Trimethylsilylation and methylation of 1-hydroxybenzotriazole 3-oxide

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Trimethylsilylation and methylation of 1-hydroxybenzotriazole 3-oxide (**1**) proceed regioselectively and afford 1-trimethylsilyloxy- and 1-methoxybenzotriazole 3-oxides, respectively. The first compound easily undergoes fast hydrolysis and methanolysis, but does not react with nitroethane at 20 °C. A fast reversible 1,5-O,O-migration of the $SiMe_3$ group is observed for this compound.

Key words: 1-hydroxybenzotriazole 3-oxide, 1-methoxybenzotriazole 3-oxide, trimethylsilyl derivative of 1-hydroxybenzotriazole 3-oxide, silylation, methylation, 1,5-O,O-migration of the $SiMe_3$ group.

Previously,[1] preparation of a new derivative of benzotriazole, 1-hydroxybenzotriazole 3-oxide (**1**), was described.

Since this compound is rather insoluble in organic solvents, its trialkylsilyl derivatives may be promising trialkylsilylating agents for C—H acids, and, in particular, for nitro compounds.

In the present report, methylation* and trimethylsilylation of triazole **1** are considered.

It has been found that the action of various methylating agents (diazomethane and methyl iodide) on triazole **1** itself, as well as on its silver salt **3**, prepared *via* potassium salt **2**, affords regioselectively only the product of *O*-methylation, *i.e.*, 1-methoxybenzotriazole 3-oxide (**4**) (see Scheme 1).

The structure of **4** was determined on the basis of its elemental analysis data, NMR and mass spectra. The presence of four signals in the ^{1}H NMR spectrum and six signals in the ^{13}C NMR spectrum of azole **4**, which corresponds to benzene ring, confirms unequivocally the structure of "unsymmetrical" *O*-methyl derivative for this compound. The assignment of signals in the ^{1}H NMR spectrum (see Experimental) was carried out on the basis of their multiplicity assuming that the most lowfield doublet (7.96 ppm) corresponds to H(2). The signals in the ^{13}C NMR spectrum of compound **4** were assigned using direct and long-range ^{13}C—^{1}H spin coupling constants through one and more bonds obtained from two-dimensional C—H-correlation spectra. The choice between C(1) and C(6) signals was made by registration of signals of only non-protonated ^{13}C atoms, taking into account that the signal of C(1) is broadened approximately twice in comparison to the C(6) signal due to ^{13}C—^{14}N spin coupling through one bond. Compound **4** exhibits thermal instability and enhanced susceptibility to mechanical actions, in particular, to trituration. According to DTA data,* the temperature, when intensive decomposition of **4** begins, is *ca.* 85 °C, *i.e.*, near its melting point. Trimethylsilyl derivative (**5**) of triazole **1** was prepared by treatment of salt **3** with chlorotrimethylsilane in acetonitrile. The structure of **5** was confirmed by its chemical transformations and the NMR data. An addition of two to three equivalents of water to a solution of compound **5** in acetonitrile leads to precipitation of triazole **1** in approximately quantitative yield, all of the Me_3Si moiety being converted into hexamethyldisiloxane as suggested by the ^{1}H NMR spectrum. Similarly, derivative **5** silylates MeOH in acetonitrile that accompanies by fast and quantitative formation of precipitate of triazole **1**. However, it appears that compound **5** does not silylate nitroethane at 20 °C in an appreciable rate, *i.e.*, **5** is not a strong silylating agent for C—H-acids.

The multiplicity and the number of signals in the NMR spectra of compound **5** indicate either its "symmetrical" structure (**5b**) or the fast (on NMR scale) and reversible 1,5-O,O-migration of the Me_3Si group (**5a** $\rightleftarrows$ **5c**). The structure **5b** can be rejected, since it contradicts the broadening of some signals in the NMR spectrum observed by us for compound **5** (see Experimental). The NMR spectra of compound **4** can be considered as reference data for derivative **5a** (or **5c**), because the chemical shifts of the benzene ring in the NMR spectra of compounds **4** and **5a** should be rather similar. With fast **5a** $\rightleftarrows$ **5c** exchange, the

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* Methyl derivative (**4**) of triazole **1** was used as the reference compound to establish the structure of trimethylsilyl derivative **1**.

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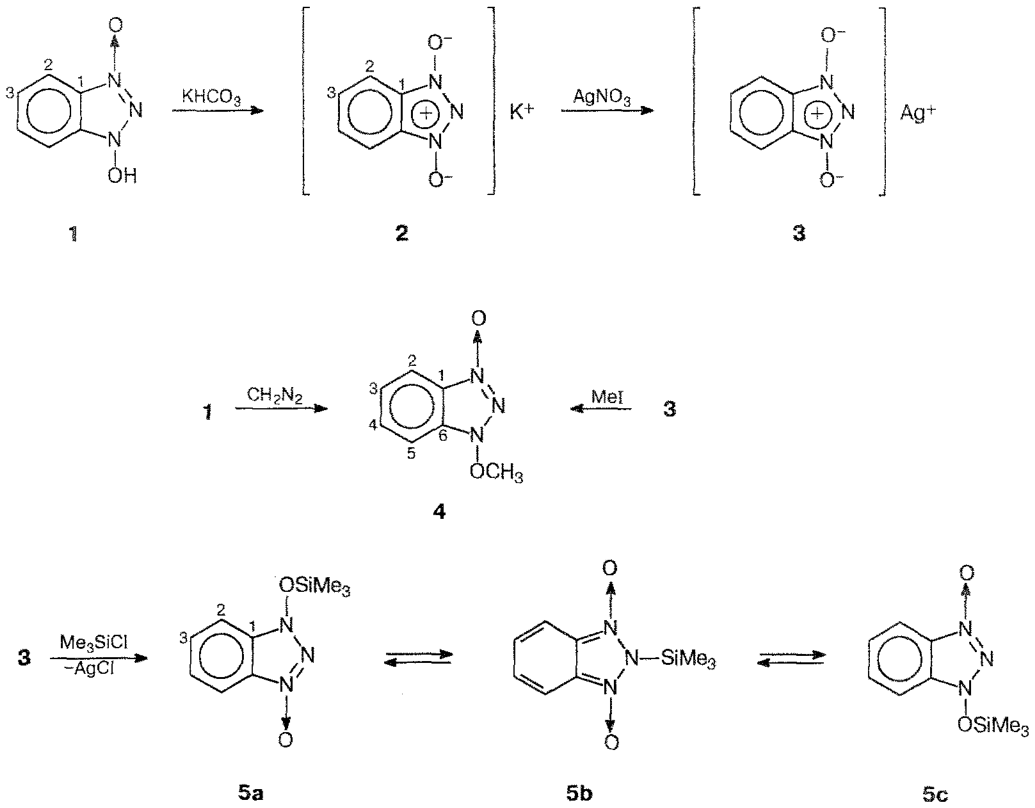
Scheme 1



corresponding signals of H(2) and H(5), H(3) and H(4), C(1) and C(6), C(2) and C(5), as well as C(3) and C(4) should collapse.

As demonstrated in Table 1, the observed signals for derivative **5** are rather close to those calculated which indirectly confirms the structure of compound **5a** and the fast **5a** $\rightleftarrows$ **5c** exchange. However, the observed temperature-dependent broadening of the signals of the Me_3Si group for derivative **5** is hard to explain disregarding participation of the symmetrical structure **5b** in the exchange as the intermediate. In such case, the 1,5-O,O-migration of the Me_3Si group should be considered as a sequence of two 1,3-O,N-shifts, and the process as whole can be expressed by the following scheme: **5a** $\rightleftarrows$ **5b** $\rightleftarrows$ **5c**. There is the need in further investigations to establish the mechanisms of exchange processes in derivatives **5**.

Experimental

The NMR spectra were registered with a Bruker AM-300 spectrometer (300.13 MHz for ^1H nuclei), and the IR spectra were recorded with a UR-20 spectrometer. The UV spectra were obtained with a Specord UV VIS spectrometer, and the mass spectra were measured with a MAT 311A spectrometer.

All the experiments on the synthesis of derivatives **4—5** were carried out in dry solvents.

1-Hydroxybenzotriazole 3-oxide (1). *o*-(2-*tert*-Butylazoxy)aniline[2] (8.5 g, 0.044 mol) in 50 mL of CH_2Cl_2 was added in one portion to perbenzoic acid (18.5 g, 0.156 mol) in CH_2Cl_2 (150 mL) cooled to 10 °C, the mixture was stirred for 2 h at 20 °C, and the precipitate was filtered off, washed with ethyl ether (2×20 mL), and dried at 20 °C (15 Torr). Triazole **1** (5.13 g, 80 %) was obtained, m.p. 127 °C (decomp.).

Silver salt of triazole 1 (3). Water (10 mL) was added to a mixture of product **1** (3 g, 0.019 mol) and $KHCO_3$ (2.1 g, 0.02 mol), and after evolution of CO_2 was ceased, the solution of potassium salt **2** was obtained. NMR (D_2O, δ, acetone as the internal standard): ^1H NMR: 7.24 (m, 2 H, H-2), 7.42 (m, 2 H, H-3); ^{13}C NMR: 111.83 (C-2, $^1J_{^1H-^{13}C}$ = 170 Hz), 126.63 (C-3, $^1J_{^1H-^{13}C}$ = 168 Hz), 127.06 (C-1). The prepared solution was neutralized with 0.1 *N* aqueous HNO_3, a solution of $AgNO_3$ (3.5 g, 0.02 mol) was added, and the yellow precipitate of silver salt **3** (4.75 g, 97 %) was filtered off. [**Caution!** *Salt* **3** *is susceptible to trituration.*]

1-Methoxybenzotriazole 3-oxide (4). ***Method A.*** CH_3I (0.35 g, 2.5 mmol) was added to a suspension of silver salt **3** (0.5 g, 2 mmol) in acetonitrile (5 mL), the mixture was stirred at 20 °C for 30 min, filtered, evaporated to 50% of its volume at 25 °C (15 Torr), and passed through a short column with silica gel 40/100 μ (ether/acetone, 5:1, as the eluent), the solvent was removed at 25 °C (15 Torr), the residue was dissolved in a minimum amount of acetonitrile and diluted with 5 mL of ether, product **4** (0.153 g) was filtered off, the filtrate was evaporated to dryness, the residue was chromatographed on a silica gel column (ether/acetone, 5:1, as the eluent), and an additional amount of product **4** (0.128 g) was isolated. The total yield of the product was 0.281 g (80 %), m.p. 88—89 °C (decomp.). Found (%): C, 51.65; H, 4.29; N, 26.86. $C_7H_7N_3O_2$. Calculated (%): C, 50.90;

H, 4.27; N, 25.44. IR (ν/cm^{-1}): 765 (s), 830 (w), 935 (m), 1045 (s), 1345 (s), 1420 (s), 1460 (m). UV (λ_{max}/nm, in CH_3CN), 340 (ε = 7600). Mass spectrum: 165 $[M]^+$, 150 $[M-CH_3]^+$, 117 $[M-OCH_3-OH]^+$, 30 $[NO]^+$. NMR ($CDCl_3$, δ, tetramethylsilane) ^1H NMR: 4.31 (s, 3 H, CH_3), 7.41 (m, 1 H, H(3), ^3J = 8.6, ^4J = 1.1 Hz), 7.59 (m, 1 H, H(5), ^3J = 8.5 Hz), 7.65 (m, 1 H, H(4)), 7.96 (m, 1 H, H(2)); ^{13}C NMR: 67.32 (OCH_3), 109.90 (C-5), 115.56 (C-2), 125.16 (C-3), 129.79 (C-1), 130.83 (C-6), 131.24 (C-4); ^{14}N NMR (δ, from CH_3NO_2): −51.0 (N=, $\Delta\nu_{1/2}$ > 1000 Hz), −84.2 (N(O), $\Delta\nu_{1/2}$ = 230 Hz).

Table 1. Comparison of the NMR spectral data for compounds **2**, **4**, and **5** (δ, ppm)

Atom	Experiment [calculated data]*		
	4 ($CDCl_3$)	**5** (CH_3CN)	**2** (D_2O)
H(2)	7.96 (d)	7.74 [7.77]	7.24
H(5)	7.59 (d)		
H(3)	7.41 (t)	7.54 [7.53]	7.42
H(4)	7.65 (t)		
C(1)	129.79	131.60 [130.3]	127.06
C(6)	130.83		
C(2)	115.56	113.55 [112.7]	111.83
C(5)	109.90		
C(3)	125.16	128.71 [128.2]	126.63
C(4)	131.24		

* The calculated values of chemical shifts for compound **5** were obtained from the data on compound **4** using the following formulas: $\delta H(2)_{calc} = (\delta H(2) + \delta H(5))/2$; $\delta H(3)_{calc} = (\delta H(3) + \delta H(4))/2$; $\delta C(1)_{calc} = (\delta C(1) + \delta C(6))/2$; $\delta C(2)_{calc} = (\delta C(2) + \delta C(5))/2$; $\delta C(3)_{calc} = (\delta C(3) + \delta C(6))/2$.

Method B. An ethereal solution of CH_2N_2 (6 mL, 0.18 mole/L) was added to a suspension of triazole **1** (0.151 mg, 1 mmol) in 10 mL of acetonitrile; after dissolution of the precipitate was completed and gas evolution ceased, the solution was evaporated at 25 °C (15Torr); derivative **4** (0.163 g, quantitative yield) was obtained, m.p. 87—88 °C (decomp.). The product was spectrally identical with the compound obtained by Method A.

1-Trimethylsiloxybenzotriazole 3-oxide (5). Chlorotrimethylsilane (0.11 g, 1 mmol) was added dropwise to salt **3** (0.25 g, 1.1 mmol) in acetonitrile (1 mL) under argon. The mixture was stirred for 5 min and filtered, CD_3CN (0.1 mL) was added, and the solution was studied by NMR (acetonitrile; δ, ppm, tetramethylsilane). ^1H NMR: 0.41 (s, 9 H, $Si(CH_3)_3$), 7.54 (m, 2 H, H(3)), 7.74 (m, 2 H, H(2)) (at −25 °C the signals of H(2) and H(3) are significantly broadened); ^{13}C NMR: −0.70 ($Si(CH_3)_3$, broadened from +20 °C to −25 °C), 113.55 (C-2), 128.71 (C-3), 131.60 (C-1) (at −25 °C the C-2 and C-3 signals are significantly broadened); ^{29}Si: 42.74 (the signal is significantly broadened from −25 °C to 20 °C). Narrow signals were absent in the ^{14}N NMR spectrum.

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