New reactions of aci-1-nitropropane trimethylsilyl ester with 4-nitronitrosobenzene in the presence of trimethylsilylating reagents

I. M. Lyapkalo, S. L. Ioffe, Yu. A. Strelenko, and V. A. Tartakovsky*

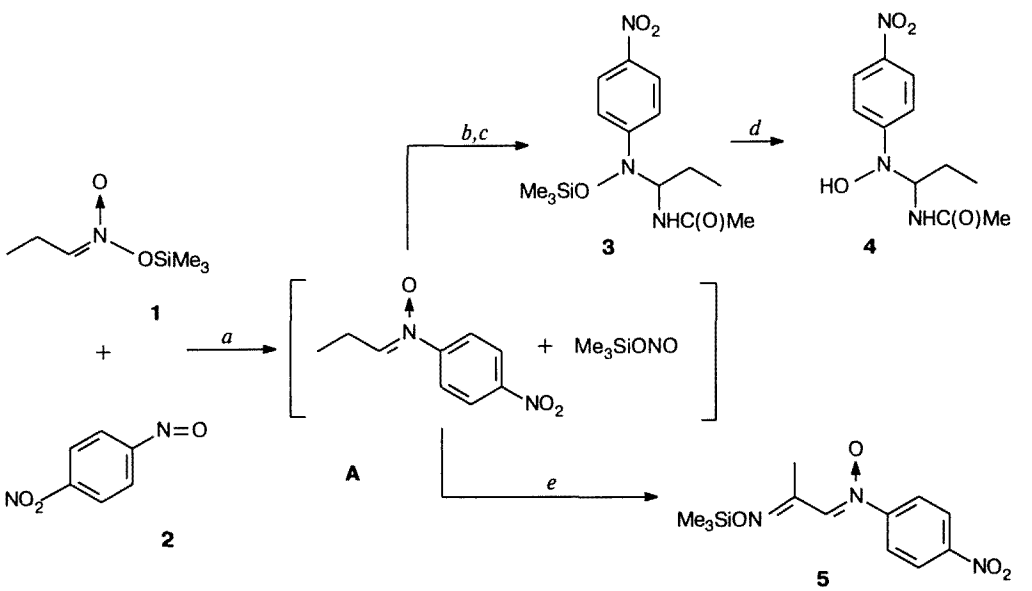
N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117913 Moscow, Russian Federation. Fax: +7 (095) 135 5328

We found new unusual reactions of trimethylsilyl ester of aci-1-nitropropane (**1**) with 4-nitronitrosobenzene (**2**) in the presence of silylating reagents (Scheme 1). The reaction of compound **1** (1.2 equiv.) with compound **2** (1 equiv.) in the presence of $MeC(OSiMe_3)=NSiMe_3$ (BSA) (2.5 equiv.) affords *N*-(4-nitrophenyl)-*N*-(1-acetylaminopropyl)-*N*-trimethylsilyloxyamine (**3**), which is converted into *N*-(4-nitrophenyl)-*N*-(1-acetylaminopropyl)hydroxylamine (**4**) on treatment with a catalytic amount of KF in MeOH.

At the same time, the reaction of compound **1** (1.3 equiv.) with compound **2** (1 equiv.) in the presence of Me_3SiCl/Et_3N (2.5 equiv.) yields 1-(4-nitrophenylimino)-2-(trimethylsilyloxyimino)propane 1-*N*-oxide (**5**) (see Scheme 1).

One may assume that 1-(4-nitrophenylimino)propane *N*-oxide (**A**) is the key intermediate of both reactions. At present, the mechanism of these transformations and the possibility of conducting them using other substances are being studied.

Scheme 1



Reagents and conditions: *a*, − 78 °C, CH_2Cl_2; *b*, $MeC(OSiMe_3)=NSiMe_3$ (BSA); *c*, MeOH; *d*, MeOH (excess), cat. *e*, Me_3SiCl/Et_3N, Me_3SiONO.

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***N*-(4-Nitrophenyl)-*N*-(1-acetylaminopropyl)-*N*-trimethylsilyloxyamine (3)**, yield 50 %, m.p. 96—99 °C (decomp.). ^{1}H NMR ($CDCl_3$), δ: 0.14 (s, 9 H, $SiMe_3$); 0.96 (br.t, 3 H, Me, ^3J = 7.3 Hz); 1.79 (br.m, 2 H, CH_2, H_A+H_B); 1.94 (br.s, 3 H, MeCO); 5.37 (br.m, 1 H CH, H_X, $^3J_{XA}$ = 9.0 Hz, $^3J_{XB}$ = 5.7 Hz); 6.60 (br.d, 1 H, NH, ^3J = 9.0 Hz); 7.32 (d, 2 H, CH_m with respect to NO_2, ^3J = 9.1 Hz); 8.15 (d, 2 H, CH_o with respect to NO_2). ^{13}C NMR, δ: −0.37 ($SiMe_3$); 10.42 (Me); 22.83 (MeCO); 25.20 (br, CH_2); 74.36 (CH); 118.26 (br, $\underline{C}H_m$ with respect to NO_2); 124.48 ($\underline{C}H_o$ with respect to NO_2); 142.81 (C−NO_2); 157.64 (C−N); 169.85 (C=O). ^{29}Si NMR (INEPT), δ: 28.04. ^{14}N NMR, δ (referred to $MeNO_2$): −12.8 ($\Delta\nu_{1/2}$, J = 850 Hz, NO_2). ^{15}N NMR (INEPT, CD_2Cl_2, −40 °C), δ (referred to $MeNO_2$)*: −251.7 (d, $\underline{N}H$, J = 88 Hz); −259.7 (d, $\underline{N}H$, J = 93 Hz). MS, *m/z*: 325 $[M]^{+\cdot}$, 267 $[M-AcNH]^+$, 251 $[M-AcNH_2-Me]^+$, 226 $[M-OSiMe_3]^+$, 211 $[M-OSiMe_3-Me]^{+\cdot}$, 210 $[M-Me_3SiOH-Me]^+$, 194 $[M-AcNHSiMe_3]$. Found (%): C, 51.58; H, 7.15; N, 12.80; Si, 8.84. $C_{14}H_{23}N_3O_4Si$. Calculated (%): C, 51.67; H, 7.12; N, 12.91; Si, 8.63.

***N*-(4-Nitrophenyl)-*N*-(1-acetylaminopropyl)hydroxylamine (4)**, yield 90 %, m.p. 153—159 °C (decomp.). ^{1}H NMR ($(CD_3)_2SO$), δ: 0.91 (br.t, 3 H, Me); 1.86 (br.m, 5 H, CH_2 + MeCO); 5.69 (br.m, 1 H CH); 7.23 (br.d, 2 H, CH_m with respect to NO_2); 8.11 (br.d, 2 H, CH_o with respect to NO_2); 8.50 (br.d, 1 H, NH); 9.55 (br.s, 1 H, OH). ^{13}C NMR, δ: 10.20 (Me); 22.38 (MeCO); 24.78 (CH_2); 67.45 (CH); 113.03 (CH_m with respect to NO_2); 125.11 (CH_o with respect to NO_2); 138.69 (C−NO_2); 155.82 (C−N); 169.71 (C=O). Found (%): C, 52.22; H, 6.04; N, 16.65. $C_{11}H_{15}N_3O_4$. Calculated (%): C, 52.17; H, 5.97; N, 16.59.

1-(4-Nitrophenylimino)-2-(trimethylsilyloxyimino)propane 1-*N*-oxide (5), yield 74 %, m.p. 101—105 °C (decomp.), ^{1}H NMR ($CDCl_3$), δ: 0.27 (s, 9 H, $SiMe_3$); 2.53 (s, 3 H, Me); 7.81 (s, 1 H, $C\underline{H}$=N); 7.99 (d, 2 H, CH_m with respect to NO_2, ^3J = 9.1 Hz); 8.34 (d, 2 H, CH_o with respect to NO_2). ^{13}C NMR, δ: −0.78 ($SiMe_3$); 12.61 (Me); 122.89 ($\underline{C}H_m$ with respect to NO_2); 124.87 ($\underline{C}H_o$ with respect to NO_2); 135.19 ($\underline{C}$H=N); 148.46 and 152.47 (C−N and C−NO_2); 157.92 ($\underline{C}$=NOSiMe$_3$). ^{29}Si NMR (INEPT), δ: 28.60. ^{14}N NMR, δ (referred to $MeNO_2$): −16.1 ($\Delta\nu_{1/2}$, J = 800 Hz, NO_2); −101.6 ($\Delta\nu_{1/2}$, J = 450 Hz, C=$\underline{N}$(O)Ar). ^{15}N NMR (INEPT, 0 °C), δ: 15.0 (C=$\underline{N}$OSiMe$_3$); −96.7 (C=$\underline{N}$(O)Ar). Found (%): C, 49.04; H, 5.72; N, 14.29; Si, 9.65. $C_{12}H_{17}N_3O_4Si$. Calculated (%): C, 48.80; H, 5.80; N, 14.23; Si, 9.51.

* Under these conditions, two $\underline{N}$H signals corresponding to the rotamers, existing due to the hindered amine rotation, can be observed.

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