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1-Organyl-2-azasilatran-3-ones

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Abstract—New 1-organyl-2-azasilatran-3-ones have been synthesized via the reaction of trifunctional silanes $RSiX_3$ (R = Et, Pr, Ph, CH_2=CH, or $ClCH_2$; X = Cl or Me_2N) with *N,N*-bis(2-hydroxyethyl)glycinamides $(HOCH_2CH_2)_2NCH_2C(O)NHR$ (R = H or Me) and their *N′,O*-trimethylsilyl derivatives. The obtained products can be hydrolyzed to give the corresponding organylsilanetriols. Lithiation of 1-methyl- and 1-phenyl-2-azasilatran-3-ones with *n*-butyllithium or their reduction with lithium aluminum hydride leads to the products of splitting of the atrane backbone $RSiBu_3$ and $RSiH_3$ (R = Me or Ph), respectively.

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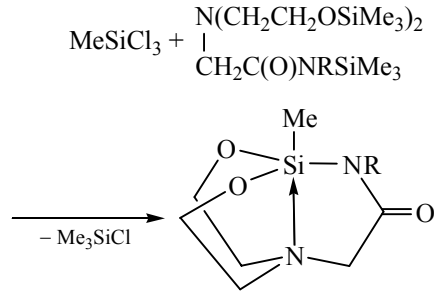
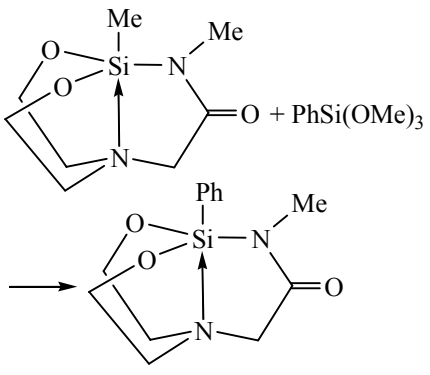
The first representatives of the silatranes class were synthesized in 1961 [1]. Over the past half-century the chemistry of these compounds has been extensively developed. Silatranes and related 2,8,9-triazasilatranes have become vast and thoroughly studied classes of organic pentacoordinated silicon compounds (for reviews, see [2–5] and references cited therein). Hypervalent bonding between the bridging Si and N atoms leads to the tricyclic cage structure and to special chemical and biological properties of the molecules. Numerous derivatives and analogues of silatranes with tricyclic backbone other than the "classical" one are known (3,7,10- and 4-substituted derivatives, silatranones, 2-carba- and homosilatranes, 2,8,9-tricarbasilatranes, and others). Important information about the symmetry, steric and electronic effects of the equatorial substituents in the bridge silicon atom trigonal bipyramidal arrangement on Si binding with the donor center can be deduced from studies of silatranes and 2,8,9-triazasilatranes analogues containing both oxygen and nitrogen atoms in the equatorial plane of the Si trigonal bipyramid. However, these closest "mixed" analogues are poorly studied. 1-Phenyl-2-azasilatrane is the first example of such compounds [6]. Using three essentially different methods, we prepared [7–9] the representatives of new cage structures class: 1-methyl-, 1,2-dimethyl-, 1-phenyl-2-methyl-, and 1-propyl-2-azasilatran-3-ones to fill in the gap. In particular, 1-methyl- and 1,2-dimethyl-2-azasilatran-3-ones were prepared via the reaction of methyltrichlorosilane with *N′*-(trimethylsilyl)-*N,N*-bis-{2-[(trimethylsilyl)oxy]-ethyl}glycinamides [7].

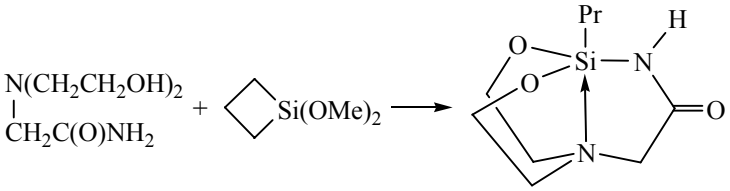


R = H, Me.

The study of the resilylation reactions of silatranes and their analogues revealed that the reaction of 1,2-dimethyl-2-azasilatran-3-one with phenyltrimethoxysilane resulted in the formation of 1-phenyl-2-methyl-2-azasilatran-3-one [8].

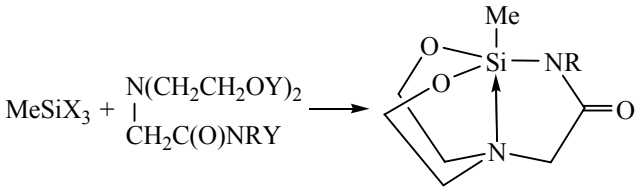


1-Propyl-2-azasilatran-3-one was synthesized via the splitting of the Si–C bond of 1,1-dimethoxy-1-silacyclobutane with *N,N*-bis(2-hydroxyethyl)glycinamide [9].



The present work aimed at finding the optimal synthetic routes to 1-organyl-2-azasilatran-3-ones and investigation of their chemical properties.

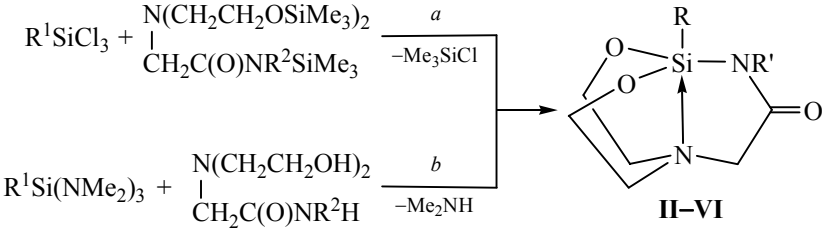
A well known method for the atrane structure formation is the reaction of two reagents containing three functional groups [2–5]. Using the reaction of methylsilanes $MeSiX_3$ with *N,N*-bis(2-hydroxyethyl) glycinamides and their *N′,O*-trimethylsilyl derivatives as a model, we studied the effects of solvent, temperature, reaction time, and the catalyst nature on the conversion of the reagents. The conversion was determined from ^{1}H NMR spectra as ratio of integral intensities of the OCH_2CH_2N fragment signals of compounds **Ia**, **Ib** and of the starting glycine derivatives. In Table 1, the reaction conditions and the respective yields of 1-methyl-2-azasilatran-3-ones (**Ia, Ib**) are given.



Ia, Ib

X = Cl, OMe, OEt, NMe_2, NEt_2, OC(O)Me; Y = H, $SiMe_3$; R = H (**a**), Me (**b**).

The results suggested that the following processes were the most promising for practical application: the reaction of $MeSiCl_3$ with *N′*-(trimethylsilyl)-*N,N*-bis {[(trimethyl-silyl)oxy]ethyl}glycinamides in boiling benzene or toluene in the presence of catalytic amounts of quinoline, and the reaction of $MeSi(NMe_2)_3$ with *N,N*-bis(2-hydroxyethyl)glycinamides either in bulk or in boiling benzene or toluene. Those two reactions were used for preparation of new 1-organyl-2-azasilatran-3-ones (**II–VI**). The conditions, degree of the conversion of starting compounds, and the yields of respective products are presented in Table 2.



II–VI

R^1 = Et, R^2 = H (**IIa**); R^1 = Et, R^2 = Me (**IIb**); R^1 = Pr, R^2 = H (**IIIa**); R^1 = Pr, R^2 = Me (**IIIb**); R^1 = Ph, R^2 = H (**IVa**); R^1 = Ph, R^2 = Me (**IVb**); R^1 = CH_2=CH, R^2 = H (**Va**); R^1 = CH_2=CH, R^2 = Me (**Vb**); R^1 = $ClCH_2$, R^2 = H (**VIa**); R^1 = $ClCH_2$, R^2 = Me (**VIb**).

Compounds **I–VI** were white or slightly yellowish amorphous powders, poorly soluble in nonpolar organic solvents. Their structure was proved by multinuclear NMR spectroscopy. Pentacoordination of the silicon atom and the tricyclic structure of the compounds were reflected in increased shielding of the ^{29}Si nuclei and by diastereotopicity of the NCH_2CH_2O methylene groups protons, similarly to that previously

Table 1. Reaction conditions and yields of 1-methyl-2-azasilatran-3-ones (**Ia, Ib**)

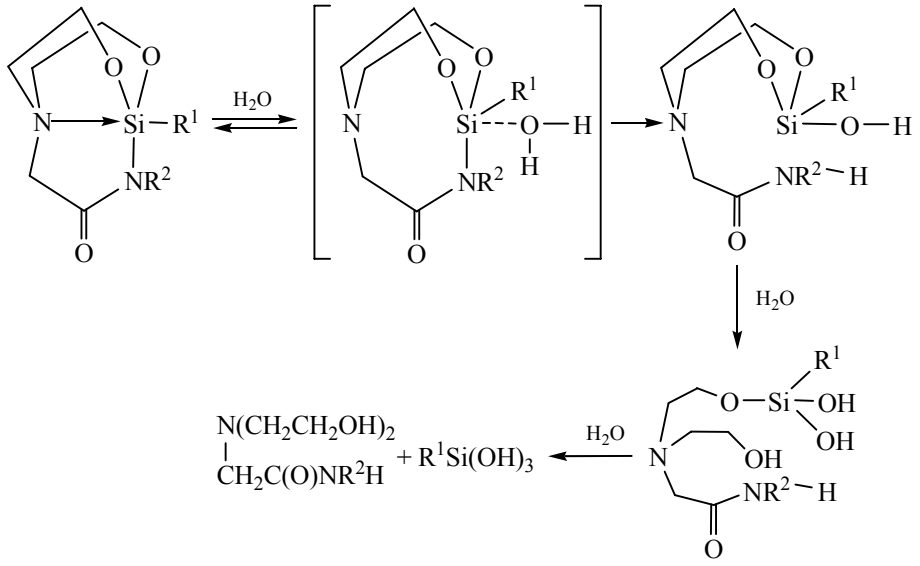
X	Y	Solvent	*T*, °C	*t*, h	Catalyst	Conversion, %	
						Ia	**Ib**
Cl[a]	H	$CHCl_3$	–10	6	–	17	23
Cl[a]	H	″	–10	20	–	21	29
Cl[a]	H	″	23	6	–	12	16
Cl[a]	H	″	61	6	–	[c]	7
Cl	Me_3Si	Et_2O	24	8	–	34	37
Cl	Me_3Si	″	24	8	Quinoline	53	49
Cl	Me_3Si	$CHCl_3$	22	8	–	32	36
Cl	Me_3Si	Benzene	22	8	–	30	27
Cl	Me_3Si	″	80	5	–	87	89
Cl	Me_3Si	″	80	5	Quinoline	97	98
Cl	Me_3Si	Hexane	69	5	–	78	84
Cl	Me_3Si	″	69	5	Quinoline	88	85
Cl	Me_3Si	Toluene	110	5	–	89	88
Cl	Me_3Si	″	110	5	Quinoline	96	98
Cl	Me_3Si	No solvent	23	4	–	93	89
OMe	H	Benzene	80	12	MeONa	38	33
OMe	H	Toluene	110	12	″	45	42
OMe[b]	H	″	110	12	″	65	70
OEt[b]	H	″	110	12	EtONa	39	37
NMe_2	H	No solvent	100	8	–	96	97
NMe_2	H	Benzene	80	12	–	91	87
NMe_2	H	″	80	18	–	96	98
NMe_2	H	Toluene	110	12	–	95	97
NEt_2	H	″	110	12	–	77	69
OC(O)Me	H	$CHCl_3$	22	6	–	18	15
OC(O)Me	H	″	22	12	–	27	40

[a] Et_3N as acceptor. [b] Molecular sieves, MS 3A. [c] Trace amounts.

observed in the NMR spectra of 1-organylsilatran-2-ones [10].

Pure compounds **I–VI** as well as their solutions were hydrolyzed when stored in the air. For example, after 1–2 days of storage, the ^{1}H NMR spectra of the 1-organyl-2-azasilatran-3-ones solutions were changed reflecting formation of the stepwise hydrolysis products.

In the case of **I–V**, after 7–10 days the only signals observed in the ^{1}H NMR spectra were those assigned to protons of the corresponding *N,N*-bis(2-hydroxyethyl)glycinamides and organylsilanetriols. ^{1}H NMR spectra of 1-phenyl-2-azasilatran-3-one and of its hydrolysis product in the range of 3–4 ppm are shown in the Figure. As seen from it, the hydrolysis products spectrum contained no signals of the NCH_2, $NCH_2C(O)$ or OCH_2 groups of the atrane backbone, whereas the signals of NCH_2, $NCH_2C(O)$ and OCH_2 groups appeared, their chemical shifts being identical to those of $(HOCH_2CH_2)_2NCH_2C(O)NH_2$. These changes were common for compounds **I–V**.

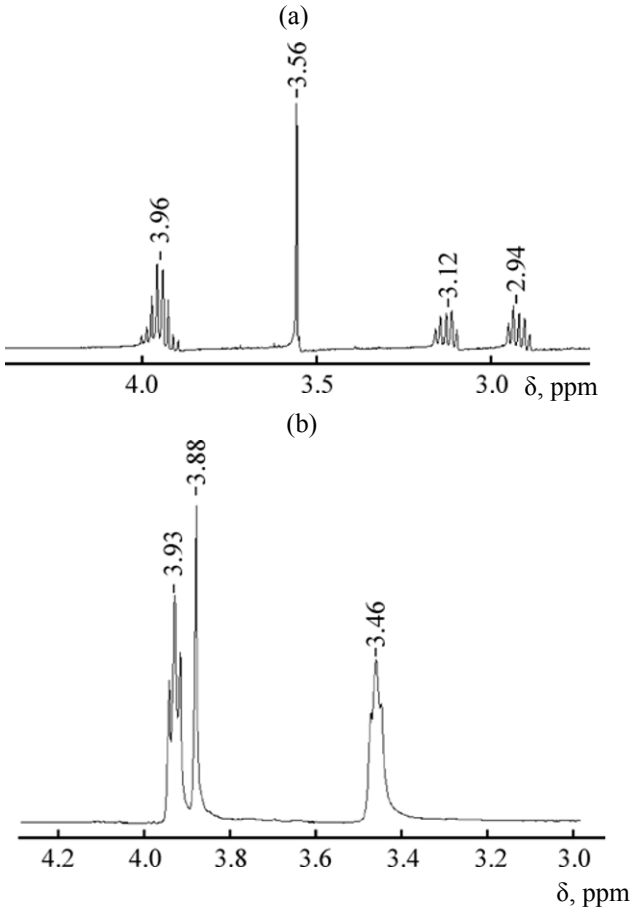


The changes in the ^{1}H NMR spectrum caused by hydrolysis of compound **VI** were more complex, likely, due to partial formation of quaternary ammonium salts. Among the signals of the silicon groups in the ^{1}H, ^{13}C, ^{29}Si NMR spectra of the hydrolysis products, the intensive signals reliably assigned to organylsilanetriols (Table 3), and weak signals (<5–7% of the major signal) of polysiloxanes were observed. Eventually, condensation of organylsilanetriols resulted in decrease of their signals intensity and in increase of polysiloxanes signals intensity. After a month, only polysiloxanes signals were observed in the spectra. All the attempts to separate the mixtures of *N,N*-bis(2-hydroxyethyl)glycinamides and organylsilanetriols failed; condensation of silanols to form polymeric products and precipitation of SiO_2 (final product of hydrolysis) were observed. Hydrolysis of compounds **I–VI** with equimolar amount of water in acetonitrile or chloroform at –15 to 25°C led to amides of *N,N*-bis(2-hydroxy-ethyl)glycine, a mixture of polysioxanes, and SiO_2.

Compounds with several OH groups at the same carbon atom are known to be very unstable and readily

Table 2. Reaction conditions and yields of 1-organyl-2-azasilatran-3-ones (**II–VI**)

Compound	Reaction	Solvent	*t*, h	Conversion, %	Yield, %
IIa	*a*	Benzene	10	88	69
IIa	*b*	Toluene	24	91	77
IIb	*a*	Benzene	10	90	73
IIb	*b*	Toluene	32	86	61
IIIa	*a*	″	12	81	62
IIIb	*a*	″	10	87	63
IVa	*a*	Benzene	8	93	81
IVa	*b*	Toluene	12	96	87
IVb	*a*	Benzene	10	94	85
IVb	*b*	Toluene	12	89	81
Va	*a*	Benzene	10	83	70
Vb	*a*	″	10	78	64
VIa	*a*	″	10	83	70
VIb	*a*	″	10	78	64



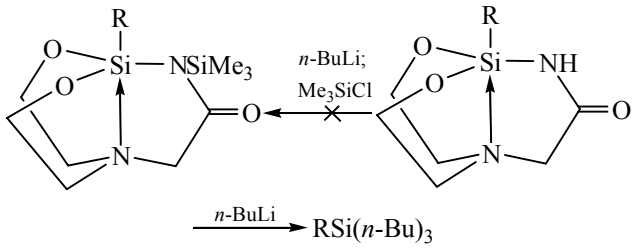
^{1}H NMR spectrum of freshly prepared solution of compound **IVa** (a) and of the same sample after 11 days storage at air (b).

dehydrating. However, similar silicon compounds, $R^1R^2Si(OH)_2$ and $RSi(OH)_3$, represent unique polyfunctional molecules which can be isolated and characterized under certain conditions. In 1959, the first stable phenylsilanetriol was obtained via hydrolysis of phenyltrichlorosilane (in the buffer solution, to prevent condensation to siloxanes occurring under acidic or alkaline conditions) [11]. Special attention to polysilanols chemistry [12–15] has arisen because they are excellent synthons of silsesquioxanes, metallosilsesquioxanes, and charged polymers in the materials chemistry. In 1982, the X-ray data were first obtained for cyclohexylsilanetriol [16], showing the presence of intermolecular hydrogen bonds. Those results were later proved by further studies of organylsilanetriols. Apparently, mild hydrolysis of 1-organyl-2-azasilatran-3-ones leaded to the formation of strong hydrogen-bonded complexes of organylsilanetriols and amides of bis(2-hydroxyethyl)glycine, stable in the solution.

Table 3. ^{1}H, ^{13}C, ^{29}Si NMR spectra parameters of organylsilanetriols $RSi(OH)_3$ (δ, ppm)

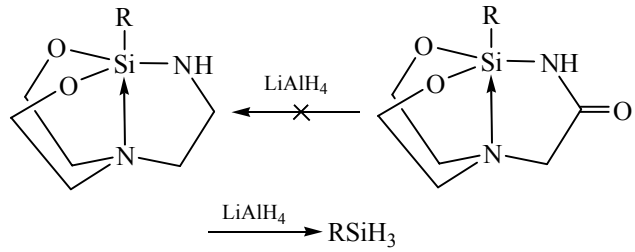
R	^{1}H	^{13}C	^{29}Si
Me	–0.47	1.84	–41.9
Et	0.68, 1.25	0.28, 6.75	–43.4
Pr	0.68, 0.95, 1.41	12.77, 16.46, 17.64	–44.2
Ph	7.28, 7.68	127.78, 130.48, 130.95, 134.8	–52.2
Vin	5.88–6.12	130.35, 136.88	–58.8

We expected to obtain the products of *N*-silylation of the 1-organyl-2-azasilatran-3-ones amide group via lithiation and subsequent silylation. However, in the products of lithiation of **Ia** and **IVa** only the corresponding methyl- and phenyltributylsilanes were detected by multinuclear NMR spectroscopy, along with unidentified tarry products.



R = Me, Ph.

An attempt to reduce the 1-organyl-2-azasilatran-3-ones amide group with lithium aluminum hydride in diethyl ether in order to synthesize 1-organyl-2-azasilatranes failed as well. According to the NMR spectra of the reaction mixtures, organylsilanes were the major products. Similar reaction of silatrane backbone splitting with organometal reagents have been described also for alkyl- and arylsilatranes [17].



R = Me, Ph.

In spite of those unsuccessful outcomes, investigation of the reduction and silylation of the 1-organyl-2-azasilatran-3-ones amide fragment seems very promising. Overcoming of the experimental obstacles will allow preparation of novel compounds series with unique physico-chemical properties and potential biological activity.

EXPERIMENTAL

IR spectra of compounds **I–VI** were recorded with Specord IR-75 and Bruker IFS 25 spectrometers in vaseline oil. NMR spectra of the compounds **I–VI** solutions (10–20 wt %) in the 1:2 $CDCl_3$–CD_2Cl_2 mixture were registered with JEOL-90Q (^{1}H, 89.5; ^{13}C, 22.5; ^{29}Si, 17.9 MHz) and Bruker DPX-400 (^{1}H, 400.1; ^{13}C, 100.6; ^{29}Si, 79.5 MHz) spectrometers using TMS or HMDS as internal standard. All reactions were carried out under carefully dried argon atmosphere. The solvents were purified via the known procedures [18]. Amide and *N*′-methylamide of *N,N*-bis(oxyethyl)-glycine were synthesized via standard procedures [19]. *N′,O*,O'-Tris(trimethylsilyl)amide and *N′,O*,O'-tris(trimethylsilyl)-*N*′-methylamide of bis(oxyethyl)glycine were synthesized as previously described [7].

Synthesis of 1-organyl-2-azasilatran-3-ones (I–VI). *a*. The solution of equimolar amount of organyltrichlorosilane in 25 ml of benzene or toluene was slowly added dropwise to the boiling solution of 1 mmol of *N*-(trimethylsilyl)-*N*′,*N*′-bis{2-[(trimethylsilyl)oxy]ethyl}glycinamide in 25 ml of the corresponding solvent containing 0.05 g of freshly distilled quinoline. The mixture was refluxed for 8–10 h, cooled to room temperature, and left in a refrigerator for 12–20 h. The precipitate formed was filtered off, washed with dry pentane, and dried in vacuum. Evaporation of the mother liquor under vacuum (25–30 mm Hg) by ~3/4 volume and subsequent incubation in a refrigerator for 12–20 h gave additionally 20–45% of the crude product.

b. The equimolar mixture of *N*′,*N*′-bis(2-oxyethyl)-glycinamide and organyltris(dimethylamino)silane (1 mmol of both) in 100 ml of dry toluene was refluxed upon stirring till the evolution of dimethylamine ceased (universal indicator paper test). The reaction mixture was evaporated to 1/5 of the initial volume under vacuum (25–30 mm Hg) and left in a refrigerator for 12–20 h. The precipitate formed was filtered off and, if necessary, purified by sublimation or crystallization.

1-Methyl-2-azasilatran-3-one (Ia). mp > 165°C (decomp.). IR spectrum, ν, cm^{-1}: 1680 (C=O), 1100 (Si–O), 3450 (NH). ^{1}H NMR spectrum, δ, ppm: –0.07 s (MeSi), 2.88 m and 3.02 m (NCH_2), 3.30 s (CH_2C=O), 3.80 m (OCH_2), 5.35 (NH). ^{13}C NMR spectrum, δ_C, ppm: –0.02 (MeSi), 54.08 (NCH_2), 56.68 (CH_2C=O), 57.85 (OCH_2), 174.32 (C=O). ^{29}Si NMR spectrum, δ_{Si}, ppm: –67.0 (27°C), –66.2 (55°C). Found, %: C 41.79; H 7.00; Si 13.90; N 13.98. $C_7H_{14}N_2O_3Si$. Calculated, %: C 41.56; H 6.98; Si 13.88; N 13.85.

1**,2-Dimethyl-2-azasilatran-3-one (Ib).** mp 174–176°C. IR spectrum, ν, cm^{-1}: 1660 (C=O), 1100 (Si–O). ^{1}H NMR spectrum, δ, ppm: 0.09 s (MeSi), 2.85 s (MeN), 2.95 m and 3.13 m (NCH_2), 3.42 s (CH_2C=O), 3.84 m (OCH_2). ^{13}C NMR spectrum, δ_C, ppm: 1.47 (MeSi), 30.34 (NMe), 53.03 (NCH_2), 55.77 ($\underline{C}H_2C$=O), 57.14 (OCH_2), 172.24 (C=O). ^{29}Si NMR spectrum, δ_{Si}, ppm: –65.7 (27°C), –65.0 (55°C). Found, %: C 43.97; H 7.73; Si 13.20; N 12.58. $C_8H_{16}N_2O_3Si$. Calculated, %: C 44.42; H 7.46; Si 12.98; N 12.95.

1-Ethyl-2-azasilatran-3-one (IIa). mp 118–120°C (decomp.). IR spectrum, ν, cm^{-1}: 1682 (C=O), 1100 (Si–O), 3455 (NH). ^{1}H NMR spectrum, δ, ppm: 0.34 (CH_2Si); 0.93 (MeC); 2.94 m and 3.07 m (NCH_2), 3.38 (CH_2C=O), 3.82 m (OCH_2), 5.25 (NH). ^{13}C NMR spectrum, δ_C, ppm: 5.02 ($SiCH_2$), 14.82 ($\underline{C}H_3C$), 54.93 (NCH_2), 57.76 ($\underline{C}H_2C$=O), 58.15 (OCH_2), 173.66 (C=O). ^{29}Si NMR spectrum: δ_{Si} –68.8 ppm. Found, %: C 44.77; H 7.61; N 13.22. $C_8H_{16}N_2O_3Si$. Calculated, %: C 44.42; H 7.46; N 12.95.

1-Ethyl-2-methyl-2-azasilatran-3-one (IIb). mp 129–132°C. IR spectrum, ν, cm^{-1}: 1660 (C=O), 1100 (Si–O). ^{1}H NMR spectrum, δ, ppm: 0.28 (CH_2Si), 0.92 s (MeC), 2.82 s (MeN), 2.92 m and 3.10 m (NCH_2), 3.44 s (CH_2C=O), 3.82 m (OCH_2). ^{13}C NMR spectrum, δ_C, ppm: 3.58 (CH_2Si), 8.98 (MeC), 30.18 (NMe), 53.10 (NCH_2), 55.68 ($\underline{C}H_2C$=O), 57.12 (OCH_2), 172.76 (C=O). ^{29}Si NMR spectrum: δ_{Si} –65.8 ppm. Found, %: C 46.53; H 7.91; N 12.22. $C_8H_{16}N_2O_3Si$. $C_9H_{18}N_2O_3Si$. Calculated, %: C 46.93; H 7.88; N 12.16.

1-Propyl-2-azasilatran-3-one (IIIa). mp 98–101°C. IR spectrum, ν, cm^{-1}: 1685 (C=O), 1100 (Si–O), 3455 (NH). ^{1}H NMR spectrum, δ, ppm: 0.53 m (CH_2Si), 0.93 m (MeC), 1.43 m (CCH_2C), 2.91 m and 3.04 m (NCH_2), 3.34 (CH_2C=O), 3.80 (OCH_2), 4.82 (NH). ^{13}C NMR spectrum, δ_C, ppm: 8.12 ($SiCH_2$), 14.82 (C$\underline{C}$C), 16.81(C$\underline{C}H_3$), 54.67 (NCH_2), 57.12 ($\underline{C}H_2C$=O), 58.05 (OCH_2), 173.72 (C=O). ^{29}Si NMR spectrum: δ_{Si} –68.2 ppm. Found, %: C 46. 72; H 7.71; N 11.35. C_9H_{18}·N_2O_3Si. Calculated, %: C 46.93; H 7.88; N 12.16.

1-Propyl-2-methyl-2-azasilatran-3-one (IIIb). mp 89–92°C. IR spectrum, ν, cm^{-1}: 1680 (C=O), 1100 (Si–O). ^1H NMR spectrum, δ, ppm: 0.51 m (CH_2Si), 0.92 m (MeC), 1.46 m (CCH_2C), 2.87 s (NMe), 2.96 m and 3.14 m (NCH_2), 3.43 c ($CH_2C=O$), 3.82 m (OCH_2). ^{13}C NMR spectrum, δ_C, ppm: 8.10 ($SiCH_2$), 14.90 ($C\underline{C}H_2C$), 16.72 ($C\underline{C}H_3$), 55.43 (NCH_2), 57.94 ($\underline{C}H_2C=O$), 58.20 (OCH_2), 172.56 (C=O). ^{29}Si NMR spectrum, δ_{Si} ppm: –67.4. Found, %: C 49.39; H 7.47; N 11.69; Si 9.79. $C_{10}H_{20}N_2O_3Si$. Calculated, %: C 49.15; H 8.25; N 11.46.

1-Phenyl-2-azasilatran-3-one (IVa). mp > 208°C (decomp.). IR spectrum, ν, cm^{-1}: 1678 (C=O), 1100 (Si–O), 3450 (NH). ^1H NMR spectrum, δ, ppm: 2.94 m and 3.12 m (NCH_2), 3.56 s ($CH_2C=O$), 3.94 m (OCH_2), 7.28 m and 7.73 m (Ph). ^{13}C NMR spectrum, δ_C, ppm: 53.28, 55.29, 58.08, 127.38, 128.64, 134.29, 139.12, 168.19. ^{29}Si NMR spectrum: δ_{Si} –80.0 ppm. Found, %: C 54.17; H 6.41; N 10.29; Si 9.79. $C_{12}H_{16}N_2O_3Si$. Calculated, %: C 54.52; H 6.10; N 10.60; Si 10.62.

1-Phenyl-2-methyl-2-azasilatran-3-one (IVb). mp 238–239°C. IR spectrum, ν, cm^{-1}: 1676 (C=O), 1100 (Si–O). ^1H NMR spectrum, δ, ppm: 2.41 s (NMe), 2.91 m and 3.08 m (NCH_2), 3.49 s ($CH_2C=O$), 3.96 m (OCH_2), 7.26 m and 7.70 m (Ph). ^{13}C NMR spectrum, δ_C, ppm: 32.1, 53.14, 55.89, 57.55, 127.41, 128.17, 135.03, 141.92, 172.55. ^{29}Si NMR spectrum: δ_{Si} –79.0 ppm. Found, %: C 55.78; H 6.13; N 10.23; Si 9.57. $C_{13}H_{18}N_2O_3Si$. Calculated, %: C 56.09; H 6.52; N 10.06; Si 10.09.

1-**Vinyl-2-azasilatran-3-one (Va).** mp >162°C (decomp.). IR spectrum, ν, cm^{-1}: 1682 (C=O), 1100 (Si–O), 3456 (NH). ^1H NMR spectrum, δ, ppm: 2.80 m and 3.06 m (NCH_2), 3.42 s ($CH_2C=O$), 3.88 m (OCH_2), 5.84 m (C=CH), 6.12 m ($CH_2=C$). ^{13}C NMR spectrum, δ_C, ppm: 53.42, 55.72, 58.38, 124.32, 128.43, 169.52. ^{29}Si NMR spectrum: δ_{Si} –82.2 ppm. Found, %: C 44.57; H 6.23; N 13.37. $C_8H_{14}N_2O_3Si$. Calculated, %: C 44.84; H 6.58; N 13.07.

1-**Vinyl-2-methyl-2-azasilatran-3-one (Vb).** mp 143–145°C. IR spectrum, ν, cm^{-1}: 1676 (C=O), 1100 (Si–O). ^1H NMR spectrum, δ, ppm: 2.36 s (NMe), 2.87 m and 3.04 m (NCH_2), 3.53 s ($CH_2C=O$), 3.90 m (OCH_2), 5.96 m (C=CH), 6.27 m ($CH_2=C$). ^{13}C NMR spectrum, δ_C, ppm: 33.4, 53.45, 55.76, 57.39, 126.42, 128.34, 172.55. ^{29}Si NMR spectrum: δ_{Si} –81.0 ppm. Found, %: C 46.93; H 6.80; N 12.06. $C_9H_{16}N_2O_3Si$. Calculated, %: C 47.34; H 7.06; N 12.27.

1-Chloromethyl-2-azasilatran-3-one (VIa). IR spectrum, ν, cm^{-1}: 1684 (C=O), 1100 (Si–O), 3450 (NH). ^1H NMR spectrum, δ, ppm: 2.72 s (CH_2Cl), 2.78 m and 2.98 m (NCH_2), 3.12 s ($CH_2C=O$), 3.85 m (OCH_2). ^{29}Si NMR spectrum: δ_{Si} –78.0 ppm. Found, %: C 35.48; H 5.83; N 11.92. $C_7H_{13}ClN_2O_3Si$. Calculated, %: C 35.52; H 5.54; N 11.83.

1-Chloromethyl-2-methyl-2-azasilatran-3-one (VIb). mp 198–201°C. IR spectrum, ν, cm^{-1}: 1678 (C=O), 1100 (Si–O). ^1H NMR spectrum, δ, ppm: 2.76 s (CH_2Cl), 2.82 s (MeN), 2.85 m and 3.04 m (NCH_2), 3.23 s ($CH_2C=O$), 3.83 m (OCH_2). ^{29}Si NMR spectrum: δ_{Si} –72.0 ppm. Found, %: C 38.39; H 6.18; N 11.19. $C_8H_{15}ClN_2O_3Si$. Calculated, %: C 38.32; H 6.03; N 11.17.

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