Russian Journal of Organic Chemistry, Vol. 39, No. 9, 2003, pp. 1358–1359. Translated from Zhurnal Organicheskoi Khimii, Vol. 39, No. 9, 2003, pp. 1430–1431.

SHORT COMMUNICATIONS

Cyclooligomerization of Acetylene with Acetonitrile to 2-Amino-3-(1-iminoethyl)-6-methylpyridine in the System KOH–CH_3CN

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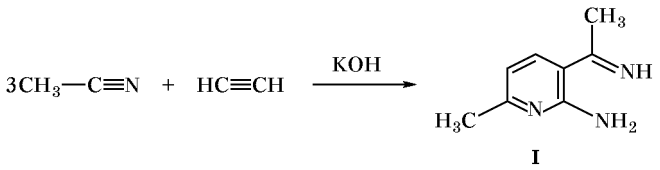
Received March 27, 2003

Cyclooligomerizations of acetylene to benzene, cyclooctatetraene, and higher cyclic polyenes in the presence of transition metal salts or complexes have been well documented [1, 2]. Analogous but less explored from the preparative viewpoint reactions occur in systems consisting of a strong base and polar aprotic solvent (superbasic medium) in the presence of alkali metal cations [3–6].

Gairns *et al.* [7] reported on the cyclization of acetylene with two molecules of acetonitrile to afford 2,4-dimethylpyrimidine (yield 8%) in the presence of potassium under pressure and at elevated temperature (16–17 atm, 175–200°C, 7 h). In the present communication we briefly describe a new cyclooligomerization of acetylene with acetonitrile, which occurs under mild conditions (–15 to 20°C, atmospheric pressure, KOH–MeCN) and leads to formation of 2-amino-3-(1-iminoethyl)-6-methylpyridine (**I**) in one preparative step (Scheme 1). Compound **I** is the product of condensation of one acetylene molecule with three molecules of acetonitrile.

Scheme 1.



I

Presumably, intermediate dimeric ambident anion **A** adds to acetylene molecule to give carbanion **C** which then gives rise to pyridine ring via addition of the third acetonitrile molecule (Scheme 2). Here, potassium cation, which is known to form complexes with one or several acetylene molecules [6, 8, 9], gives rise to a complex with acetonitrile and acts as a coordinating center (template).

2-Amino-3-(1-iminoethyl)-6-methylpyridine (I). Acetonitrile, 7.83 g (190 mmol) was saturated with acetylene at 18–20°C over a period of 15 min. The solution was cooled to –15°C, 0.66 g (11.8 mmol) of finely powdered potassium hydroxide (preliminarily calcined for 5 h at 450–500°C) was added, and acetylene was bubbled through the mixture for 2 h at –15°C. The mixture was allowed to warm up to 18–20°C, while continuously bubbling acetylene (6 h), and the resulting dark brown mixture was left overnight. The solid precipitate, 1.4 g, was filtered off and washed with 10 g of diethyl ether. The washings were combined with the filtrate, 3.04 g, which consisted mainly of acetonitrile, dried over $MgSO_4$, and evaporated under reduced pressure. The dark residue (0.24 g) was treated with 10 ml of boiling hexane to isolate 0.01 g of light yellow needles with mp 133–134°C. IR spectrum (KBr), ν, cm^{-1}: 3420, 3300, 3139 (C–H, pyridine), 2923, 2855 (C–H, CH_3), 1612, 1589 sh, 1549 (pyridine), 1464, 1440, 1388, 1374, 1284, 1248, 1231, 1196, 1164, 1087, 1051, 1036, 979, 932, 863, 795, 770, 698, 588, 574, 553, 523. ^1H NMR spectrum, δ, ppm: 9.32 br.s (1H, NH), 7.55 d (1H, 4-H, $^3J_{4,5}$ = 8.1 Hz), 7.35 br.s (2H, NH_2), 6.38 d (1H, 5-H, $^3J_{4,5}$ = 8.1 Hz), 2.39 s (3H, $CH_3C{=}N$), 2.37 s (3H, 6-CH_3). ^{13}C NMR spectrum, δ_C, ppm: 174.26 (C=NH), 159.94 (C^6), 158.26 (C^2), 138.86 (C^4), 111.50 (C^5), 110.98 (C^3), 28.22 ($\mathbf{C}H_3C{=}N$), 24.42 (6-CH_3). Mass spectrum, *m*/*z* (I_{rel}, %): 149 (100), 148 (20), 132 (63), 109 (23), 108 (29), 42 (13), 28 (14). Found, %: C 63.73; H 7.77;

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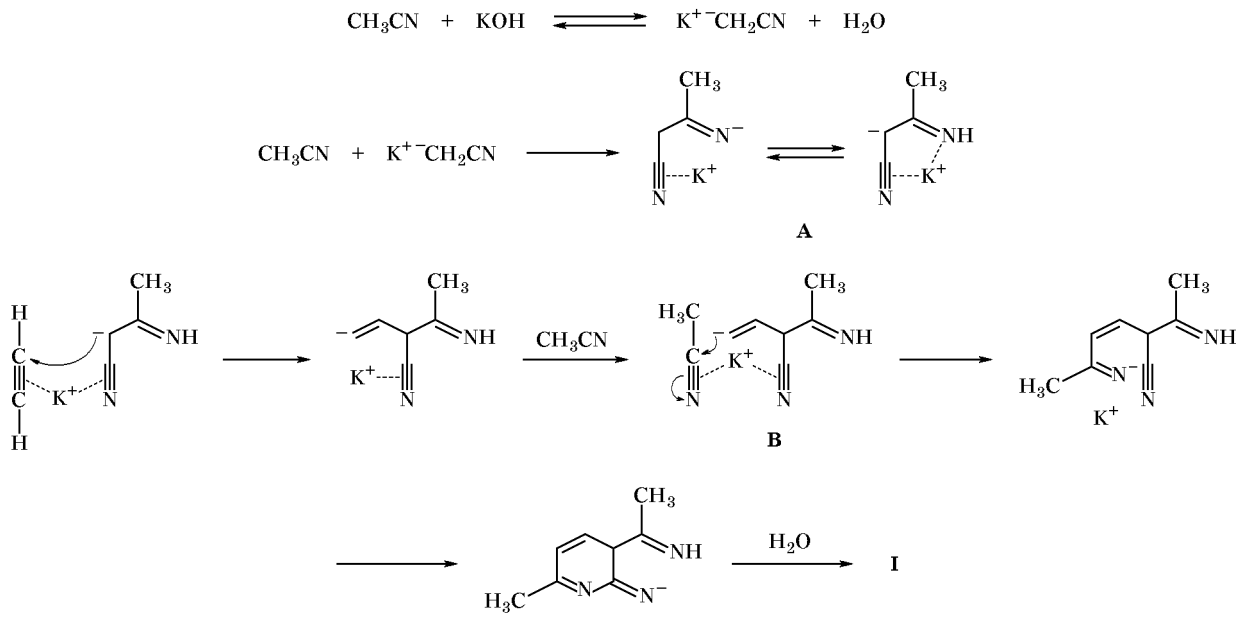
Scheme 2.



N 27.63. $C_8H_{11}N_3$. Calculated, %: C 64.40; H 7.43; N 28.16.

The ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 250 spectrometer (250.1 and 62.9 MHz, respectively) from 0.1 or 5–10 wt % solutions in $CDCl_3$ using HMDS as internal reference. The IR spectra were measured on Specord 75IR and Bruker IFS-25 spectrometers. The mass spectra were obtained on a Finnigan GCQ instrument with direct sample admission into the ion source. Commercial acetonitrile was distilled over P_2O_5. The structure of 2-amino-3-(1-iminoethyl)-6-methylpyridine (**I**) was also proved by X-ray analysis (the results will be reported in a separate communication).

Despite the poor yield (which, however, may be increased by optimizing the reaction conditions), the above one-pot chemo- and regioselective synthesis of pyridine derivative **I** possessing a rare combination of functional groups may be of practical importance provided that such building block would be needed. The procedure is based on readily accessible initial reactants and is very simple, and any amount of the product can be prepared.

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