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The Products of Substitution and Cyclization in the Reaction of (2-Bromoethyl)(3-chloropropyl)dimethylsilane with Triflamide

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Abstract—In order to synthesize the first seven-membered *N*-triflylazasilacycloalkane the reaction of triflamide with (2-bromoethyl)(3-chloropropyl)dimethylsilane was studied. Depending on the reaction conditions bis(3-chloropropyl)tetramethyldisiloxane, 3-trifluoromethylsulfonylaminopropyl(3-chloropropyl)-tetramethyldisiloxane, (2-triflamidoethyl)(3-chloropropyl)dimethylsilane, bis(3-triflamidopropyl)tetramethyldisiloxane, and the target 4,4-dimethyl-1-(trifluoromethylsulfonyl)-1,4-azasilepane have been isolated. In all cases the halogen atom in the β-bromoethyl group is replaced first. Low-temperature ^{1}H NMR spectroscopy showed that the prepared seven-membered heterocycle is conformationally flexible.

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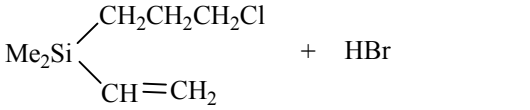
Heterocyclic compounds with the nitrogen and silicon atoms in 1,3- and 1,4-positions of the ring as well as their derivatives have been actively studied in two recent decades since they possess interesting chemical properties, different types of biological activity showing hypotensive, ganglion blocking, neurotropic, and other effects [1–7] and demonstrate an interesting conformational behavior [8–11].

In general, the synthesis of five- and six-membered organosilicon azaheterocycles is mainly performed by the reaction of ω,ω'-di(haloalkyl)silanes with amines, or by the method of intramolecular cyclization of (ω-haloalkyl)(ω'-aminoalkyl)silanes, which can be considered as intermediates in the former reaction [2, 3, 12–19].

The synthesis of seven-membered Si,N-heterocycles was always a challenge, that is why there are few examples of their synthesis. Thus in [20] the synthesis of l-butyl-3,3-dimethyl-3-sila-l-azasilacycloheptane from δ-bromobutyl(bromomethyl)dimethylsilane and butylamine in 43% yield was described. Mironov et al. [21] have synthesized the organosilicon lactam, 3,3-dimethyl-1,3-azasilepan-7-one, in 70% yield by heating 4-[(chloromethyl)dimethylsilyl]butanamide with sodium methoxide in methanol. 2,4,4-Trimethyl-1-phenyl-1,4-azasilepane was obtained in an extremely low yield (3%) in the reaction of aniline with chloropropyl(allyl)dimethylsilane [18], and its 2-unsubstituted analog was synthesized in 36% yield by the reaction with vinyl(3-phenylaminopropyl)dimethylsilane [19]. A complex condensed heterocycle, an ester of 5,5-dimethyl-8,9-dioxo-1-aza-5-silabicyclo[5.2.0]nonane-2-carboxylic acid, was decomposed with the formation (among other products) of two simpler seven-membered Si,N-heterocycles, the esters of 4,4-dimethyl-1,4-azasilepane-7-carboxylic and -2,7-dicarboxylic acids [22]. The stereocontrolled synthesis of a series of six-membered Si,N-heterocycles as well as their seven-membered analog, (*R*)-benzyl-3,3-diphenyl-2-propyl-1,3-azasilepane-1-carboxylate in good yield has been described [23]. In the latter case, the nitrogen atom is protected by the carboxybenzyl group. We failed to find seven-membered Si,N-heterocycles bearing a protecting sulfonyl group at the nitrogen atom, although their organic analogs, such as 1-tosylazepane, are well known and were prepared by the base-catalyzed cyclization of *N*-(6-bromoalkyl)-sulfonamides [24].

In the course of our studies on the synthesis and investigation of the properties of *N*-triflyl substituted

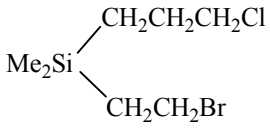
Si,N-heterocycles based on the reaction of heterocyclization of dimethyldi(ω,ω'-haloalkyl)silanes with trifluoromethanesulfonamide (triflamide) we have synthesized new five- and six-membered Si,N-heterocycles with the endocyclic nitrogen and silicon atoms possessing the triflyl group at nitrogen [25–27]. The reactions were performed in the presence of triethylamine, the products were formed in moderate yields of 42–50%. In the present work, with the aim to synthesize the seven-membered analog of the earlier obtained N-triflylazasilacycloalkanes the reaction of triflamide **I** with (2-bromoethyl)(3-chloropropyl)dimethylsilane **II** has been studied. The starting silane **II** was prepared by the free-radical hydrobromination of (3-chloropropyl)dimethyl(vinyl)silane in 83% yield by the known procedure [13].



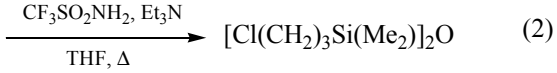
$$Me_2Si(CH_2CH_2CH_2Cl)(CH{=}CH_2) + HBr \xrightarrow[\text{hexane, Ar}]{(PhCOO)_2} Me_2Si(CH_2CH_2CH_2Cl)(CH_2CH_2Br) \quad (1)$$

II

The attempt to perform the reaction of silane **II** with triflamide under the conditions optimal for the synthesis of the earlier prepared five- [27] and six-membered cycles [26] (THF, **I**:**II**:Et_3N = 2:1:2) failed. At room temperature or in the absence of triethylamine the reaction does not proceed, and only after reflux for 7–13 h the conversion was 47–50%. Therewith no fluorine-containing products were detected by the ^1H and ^{19}F NMR spectroscopy. From the ^{29}Si NMR spectroscopy, the reaction mixture, apart from the starting silane **II**, contained silanols (δ_{Si} ~15 ppm) and siloxanes (δ_{Si} ~8 ppm), in particular, bis(3-chloropropyl)tetramethyldisiloxane (**III**).



II



$$\xrightarrow[\text{THF, }\Delta]{CF_3SO_2NH_2,\ Et_3N} [Cl(CH_2)_3Si(Me_2)]_2O \quad (2)$$

III

The formation of siloxane **III** was proved by the coincidence of the signals of the reaction mixture with the signals of the independently synthesized sample. The reaction of silane **II** with the sodium salt of triflamide in THF proceeds similar to reaction (2) (the reaction was carried out in the presence of the phase transfer catalyst triethylbenzylammonium chloride because the salt was insoluble in THF).

In methanol, as in THF, the reaction does not occur at room temperature. At reflux over 7 h in the presence of triethylamine the starting silane **II** is completely consumed. According to the NMR spectroscopy data, the reaction mixture contains mainly siloxanes. By the use of column chromatography, we succeeded to isolate siloxane **III** (yield 10%) and the product of substitution of one chlorine atom in it by the triflamide residue, 3-trifluoromethylsulfonylaminopropyl(3-chloropropyl)tetramethyldisiloxane (**IV**) (yield 3.5%).

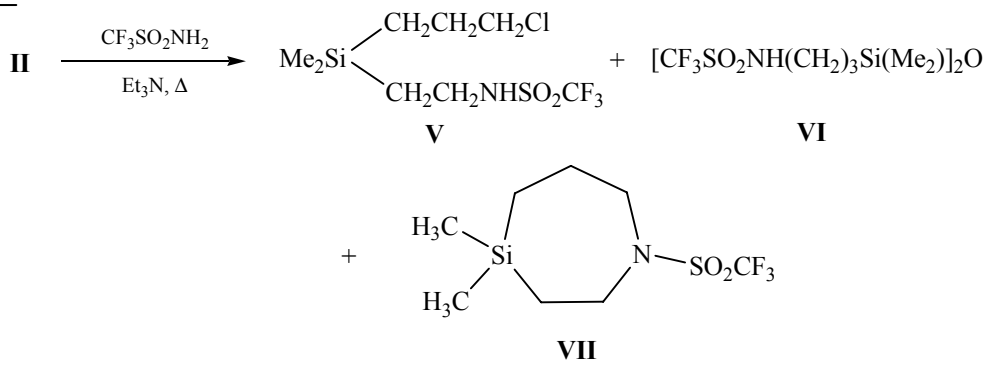
$$\mathbf{II} \xrightarrow[\text{MeOH, }\Delta]{CF_3SO_2NH_2,\ Et_3N} \mathbf{III} + CF_3SO_2NH(CH_2)_3Si(Me_2)OSi(Me_2)(CH_2)_3Cl \quad (3)$$

IV

Apparently, complete conversion of silane **II** in methanol, as distinct from the reaction in THF, is due to an easier cleavage of the Si–C bond in the bromoethyl fragment (β-effect) in a proton-donor medium [28]. This was confirmed by an independent synthesis of siloxane **III**: it was obtained by the reflux of silane **II** in methanol and isolated by column chromatography in 36% yield. Siloxane **III** can react with triflamide to afford unsymmetrical disiloxane **IV**. The structure of siloxanes **III** and **IV** was proved by NMR spectroscopy. The ^1H and ^{13}C NMR spectra of symmetrical siloxane **III** contain the signals of the $SiMe_2$ group and three signals of the methylene groups of the $Si(CH_2)_3Cl$ fragment, and the ^{29}Si NMR spectrum contains one signal at 7.64 ppm. In the unsymmetrical siloxane **IV** the number of signals in all NMR spectra is doubled due to the presence of two nonequivalent fragments $Si(CH_2)_3Cl$ and $Si(CH_2)_3N$. The assignment of the signals in the ^1H and ^{13}C NMR spectra to the chloropropyl and the triflamidopropyl fragments was performed by the use of two-dimensional spectra ^1H–^1H COSY and ^1H–^{13}C HSQC and was based on different splitting pattern of the CH_2Cl and CH_2N signals in the ^1H NMR spectra: the former signal is a triplet, whereas the latter one is a quartet due to close coupling constants $^3J_{CH–CH}$ and $^3J_{CH–NH}$.

Earlier we have shown that the reaction of triflamide with (chloromethyl)trimethylsilane is sharply retarded when performed in THF or methanol in the

presence of excess triethylamine as compared to the reaction in triethylamine as a solvent [29]. The same effect was observed in the reaction of triflamide with silane **II**. The composition of the products formed did not change qualitatively when the reaction was carried out in triethylamine. At room temperature the reaction does not take place, but upon heating to 50–60°C a spontaneous heating of the reaction mixture to 70–90°C occurs and after 3 h at 70–75°C the conversion of the starting silane **II** reaches 100%. The reaction with small excess of triflamide with respect to silane **II** leads to the formation of (2-triflamidoethyl)(3-chloropropyl)dimethylsilane (**V**), bis(3-triflamidopropyl)tetramethyldisiloxane (**VI**), and 4,4-dimethyl-1-(trifluoromethylsulfonyl)-1,4-azasilepane (**VII**) according to reaction (4).



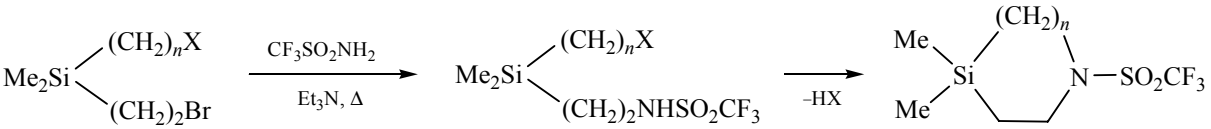
(4)

The results of monitoring reaction (4) by ^{1}H NMR spectroscopy are presented in the table.

Compound **V** is the intermediate on the way of transformation of silane **II** to the product of heterocyclization **VII**. This process is general for dihalosilanes $Me_2Si(CH_2CH_2Br)(CH_2)_nX$ [reaction (5)].

In all cases, the halogen atom in the β-bromoethyl group is replaced first, but the five- and six-membered heterocycles are formed immediately, so that the intermediate products of monosubstitution cannot be even detected in the reaction mixture, whereas in the synthesis of the seven-membered cycle it is formed, according to NMR data, in up to 50% yield. Apparently, this is due to a lower rate of cyclization of compound **V** because of more remote groups NH and CH_2Cl.

Products **V**–**VII** were isolated as individual compounds by column chromatography, their structure and composition was proved by IR, ^{1}H, ^{13}C, ^{19}F, ^{29}Si NMR spectroscopy and elemental analysis, and by independent synthesis. Thus, in the ^{1}H and ^{13}C NMR spectra of the product of monosubstitution **V**, apart from the signals of the Me_2Si group, the signals of five different methylene groups are observed, in the IR and



(5)

n = 1, X = Cl [27]; *n* = 2, X = Br, [26]; *n* = 3, X = Cl.

Conditions of reaction (4) and yields of the products

II : Et_3N	Time, h	*T*, °C	Conversion, %	**V**, %	**VI**, %	**VII**, %
1:4	1	72	72	39	30	3
1:4	2	72	84	40	30	14
1:4	3	72	100	50	34	16
1:7	0.5	80–86	80	12	45	Traces[a]
1:4	6	85–90	100	Traces	70	20[b]

[a] Yield of unidentified products of decomposition 23%. [b] Yield of unidentified products of decomposition 10%.

^{1}H NMR spectra the NH signal is present, and the ^{13}C and ^{19}F NMR spectra contain the signal of the CF_3 group. Note the absence of the product of monosubstitution of chlorine atom in silane **II**, which is indicative of a higher reactivity of the β-bromoethyl group as compared to the γ-chloropropyl group. Since in reaction (4) the precipitate comprising the mixture of hydrohalides $Et_3N{\cdot}HCl$ and $Et_3N{\cdot}HBr$ is formed, for the independent assessment of the relative reactivity of the γ-chloropropyl and β-bromoethyl groups we have used the method of X-ray energy dispersive microanalysis and examined the specimens taken after 30 min and after 2 h from the beginning of the reaction. After 30 min the averaged ratio Br/Cl in the mixture of the salts was 2:1, whereas after 2 h it was 1:6, that is, in the first step the substitution takes place in the 2-bromoethyl group and only then in the 3-chloropropyl group.

The positions of the methylene group signals in the ^{1}H NMR spectra of siloxanes **VI** and **III** practically coincide. The difference is that the spectrum of siloxane **VI** contains the triplet of the NH group, and the signal of the NCH_2 looks like a quartet due to additional splitting on the NH proton, rather than a triplet as in the spectrum of compound **III**. Siloxane **VI** is, apparently, the product of bis-triflamidation of siloxane **III**, which is an intermediate formed by β-cleavage of silane **II**. Indeed, an independent experiment has shown that siloxane **III** reacts with triflamide to give siloxane **VI** in 90% yield, as shown the ^{1}H NMR spectroscopy data.

$$\mathbf{III} + CF_3SO_2NH_2 \xrightarrow[Et_3N,\ \Delta]{} \mathbf{VI} \qquad (6)$$

Siloxane **III** was also detected under the conditions of reaction (4) in the initial stage (15–30 min) at a lower temperature (below 63°C).

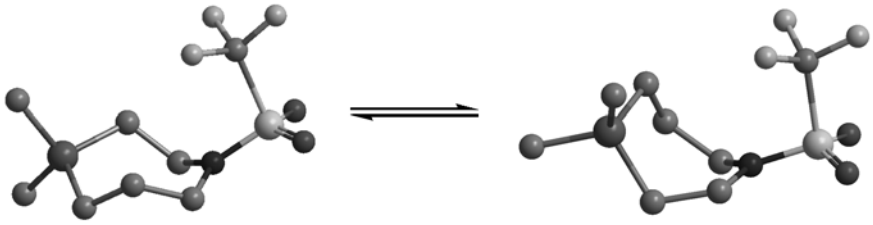
The use of 7-fold excess of triethylamine accelerates reaction (4): the conversion reaches 80% after 30 min. The content of product **V** decreases to 12%, but the product of heterocyclization **VII** is present only in trace amounts. Therewith, the content of siloxane **VI** increases to 45% (see the table), apparently, due to a faster β-cleavage of the starting silane **II**. The optimal conditions for preparation of heterocycle **VII** were found to be the following: the use of the ratio **II**:**I**:Et_3N = 1:2:4 and reflux at 85–90°C in the course of 6 h. Under these conditions, according to the ^{1}H NMR data, the conversion was 100% and the reaction mixture contained only products **VI** and **VII** in the ratio 7:2. The isolated yield of siloxane **VI** after column chromatography was 37%, and of heterocycle **VII**, 16%. Compounds **V** and **VII** containing the triflamide residue in the β-position to the silicon atom, are rather stable and do not decompose at storage for half a year.

In the ^{1}H NMR spectrum of compound **VII** in $CDCl_3$ at room temperature four signals are observed: broadened singlets at 0.8 and 1.1 ppm belonging to the $SiCH_2$ groups in the $(CH_2)_3$ and $(CH_2)_2$ fragments, respectively, a multiplet of the CCH_2C group, and a very broad signal at 2.5–4.5 ppm belonging to two nonequivalent NCH_2 groups. The observed broadening is caused by the lability of the seven-membered ring. When the temperature of the sample was increased to 70°C, the solution was degassed, and the spectrum was taken in an argon atmosphere, the $SiCH_2$ signals showed a multiplet structure and the NCH_2 signals appeared as two separate broadened singlets at 3.4 and 3.6 ppm. Two-dimensional homonuclear spectrum ^{1}H–^{1}H COSY at 70°C allowed to unambiguously assign all signals: the protons of the 6-CH_2 group give cross peaks with the protons of the 5-$SiCH_2$ and 7-NCH_2 groups, and the protons of the 3-$SiCH_2$ group, with the protons of the 2-NCH_2 group.

The observed variations in the ^{1}H NMR spectrum at higher temperatures prompted us to investigate the dynamics of the process at low temperatures. The results are shown in Fig. 1. As follows from the spectra, all signals are split to the sgnals of the axial and equatorial Si-methyl groups and the axial and equatorial protons of the methylene groups of the ring. From the temperature of coalescence and the difference in the chemical shifts of the signals of protons of the 2-CH_2, 3-CH_2, 5-CH_2, 7-CH_2 groups as well as of the SiMe protons and using the Eyring equation, where $k = \Delta\nu/0.45$, the free energy was calculated. It turned out to be practically the same for all pairs of the signals and was equal to 13.5 kcal/mol.

$$\Delta G_c^{\neq} = 1.986T_c[23.76 + 2.303(\log T_c - \log k)].$$

Apparently, this value is a barrier to the ring inversion, but the structure and the energy of the interconverting conformers is the subject of a separate investigation in view of the presence of two heteroatoms in the seven-membered ring, which may occupy different nonequivalent positions, and the triflyl group which may be differently oriented with respect to the ring. Equilibrium (7) illustrates only one of many possibilities.



(7)

In Fig. 2, the low-temperature ^{1}H–^{1}H COSY spectrum of heterocycle **VII** is given in the range of protons of the ring methylene groups. The pattern of splitting and the presence of the corresponding cross peaks allow an unambiguous assignment of the observed signals to the axial and equatorial protons in the ring. As is seen, in accordance with the general rule, in all cases the axial protons resonate at a stronger field. All signals are completely resolved, except for the overlapping signals of the 5-CH_{eq} and 3-CH_{ax} protons at 0.9 ppm.

An attempt to perform cyclization of compound **V** by the action of NaH in THF employing the procedure used for the cyclization of (γ-hydroxy)-α-silylamines and their derivatives [23] failed; even upon heating to 50°C in the course of 5 h the starting product **V** was recovered, probably, due to the low basicity of the triflamide nitrogen atom.

EXPERIMENTAL

^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra were recorded from $CDCl_3$ solutions on a Bruker DPX 400 spectrometer (400, 100, 376, and 79.5 MHz, respectively). Chemical shifts are given relative to TMS (^{1}H, ^{13}C, ^{29}Si) and CCl_3F (^{19}F). The assignment of the signals in ^{1}H and ^{13}C NMR spectra was performed by the use of

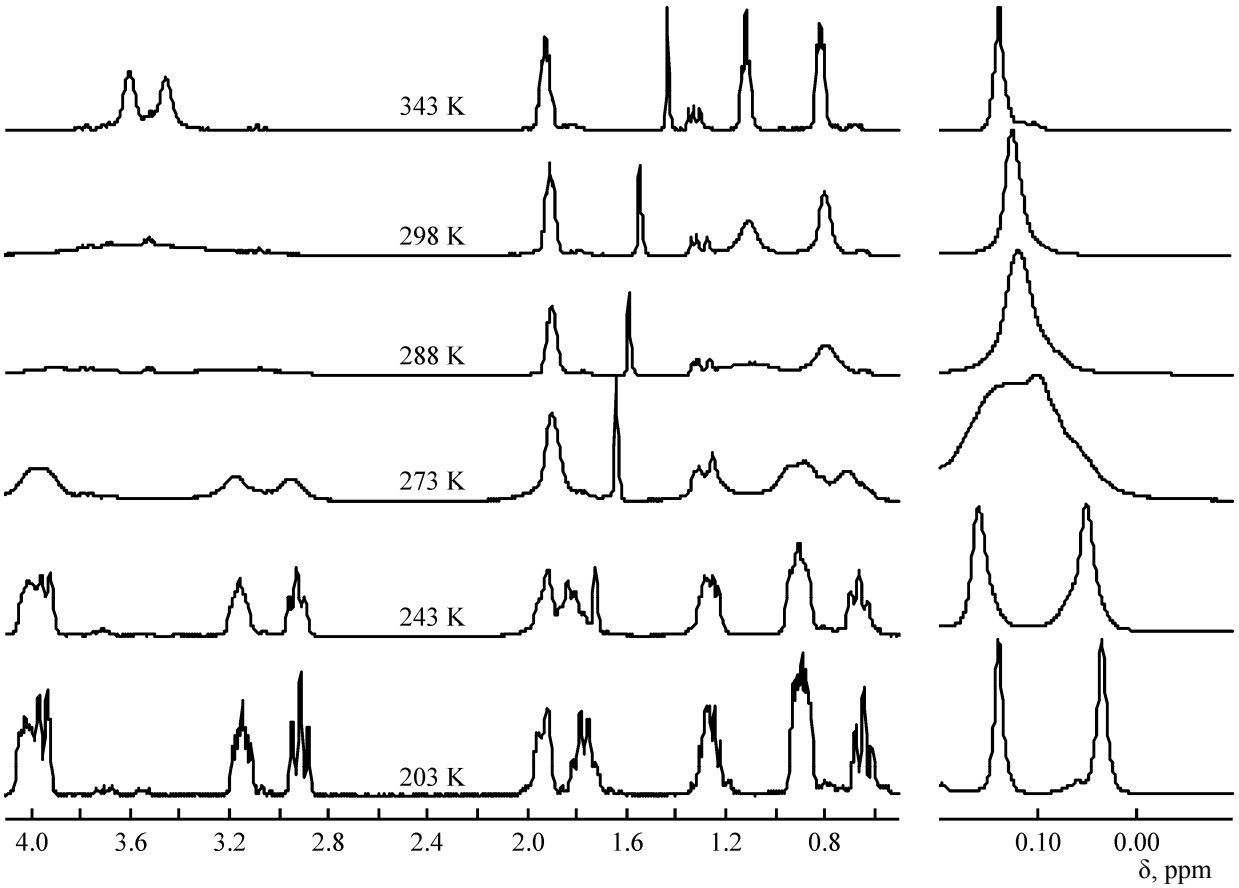


Fig. 1. ^{1}H NMR spectra of 4,4-dimethyl-1-(trifluoromethylsulfonyl)-1,4-azasilepane (**VII**) in $CDCl_3$ in the temperature range from 70 to –70°C.

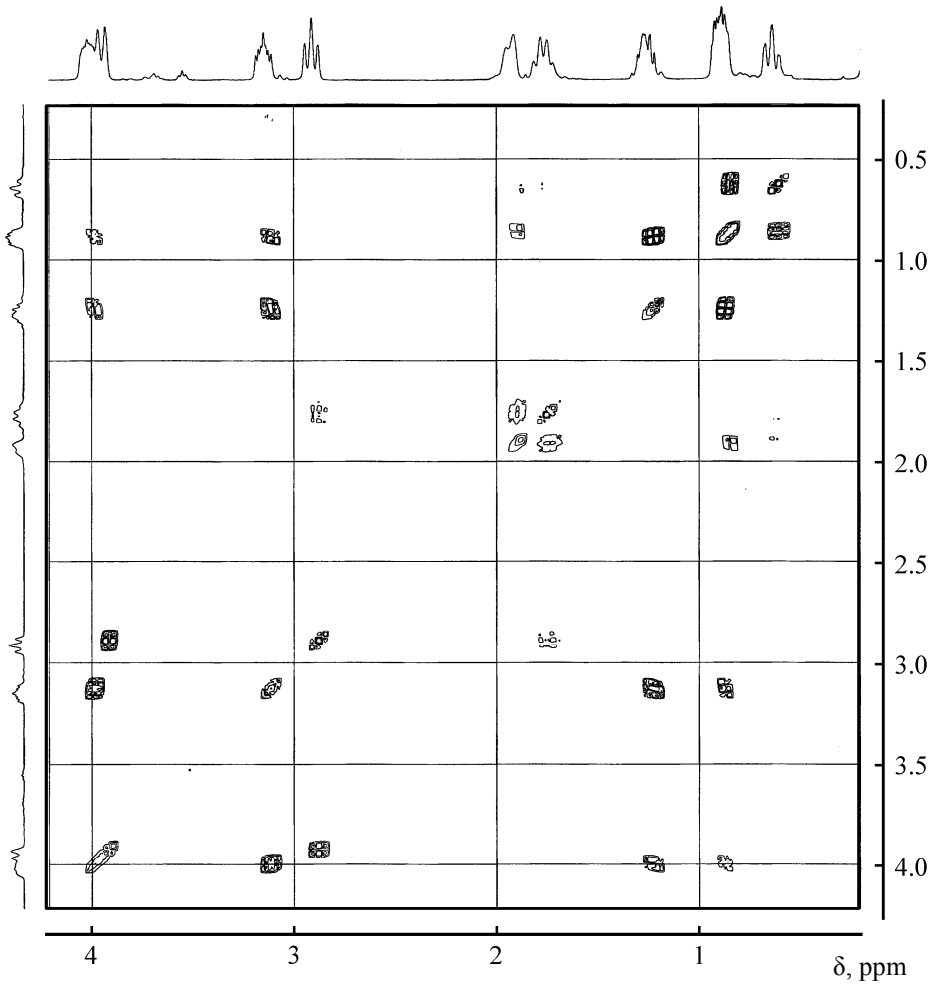


Fig. 2. ^{1}H–^{1}H COSY spectrum of 4,4-dimethyl-1-(trifluoromethylsulfonyl)-1,4-azasilepane (**VII**) at –70°C in $CDCl_3$.

two-dimensional spectra ^{1}H–^{1}H COSY, ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC. IR spectra were taken on a Bruker Vertex 70 spectrometer in thin layer. X-ray energy dispersive microanalysis was performed on a RES Hitachi TM 3000.

(2-Bromoethyl)(3-chloropropyl)dimethylsilane (II). Through a solution of 5.257 g (22 mmol) of (3-chloropropyl)dimethyl(vinyl)silane and 0.05 g (0.2 mmol) of benzoyl peroxide in 40 ml of anhydrous hexane dried gaseous HBr was bubbled in the course of 6 h in an argon atmosphere under UV irradiation and stirring. The reaction mixture was left overnight at room temperature, the excess of HBr was removed by passing argon, and hexane was distilled off at the atmospheric pressure. After vacuum distillation of the residue 6.51 g (83%) of silane **II** was isolated, bp 131–132°C (10 mm Hg), n_D^{25} 1.4900. IR spectrum, ν, cm^{-1}: 2954, 1420, 1250, 1030, 835. ^{1}H NMR spectrum, δ, ppm: 0.06 s (6H, $SiMe_2$), 0.67 m (2H, $C\underline{H}_2CH_2CH_2Cl$), 1.40 m (2H, $CH_2\underline{C}H_2CH_2Br$), 1.76 m (2H, $CCH_2\underline{C}$), 3.50 t (2H, CH_2Cl, ^{3}J 7.0 Hz), 3.55 m (2H, CH_2Br). ^{13}C NMR spectrum, δ_C, ppm: –3.68 (SiMe), 12.58 ($Si\underline{C}CC$), 22.31 ($Si\underline{C}CBr$), 27.50 ($C\underline{C}C$), 31.24 (CBr), 47.63 (CCl). ^{29}Si NMR spectrum: δ_{Si} 2.62 ppm. The assignment is proved by the presence of cross peaks between the signals at 0.67 and 1.76 ppm, 1.76 and 3.50 ppm, 1.49 and 3.55 ppm in the ^{1}H–^{1}H COSY spectrum, and in the ^{1}H–^{13}C HSQC spectrum, by the presence of the cross peaks between the signals at 0.67, 1.49, 1.76, 3.50 and 3.55 ppm in the ^{1}H NMR spectrum and the signals at 12.58, 22.31, 27.50, 47.63 and 31.24 ppm, respectively, in the ^{13}C NMR spectrum. Found, %: C 34.22; H 6.77; Br 32.85; Cl 14.57; Si 11.03. $C_7H_{16}BrClSi$. Calculated, %: C 34.51; H 6.62; Br 32.79; Cl 14.55; Si 11.49.

Reaction of (2-bromoethyl)(3-chloropropyl)dimethylsilane with triflamide. *a*. To the solution of 0.436 g (1.8 mmol) of silane **II** and 0.533 g (3.6 mmol)

of triflamide **I** in 3 ml of anhydrous THF the solution of 0.362 g (3.6 mmol) of triethylamine in 1 ml of THF was added in an argon atmosphere in the course of 10 min. The reaction mixture was refluxed for 13 h, then the solvent was removed. The residue, according to the ^{1}H, ^{13}C, ^{29}Si, ^{19}F NMR spectroscopy data, consisted of the starting silane **II** (50%) and siloxane **III** (32%).

b. To the solution of 0.345 g (1.4 mmol) of silane **II** the solution of 0.422 g (2.8 mmol) of triflamide and 0.286 g (2.8 mmol) of triethylamine in 2 ml of methanol was added dropwise during 15 min. The reaction mixture was refluxed for 6–7 h, methanol was removed, the residue was stirred with hexane, the solution separated from the precipitate containing triflamide, triethylamine salts and silanols. The hexane solution was evaporated to give 0.08 g of liquid residue, which contained, according to the ^{1}H, ^{19}F NMR spectroscopy data, bis-(3-chloropropyl)tetramethyldisiloxane **III**, 3-trifluoro-methylsulfonylaminopropyl-(3-chloropropyl)tetra-methyldisiloxane **IV** in the ratio 5:1, and unidentified impurities. Individual products **III** and **IV** were isolated by column chromatography on silica ICN by gradient elution with hexane–ether from 100:1 to 1:1.

c. To the mixture of 0.884 g (3.6 mmol) of 3-chloropropyl(2-bromoethyl)dimethylsilane (**II**) and 1.08 g (7.2 mmol) of triflamide 1.47 g (2.1 ml, 14.6 mmol) of triethylamine was added dropwise at stirring in the course of 15 min. The reaction mixture was heated till the beginning of exothermic reaction (70°C), stirred for 6.5 h at 88–92°C, cooled, 6 ml of water was added, and the product was extracted with ether (3×3 ml). The organic layer was dried over Na_2SO_4, solvent was removed to obtain 1.243 g of crude product, consisting, according to the ^{1}H NMR data, of 4,4-dimethyl-1-(trifluoromethylsulfonyl)-1,4-azasilepane (**VII**) and siloxane **VI** in the ratio 2:7 and triethylamine; no starting silane **II** was detected. The yield of the crude product **VII** was 25%, of siloxane **VI**, 61%. Analytically pure samples were obtained by column chromatography on silica Geduran Si 60 (Merck) in the system hexane–ether, from 80:1 to 20:1.

Bis(3-chloropropyl)tetramethyldisiloxane (III). The yield after chromatographic separation 10%, R_f 0.94. IR spectrum, ν, cm^{-1}: 2957 (CH_2), 1412 (SiC), 1257 (SiMe), 1051 (SiOSi), 796 (CH_2Cl). ^{1}H NMR spectrum, δ, ppm: 0.08 s (12H, $SiMe_2$), 0.63 m (4H, $SiCH_2$), 1.79 m (4H, CH_2), 3.51 t (4H, CH_2Cl, ^{3}J 7.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 0.24 (SiMe), 15.87 (SiC), 27.03 (C<u>C</u>C), 47.78 (CCl). ^{29}Si NMR spectrum: δ_{Si} 7.64 ppm.

3-Trifluoromethylsulfonylaminopropyl(3-chloropropyl)tetramethyldisiloxane (IV). Yield after chromatographic separation 3.5%, R_f 0.47. ^{1}H NMR spectrum, δ, ppm: 0.09 s (6H, $SiMe_2$), 0.1 s (6H, $SiMe_2$), 0.55 m (2H, $\underline{CH_2}CH_2CH_2N$), 0.65 m (2H, $\underline{CH_2}CH_2CH_2Cl$), 1.67 m (2H, $NCH_2\underline{CH_2}$), 1.79 m (2H, $ClCH_2\underline{CH_2}$), 3.30 m (2H, NCH_2), 3.53 m (2H, $ClCH_2$), 4.98 br. s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 0.22 (SiMe); 14.93 (<u>C</u>CCN), 15.80 (<u>C</u>CCCl), 24.45 (<u>C</u>CN), 27.00 (<u>C</u>CCl), 47.09 (NC), 47.81 (ClC), 119.67 q (CF_3, $^{1}J_{CF}$ 319.0 Hz). ^{19}F NMR spectrum: δ_F –77.49 ppm. ^{29}Si NMR spectrum, δ_{Si}, ppm: 7.81, 8.41. The assignment is proved by the presence of cross peaks between the signals at 0.55 and 1.67 ppm, 0.65 and 1.79 ppm, 1.67 and 3.30 ppm, and 1.79 and 3.53 ppm in the ^{1}H–^{1}H COSY spectrum, and in the ^{1}H–^{13}C HSQC spectrum by the presence of the cross peaks between the signals at 0.55, 0.65, 1.67, 1.79, 3.30 and 3.53 ppm in the ^{1}H NMR spectrum and the signals at 14.93, 15.80, 24.45, 27.00, 47.09 and 47.81 ppm, respectively, in the ^{13}C NMR spectrum. Found, %: C 32.60; H 6.21; N 3.49; S 7.91. $C_{11}H_{25}ClF_3NO_3SSi_2$. Calculated, %: C 33.04; H 6.25; N 3.50; S 8.01.

2-Trifluoromethylsulfonylaminoethyl(3-chloropropyl)dimethylsilane (V). To the mixture of 0.403 g (1.65 mmol) of 2-bromoethyl(3-chloropropyl)dimethylsilane **II** and 0.342 g (2.3 mmol) of triflamide 0.669 g (6.62 mmol) of triethylamine was added dropwise in the course of 10 min. The reaction mixture was heated to 50°C, then it spontaneously heated to 72°C and was stirred at this temperature for 3.5 h. After the completion of the reaction, 8 ml of water was added, the product was extracted with ether (3×3 ml), the extract was dried over Na_2SO_4, the solvent was removed to afford 0.341 g of crude product consisting, according to the ^{1}H, ^{13}C, ^{29}Si, ^{19}F NMR data, of product **V**, a mixture of siloxanes (mainly **VI**), and heterocycle **VII** in the ratio 3:2:1. Pure product **V** (0.112 g, 22%) was isolated by column chromatography on silica (Geduran, Merck), with eluent hexane–ether, from 10:1 to 1:1, R_f 0.45 (hexane:ether = 2:1). IR spectrum, ν, cm^{-1}: 3317 (NH), 2456 (CH_2), 1432 (SiC), 1372 (SO_2), 1254 (SiMe), 1232, 1193 (CF_3), 1146 (SO_2), 1047 (SN), 911 (CN), 736 (CCl), 606 (CF_3). ^{1}H NMR spectrum, δ, ppm: 0.07 s (6H, $SiMe_2$), 0.67 m (2H, $Si\underline{CH_2}CH_2CH_2Cl$), 0.98 m (2H, $Si\underline{CH_2}CH_2N$), 1.76 m (2H, $CH_2C\underline{H_2}CH_2$), 3.36 m (2H, CH_2N), 3.52 t (2H, CH_2Cl, ^{3}J 7.0 Hz). ^{13}C NMR

spectrum, δ_C, ppm: –3.66 (SiMe), 12.53 (SiCCCCl), 17.82 (SiCCN), 27.25 (CCC), 41.51 (CN), 47.62 (CCl), 121.3 q (CF_3, *J* 319.3 Hz). ^{19}F NMR spectrum: δ_F –77.42 ppm. ^{29}Si NMR spectrum: δ_{Si} 2.04 ppm. Found, %: C 30.51; H 5.26; Cl 11.58; F 17.70; N 4.55; S 10.84. $C_8H_{17}ClF_3NO_2SSi$. Calculated, %: C 30.81; H 5.49; Cl 11.37; F 18.28; N 4.49; S 10.28.

Bis(3-trifluoromethanesulfonylaminopropyl)tetramethyldisiloxane (VI). Yield after chromatographic separation 37%, R_f 0.61. IR spectrum, ν, cm^{-1}: 3316 (NH), 2957 (CH_2), 1434 (SiC), 1371 (SO_2), 1257 (SiMe), 1239 (CF_3), 1192 (CF_3), 1147 (SO_2), 1069 (SN), 1050 (SiOSi), 841 (CN), 797 (CS), 610 (CF_3). ^1H NMR spectrum, δ, ppm: 0.01 s (12H, $SiMe_2$), 0.55 m (4H, $SiCH_2$), 1.64 m (4H, CCH_2C), 3.28 q (4H, NCH_2, *J* 6.7 Hz), 5.20 br. t (2H, NH *J* 6.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 0.04 (SiMe), 14.78 (SiC), 24.37 (CCC), 47.07 (NC), 119.67 q (CF_3, *J* 319.0 Hz). ^{19}F NMR spectrum: δ_F –74.48 ppm. ^{29}Si NMR spectrum: δ_{Si} 8.38 ppm. Found, %: C 28.37; H 5.21; F 22.06; N 5.11; S 12.31. $C_{12}H_{26}F_6N_2O_5S_2Si_2$. Calculated, %: C 28.13; H 5.08; F 22.26; N 5.47; S 12.50.

4,4-Dimethyl-1-(trifluoromethylsulfonyl)-1,4-azasilepane (VII). Yield after chromatographic separation 16%, R_f 0.86. IR spectrum, ν, cm^{-1}: 2954 (CH_2), 1464 (SiC), 1386 (SO_2), 1253 (SiMe), 1225 (CF_3), 1183 (CF_3), 1137 (SO_2), 1067 (SN), 1018 (CN), 837 (CS), 590 (CF_3). ^1H NMR spectrum (343 K), δ, ppm: 0.10 s (6H, $SiMe_2$), 0.78 m (2H, 5-CH_2), 1.08 m (2H, 3-CH_2), 1.89 m (2H, 6-CH_2), 3.42 br. s (2H, 7-CH_2), 3.57 br. s (2H, 2-CH_2). ^{13}C NMR spectrum, δ_C, ppm: –2.08 (SiMe), 14.04 (C^5), 17.44 (C^3), 25.49 (C^6), 48.82 (C^2), 53.91 (C^7), 120.48 q (CF_3, *J* 323.2 Hz). ^{19}F NMR spectrum: δ_F –74.44 ppm. ^{29}Si NMR spectrum: δ_{Si} 4.3 ppm. In the ^1H–^1H COSY spectrum at 70°C cross peaks are observed between the signals at 0.78 and 1.89 ppm, 1.08 and 3.57 ppm, 1.89 and 3.42 ppm. ^1H NMR spectrum (203 K), δ, ppm: 0.03 s (3H, $SiMe_{ax}$), 0.14 s (3H, $SiMe_{eq}$), 0.64 d. d. d (1H, 5-CH_{ax}, $^2J_{5ax–5eq} \approx {}^3J_{5ax–6ax} \approx 14.0$, $^3J_{5ax–6eq}$ 3.3 Hz), 0.89 m (2H, 5-CH_{eq} + 3-CH_{ax}), 1.26 m (1H, 3-CH_{eq}), 1.77 m (1H, 6-CH_{ax}), 1.94 br. d (1H, 6-CH_{eq}, $^2J_{6ax–6eq}$ 14.8 Hz), 2.91 d. d (2-CH_{ax}, $^2J_{2ax–2eq}$ 14.4, $^3J_{2ax–3ax}$ 12.6 Hz), 3.15 d. d. d (1H, 7-CH_{ax}, $^2J_{7ax–7eq}$ 14.7, $^3J_{7ax–6ax}$ 10.5, $^3J_{7ax–6eq}$ 5.4 Hz), 3.95 br. d (1H, 2-CH_{eq}, $^2J_{2ax–2eq}$ 14.4 Hz), 4.02 m (1H, 7-CH_{eq}). Found, %: C 35.09; H 5.71; N 4.92. $C_8H_{17}F_3NO_2SSi$. Calculated, %: C 34.91; H 5.82; N 5.09.

Methanolysis of (2-bromoethyl)(3-chloropropyl) dimethylsilane. A mixture of 0.272 g of silane **II** in 1.5 ml of methanol was refluxed for 6 h, methanol was removed to afford 0.202 g of the liquid residue containing, according to the ^1H, ^{13}C, ^{29}Si NMR data, 74% of siloxane **III**. Pure siloxane **III** was isolated by column chromatography on silica, eluent hexane–ether (from 8:1 to 1:1) in 47% yield. Physicochemical constants coincided with the literature data [30], NMR spectra were identical to those for the samples obtained in methanol and THF.

Reaction of bis(3-chloropropyl)dimethyldisiloxane III with triflamide. A mixture of siloxane **III** (0.085 g, 0.3 mmol), triflamide (0.088 g, 0.6 mmol) and triethylamine (1.196 g, 1.2 mmol) was kept at room temperature for 20 h. No changes occur according to NMR data. The mixture was heated to 78–82°C for 8 h, decomposed with water, extracted with ether, the extract was dried over Na_2SO_4, the solvent removed in a vacuum. According to the ^1H, ^{13}C, ^{29}Si, ^{19}F NMR data, siloxane **VI** was formed in 90% yield.

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