyclohexanes as well as study of the products properties are topical issues of modern organic chemistry, due to the compounds high reactivity and their promising applications in synthesis of polyorganopolysiloxane block-copolymers [1, 2], carbon-functionalized organosiloxanes [3], crosslinking agents [4], and modifiers of particles surface [5].

Generally, azasilacyclopentanes and azasilacyclohexanes are prepared via the intramolecular condensation of organosilicon amines containing alkoxy group adjacent to silicon atom and the N–H or N–$SiMe_3$ group in the organic substituent at silicon atom.

N-Alkyl-, *N*-vinyl-, *N*-allyl-, and *N*-benzyl-substituted azasilacyclopentanes **I** are formed with yields of more than 30% via cyclization of 3-(*N*-organylamino)propyltrialkoxysilanes in the presence NH_4Cl [6, 7] (Scheme 1).

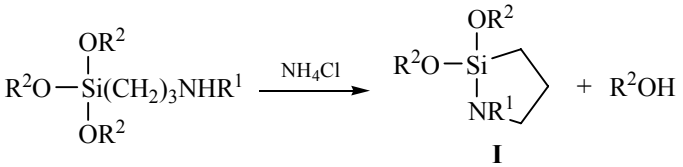
However, authors of [6, 7] have noted the low yield of 2,2-diethoxy-1-aza-2-silacyclopentane (5–7%) in course of condensation of 3-aminopropyltri-ethoxysilane; furthermore, attempts to prepare 2,2-dimethoxy-1-aza-2-silacyclopentane via condensation of 3-aminopropyltrimethoxysilane have failed.

2,2-Dimethoxy-1-aza-5,5-dialkyl-2-silacyclohexanes **II** have been prepared via heating of (4-amino-3,3-dialkylbutyl)trimethoxysilanes in the presence of sodium methoxide [8].



II

Scheme 1.



I

R^1 = Me, Et, *p*-Bu, *t*-Bu, Bn, Ph, Vin, All; R^2 = Me, Et.

Reaction of 3-aminopropyltriethoxysilane with hexamethyldisilazane **III** has yielded 1-(trimethylsilyl)-2,2-diethoxy-1-aza-2-silacyclopentane [9].

In this work, we aimed at developing the procedure to prepare silylated derivatives of azasilacyclopentanes via catalyzed intramolecular cyclization of amino-containing alkoxysilanes and alkoxydisiloxanes $(CH_3)_a$ $(CH_3O)_b[(CH_3)_3SiO]_cSi(CH_2)_3NH_2$ (a = 1, b = 2, c = 0; a = 1, b = 1, c = 1; a = 0, b = 2, c = 1) in the presence of hexamethyldisilazane. Structure and ^{1}H и ^{29}Si NMR spectral features of the prepared azasilacyclopentanes as well as their reactivity in the presence of nucleophilic agents have been studied.

3-Aminopropylmethyldimethoxysilane **IV** in the presence of compound **III** (molar ratio of 1 : 1) and NH_4Cl at 80°C underwent condensation to give 1-(trimethylsilyl)-2-methyl-2-methoxy-1-aza-2-silacyclopentane **V**; equimolar amounts of trimethylmethoxysilane **VI** and ammonia were formed as well.

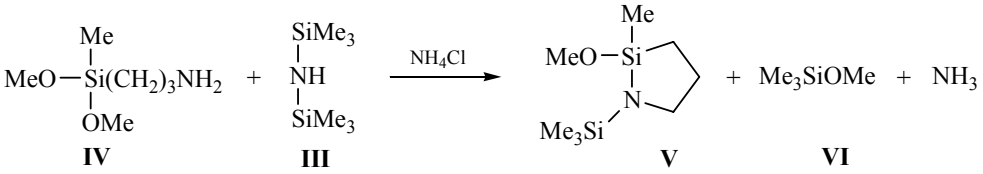
The reaction was complete within 15 h. When $(NH_4)_2SO_4$ was used as catalyst instead of NH_4Cl, the reaction was noticeable only at 120°C. In the absence of any catalyst, no reaction occurred upon prolonged heating of the silane **IV** at 180°C or upon heating of mixture of compounds **IV** and **III** at 130°C.

Two possible ways of formation of the silacyclopentane **V** were suggested (Scheme 2).

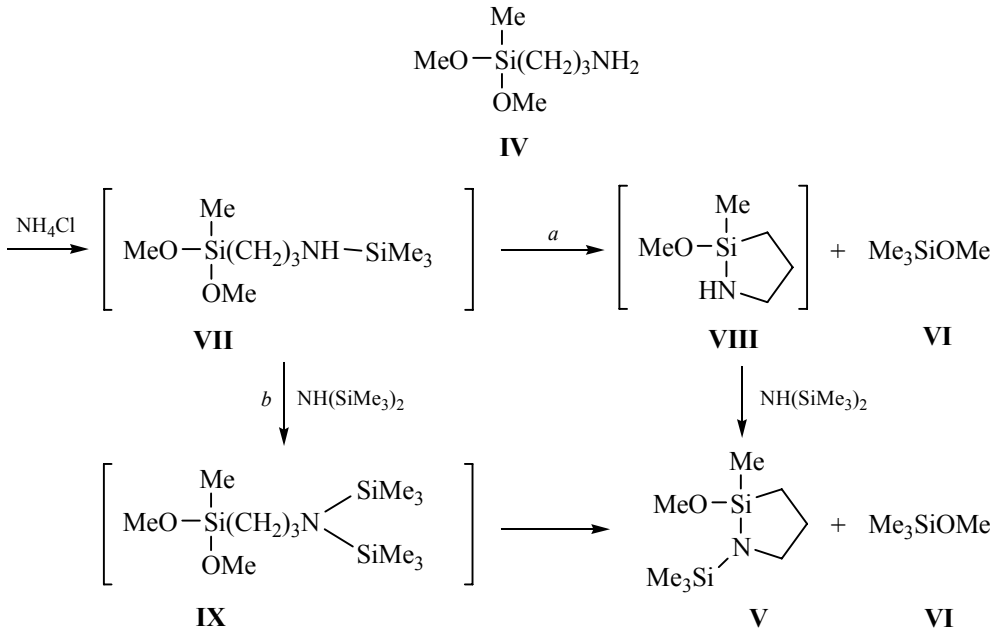
Gas-liquid chromatography studies did not reveal possible intermediate products of silylation of the silane **IV**: 3-(*N*-trimethylsilyl)propylmethyldimethoxysilane **VII**, 2-methyl-2-methoxy-1-aza-2-silacyclopentane **VIII**, or 3-[*N*,*N*-bis(trimethylsilyl)propyl]methyldimethoxysilane **IX** in the reaction mixture. However, their formation could not be explicitly excluded, as their absence could be due to their high reactivity under conditions of the reaction or the analysis (Scheme 3).

^{1}H NMR spectrum of the parent silane **IV** contained triplets of the C^3H_2 and C^5H_2 protons and a multiplet of the C^4H_2 group. Composition and structure of compound **V** were confirmed by ^{1}H, ^{29}Si, and ^{13}C NMR spectroscopy data.

Scheme 2.



Scheme 3.



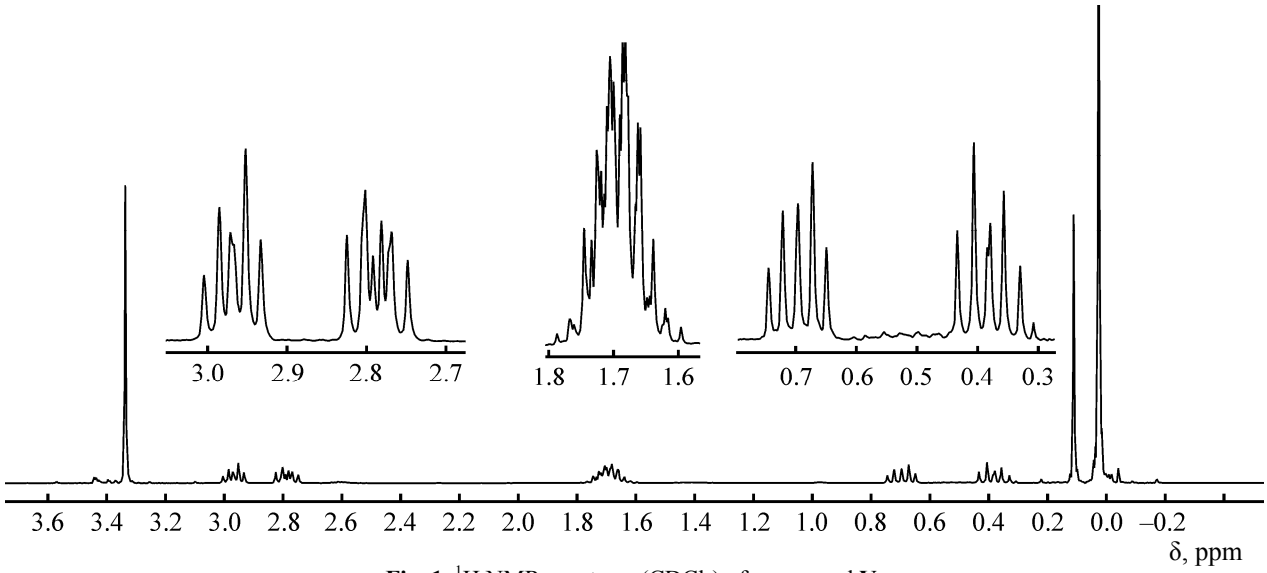


Fig. 1. ^{1}H NMR spectrum ($CDCl_3$) of compound **V**.

Protons of the C^3H_2 and C^5H_2 methylene groups of compound **V** were magnetically nonequivalent, therefore, in the ^{1}H NMR spectrum (Fig. 1) there were two sets of signals of equal integral intensity assigned to the C^3H and C^3H' atoms ($\Delta_3 = \delta_3 - \delta_3' = 0.32$ ppm) and to C^5H and C^5H' atoms ($\Delta_5 = \delta_5 - \delta_5' = 0.18$ ppm), along with the multiplet assigned to the C^4H_2 protons. Magnetic nonequivalence of the geminal protons of methylene groups arose from asymmetry of the silicon atom surrounding as well as the cyclic structure.

The cyclic structure of compound **V** was confirmed by 2D NMR measurements (HMBC), ^{1}H–^{29}Si and ^{1}H–^{15}N. In the ^{1}H–^{15}N NMR spectrum, a cross peak of the nitrogen atom and protons of the methyl group adjacent to silicon atom in the cycle was observed (spin-spin interaction via the three bonds, H–C–Si^2–N). In the ^{1}H–^{29}Si NMR spectrum, the key proofs of the cyclic structure were cross peaks of C^5H and C^5H' protons with Si^2 atom (interaction via the Si^2–N–C^5–H bonds). Noteworthily, in the parent acyclic compound **IV**, there were no cross peaks of the Si–C–C–C–H atoms, separated with four σ bonds.

The presence of different conformations of the cyclic structure did not contribute much to the ^{1}H NMR spectrum of compound **V**. That was confirmed by ^{1}H NMR studies of 1-(trimethylsilyl)-2,2-dimethoxy-1-aza-2-silacyclopentane **X**: The latter compound did not contain an asymmetric silicon atom, and no splitting of the CH_2 protons (possible due to the presence of different conformers) was observed. Compound **X** was prepared via the interaction of 3-aminopropyltrimethoxysilane **XI** with hexamethyldisilazane. 1-(Trimethylsilyl)-2-methoxy-2-trimethylsiloxy-1-aza-2-silacyclopentane **XII** and 1-(trimethylsilyl)-2-methyl-2-trimethylsiloxy-1-aza-2-silacyclopentane **XIII**, bearing silicon atom substituted with trimethylsiloxy group, were prepared via the following two-stage route. First, interesterification of the silanes **XI** and **IV** with trimethylsilanol was performed, and then the so formed 1,1,1-trimethyl-3,3-dimethoxy-3-(3-aminopropyl)disiloxane **XIV** and 1,1,1,3-tetramethyl-3-methoxy-3-(3-aminopropyl)disiloxane **XV** were catalytically cyclized (Scheme 4).

Compounds **XII** and **VIII** containing asymmetric silicon atoms were prepared via interaction of the disiloxanes **XIV** and **XV**, respectively, with equimolar amount of hexamethyldisilazane in the presence of NH_4Cl with simultaneous distillation off of trimethylmethoxysilane.

Signals of the CH_2 groups in the ^{1}H NMR spectrum of compound **XIII** were similar to those in the spectrum of the silacyclopentane **V**. In particular, the spectrum of compound **XIII** contained the two sets of proton signals with equal integral intensity, assigned to C^3H and C^3H' ($\Delta_3 = \delta_3 - \delta_3' = 0.12$ ppm) and to C^5H and C^5H' ($\Delta_5 = \delta_5 - \delta_5' = 0.17$ ppm), along with a multiplet assigned to the C^4H_2 protons.

Signals of the CH_2 groups in the ^{1}H NMR spectrum of silacyclopentane **XII** (Fig. 2) differed from those in the spectrum of compounds **V** (Fig. 1) and **X** (Fig. 3): signal of the C^5H_2 protons appeared as triplet, and

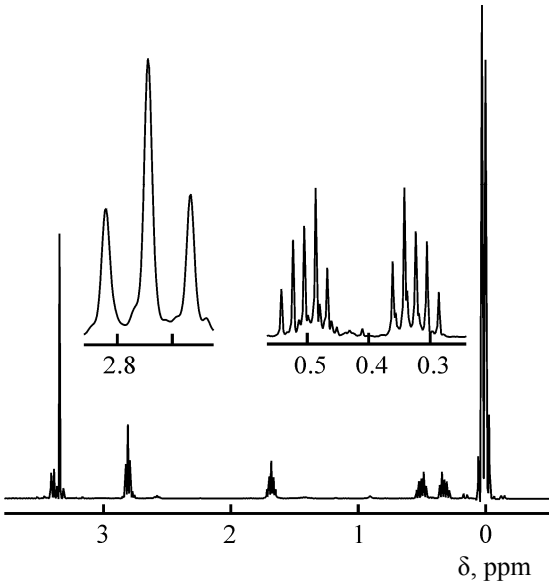


Fig. 2. ^{1}H NMR spectrum ($CDCl_3$) of compound **XII**.

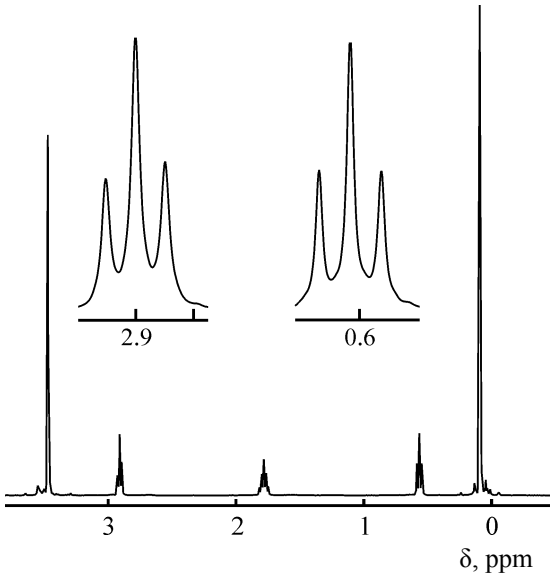
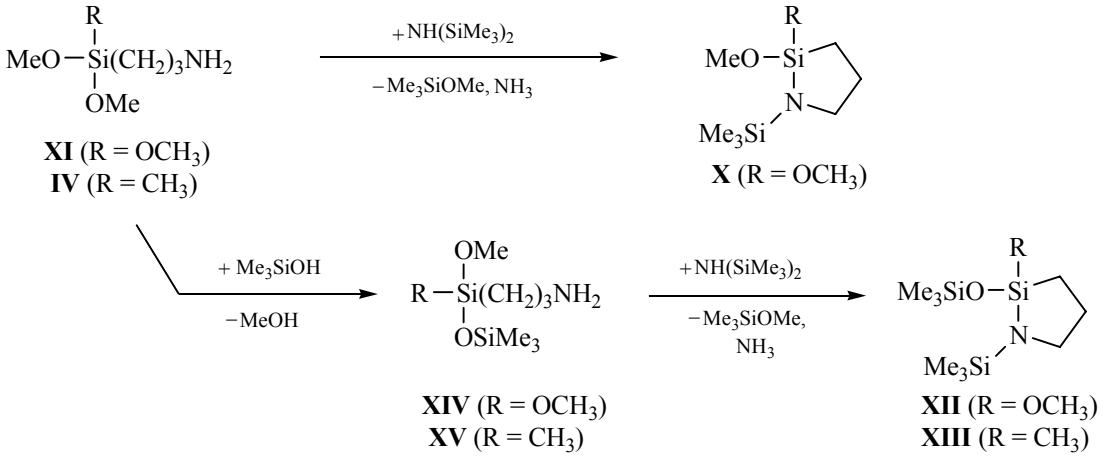


Fig. 3. ^{1}H NMR spectrum ($CDCl_3$) of compound **X**.

protons of C^3H and C^3H' resonated as pair of sets of signals with $\Delta_3 = \delta_3 - \delta_3' = 0.19$ ppm. The spectral data showed that the presence of two different substituents at the same silicon atom of compound **XII** affected the protons of C^3H_2 group only.

Alternatively, compound **XIII** was prepared (yield of 48%) via catalytic rearrangement of the silacyclopentane **V** and hexamethyldisiloxane in the presence of 0.5 wt % of KOH at 120°C (upon simultaneous distillation off of the silane **VI**) (Schemes 5, 6).

Scheme 4.



XI (R = OCH_3)
IV (R = CH_3)

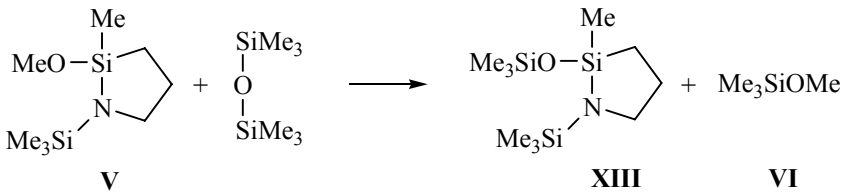
X (R = OCH_3)

XIV (R = OCH_3)
XV (R = CH_3)

XII (R = OCH_3)
XIII (R = CH_3)

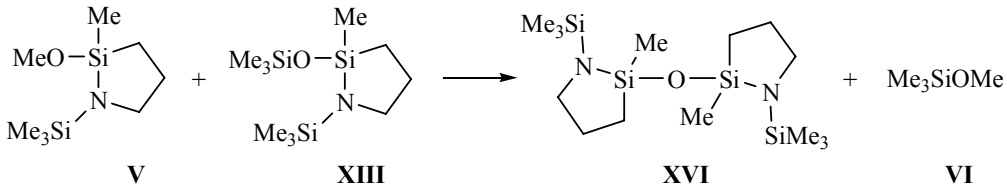
R = OCH_3 (**XI, X, XII**), CH_3 (**IV, XV, XIII**).

Scheme 5.



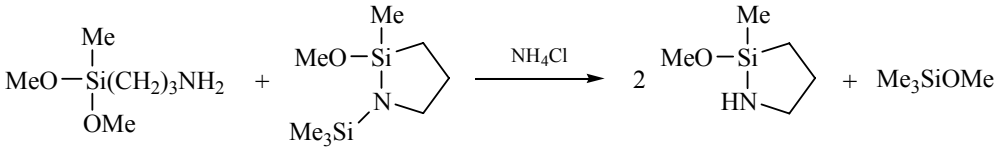
V **XIII** **VI**

Scheme 6.



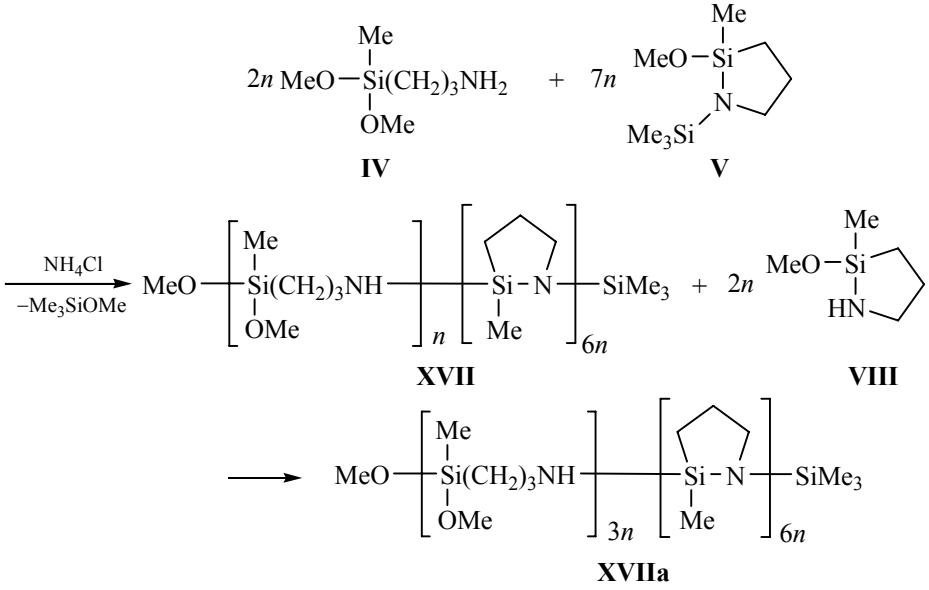
V **XIII** **XVI** **VI**

Scheme 7.



IV **V** **VIII** **VI**

Scheme 8.



XVII **VIII**

XVIIa

The interaction of silacyclopentanes **V** and **VIII** at 165°C in the presence of sodium trimethylsinanolate yielded 2,2'-oxybis[1-(trimethylsilyl)-2-methyl-1-aza-2-silacyclopentane] **XVI**.

Thus, the catalytic rearrangement occurred with participation of the Si–OMe (**V**) and Si–O–$SiMe_3$ (**XIII**) groups exclusively, the cyclic structure being preserved.

Asymmetry of silicon atom in the cyclic structures led to identical signals of CH_2 groups in the ^1H NMR spectra of compounds **XVI**, **V**, and **XIII**. Similarly to the case of the silacyclopentane **V** (Fig. 1), ^1H NMR spectrum of compound **XVI** contained two sets of proton signals, of equal integral intensity, assigned to C^3H ($C^{3'}H$) and C^3H' ($C^{3'}H'$) ($\Delta_3 = \delta_3 - \delta_3' = 0.15$ ppm) and to C^5H ($C^{5'}H$) and C^5H' ($C^{5'}H'$) c ($\Delta_5 = \delta_5 - \delta_5' = 0.17$ ppm), along with multiplet signal of C^4H_2 ($C^{4'}H_2$).

Presence of two asymmetric centers in compound **XVI** led to splitting of signals of silicon atoms of the cyclic part of the molecule in the ^{29}Si NMR spectra. Symmetry of the signal shape was due to the presence of two diastereomers of the 1-aza-2-silacyclopentane part in the 1 : 1 ratio.

We attempted to prepare 2-methyl-2-methoxy-1-aza-2-silacyclopentane **VIII** via interaction of compounds **IV** and **III** at 2 : 1 molar ratio; the reaction

was run at 100°C till complete consumption of hexamethyldisilazane. In course of the reaction, 1 mol of methyltrimethoxysilane was liberated. Gas-liquid chromatography analysis of the reaction mixture revealed that only compounds **IV** and **V** were present in equimolar ratio, whereas the expected product **VIII** was not found. Further heating at 160°C led to appearance of the new signal in the chromatogram, with lower retention time as compared with those of compounds **IV** and **V**. Intensity of the new peak increased with longer reaction run, the highest content of the product being of 20%. The product could not be isolated by distillation: a mixture of compounds **IV** and **V** was distilled, containing about 5% of the unknown compound. Probably, the product structure corresponded to that of compound **VIII** formed via the Scheme 7.

Upon prolonged heating of the reaction mixture and distillation off of the formed trimethylmethoxysilane, compound **V** polymerized. After elimination of the low molecular weight admixtures **IV** and **VIII** by distillation in high vacuum, the polymer product soluble in chloroform was obtained with yield of 84%. ^{1}H NMR data showed that the polymer contained 1-aza-2-silacyclopentane and linear aminopropylsilane units (**XVIIa**).

1-Aza-2-silacyclopentane fragments were assigned to the broadened signals of methylene protons C^3H (C^3H') δ_3 = 0.30–0.90 ppm, C^4H_2 δ_4 = 1.60–1.90 ppm, and C^5H (C^5H') δ_5 = 2.70–3.20 ppm. Integral intensities ratio of the signals of CH_2 protons in the ^{1}H NMR spectrum was the same. The linear 3-aminopropylsilane units were assigned to the broadened signals of protons at C^1H_2 δ_1 = 0.30–0.90 ppm, C^2H_2 δ_2 = 1.30–1.60 ppm, and C^3H_2 δ_3 = 2.55–2.70 ppm. According to the ^{1}H NMR data, ratio of the linear and the cyclic units in the polymer was of 1 : 2.

We suggested the Scheme 8 of formation of compound **XVIIa**.

Compound **IV** underwent condensation with the silacyclopentane **V** to form compound **VIII** and polymer **XVII**. In turn, the silacyclopentane **VIII** could polymerize with the ring opening, thus enriching polymer **XVII** with linear aminopropylsilane units.

Polymer **XVIIa** reacted with trimethylsilanol to form 1,1,1,3-tetramethyl-3-methoxy-3-(3-aminopropyl)disiloxane **XV** and 1,1,1,3,5,5,5-heptamethyl-3-(3-aminopropyl)trisiloxane, their formation being in agreement with the suggested structure of compound **XVIIa**.

To conclude, in this work we elaborated a method to prepare silylated azasilacyclopentanes starting with amino-containing alkoxydisiloxanes. Cyclic structure of the prepared products was confirmed by ^{1}H, ^{13}C, ^{15}N, and ^{29}Si NMR spectroscopy; the effect of nature of substituents at asymmetric silicon atom in the cycle on magnetic properties of geminal methylene protons was demonstrated. Chemical transformations of the azasilacyclopentanes Si–O bonds in course of interaction with nucleophilic were studied; the cyclic structure was preserved. Such reactions are of interest in view of synthesis of new reactive organosilicon monomers and oligomers.

EXPERIMENTAL

^{1}H, ^{13}C, ^{29}Si, and ^{15}N NMR spectra were recorded using the Bruker Avance II instrument (300 MHz, $CDCl_3$, TMS as internal standard).

1-(Trimethylsilyl)-2-methyl-2-methoxy-1-aza-2-silacyclopentane (V). A mixture of 163.07 g (1 mol) of 3-aminopropylmethyldimethoxyxilane **IV**, 161.03 g (1 mol) of hexamethyldisilazane **III**, and 3.24 g of ammonium chloride (1%) was incubated at 110°C during 15 h. Trimethylmethoxysilane was distilled off during the reaction. Yield of distilled product **V** 173.77 g (85.6%), purity of 98%, mp 111–112°C (70 mmHg), n_D^{20} 1.4390. ^{1}H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm: 0.03 s (9H, Me_3Si), 0.11 s (3H, Me), 0.38 d.t (1H, C^3H, ^2J 14.5, ^3J 8.2 Hz), 0.70 d.t (1H, C^3H', ^2J 14.5, ^3J 6.9 Hz), 1.59–1.79 m (2H, C^4H_2), 2.79 d.d.d (1H, C^5H, ^2J 10.0, ^3J 7.0, 6.0 Hz), 2.97 d.t (1H, C^5H', ^2J 10.0, ^3J 5.7 Hz), 3.34 s (3H, MeO). ^{13}C NMR spectrum (75.5 MHz, $CDCl_3$), δ_C, ppm: –1.48 (Me), –0.36 ($NSiMe_3$), 9.5 (C^3), 25.92 (C^4), 47.03 (C^5), 49.66 (MeO). ^{29}Si NMR spectrum (59.6 MHz, $CDCl_3$), δ_{Si}, ppm (assigned basing on the ^{1}H–^{29}Si HMBC spectrum): 2.42 ($NSiMe_3$), 13.29 (Si^2). ^{15}N NMR spectrum (30.4 MHz, $CDCl_3$): δ_N 38.06 ppm (N^1).

1-(Trimethylsilyl)-2,2-dimethoxy-1-aza-2-silacyclopentane (X). A mixture of 179.03 g (1 mol) of 3-aminopropyltrimethoxysilane **XI**, 161.02 g (1 mol) of hexamethyldisilazane **III**, and 3.40 g of ammonium chloride (1%) was incubated at 100°C during 9 h. Trimethylmethoxysilane was distilled off during the reaction. Yield of distilled product **X** 180.02 g (82.2%), purity of 99%, mp 141–142°C (73 mmHg), n_D^{20} 1.4345. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ,

ppm: 0.09 s (9H, $NSiMe_3$), 0.56 t (2H, C^3H_2, ^3J 7.7 Hz), 1.78 t. t (2H, C^4H_2, ^3J 7.7, 6.9 Hz), 2.91 t (2H, C^5H_2, ^3J 6.2 Hz), 3.47 s (6H, MeO). ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$), δ_C, ppm: –1.11 ($NSiMe_3$), 4.12 (C^3), 24.89 (C^4), 44.86 (C^5), 49.65 (MeO). ^{29}Si NMR spectrum (79.5 MHz, $CDCl_3$), δ_{Si}, ppm: 2.49 ($NSiMe_3$), –14.30 (Si^2).

1-(Trimethylsilyl)-2-methoxy-2-trimethylsiloxy-1-aza-2-silacyclopentane (XII). A mixture of 237.06 g (1 mol) of 1,1,1-trimethyl-3,3-dimethoxy-3-(3-aminopropyl)disiloxane **XIV**, 161.02 g (1 mol) of hexamethyldisilazane **III**, and 3.98 g of ammonium chloride (1%) was incubated at 120°C during 20 h. Trimethylmethoxysilane was distilled off during the reaction. Yield of distilled product **XII** 194.45 g (70.2%), purity of 98%, mp 149–150°C (85 mmHg), n_D^{20} 1.4270. ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 0.03 s (9H, $OSiMe_3$), 0.00 s (9H, $NSiMe_3$), 0.31 d.t (1H, C^3H, ^2J 15.0, ^3J 7.6 Hz), 0.50 d.t (1H, C^3H', ^2J 15.0, ^3J 7.6 Hz), 1.61–1.73 m (2H, C^4H_2), 2.80 t (2H, C^5H_2, ^3J 6.1 Hz), 3.34 s (3H, MeO). ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$), δ_C, ppm: –0.73 ($NSiMe_3$), 1.46 ($OSiMe_3$), 6.63 (C^3), 25.08 (C^4), 44.93 (C^5), 49.75 (MeO). ^{29}Si NMR spectrum (79.5 MHz, $CDCl_3$), δ_{Si}, ppm: –23.72 (Si^2), 2.14 ($NSiMe_3$), 8.21 ($OSiMe_3$).

1-(Trimethylsilyl)-2-methyl-2-trimethylsiloxy-1-aza-2-silacyclopentane (XIII). A mixture of 221.04 g (1 mol) of 1,1,1,3-tetramethyl-3-methoxy-3-(3-aminopropyl)disiloxane **XV**, 161.04 g (1 mol) of hexamethyldisilazane **III**, and 3.82 g of ammonium chloride (1%) was incubated at 125°C during 24 h. Trimethylmethoxysilane was distilled off during the reaction. Yield of distilled product **XIII** 184.53 g (70.7%), purity of 97%, mp 99–100°C (17 mmHg), n_D^{20} 1.4295. ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm: 0.08 s (9H, $OSiMe_3$), 0.078 s (9H, $NSiMe_3$), 0.16 s (3H, Me), 0.46 d.t (1H, C^3H, ^2J 14.0, ^3J 8.0 Hz), 0.58 d.t (1H, C^3H', ^2J 14.0, ^3J 6.9 Hz), 1.69–1.79 m (2H, C^4H_2), 2.83 d.t (1H, C^5H, ^2J 10.0, ^3J 6.5 Hz), 3.00 d.t (1H, C^5H', ^2J 9.9, ^3J 5.7 Hz). ^{13}C NMR spectrum (75.5 MHz, $CDCl_3$), δ_C, ppm: –0.03 ($NSiMe_3$), 1.12 (Me), 1.93 ($OSiMe_3$), 12.68 (C^3), 25.78 (C^4), 46.92 (C^5). ^{29}Si NMR spectrum (59.6 MHz, $CDCl_3$), δ_{Si}, ppm: 2.08 ($NSiMe_3$), 6.12 ($OSiMe_3$), 1.72 (Si^2).

1,1,1-Trimethyl-3,3-dimethoxy-3-(3-aminopropyl)disiloxane (XIV). 90.00 g (1 mol) of trimethylsilanol was added dropwise to 179.02 g (1 mol) of 3-aminopropyltrimethoxysilane **XI** during 3 h at room temperature. The formed methanol was distilled in vacuum. Yield of distilled product **XIV** 210.50 g (88.8%), purity of 97%, mp 138–139°C (85 mmHg), n_D^{20} 1.4238. ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm: 0.11 s (9H, $OSiMe_3$), 0.51–0.58 m (2H, C^1H_2), 1.43–1.53 m (2H, C^2H_2), 1.15 br.s (2H, NH_2), 2.63 t (2H, C^3H_2, ^3J 7.0 Hz), 3.48 s (6H, MeO). ^{29}Si NMR spectrum (59.6 MHz, $CDCl_3$), δ_{Si}, ppm: –49.81 (Si), 8.59 ($OSiMe_3$).

Silane (XI). ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm: 0.58–0.65 m (2H, C^1H_2), 1.25 br.s (2H, H_2N), 1.47–1.57 m (2H, C^2H_2), 2.65 t (2H, C^3H_2, ^3J 7.0 Hz), 3.54 s (9H, MeO). ^{29}Si NMR spectrum (59.6 MHz, $CDCl_3$): δ_{Si} –42.45 ppm (Si).

1,1,1,3-Tetramethyl-3-methoxy-3-(3-aminopropyl)disiloxane (XV). 90.00 g (1 mol) of trimethylsilanol was added dropwise to 163.06 g (1 mol) of 3-aminopropylmethyldimethoxysilane **IV** during 3 h at room temperature. The formed methanol was distilled off in vacuum. Yield of distilled product **XV** 189.2 g (85.6%), purity of 99%, mp 88–89°C (15 mmHg), n_D^{20} 1.4251. ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm: 0.03 s (3H, Me), 0.08 s (9H, $OSiMe_3$), 0.48–0.54 m (2H, C^1H_2), 1.40–1.50 m (2H, C^2H_2), 1.61 br.s (2H, NH_2), 2.64 t (2H, C^3H_2, ^3J 7.0 Hz), 3.43 s (3H, MeO). ^{29}Si NMR spectrum (59.6 MHz, $CDCl_3$), δ_{Si}, ppm: –12.75 (Si), 6.36 ($OSiMe_3$).

Silane (IV). ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm: –0.10 s (3H, Me), 0.37–0.45 m (2H, C^1H_2), 0.93 br.s (2H, H_2N), 1.23–1.35 m (2H, C^2H_2), 2.46 t (2H, C^3H_2, ^3J 7.0 Hz), 3.30 s (6H, MeO). ^{29}Si NMR spectrum (59.6 MHz, $CDCl_3$): δ_{Si} –2.61 ppm (Si).

2,2'-Oxybis-[1-(trimethylsilyl)-2-methyl-1-aza-2-silacyclopentane] (XVI). A mixture of 203.03 g (1 mol) of 1-(trimethylsilyl)-2-methyl-2-methoxy-1-aza-2-silacyclopentane **V**, 261.02 g (1 mol) of 1-(trimethylsilyl)-2-methyl-2-trimethylsiloxy-1-aza-2-silacyclopentane **XIII**, and 3.25 g of sodium trimethylsilanolate (0.7%) was incubated at 160°C during 15 h. Trimethylmethoxysilane was distilled off during the reaction. Yield of the distilled product **XVI** 86.40 g (24%), purity of 97%, mp 116–117°C (2 mmHg), n_D^{20} 1.4580. ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 0.06 s (18H, N^1SiMe_3, $N^{1'}SiMe_3$), 0.16 s (6H, Si^2Me, $Si^{2'}Me$), 0.45 d.t. (2H, C^3H, $C^{3'}H$, ^2J 14.0, ^3J 8.0 Hz), 0.60 and 0.61 d.t (2H, C^3H', $C^{3'}H'$, ^2J 14.0, ^3J 7.0 Hz), 1.69–1.76 m (4H, C^4H_2, $C^{4'}H_2$), 2.82 d.t (2H, C^5H, $C^{5'}H$, ^2J 14.0, ^3J 6.2 Hz), 2.99 d.t (2H, C^5H', $C^{5'}H'$, ^2J 10.0, ^3J 5.9 Hz). ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$), δ_C, ppm: –0.09 ($NSiMe_3$), 0.96 (Si^2Me), 1.02

($Si^{2'}Me$), 12.56 (C^3, $C^{3'}$), 25.75 (C^4, $C^{4'}$), 46.89 (C^5, $C^{5'}$). ^{29}Si NMR spectrum (79.5 MHz, $CDCl_3$), δ_{Si}, ppm: 0.56 (Si^2), 0.63 ($Si^{2'}$), 2.02 (N^1SiMe_3, $N^{1'}SiMe_3$).

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