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THE REACTION OF 3,5-DICHLORO-PYRID-2-YLHYDRAZINE WITH 2-CHLORO-3',4'-DIHYDROXYACETOPHENONE

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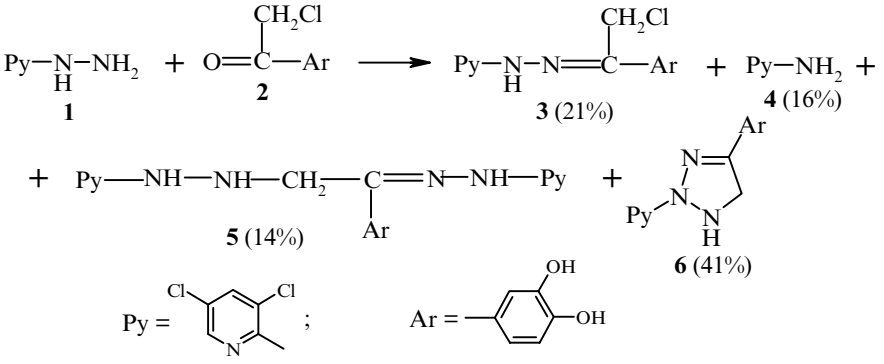
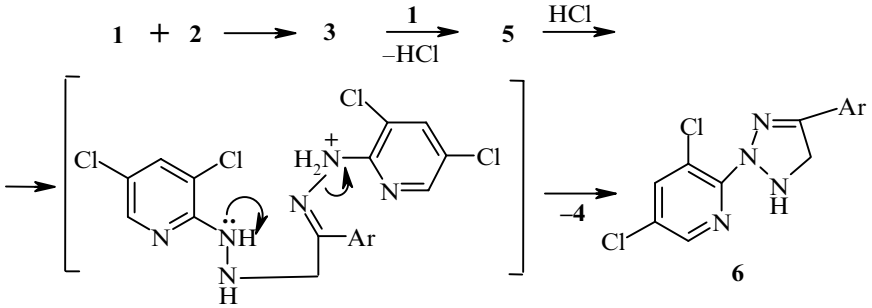
While studying the reaction of 3,5-dichloropyrid-2-ylhydrazine (**1**) with various aldehydes and ketones with the aim of synthesizing hetaryl-substituted hydrazones – synthons for the preparation of polyheterocyclic compounds [1] – we established that, according to chromato-mass spectrometric data, in the case of 2-chloro-3',4'-dihydroxyacetophenone (**2**) three different compounds, which we isolated by HPLC, were formed along with the desired hydrazone **3**.



The following scheme may be proposed for the formation of these compounds:



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2-Chloro-3',4'-dihydroxyacetophenone N-(3,5-Dichloropyrid-2-yl)hydrazone (3). Yield 21%; mp 278-280°C (dec.). IR spectrum (KBr), ν, cm^{-1}: 1628 (C≡N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, *J* (Hz): 3.30 (2H, s, CH_2Cl); 5.64 (2H, br. s, OH); 7.05 (1H, m, J_{AC} = 2.4, H_C); 7.28 (1H, m, J_{BC} = 7.6, H_B); 7.33 (1H, m, J_{AB} = 0.2, H_A); 7.82-7.88 (2H, m, 4-H and 6-H of pyridine); 8.32 (1H, br. s, NH). Mass spectrum, *m/z* (I_{rel}, %): 345 (M^+, 18), 310 (18), 161 (100). Found, %: C 44.95; H 2.90; N 12.18. $C_{13}H_{10}Cl_3N_3O_2$. Calculated, %: C 45.05; H 2.91; N 12.12.

2-Amino-3,5-dichloropyridine (4). Yield 16%; mp 78-79.5°C (lit. mp 81-83°C [2]). Mass spectrum, *m/z* (I_{rel}, %): 162 (M^+, 100).

ω-[N^1-(3,5-dichloropyrid-2-yl)hydrazino]-3,4-dihydroxyacetophenone N-(3,5-Dichloropyrid-2-yl)-hydrazone (5). Yield 14%; mp 184-186°C. IR spectrum (KBr), ν, cm^{-1}: 1645 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, *J* (Hz): 3.84 (2H, m, CH_2); 5.20 (2H, br. s, OH); 6.04-6.10 (2H, br. s, NH); 8.20 (1H, br. s, NH); 7.00 (1H, m, J_{AC} = 3.0, H_C); 7.16 (1H, m, J_{BC} = 8.2, H_B); 7.44 (1H, m, J_{AB} = 0.2, H_A); 7.62-7.84 (4H, m, H_{arom}). Mass spectrum , *m/z* (I_{rel}, %): 486 (M^+, 5), 451 (24), 416 (100). Found, %: C 44.18; H 2.80; N 17.11. $C_{18}H_{14}Cl_4N_6O_2$. Calculated, %: C 44.29; H 2.89; N 17.22.

2-(3,5-Dichloropyrid-2-yl)-4-(3,4-dihydroxyphenyl)-1H-Δ^3-1,2,3-triazoline (6). Yield 41%; mp 252°C (dec.). UV spectrum (EtOH), λ_{max}, nm (log ε): 254 (3.9), 292 (4.2), 335 (4.12), 380 (4.02). IR spectrum (KBr), ν, cm^{-1}: 3330 (NH), 1605 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, *J* (Hz): 2.86 (1H, unsym. d, J_{AB} = 18.0, $H_{A'}$ or $H_{B'}$ of triazoline); 3.34 (1H, unsym. d, J_{AB} = 18.0, $H_{B'}$ or $H_{A'}$ of triazoline); 5.34 (2H, br. s, OH); 6.28 (1H, br. s, NH); 7.08 (1H, m, J_{AC} = 2.3, H_C); 7.24 (1H, m, J_{BC} = 9.0, H_B); 7.32 (1H, m, J_{AB} = 0.3, J_{AC} = 2.3, H_A); 7.74-7.80 (2H, m, 4-H and 6-H of pyridine). Mass spectrum , *m/z* (I_{rel}, %): 324 (M^+, 8.5), 296 (74), 289 (22), 261 (25). Found, %: C 47.85; H 3.14; N 17.21. $C_{13}H_{10}Cl_2N_4O_2$. Calculated, %: C 48.02; H 3.10; N 17.23.

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