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# SYNTHESIS OF PYRROLO[c]- AND PYRROLO[i]PHENANTHRIDINES

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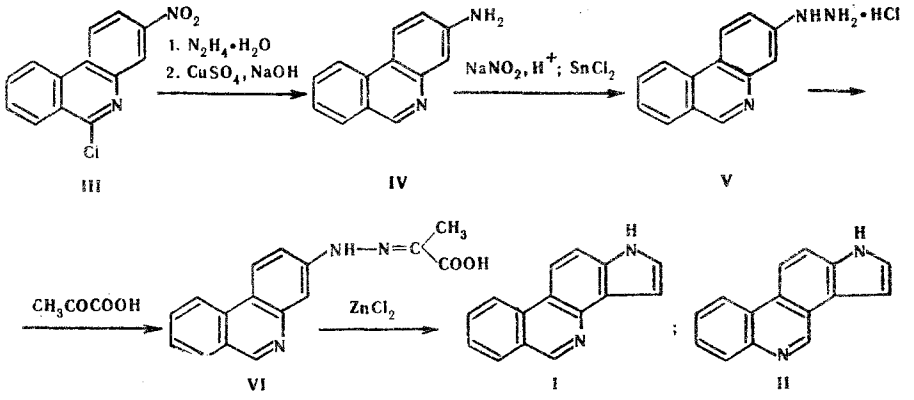
We have synthesized the previously unknown 1H-pyrrolo[2,3-c]- and 1H-pyrrolo[3,2-i]-phenanthridines (I and II), which are analogs of benzophenanthridine alkaloids [1].

The previously undescribed 3-aminophenanthridine (IV), with mp 139-140°C, was synthesized in 40% yield from 3-nitro-6-chlorophenanthridine (III) [2] by the action of hydrazine hydrate with subsequent decomposition of the intermediately formed hydrazine with aqueous $CuSO_4$ solution [3]. The structure of the amine obtained was confirmed by IR, UV, and PMR spectroscopy and mass spectrometry.




Diazotization of amine IV with subsequent reduction yielded 3-phenanthridylhydrazine hydrochloride (V), which gave the corresponding hydrazone VI on treatment with pyruvic acid. Cyclization of hydrazone VI by fusing with anhydrous $ZnCl_2$ [4] led to I, with mp 271-272°C, in 15% yield. PMR spectrum (in DMSO): 11.82 (broad s), 9.84 (s), 8.51 (dd), 8.03 (dd), 7.65 (dd), and 7.36 ppm (m); $J_{AB} \approx 8.8$ Hz. UV spectrum (in alcohol), $\lambda_{max}$ (log $\varepsilon$): 215 (4.69), 261 (4.79), 337 (4.22), 352 (4.19), and 370 nm (4.20). Mass spectrum: $M^+$ 218.

Pyrrolophenanthridine II, with mp 267-268°C, was also obtained from a mixture of pyruvic acid 3- and 8-phenanthridylhydrazones, synthesized by a similar method from a mixture of 3-nitro-6-chloro- and 8-nitro-6-chlorophenanthridines (products of the Beckmann rearrangement of stereoisomeric 2-nitrofluorenone oximes [2]), by cyclization with $ZnCl_2$. PMR spectrum (in DMSO): 11.63 (broad s), 9.39 (s), 8.46 (dd), 7.82 (dd), 7.52 (dd), and 7.18 ppm (m); $J_{AB} \approx 8.8$ Hz. UV spectrum (in alcohol), $\lambda_{max}$ (log $\varepsilon$): 208 (4.56), 220 (4.55), 240 (4.82), 254 (4.69), 275 (4.54), and 345 nm (4.08). Mass spectrum: $M^+$ 218.

The results of elementary analysis of the compound obtained were in agreement with the calculated values.

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# RING-CHAIN TAUTOMERISM OF 1-BENZOYL-2-BENZYL-5-HYDROXYPYRAZOLIDINE

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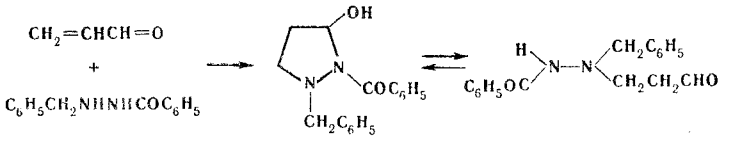
UDC 547.772.2'774'775'234.23:543.422:541.623

We have found that the product of the reaction of 1-benzoyl-2-benzylhydrazine with acrolein in nonpolar solvents ($CCl_4$, $CDCl_3$) has the cyclic 1-benzoyl-2-benzyl-5-hydroxypyrazolidine structure (A). The product was isolated in 80% yield and had mp 107°C and $R_f$ 0.53 [activity II $Al_2O_3$, chloroform–methanol (50:1)]. Found: C 72.5; H 6.6; N 10.0%. $C_{17}H_{18}N_2O_2$. Calculated: C 72.3; H 6.4; N 9.9%. The IR spectrum of the product does not contain a band of vibrations of an aldehyde carbonyl group at 1700-1720 $cm^{-1}$ but does contain a band of OH absorption at 3340 $cm^{-1}$ and a band of "amide" carbonyl absorption at 1650 $cm^{-1}$. $^{13}C$ NMR spectrum (CFT-20, $CDCl_3$): 168.2 (s, C=O), 82.4 [d, J = 164 Hz, $C_{(5)}$], 61.7 (t, J = 142 Hz, $CH_2Ph$), 50.4 [t, J = 148 Hz, $C_{(3)}$], and 31.8 ppm [t, J = 136 Hz, $C_{(4)}$].* The carbon atoms of the aromatic rings give a group of signals at 127-136 ppm.

The same compound exists partially (∼10%) in linear tautomeric form B in polar solvents ($d_6$-DMSO, $CD_3OD$).




A B

The existence of the B form is proved by the appearance of an additional band of vibrations of an aldehyde carbonyl group at 1710 $cm^{-1}$, as well as by a set of signals corresponding to a linear structure in the PMR spectrum. PMR spectrum (Bruker WP-200, $d_6$-DMSO), δ: form A: 2.70-3.10 (4H, m, 3- and 4-H), 3.50 (AB system, J = 22 Hz, $CH_2Ph$), 5.85 (1H, broad s, OH), 6.40 (1H, m, 5-H), and 6.90-7.70 (10H, m, aromatic protons); form B: 2.55 (2H, dt, $J_1$ = 6 Hz, $J_2$ = 1.5 Hz, $COCH_2$), 3.22 (2H, t, J = 6 Hz, $CH_2N$), 4.08 (2H, s, $CH_2Ph$), 6.90-7.70 (10H, m, aromatic protons), 9.52 (1H, broad s, NH), and 9.68 ppm (1H, t, J = 1.5 Hz, CHO).

This is the first known example of tautomerism of a β-hydrazino carbonyl compound, viz., 5-hydroxypyrazolidine (A ⇄ B).

*Compare with the data presented by I. P. Bezhan, K. N. Zelenin, and V. V. Pinson in Zh. Org. Khim., 18, 493 (1982).

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