Unusual transformation of 2-nitropropane under the conditions of trimethylsilylation

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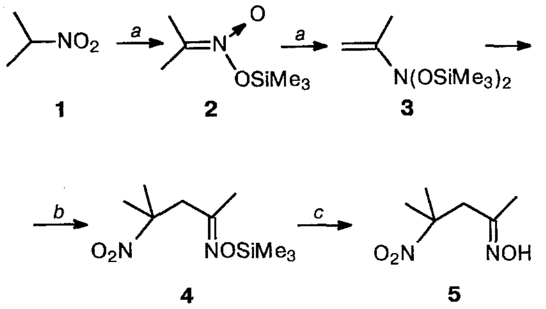
Under the standard conditions of trimethylsilylation[1] of 2-nitropropane (**1**) (1.5 equiv. of Me_3SiCl—Et_3N in MeCN, 36 h at 5—15 °C) we unexpectedly obtained 4-methyl-4-nitro-2-trimethylsilyloximinopentane (**4**) (Scheme 1), yield 60 %, b.p. 62—64 °C (0.5 Torr), $n^{20}{}_D$ 1.4503. ^1H NMR ($CDCl_3$), δ: 0.15 (s, 9 H, $SiMe_3$); 1.62 (s, 6 H, Me_2); 1.80 (s, 3 H, Me); 2.84 (s, 2 H, CH_2). ^{13}C NMR: −0.18 ($SiMe_3$); 15.71 (Me); 27.04 (Me_2); 46.14 (CH_2); 86.46 (C—NO_2); 157.03 (C=N). ^{29}Si (INEPT): 24.55. ^{14}N NMR ($MeNO_2$), δ: 17.7 ($\Delta\nu_{1/2}$ = 400 Hz, NO_2). MS, *m/z*: 186 $[M-NO_2]^+$. **2**. Found (%): C, 46.68; H, 8.63; N, 12.14; Si, 11.83. $C_9H_{20}N_2O_3Si$. Calculated (%): C, 46.52; H, 8.68; N, 12.06; Si, 12.09.

Scheme 1



Reagents and conditions: *a*. Me_3SiCl—Et_3N in MeCN; *b*. **2** or **1**; *c*, MeOH

Treatment of compound **4** with methanol afforded the crystalline oxime of 4-methyl-4-nitropentan-2-one (**5**), yield 85 %, m.p. 63—64 °C (from hexane). NMR ($(CD_3)_2CO$), δ, ^1H: 1.61 (s, 6 H, Me_2); 1.79 (s, 3 H, Me); 2.85 (s, 2 H, CH_2); 9.85 (br.s, 1 H, OH). ^{13}C: 14.68 (Me); 26.32 (Me_2); 46.03 (CH_2); 87.23 (C—NO_2); 152.60 (C=N). ^{14}N ($MeNO_2$), δ: 22.8 ($\Delta\nu_{1/2}$ = 210 Hz, NO_2). ^{15}N (INEPT): 22.11 (NO_2); −23.08 (C=NOH). MS, *m/z*: 114 $[M-NO_2]^+$, 113 $[M-HNO_2]^{+\cdot}$. IR, ν/cm^{-1}: 1540, 1350 (NO_2). **3**. Found (%): C, 44.95; H, 7.52; N, 17.44. $C_6H_{12}N_2O_3$. Calculated (%): C, 44.99; H, 7.55; N, 17.49.

When nitroalkane **1** was silylated with one equivalent of Me_3SiCl—Et_3N, the starting compound **1**, silylnitronate **2** (see Ref. 2), and 2-[*N,N*-bis(trimethylsilyloxy)amino]propene (**3**), which had been previously prepared by treatment of 2-nitropropane **1** with trimethylsilyltriflate,[3] were detected in the reaction mixture by NMR spectroscopy. The ratio between compounds **1**, **2**, and **3** depends on the quantity of the silylating agent and indicates that the **1** → **2** and **2** → **3** reactions occur at similar rates.

Compound **4** results from the reaction of enamine **3** with either silylnitronate **2**, according to a concerted mechanism, or with the initial **1** under conditions of basic catalysis by Et_3N. Thus, Me_3SiCl—Et_3N in MeCN cannot be advised for the preparation of pure silylnitronate **2**, but it can be used to generate this compound under the conditions in which it is scavenged by activated olefins.[1]

The transformations of nitroalkane **1** observed are the first example of the formation of a new C—C bond during silylation of nitroparaffins. Currently we are studying the mechanism and the fields of application of these transformations in the synthesis.

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