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Cyclocondensation of 1*H*-Indol-2-amine with Pentane-2,3,4-trione 3-Arylhydrazones

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Abstract—3-(Aryldiazenyl)-2,4-dimethyl-9*H*-pyrido[2,3-*b*]indoles were synthesized for the first time by cyclocondensation of 1*H*-indol-2-amine with pentane-2,3,4-trione 3-arylhydrazones.

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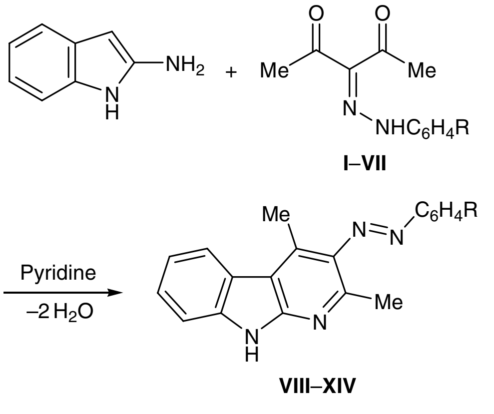
Insofar as both nitrogen atoms and carbon atom in position *3* are reactive centers in the 1*H*-indol-2-amine molecule, it reacts with β-diketones to give pyrido[2,3-*b*]indoles or pyrimido[1,2-*a*]indoles. The condensation direction strongly depends on the reaction conditions and initial reactants [1, 2]. Reactions of 1*H*-indol-2-amine with pentane-2,3,4-trione 3-arylhydrazones **I–VII** were not studied previously.

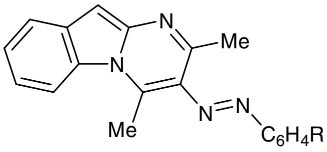
We have found that cyclocondensation of arylhydrazones **I–VII** with 1*H*-indol-2-amine occurs under mild conditions (room temperature) in pyridine. These reactions in 72 h lead to the formation of orange products that are poorly soluble in common organic solvents. The products were identified as 3-(aryldiazenyl)-2,4-dimethyl-9*H*-pyrido[2,3-*b*]indoles **VIII–XIV** whose yields ranged from 19 to 67% (Scheme 1). The product structure was confirmed by their elemental analyses and IR, ^{1}H NMR, and mass spectra. The elemental composition of **VIII–XIV** suggests that the condensation of hydrazones **I–VIII** with 1*H*-indol-2-amine is accompanied by elimination of two water molecules.

Scheme 1.



I, **VIII**, R = 2-Cl; **II**, **IX**, R = 2-Br; **III**, **X**, R = 2-I; **IV**, **XI**, R = 2-Me; **V**, **XII**, R = 3-NO$_2$; **VI**, **XIII**, R = 4-Br; **VII**, **XIV**, R = 4-COOEt.

The IR spectra of **VIII–XIII** lack absorption in the region 1640–1720 cm^{-1}, indicating that both carbonyl groups in initial arylhydrazones **I–VII** are involved in the condensation. The band at 1723 cm^{-1} in the IR spectrum of **XIV** was assigned to stretching vibrations of the ester carbonyl group. Compounds **VIII–XIV** displayed an absorption band in the region 3100–3380 cm^{-1} due to stretching vibrations of the NH group; the presence of this band confirms that compounds **VIII–XIV** have the structure of pyrido[2,3-*b*]indoles rather than pyrimido[1,2-*a*]indoles like **XV**.



XV

In the ^{1}H NMR spectra of **VIII–XIV** in trifluoroacetic acid we observed two singlets at δ 2.40–2.83 ppm from protons of the methyl groups and a multiplet in the region δ 6.80–8.36 ppm from the aromatic protons. No signal assignable to the 10-H proton of pyrimido[1,2-α]indole structure was present; according to published data, such signal is usually located in a stronger field, e.g., at δ 6.48 ppm for 8-chloro-2,3-dimethylpyrimido[1,2-*a*]indole [1].

The mass spectra of **VIII** and **X–XIV** contained the molecular ion peaks (*m*/*z* 334, 426, 314, 345, 378, and 373, respectively). The subsequent fragmentation of the molecular ions of **VIII** and **X–XIV** includes elimination of substituent from the aryl group and loss of the aryl group and nitrogen molecule to give a stable fragment ion with *m*/*z* 195. This ion was previously assigned the structure of 3,5-dimethylpyrido[2,3-*b*]-indolium [2]. Decomposition of the latter leads to ions with *m*/*z* 168 and 155 as a result of elimination of HCN and CH_2CN, respectively; and expulsion of methyl group leads to fragment ion with *m*/*z* 140.

EXPERIMENTAL

The ^1H NMR spectra were recorded from solutions in trifluoroacetic acid on a Bruker Avance DRX-200 spectrometer (200 Hz). The mass spectra were run on a Finnigan MAT-8200 instrument. The IR spectra were obtained on a Vector 22 spectrometer from samples prepared as KBr pellets.

Initial pentane-2,3,4-trione 3-arylhydrazones **I–VII** were synthesized according to the procedure described in [3].

3-Aryldiazenyl-2,4-dimethyl-9*H*-pyrido[2,3-*b*]-indoles VIII–XIV (*general procedure*)**.** A mixture of 0.2 g (1.5 mmol) of 1*H*-indol-2-amine, 1.5 mmol of arylhydrazone **I–VII**, and 3 ml of anhydrous pyridine was stirred for 72 h at 20°C. The orange precipitate was filtered off and washed with water (until the pyridine odor disappeared), 5 ml of alcohol, and 5 ml of diethyl ether.

3-(2-Chlorophenyldiazenyl)-2,4-dimethyl-9*H*-pyrido[2,3-*b*]indole (VIII). Yield 0.34 g (68%), mp 282–285°C. IR spectrum, ν, cm^{-1}: 3320–3180 (NH). ^1H NMR spectrum, δ, ppm: 2.52 s (3H, CH_3), 2.78 s (3H, CH_3), 6.87–7.81 m (8H, H_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): 334 (35) $[M]^+$, 299 (24), 223 (4), 195 (100), 179 (6), 168 (10), 155 (6), 140 (8), 127 (16), 111 (8), 75 (6). Found, %: C 67.74; H 4.73; Cl 10.60; N 16.31. $C_{19}H_{15}ClN_4$. Calculated, %: C 68.16; H 4.52; Cl 10.59; N 16.73.

3-(2-Bromophenyldiazenyl)-2,4-dimethyl-9*H*-pyrido[2,3-*b*]indole (IX). Yield 0.28 g (49%), mp 281–283°C. ^1H NMR spectrum, δ, ppm: 2.56 s (3H, CH_3), 2.81 s (3H, CH_3), 6.91–7.83 m (8H, H_{arom}). Found, %: C 60.50; H 4.47; Br 21.00; N 14.82. $C_{19}H_{15}BrN_4$. Calculated, %: C 60.17; H 3.99; Br 21.07; N 14.77.

3-(2-Iodophenyldiazenyl)-2,4-dimethyl-9*H*-pyrido[2,3-*b*]indole (X). Yield 0.29 g (45%), mp 282–284°C. IR spectrum, ν, cm^{-1}: 3300–3100 (NH). ^1H NMR spectrum, δ, ppm: 2.59 s (3H, CH_3), 2.83 s (3H, CH_3), 7.17–7.61 m (8H, H_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): 426 (30) $[M]^+$, 299 (26), 223 (7), 195 (100), 179 (6), 168 (8), 155 (6), 140 (8), 127 (11), 76 (11). Found, %: C 53.49; H 3.76; I 29.80; N 12.86. $C_{19}H_{15}IN_4$. Calculated, %: C 53.54; H 3.55; I 29.77; N 13.14.

2,4-Dimethyl-3-(2-methylphenyldiazenyl)-9*H*-pyrido[2,3-*b*]indole (XI). Yield 0.09 g (19%), mp 250°C. IR spectrum, ν, cm^{-1}: 3100–3293 (NH). ^1H NMR spectrum, δ, ppm: 2.23 s (3H, CH_3), 2.45 s (3H, CH_3), 2.71 s (3H, CH_3), 6.79–7.81 m (8H, H_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): 314 (52) $[M]^+$, 313 (12), 299 (8), 271 (4), 223 (4), 195 (100), 179 (5), 168 (8), 155 (6), 140 (5), 127 (10), 91(22), 65 (8). Found, %: C 75.94; H 6.05; N 17.35. $C_{20}H_{18}N_4$. Calculated, %: C 76.41; H 5.77; N 17.82.

2,4-Dimethyl-3-(3-nitrophenyldiazenyl)-9*H*-pyrido[2,3-*b*]indole (XII). Yield 0.26 g (50%), mp 291–294°C. IR spectrum, ν, cm^{-1}: 3312–3220 (NH). ^1H NMR spectrum, δ, ppm: 2.52 s (3H, CH_3), 2.78 s (3H, CH_3), 7.19–8.36 m (8H, H_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): 345 (17) $[M]^+$, 299 (8), 223 (6), 195 (100), 179 (6), 168 (9), 155 (7), 140 (5), 127 (10). Found, %: C 65.93; H 4.94; N 19.84. $C_{19}H_{15}N_5O_2$. Calculated, %: C 66.08; H 4.38; N 20.28.

3-(4-Bromophenyldiazenyl)-2,4-dimethyl-9*H*-pyrido[2,3-*b*]indole (XIII). Yield 0.29 g (51%), mp 294–297°C. IR spectrum, ν, cm^{-1}: 3380–3110 (NH). ^1H, δ, ppm: 2.40 s (3H, CH_3), 2.66 s (3H, CH_3), 7.19–7.90 m (8H, H_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): 378 (24) $[M]^+$, 377 (8), 299 (15), 223 (4), 195 (100), 179 (7), 168 (9), 155 (16), 140 (7), 127 (12), 76 (7). Found, %: C 59.70; H 4.15; Br 21.4; N 14.42. $C_{19}H_{15}BrN_4$. Calculated, %: C 60.17; H 3.99; Br 21.07; N 14.77.

Ethyl 4-(2,4-dimethyl-9*H*-pyrido[2,3-*b*]indol-3-yldiazenyl)benzoate (XIV). Yield 0.27 g (48%), mp 258–262°C. IR spectrum, ν, cm^{-1}: 1723 (C=O), 3100–3300 (NH). ^1H NMR spectrum, δ, ppm: 0.99 t (3H, CH_3), 2.48 s (3H, CH_3), 2.74 s (3H, CH_3), 4.02–4.06 q (2H, CH_2), 7.13–7.82 m (8H, H_{arom}). Mass spectrum, m/z (I_{rel}, %): 372 (35) $[M]^+$, 343 (8), 327 (3), 299 (15), 223 (3), 195 (100), 179 (4), 168 (7), 155 (6), 140 (4), 127 (4), 76 (3). Found, %: C 71.23; H 6.04; N 15.38. $C_{22}H_{20}N_4O_2$. Calculated, %: C 70.95; H 5.41; N 15.04.

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