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Multi-channel annulation of acetylene with 3-methyl-7,8-dihydrocinnolin-5(6*H*)-one oxime in the KOH/DMSO superbasic system

Olga V. Petrova, Lyubov N. Sobenina, Igor A. Ushakov, Arsalan B. Budaev, Andrei V. Ivanov, Vladimir A. Samsonov, Aleksei Ya. Tikhonov and Boris A. Trofimov

General Information. IR spectra were obtained on a "Bruker IFS-25" spectrometer (KBr pellets in 400-4000 cm^{-1} region). ^{1}H (400 MHz), ^{13}C (100 MHz), ^{15}N (41 MHz) NMR spectra were recorded on a "Bruker Avance 400" instrument in $CDCl_3$ or DMSO-d_6. The assignment of signals in the ^{1}H NMR spectra was made using COSY and NOESY experiments. Resonance signals of carbon atoms were assigned based on ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC experiments. The values of the δ ^{15}N were measured through the 2D NMR ^{1}H-^{15}N HMBC experiment. The ^{1}H chemical shifts (δ) were referenced to HMDS (0.05 ppm) in $CDCl_3$ and the residual deuterated solvent (2.50 ppm for DMSO-d_6), the ^{13}C chemical shifts were expressed with respect to the deuterated solvent (77.10 ppm for $CDCl_3$, 39.50 ppm for DMSO-d_6), and ^{15}N - $MeNO_2$ (0.0 ppm), respectively. The values of the δ ^{15}N were measured through the 2D ^{1}H-^{15}N HMBC experiment. The C, H, N microanalyses were performed on a Flash EA 1112 CHNS-O/MAS analyzer. Melting points (uncorrected) were determined with melting point SMP3 (Stuart Scientific). The starting 3-methyl-7,8-dihydrocinnolin-5(6*H*)-one oxime was obtained by procedure described.[1]

Reaction of oxime 1 with acetylene in KOH/DMSO system

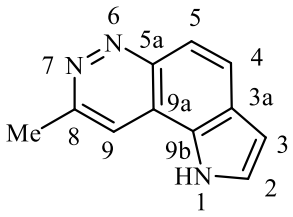
The acetylene was passed through the stirred mixture of oxime (as monohydrate) **1** (1.125 g, 5.8 mmol) and KOH (0.410 g, 6.3 mmol) in DMSO (16 ml) at 140 °C for 12 h (until disappearance of the oxime signal at 11.95 (OH) ppm and 2.59 (Me) ppm in the ^{1}H NMR spectra of the reaction mixture aliquot). After cooling to room temperature the reaction mixture was diluted with brine (80 ml) and NH_4Cl (0.337 g, 6.3 mmol) was added. The obtained solution was

1 V.A. Samsonov, L.B. Volodarskii, I,Yu. Bagryanskaya and Yu.V. Gatilov, *Chem. Heterocycl. Compd*., 1996, **32**, 907 (*Khim. Geterotsikl. Soedin.*, 1996, 1055).

extracted with diethyl ether (8×40 ml), the ether extracts were washed with water (4×40 ml) and dried over K_2CO_3. The residue after removing diethyl ether (0.344 g, dark red oil) was diluted with methanol (2 ml) and precipitated crystals were filtered off and dried to afford pyrrole **2** (0.020 g, 1.8%). Next, the aqueous layer was extracted with CH_2Cl_2 (6×40 ml), the extracts were washed with water (3×50 ml) and dried over K_2CO_3. The residue after removing the solvent (0.274 g, brown oil) was diluted with methanol (1.5 ml) and precipitated crystals were filtered off and dried to give the second crop of pyrrole **2** (0.007 g, 0.7%); total yield 2.5%.

The compounds **3-7** were isolated by column chromatography (Al_2O_3, eluent *n*-hexane, *n*-hexane/CH_2Cl_2 5:1, 3:1, 1:1 and CH_2Cl_2) of the mixture obtained after separating pyrrole **2**. The pyrrole **3** was isolated as a 1:1 mixture with pyrrole **4** (^{1}H NMR).

8-Methyl-1*H*-pyrrolo[2,3-*f*]cinnoline (2).



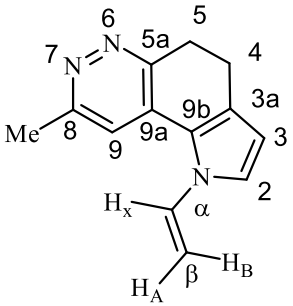
Yield 0.027 g (2.5%), mp > 284 ºC (MeOH). IR (KBr), ν, cm^{-1}: 3438, 3142, 3074, 2979, 2888, 2807, 1612, 1568, 1492, 1446, 1395, 1373, 1191, 1147, 1112, 1035, 920, 883, 812, 799, 744, 701.

^{1}H NMR (DMSO-d_6), δ: 2.86 (s, 3H, Me), 6.72 (m, 1H, H-3), 7.67 (m, 1H, H-2), 7.88 (m, 1H, H-4), 8.00 (m, 1H, H-5), 8.31 (m, 1H, H-9), 12.57 (br. s, 1H, NH).

^{13}C NMR (DMSO-d_6), δ: 21.9 (Me), 103.9 (C-3), 114.6 (C-9), 116.6 (C-3a), 119.9 (C-2), 125.2 (C-5), 125.8 (C-9b), 126.4 (C-9a), 126.8 (C-4), 147.1 (C-5a), 152.8 (C-8).

Found (%): C, 72.37; H, 4.67; N, 22.75. Calc. for $C_{11}H_9N_3$ (%): C, 72.11; H, 4.95; N, 22.94.

8-Methyl-1-vinyl-4,5-dihydro-1*H*-pyrrolo[2,3-*f*]cinnoline (3).



Yield 0.021 g (1.7%) from the mixture (1:1, 0.042 g) with pyrrole **4**.

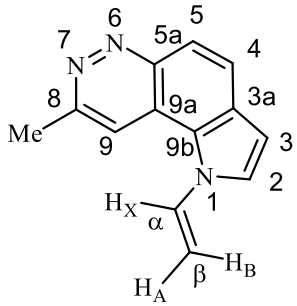
^{1}H NMR ($CDCl_3$), δ: 2.61 (s, 3H, Me), 2.80 (m, 2H, CH_2-4), 3.19 (m, 2H, CH_2-5), 5.00 (d, *J* 8.5 Hz, 1H, H_A), 5.32 (d, *J* 15.4 Hz, 1H, H_B), 6.15 (d, *J* 2.5 Hz, 1H, H-3), 7.03 (m, 2H, H-2, H-9), 7.11 (dd, *J* 8.5, 15.4 Hz, 1H, H_X).

^{13}C NMR ($CDCl_3$), δ: 21.5 (CH_2-4), 22.5 (CH_3), 30.2 (CH_2-5), 103.8 (C_β), 109.3 (C-3), 115.6 (C-9), 124.0 (C-9b), 124.8 (C-2), 127.2 (C-3a), 129.0 (C-9a), 132.1 (C_α), 155.9 (C-5a), 158.2 (C-8).

^{15}N NMR ($CDCl_3$), δ: – 214.0 (N^1), -10.6 (N^7), -1.0 (N^6).

MS, *m/z*: 211 $[M]^{+\bullet}$.

8-Methyl-1-vinyl-1*H*-pyrrolo[2,3-*f*]cinnoline (4).



Yield 0.098 g (8.1%) and 0.021 g (1.7%) from the mixture (1:1, 0.042 g) with pyrrole **3**, total yield 0.119 g (9.8%), mp 124-126ºC (*n*-hexane). IR (KBr), ν, cm^{-1}: 3088, 3037, 2992, 2923, 2858 (CH_3), 1636, 1604, 1557, 1492, 1446, 1419, 1376, 1319, 1227, 1037, 963, 891, 878, 823, 740, 702.

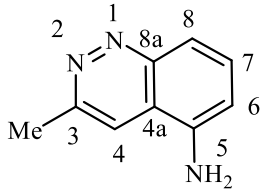
^{1}H NMR ($CDCl_3$), δ: 2.92 (s, 3H, Me), 5.26 (d, *J* 8.3 Hz, 1H, H_A), 5.51 (d, *J* 15.3 Hz, 1H, H_B), 6.72 (d, *J* 3.1 Hz, 1H, H-3), 7.44 (d, *J* 3.1 Hz, 1H, H-2), 7.59 (dd, *J* 8.3, 15.3 Hz, 1H, H_X), 7.87 (d, *J* 8.8 Hz, 1H, H-4), 7.95 (s, 1H, H-9), 8.08 (d, *J* 8.8 Hz, 1H, H-5).

^{13}C NMR($CDCl_3$), δ: 22.6 (Me), 105.9 (C-3), 106.9 (C_β), 115.1 (C-9), 117.6 (C-3a), 123.0 (C-5), 125.2 (C-9b), 125.0 (C-4), 128.5 (C-2), 128.7 (C-9a), 133.1 (C_α), 148.3 (C-5a), 153.2 (C-8).

^{15}N NMR ($CDCl_3$), δ: – 217.8 (N^1), 18.5 (N^7), 31.6 (N^6).

MS, *m/z*: 209 $[M]^{+\bullet}$. Found (%): C, 74.38; H, 5.59; N, 20.03. Calc. for $C_{13}H_{11}N_3$ (%): C, 74.62; H, 5.30; N, 20.08.

3-Methylcinnolin-5-amine (5).



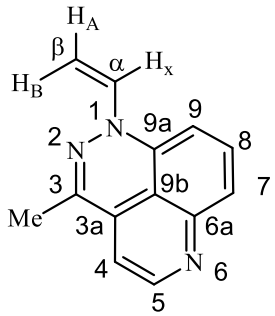
Yield 0.015 g (1.6%), mp 188-190 ºC (*n*-hexane). IR (KBr), ν, cm^{-1}: 3444, 3309, 3140, 1648, 1579, 1453, 1384, 1328, 1304, 1170, 1102, 881, 816, 766.

^{1}H NMR ($CDCl_3$), δ: 2.92 (s, 3H, Me), 4.32 (br. s, 2H, NH_2), 6.89 (d, *J* 7.3 Hz, 1H, H-6), 7.53 (m, 1H, H-7), 7.62 (s, 1H, H-4), 7.92 (d, *J* 8.6 Hz, 1H, H-8).

^{13}C NMR ($CDCl_3$), δ: 22.3 (Me), 112.5 (C-6), 115.7 (C-4), 117.9 (C-4a), 119.9 (C-8), 130.1 (C-7), 140.9 (C-5), 150.0 (C-8a), 152.7 (C-3).

Found (%): C, 68.12; H, 5.57; N, 26.31. Calc. for $C_9H_9N_3$ (%): C, 67.90; H, 5.70; N, 26.40.

3-Methyl-1-vinyl-1*H*-pyrido[4,3,2-*de*]cinnoline (6).



Yield 0.014 g (1.2%), mp 120-122ºC (*n*-hexane). IR (KBr), ν, cm^{-1}: 3091, 3055, 2953, 2920, 2853, 1623, 1580, 1505, 1463, 13486, 1324, 1248, 1176, 1059, 956, 900, 856, 821, 752, 682.

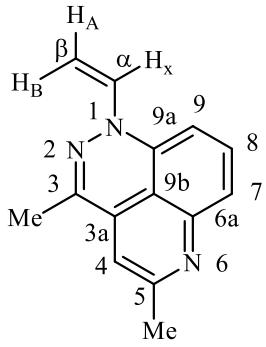
^{1}H NMR ($CDCl_3$), δ: 2.31 (s, 3H, Me), 4.80 (d, *J* 8.6 Hz, 1H, H_A), 5.56 (d, *J* 14.9 Hz, 1H, H_B), 6.70 (d, *J* 4.7 Hz, 1H, H-4), 6.75 (d, *J* 8.0 Hz, 1H, H-9), 7.04 (dd, *J* 8.6, 14.9 Hz, 1H, H_X), 7.46 (d, *J* 8.5 Hz, 1H, H-7), 7.58 (dd, *J* 8.0, 8.5 Hz, 1H, H-8), 8.70 (d, *J* 4.7 Hz, 1H, H-5).

^{13}C NMR ($CDCl_3$), δ: 18.7 (Me), 99.5 (C_β), 100.9 (C-9), 107.6 (C-4), 118.4 (C-7), 120.3 (C-9b), 130.9 (C-8), 131.80 (C-3), 131.83 (C_α), 135.9 (C-9a), 142.9 (C-3a), 149.2 (C-6a), 152.9 (C-5).

^{15}N NMR ($CDCl_3$), δ: – 209.8 (N^1), – 83.9 (N^6), – 64.2 (N^2).

MS, *m/z*: 209 $[M]^{+\bullet}$. Found (%): C, 74.83; H, 5.08; N, 20.09. Cacl. for $C_{13}H_{11}N_3$ (%): C, 74.62; H, 5.30; N, 20.08.

3,5-Dimethyl-1-vinyl-1*H*-pyrido[4,3,2-*de*]cinnoline (7).



Yield 0.007 g (0.5%), mp. 112-114 ºC (*n*-hexane), IR (KBr), ν, cm^{-1}:, 2923, 2855, 1738, 1702, 16230, 1595, 1518, 1463, 1361, 1331, 1284, 1255, 1176, 833, 756.

^{1}H NMR ($CDCl_3$), δ: 2.30 (s, 3H, 3-Me), 2.61 (s, 3H, 5-Me), 4.77 (d, *J* 8.7 Hz, 1H, H_A), 5.54 (d, *J* 14.8 Hz, 1H, H_B), 6.57 (s, 1H, H-4), 6.68 (d, *J* 8.3 Hz, 1H, H-9), 7.05 (dd, *J* 8.7, 14.8 Hz, 1H, H_X), 7.34 (d, *J* 8.4 Hz, 1H, H-7), 7.51 (dd, *J* 8.3, 8.4 Hz, 1H, H-8).

^{13}C NMR ($CDCl_3$), δ: 18.7 (3-Me), 25.7 (5-Me), 99.1 (C_β), 100.5 (C-9), 108.1 (C-4), 117.8 (C-7), 118.9 (C-9b), 131.0 (C-8), 131.9 (C_α), 132.0 (C-3a), 135.8 (C-9a), 142.8 (C-3), 148.9 (C-6a), 161.5 (C-5).

^{15}N NMR ($CDCl_3$), δ: – 211.2 (N^1), – 90.5 (N^6), – 64.9 (N^2).

MS, *m/z*: 223 $[M]^{+\bullet}$.