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SYNTHESIS AND STRUCTURE OF 1- AND 2-ISOMERS OF (TRIMETHOXYSILYLMETHYL)- AND (SILATRANYLMETHYL)BENZOTRIAZOLE

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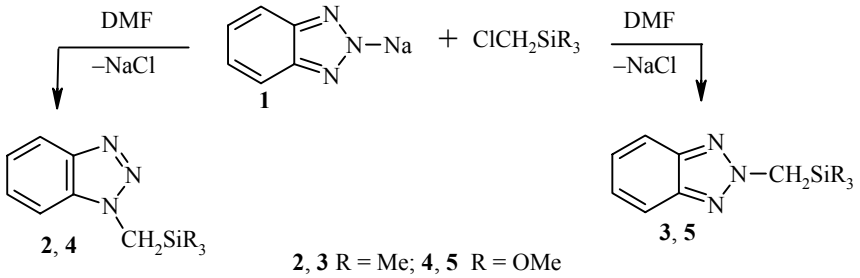
We have synthesized 1- and 2-(trimethylsilylmethyl)- and 1- and 2-(trimethoxysilylmethyl)benzotriazoles by reaction of 1,2,3-benzotriazolylsodium with trimethyl- or trimethoxy(chloromethyl)silane. We obtained 1- and 2-(silatranylmethyl)benzotriazoles by transesterification of the latter with triethanolamine.

Keywords: 1- and 2-silatranylmethylbenzotriazole, 1- and 2-trimethoxysilylmethylbenzotriazole.

Organosilicon derivatives of nitrogen-containing heterocycles have found broad application in organic synthesis, including as precursors of drugs, pesticides, and other biologically active substances [1-4].

In recent years, N-organosilicon derivatives of benzotriazole have attracted special attention [5-8]. However, compounds of this type, containing an organosilicon substituent in the 2 position of the heterocycle, have not yet been isolated. We have studied the reaction of (2-benzotriazolyl)sodium (**1**) with trimethyl- or trimethoxy(chloromethyl)silane in DMF in the presence of 18-crown-6, and consequently have isolated the corresponding individual 1- and 2-substituted organosilicon derivatives of benzotriazole **2-5** (see Table 1).



* The authors are pleased to dedicate this paper to the brilliant Latvian scientist and President of the Latvian Academy of Sciences, Janis Stradins. We have been fortunate to work together with this remarkably learned and charming man for many years. We offer our heartfelt wishes for new scientific triumphs, continued creative enthusiasm, and good health for many years more to our friend on his birthday.

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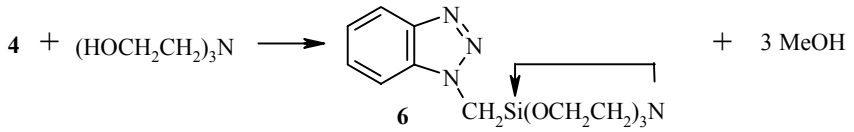
The sodium derivative **1** was obtained by reaction of 1H-1,2,3-benzotriazole with a methanol solution of sodium methoxide. We previously have demonstrated the formation of 2-benzotriazolylsodium (rather than the 1-isomer) in this case [9].

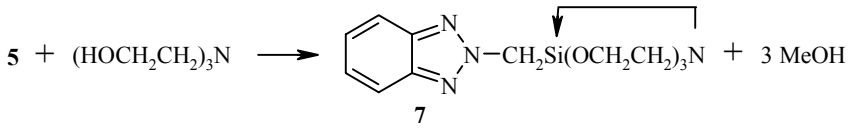
Compounds **3-5** were previously unknown. 1-(Trimethylsilylmethyl)benzotriazole (**2**) was described by A. R. Katritzky [5].

Simultaneous formation of the 1- and 2-isomers obviously is due to the dual reactivity of 1,2,3-benzotriazole anion [6].

Organosilicon derivatives **3-5** are yellowish liquids, while compound **2** is a crystalline substance. Compounds **4** and **5** are hydrolytically unstable.

By transesterification of 1- and 2-(trimethoxysilylmethyl)benzotriazoles **4** and **5** with triethanolamine, we obtained the corresponding 1- (**6**) and 2-(silatranylmethyl)benzotriazoles (**7**) in practically quantitative yield.





Silatrane derivatives **6** and **7** are colorless crystals that are soluble in DMF and DMSO (see Table 1). The crystals of compound **6** become cloudy during storage.

In the ^{1}H and ^{13}C NMR spectra, the chemical shifts of the benzotriazole ring of compounds **4-7** and also 1- and 2-methylbenzotriazoles [10] are practically identical (Table 2). The chemical shifts of the protons in the exocyclic –N–CH_2Si moiety of compounds **4-7** are also similar. Shielding of the ^{13}C nuclei of this moiety in 1-substituted compounds **4** and **6** is ~10 ppm higher than in 2-substituted compounds **5** and **7**.

The resonance in the ^{29}Si NMR spectra of silatrane derivatives **6** and **7** is shifted upfield by ~25 ppm compared with trimethoxysilylmethyl derivatives **4** and **5.** This is due to the fact that the silicon atom is pentacoordinated in compounds **6** and **7** while in compounds **4** and **5** it is tetracoordinated. At the same time, the difference in the position of the organosilicon substituent (1- or 2-) in compounds **4-7** has almost no effect on the ^{29}Si chemical shift. In this case, in the NMR spectra of tetravalent silicon derivatives **4** and **5**, the signals from the ^{13}C atoms of the –N–CH_2Si moiety are shifted upfield by more than 7 ppm compared with signals from the corresponding silatranes **6** and **7**.

The ^{15}N NMR spectra of compounds **4, 5** and **6, 7** most rigorously prove the position of the substituent on the benzotriazole ring (Table 2). The number of resonance signals from the nitrogen nuclei of this heterocycle is determined by the symmetry of the molecule, while the substantial difference in the chemical shifts is determined by the hybridization and position of the nitrogen atoms.

The chemical shifts of the ^{15}N atoms of compounds **4** and **5** are no more than 1-5 ppm different from the known values for 1- and 2-methylbenzotriazoles [11]. Shielding of the $N_{(1)}$ atom of benzotriazole **6** is 12 ppm lower while that of the $N_{(3)}$ is 5 ppm higher than the shielding intrinsic to the corresponding atoms of compound **4**.

The position of the resonance signal from the nitrogen atom of the silatrane skeleton is approximately the same in the NMR spectra of compounds **6** and **7**. Thus according to the ^{15}N NMR spectra of compounds **4-7**, the nature of the organosilicon substituent has little effect on the electron density of all the N atoms. However, the latter significantly depends on its position (1 or 2).

TABLE 1. Physicochemical Characteristics of Synthesized Compounds **2-7**

Compound	Empirical formula	Found, % / Calculated, %				bp, °C (mm Hg)	mp, °C	Yield %
		C	H	N	Si			
2	$C_{10}H_{15}N_3Si$	58.78 / 58.49	7.77 / 7.36	20.58 / 20.46	13.79 / 13.68		41-43	62
3	$C_{10}H_{15}N_3Si$	58.18 / 58.49	7.55 / 7.36	20.60 / 20.46	13.93 / 13.68	112 (5)		30
4	$C_{10}H_{15}N_3O_3Si$	47.44 / 47.41	5.70 / 5.97	16.27 / 16.59	11.48 / 11.09	152-153 (3)		60
5	$C_{10}H_{15}N_3O_3Si$	47.75 / 47.41	5.84 / 5.97	17.04 / 16.59	11.25 / 11.09	118-120 (3)		29
6	$C_{13}H_{18}N_4O_3Si$	51.12 / 50.96	6.05 / 5.92	18.51 / 18.29	9.29 / 9.17		209-211	96
7	$C_{13}H_{18}N_4O_3Si$	50.79 / 50.96	6.18 / 5.92	18.56 / 18.29	9.07 / 9.17		275	94

The extremely low solubility of compound **7** did not make it possible to determine the ^{15}N NMR chemical shifts for its hetaryl ring.

The benzoid and quinoid structures of 1-organosilicon derivatives **2**, **4**, **6** and the corresponding 2-substituted compounds **3, 5, 7** affect their IR spectra [9]. In the IR spectra of the 1-isomers **2, 4, 6**, we observe frequencies at 665-670, 1588-1591, 1614-1615 cm^{-1}, while in the spectra of the 2-isomers **3, 5, 7** we see frequencies at 623-625, 1567-1569 cm^{-1}. In the IR spectra of compounds **2-7**, the absorption frequencies for the organosilicon CH_2SiR_3 substituents are practically independent on their position in the heterocycle (1- or 2-). For compounds **2** and **3** (R = Me), they appear at 743 and 746, 843 and 846, 1248 and 1251 cm^{-1} respectively, for compounds **4** and **5** (R = OMe) they appear at 838 and 844, 1090 and 1090, 2845 and 2845 cm^{-1} respectively, while for derivatives of compounds **6** and **7** (R = 1/3 $(OCH_2CH_2)_3N$) they appear at 583 and 578, 641 and 651, 784 and 789, 812 and 819, 915 and 913, 938 and 938, 1085 and 1087, 1126 and 1123 cm^{-1} respectively.

In the UV spectra of solutions of compounds **2** and **4** in MeCN, there are two absorption maxima in the 270-290 nm and 250-270 nm regions, confirming that they are 1-substituted benzotriazoles [12-14]. In the UV spectra of solutions of compounds **3** and **5**, we observe one maximum in the 270-285 nm region, matching that observed for 2-H-, 2-Me-, and 2-Na-benzotriazoles.

Under electron impact, benzotriazoles **4** and **5** do not decompose identically. In the mass spectrum of compound **4**, there is no peak for the molecular ion, which readily loses an N_2 molecule to form the ions $[M–N_2]^{+\cdot}$ 225 (100) and $[M+H–N_2]^+$ 226 (47).*

Initial elimination of an N_2 molecule is a typical process for 1,2,3-benzotriazole and its 1-methyl-, 1-vinyl-, and 1-methoxy derivatives [15]. Further decomposition of the ions formed is due to elimination of the $^{\cdot}OCH_3$ radical (ion 194 (2)) and an HCN molecule (ion 167 (16)). In the spectrum of compound **4**, the intensity is high for the ion peak $[Si(OMe)_3]^+$ 121 (50) and the ion peaks due to decomposition of the benzotriazole ring, 105 (6), 91 (70), 77 (15).

A characteristic feature of fragmentation of compound **5** is the presence in the mass spectrum of an intense molecular ion peak $[M+H]^+$ 253 (95), 254 (45), and also the virtual absence of the ion peaks $[M–N_2]^{+\cdot}$ 225 (2) and 194 (1). In the mass spectrum of compound **5** there are also peaks for the ions $[Si(OMe)_3]^+$ 121 (100), $[C_7H_7]^+$ 91 (77), $[C_6H_5]^+$ 77 (4).

Thus, fragmentation of compounds **4** and **5**, as for arylbenzotriazoles [16], allows us to unambiguously confirm their structure.

* Here and in the following, we give the values of *m*/*z* (*I*, %) values.

TABLE 2. ^{1}H, ^{13}C, ^{15}N, and ^{29}Si NMR Spectral Characteristics of Compounds **4-7***

Compound	Chemical shifts, δ, ppm (*J*, Hz)														
	4-H	7-H	5-H	6-H	C(4)	C(7)	C(5)	C(6)	C(8)	C(9)	N(1)	N(3)	N(2)	$N_{(CH2)3N}$	Si
4	7.95 d (^{3}J = 8.0)	7.54 d (^{3}J = 8.0)	7.26 dd (^{3}J = 8.0)	7.38 dd (^{3}J = 8.0)	111.49	108.79	123.32	126.43	133.04	144.57	-160.0	-45.1	-1.1		-55.6
5	7.78		7.26		117.47		125.69		144.30		-61.4		-114.6		-56.4
6	7.97 d (^{3}J = 8.3)	7.72 d (^{3}J = 8.0)	7.27 dd (^{3}J = 8.3)	7.36 dd (^{3}J = 8.0)	119.08	111.76	122.57	125.21	133.84	145.77	-148.4	-50.0	-0.8	-350.4	-80.4
7	7.80		7.23		117.66		124.52		144.17					-350.6	-81.3

* ^{1}H NMR spectrum, δ, ppm (*J*, Hz): **4** – 3.54 (OCH_3), 4.14 (CH_2); **5** – 3.59 (OCH_3), 4.46 (CH_2); **6** – 2.86 (NCH_2, ^{3}J = 5.9), 3.76 (OCH_2, ^{3}J = 5.9), 4.04 (CH_2); **7** – 2.80 (NCH_2, ^{3}J = 5.8), 3.77 (OCH_2, ^{3}J = 5.8), 4.29 (CH_2); ^{13}C NMR spectrum, δ, ppm: **4** – 32.31 (CH_2), 50.30 (OCH_3); **5** – 42.13 (CH_2), 51.00 (OCH_3); **6** – 40.05 (CH_2), 51.22 (NCH_2), 57.09 (OCH_2); **7** – 49.19 (CH_2), 51.30 (NCH_2), 57.31 (OCH_2).

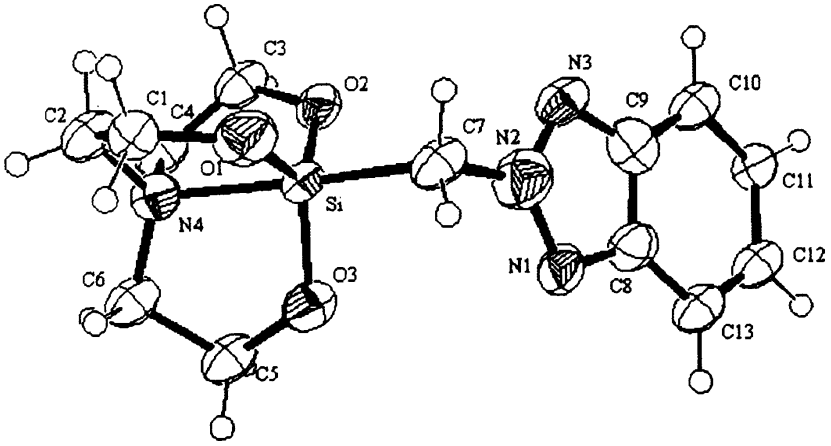
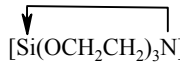


Fig. 1. 2-(1-Silatranylmethyl)benzotriazole **7**.

The mass spectra of compounds **6** and **7** are rather sparse. They contain a maximum peak for the silatrane skeleton ion 174 (100) and low-intensity ion peaks due exclusively to its decomposition (the ions 144 (7), 130 (1)). Minor decomposition of these ions is due to breaking of the C–Si bond in the molecular ion, with the appearance of a positive charge on the silatrane skeleton



$[Si(OCH_2CH_2)_3N]^+$.

The intensity of the molecular ion peak for silatrane derivatives **6** and **7** is ~2%.

The molecular structure of compound **7** was established by X-ray diffraction analysis [17]. The coordination polyhedron of the Si atom in the molecule of compound **7** has the trigonal bipyramid configuration typical of silatranes, with the N(4) and C(7) atoms in axial positions, while the equatorial vertices of this polyhedron are occupied by O(1), O(2), O(3) atoms (Fig. 1).

The interatomic distances N(4)→Si and Si–C(7) are respectively equal to 2.089(4) Å and 1.908(5) Å. The bond lengths and bond angles in the benzotriazole moiety of compound **7** are close to those observed in the 2H-benzotriazole molecule [12].

EXPERIMENTAL

^1H, ^{13}C, ^{15}N, ^{29}Si spectra of the synthesized compounds were taken on a Bruker DPX-400 spectrometer (400 MHz (^1H), 40 MHz (^{15}N), 100 MHz (^{13}C), 79 MHz (^{29}Si)) in $CDCl_3$, internal standard TMS (for ^1H, ^{13}C, and ^{29}Si nuclei) and $Me^{15}NO_2$ (for ^{15}N nuclei). We used the INEPT pulse sequence to obtain the ^{29}Si NMR spectra. The ^{15}N NMR chemical shifts were measured from inverse two-dimensional ^1H-^{15}N spectra by the HMBCGP technique. The accuracy of the chemical shift measurements for the ^1H and ^{13}C nuclei was 0.01 ppm and 0.02 ppm respectively, and 0.1 ppm for ^{15}N and ^{29}Si. The UV spectra of solutions of the compounds were obtained on a Specord UV-vis spectrophotometer; the IR spectra were obtained on a Specord IR-75 spectrometer in a microlayer or in KBr disks; the mass spectra were obtained on an LKB-2091 mass spectrometer, ionizing potential 60 eV, with direct injection of the sample into the ion source (T_{source} = 250°C).

1-(Trimethoxysilylmethyl)benzotriazole (4) and 2-(Trimethoxysilylmethyl)benzotriazole (5). Trimethoxy(chloromethyl)silane (5.46 g, 32 mmol) was added to solution of 1,2,3-benzotriazolylsodium (**1**) (4.52 g, 32 mmol) and 18-crown-6 (0.063 g) in freshly distilled DMF (50 ml). The reaction mixture was stirred for 2 h at 25-30°C. The NaCl precipitate was filtered off. When the filtrate was distilled under vacuum, 2.35 of compound **5** and 5.03 g of compound **4** were isolated.

Compounds 2 and 3 were obtained similarly. When the reaction mixture was stored at room temperature, crystals of **2** precipitated from it, which were filtered off and washed with hexane; yield 7.38 g. When the filtrate was distilled under vacuum, compound **3** (3.69 g) was isolated.

1-(Silatranylmethyl)benzotriazole (6). Mixture of compound **4** (4.31 g, 17 mmol) and triethanolamine (2.54 g, 17 mmol) was stirred for 10 min at 25°C. The white precipitate was recrystallized from a chloroform–hexane mixture, 1:1. Silatrane **6** (5.01 g) was isolated.

Its 2-isomer **7** was obtained similarly.

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