ISSN 1070-4280, Russian Journal of Organic Chemistry, 2006, Vol. 42, No. 10, pp. 1568–1569. © Pleiades Publishing, Inc., 2006.
Original Russian Text © B.F. Kukharev, V.K. Stankevich, N.A. Lobanova, E.Kh. Sadykov, V.A. Kukhareva, 2006, published in Zhurnal Organicheskoi Khimii, 2006, Vol. 42, No. 10, pp. 1579–1580.

SHORT COMMUNICATIONS

Unexpected Product in the Reaction of 2-Hydrazinoethanol with Acetylene

B. F. Kukharev, V. K. Stankevich, N. A. Lobanova, E. Kh. Sadykov, and V. A. Kukhareva

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences,
ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: irk_inst_chem@irioch.irk.ru

Received January 4, 2006

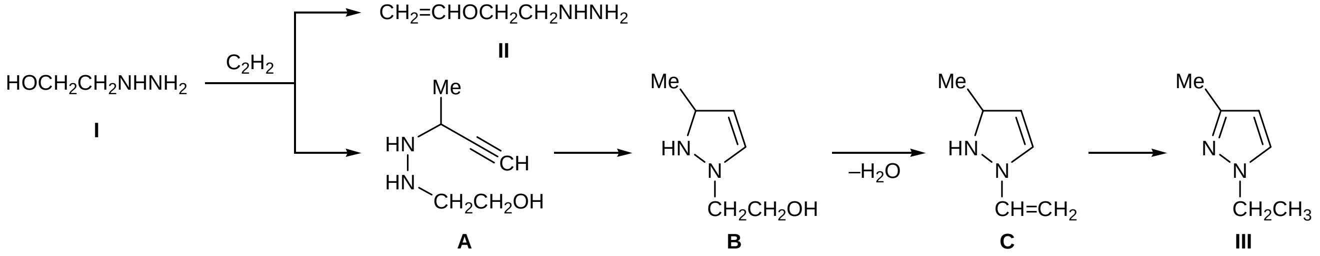
DOI: 10.1134/S1070428006100289

We previously presumed that base-catalyzed vinylation of 2-hydrazinoethanol (**I**) should be complicated owing to possible cleavage of the nitrogen–nitrogen bond; therefore, the yield of (2-vinyloxyethyl)hydrazine should be poor [1]. With a view to identify products formed in this reaction, we examined vinylation of compound **I** in DMSO in the presence of KOH. The expected (2-vinyloxyethyl)hydrazine (**II**) was isolated in only 19% yield. However, from the reaction mixture (which contained tars) we also isolated 39% of an unexpected product, 1-ethyl-3-methyl-1*H*-pyrazole (**III**).

Presumably, the reaction of 2-hydrazinoethanol (**I**) with acetylene initially gives 2-[2-(1-methylprop-2-yn-1-yl)hydrazino]ethanol **A**, by analogy with the formation of the corresponding *N*-(1-methylprop-2-yn-1-yl) derivatives in the vinylation of secondary amines [2]. Next follows intramolecular cyclization to dihydropyrazole **B**, which is well known for *N*-(prop-2-yn-1-yl)-hydrazines [3], and base-catalyzed dehydration to give 3-methyl-1-vinyl-2,3-dihydro-1*H*-pyrazole **C**. Intramolecular hydrogen transfer in the latter yields final pyrazole **III**.

The structure of compound **III** was confirmed by the ^{1}H, ^{13}C, and ^{15}N NMR spectra. The ^{15}N NMR spectrum was recorded using gradient-pulse inversed heteronuclear correlation technique (HMBC). It contained two signals at δ_N –164.82 and –76.46 ppm, which were assigned to the ^{15}N isotope in the NEt and N=CH groups, respectively, taking into account published data [4].

1-Ethyl-3-methyl-1*H*-pyrazole (III). A mixture of 100 ml of DMSO, 22.8 g (0.3 mol) of 2-hydrazinoethanol (**I**), and 2.3 g of potassium hydroxide was saturated with acetylene under a pressure of 12 atm and was then heated for 6 h at 120–130°C. The mixture was poured into 200 ml of water and treated with diethyl ether (3 × 100 ml). The extract was dried over K_2CO_3 and evaporated, and the residue was distilled under reduced pressure. Yield 12.9 g (39%), bp 72–74°C (40 mm); published data [5]: bp 143°C (760 mm; d_4^{20} = 0.9488, n_D^{20} = 1.4729. IR spectrum (neat), ν, cm^{-1}: 600, 625, 695, 740, 870, 910, 940, 965, 990, 1030, 1075, 1090, 1160, 1190, 1200, 1230, 1270, 1315, 1345, 1355, 1370, 1410, 1440, 1475, 1515, 1585, 1640, 2865, 2920, 2970, 3100. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.44 t (3H, $CH_2C\mathbf{H}_3$, ^{3}J = 7.3), 2.27 s (3H, 3-CH_3), 4.08 q (2H, $C\mathbf{H}_2CH_3$, ^{3}J = 7.3), 5.98 d (1H, 4-H, $^{3}J_{4,5}$ = 2.0), 7.25 d (1H, 5-H, $^{3}J_{4,5}$ = 2.0). ^{13}C NMR spectrum, δ_C, ppm: 13.53 ($CH_2\mathbf{C}H_3$), 15.66 (3-CH_3), 46.56 (CH_2), 104.69 (C^4), 128.85 (C^5), 148.19



(C^3). ^{15}N NMR spectrum, δ_N, ppm: –164.82 (NEt), –76.46 (C=N). Found, %: C 65.96; H 9.36; N 21.62. MR_D 32.56. $C_6H_{10}N_2$. Calculated, %: C 65.42; H 9.15; N 25.43. MR_D 32.35.

(2-Vinyloxyethyl)hydrazine (II) was isolated by distillation of the same extract. Yield 4.3 g (19%), bp 75–77°C (12 mm), d_4^{20} = 0.9846, n_D^{20} = 1.4571; published data [1]: bp 77–78°C (13 mm), d_4^{20} = 0.9848, n_D^{20} = 1.4574.

The ^1H, ^{13}C, and ^{15}N NMR spectra were recorded at 26°C from solutions in $CDCl_3$ on a Bruker DPX-400 spectrometer at 400, 100, and 40 MHz, respectively; the chemical shifts were measured relative to HMDS (^1H and ^{13}C) or $MeNO_2$ (^{15}N) as internal reference. The IR spectrum was obtained on a Specord 75IR spectrometer. The purity of compounds **I** and **II** was checked by GLC on an LKhM-80 chromatograph equipped with a thermal conductivity detector and a steel column (3×3000 mm) packed with 3% of OV-17 on Inerton Super (0.160–0.200 mm); oven temperature programming from 60 to 180°C at 4 deg/min; carrier gas helium.

Dimethyl sulfoxide and KOH were commercial products; freshly prepared 2-hydrazino-ethanol (**I**) was used; their purity was no less than 99.5% (GLC); commercial acetylene had a purity of 99%.

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