Alkynyl-substituted nitronyl nitroxides

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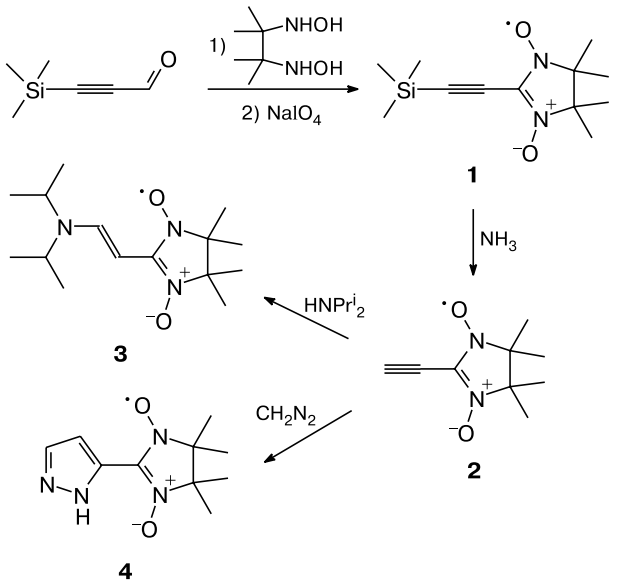
All earlier attempts to synthesize alkynyl-substituted nitronyl and imino nitroxides[1] have failed. We succeeded in synthesizing 4,4,5,5-tetramethyl-2-trimethylsilylethynyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide (**1**) and 2-ethynyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide (**2**) (Scheme 1). The structures of compounds **1** and **2** were established by X-ray diffraction (Fig. 1,*a*,*b*).

Scheme 1



The presence of the triple bond in molecules **1** and **2** is evidenced by the C(8)—C(9) bond length (~1.2 Å; see Table 1). The presence of the nitronyl nitroxide fragment adjacent to the triple bond is responsible for polarization of this bond and high reactivity. For example, compound **2** undergoes 1,3-dipolar cycloaddition with CH_2N_2 under mild conditions to give the already known[2,3] pyrazol-5-yl-substituted nitronyl nitroxide. In the reaction with $HNPr^i_2$, compound **2** is subjected to the regioselective nucleophilic attack (see Scheme 1) to form compound **3**. The structure of the latter was established by X-ray diffraction (Fig. 1,*c*).

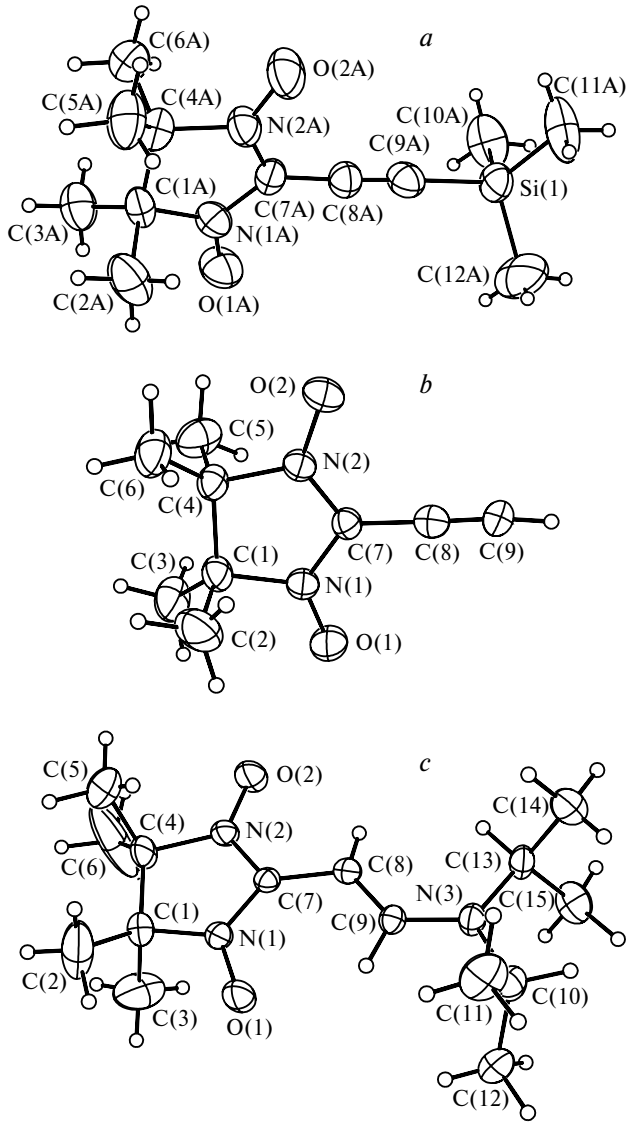


Fig. 1. Molecular structures of compounds **1** (*a*), **2** (*b*), and **3** (*c*).

The IR spectra were recorded in KBr pellets on a Bruker Vector-22 spectrophotometer in the 400—4000 cm^{-1} region. The melting points were determined on a Boetius hot-stage apparatus. Microanalyses were carried out on a Carlo Erba 1106 analyzer at the Vorozhtsov Novosibirsk Institute of Organic

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Table 1. Selected bond lengths (*d*) in molecules **1**, **2**, and **3**

Bond	1			2	3
N(1)—O(1)	1.282(5)	1.258(5)	1.283(5)	1.259(2)	1.293(4)
N(2)—O(2)	1.279(5)	1.286(5)	1.281(6)	1.274(2)	1.288(4)
N(1)—C(7)	1.340(6)	1.355(6)	1.343(6)	1.353(3)	1.344(5)
N(2)—C(7)	1.352(6)	1.332(6)	1.340(6)	1.319(2)	1.349(5)
C(7)—C(8)	1.427(7)	1.408(7)	1.406(8)	1.420(3)	1.412(6)
C(8)—C(9)	1.199(7)	1.203(7)	1.203(7)	1.106(3)	1.342(6)
C(9)—Si	1.860(6)	1.860(6)	1.841(6)		
Si—C	1.823(8)	1.836(8)	1.615(14)		
	1.828(7)	1.841(6)	1.617(17)		
	1.862(7)	1.840(8)	1.790(12)		

Chemistry of the Siberian Branch of the Russian Academy of Sciences. The magnetochemical measurements, which were performed by V. N. Ikorskii on a SQUID MPMS-5S magnetometer (Quantum Design), demonstrated that the effective magnetic moments of compounds **1—3** are close to 1.73 μ_B (300 K).

4,4,5,5-Tetramethyl-2-trimethylsilylethynyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide (1) was synthesized according to the classical Ullman method.[4] 3-(Trimethylsilyl)propiolaldehyde was condensed with 2,3-bis(hydroxyamino)-2,3-dimethylbutane[5] in MeOH giving rise to 4,4,5,5-tetramethyl-2-trimethylsilylethynylimidazolidine-1,3-diol, which was oxidized (without isolation) with $NaIO_4$ in a two-phase H_2O—CH_2Cl_2 system. The yield was 20%, m.p. 130—135 °C (with decomp.). IR, ν/cm^{-1}: 663, 764, 848, 941, 1025, 1169, 1250, 1372, 1418, 1630, 2113, 2981. Found (%): C, 56.4; H, 8.7; N, 11.9. $C_{12}H_{21}N_2O_2Si$. Calculated (%): C, 56.9; H, 8.4; N, 11.1.

2-Ethynyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide (2) was synthesized by cleaving the Si—C bond in compound **1** (60 mg, 0.24 mmol) with a 15% NH_3 solution in MeOH (see Refs 6 and 7). The yield was 20 mg (47%), m.p. 102—105 °C (with decomp.). IR, ν/cm^{-1}: 704, 756, 870, 1136, 1170, 1216, 1375, 1418, 1448, 2116, 2985, 3210. Found (%): C, 59.7; H, 7.3; N, 15.5. $C_9H_{13}N_2O_2$. Calculated C, 59.7; H, 7.2; N, 15.5.

(*E*)-2-[2-(Diisopropylamino)vinyl]-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide (3). A solution of compound **2** (18 mg, 0.1 mmol) and $HNPr^i_2$ (0.3 mL) in C_6H_6 (3 mL) was stirred at 50—60 °C for 1 h. The solvent was distilled off, and the crystalline compound was recrystallized from a mixture of CH_2Cl_2 and hexane. The yield was 20 mg (71%), m.p. 184—185 °C. IR, ν/cm^{-1}: 775, 869, 940, 988, 1010, 1054, 1099, 1132, 1194, 1213, 1283, 1314, 1365, 1386, 1410, 1443, 1615, 2871, 2933, 2973, 3079. Found (%): C, 63.9; H, 10.2; N, 14.9. $C_{15}H_{28}N_3O_2$. Calculated (%): C, 63.8; H, 10.0; N, 14.9.

X-ray diffraction study. Crystals suitable for X-ray diffraction study were grown by slow evaporation of solutions of compounds **1—3** in a mixture of CH_2Cl_2 and heptane. X-ray diffraction data sets were collected on a SMART APEX CCD Bruker AXS diffractometer (Mo-Kα, λ = 0.71073 Å, T = 295 K). Absorption corrections were applied using the Bruker SADABS software (Version 2.10). The structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for all nonhydrogen atoms. The positions of H atoms were calculated theoretically. The H atoms of the methyl groups were refined isotropically in the rigid-body approximation All calculations associated with the structure solution and refinement were carried out with the use of the Bruker SHELXTL program package (Version 6.14). Nitroxide **1** (CCDC-277835): $C_{12}H_{21}N_2O_2Si$, M = 253.40, crystals are triclinic, space group $P\bar{1}$, a = 10.850(6) Å, b = 12.433(7) Å, c = 18.070(10) Å, α = 77.444(11)°, β = 86.832(12)°, γ = 81.093(11)°, V = 2350(2) Å^3; Z = 6, 8584 measured reflections (1.70 < θ < 23.31°), of which 6383 reflections with $I > 2\sigma(I)$, ρ_{calc} = 1.074 g cm^{-3}, μ = 1.44 cm^{-1}, R_1 = 0.0811, wR_2 = 0.2108. Nitroxide **2** (CCDC-277836): $C_9H_{13}N_2O_2$, M = 181.21, crystals are orthorhombic, space group *Pbca*, a = 11.055(3) Å, b = 11.691(3) Å, c = 15.436(4) Å, V = 1995.1(8) Å^3, Z = 8, 20845 measured reflections (2.64 < θ < 29.56°), of which 2683 reflections with $I > 2\sigma(I)$, ρ_{calc} = 1.207 g cm^{-3}, μ = 0.87 cm^{-1}, R_1 = 0.0780, wR_2 = 0.1602. Nitroxide **3**: $C_{15}H_{28}N_3O_2$, M = 282.40, crystals are orthorhombic, space group *Pbca*, a = 13.672(2) Å, b = 12.588(2) Å, c = 19.948(3) Å, V = 3433.1(7) Å^3, Z = 8, 19021 measured reflections (2.04 < θ <23.31°), of which 2478 reflections with $I > 2\sigma(I)$, ρ_{calc} = 1.093 g cm^{-3}, μ = 0.73 cm^{-1}, R_1 = 0.0883, wR_2 = 0.2217.

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