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NEW HETEROCYCLIC SYSTEM — PYRIDAZINO[3,4-*c*]CINNOLINE

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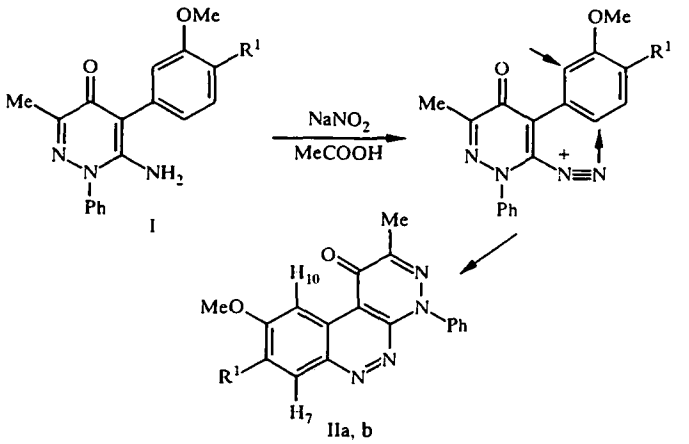
1,5-Diaryl-6-hydroxy-3-methyl-4-pyridazinones are formed upon the diazotization of 6-amino-5-aryl-3-methyl-1-phenyl-4-pyridazinones (I) using sodium nitrite in acetic acid with subsequent treatment of the reaction mixture with water [1].

The introduction of electron-donor groups in the *meta* position of the 5-phenyl ring facilitates intramolecular azocoupling of the diazonium salt formed in the first step, which leads to closure of the cinnoline ring and formation of a new heterocyclic system, namely, pyridazino[3,4-*c*]cinnoline (II).



I. II a R^1 = H, b R^1 = OMe

Of the two possible directions of electrophilic attack, only the attack leading to products IIa and IIb occurs. The finding of downfield singlets at 9.04 ppm for 10-H and 7.89 ppm for 7-H in the case of IIb and doublets at 9.11 ppm for 10-H (J_{10}^8 = 2.5 Hz) and 8.51 ppm for 7-H (J_7^8 = 9 Hz) in the case of IIa is unequivocal evidence supporting this conclusion.

2-Methyl-9-methoxy-4-phenyl-1(4H)-oxopyridazino[3,4-*c*]cinnoline (IIa) was obtained in 85% yield, mp 222°C (from DMF), R_f 0.66 (9:1 chloroform–methanol on Silufol UV-254). IR spectrum (KBr): 3100-3020 (=C–H), 2980-2920 (–CH_3), 1610-1590 cm^{-1} (O=C=C–C=C–N=N–). PMR spectrum at 100 MHz in DMSO-d_6: 2.41 (3H, s, CH_3), 4.04 (3H, s, CH_3O), 7.3-7.8 (6H, m, Ph and 8-H), 8.51 (1H, d, J_7^8 = 9 Hz, 7-H), 9.11 ppm (1H, d, J_{10}^8 = 2.5 Hz, 10-H). Found: N, 17.6%. Calculated for $C_{18}H_{14}N_4O_2$: N, 17.6%.

2-Methyl-8,9-dimethoxy-4-phenyl-1(4H)-oxopyridazino[3,4-*c*]cinnoline (IIb) was obtained in 87% yield, mp 284°C (from DMF), R_f 0.59 (9:1 chloroform–methanol on Silufol UV-254). IR spectrum (KBr): 3120-3040 (=C–H), 2980-2920 (–CH_3), 1610-1595 cm^{-1} (O=C=C–C=C–N=N–). PMR spectrum at 100 MHz in DMSO-d_6: 2.39 (3H, s, CH_3), 4.03 (6H, s, $2CH_3O$), 7.55-7.75 (6H, m, Ph and 8-H), 7.89 (1H, s, 7-H), 9.04 ppm (1-H, s, 10-H). Found: N, 16.2%. Calculated for $C_{19}H_{16}N_4O_3$: N, 16.1%.

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