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SYNTHESIS OF NOVEL 3,5-DIAMINO-4-(2-CYANO-ARYLAZO)PYRAZOLES

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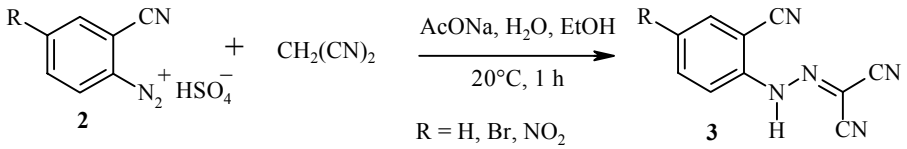
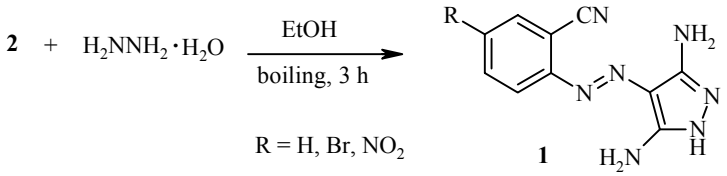
We have synthesized for the first time 3,5-diamino-4-(2-cyanoarylazo)pyrazoles **1**, containing an azo and a cyano group in the 1 and 2 positions of the benzene ring, and a bromine atom or a nitro group in the 4 position. Such compounds may be valuable starting materials in syntheses of compounds in aromatic and heterocyclic series.

With the objective of obtaining starting materials for compounds **1**, the 2-cyanoaryldiazonium bisulfates **2**, obtained by treatment of 3-hydrazones of isatin and its 5-bromo- or 5-nitro derivative with nitrosylsulfuric acid [1], underwent *in situ* a condensation reaction with malonic acid dinitrile. (2-Cyanoaryl)hydrazones of mesoxalic acid dinitrile **3** were obtained in 67%-84% yields.



Hydrazones **3** easily enter into the cyclocondensation reaction with hydrazine hydrate, and lead to 3,5-diamino-4-(2-cyanoarylazo)pyrazoles **1** in 54.5%-78% yields.



(2-Cyanophenyl)hydrazone of Mesoxalic Acid Dinitrile (3) (R = H). A suspension of 2-cyanophenyldiazonium bisulfate **2** (R = H), obtained from isatin 3-hydrazone (1 g, 0.0062 mol) [1], was poured over a mixture of water (50 ml) and ice (50 g). A solution of malonic acid dinitrile (0.41 g, 0.0063 mol) in alcohol (10 ml) was added to the mixture formed with stirring and cooling with ice; while stirring was continued, a solution of sodium acetate (10 g) in water (50 ml) was added. The reaction mixture was stirred for

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1.5 h at room temperature, water (150 ml) was added, and it was heated on a water bath at 50°C for 15 min and then cooled down to room temperature. The precipitate was washed on the filter with water, dried in air, and recrystallized from a water–DMF mixture. Yield 0.92 g (76%); mp 162-163°C. IR spectrum (KBr), ν, cm^{-1}: 2232 (CN), 1621 (C=N), 3270 (N–H). UV spectrum (EtOH), λ_{max}, nm (log ε): 203.2 (2.09), 216.8 (1.94) (inflection point), 257.6 (1.83), 319.2 (1.59) (inflection point), 350.4 (1.65), 398.4 (1.57 (inflection point). Found, %: C 62.01; H 2.37; N 36.31. $C_{10}H_5N_5$. Calculated, %: C 61.53; H 2.58; N 35.88.

Other hydrazones **3** were obtained similarly from the corresponding bisulfates **2** and malonic acid dinitrile.

(4-Bromo-2-cyanophenyl)hydrazone of Mesoxalic Acid Dinitrile (3) (R = Br). Yield 83.8%; mp 175-176°C (H_2O–DMF). IR spectrum (KBr), ν, cm^{-1}: 2240 (CN), 1615 (C=N), 3240 (N–H). UV spectrum (EtOH), λ_{max}, nm (log ε): 205.6 (1.91), 216.0 (1.83) (inflection point), 268.0 (1.56), 348.0 (1.45), 403.2 (1.56). Found, %: C 43.29; H 1.43; N 26.17. $C_{10}H_4BrN_5$. Calculated, %: C 43.82; H 1.47; N 25.68.

(2-Cyano-4-nitrophenyl)hydrazone of Mesoxalic Acid Dinitrile (3) (R = NO_2). Yield 66.9%; mp 201-202°C (H_2O–DMF). IR spectrum (KBr), ν, cm^{-1}: 2182 (CN), 1628 (C=N), 3240 (N–H), 1564, 1368 (NO_2). UV spectrum (EtOH), λ_{max}, nm (log ε): 203.2 (2.03), 221.6 (1.94), 263.2 (1.61), 320.8 (1.79). Found, %: C 50.13; H 1.87; N 35.27. $C_{10}H_4N_6O_2$. Calculated, %: C 50.00; H 1.68; N 34.89.

3,5-Diamino-4-(2-cyanophenyl)azopyrazole (1) (R = H). Hydrazine hydrate (1 ml, 0.02 mol) was added to hydrazone **3** (R = H) (0.78 g, 0.004 mol) in alcohol (30 ml). The mixture was boiled for 3 h; most of the liquid was driven off under vacuum. The residue was filtered off, washed on the filter with alcohol, dried in air, and recrystallized from propanol. Yield 0.496 g (54.5%); mp 165-167°C. IR spectrum (KBr), ν, cm^{-1}: 2222 (CN), 1414 (N=N), for NH_2, 3436 (N–H), 1658 (C–N), 3360 (N–H). UV spectrum (EtOH), λ_{max}, nm (log ε): 207.2 (2.00), 228.0 (1.70) (inflection point), 271.2 (1.81), 327.2 (1.81), 377.6 (1.51). Found, %: C 52.37; H 3.96; N 42.78. $C_{10}H_9N_7$. Calculated, %: C 52.87; H 3.99; N 43.17.

Other compounds **1** were obtained similarly from the corresponding **3** and hydrazine hydrate.

4-(4-Bromo-2-cyanophenyl)azo-3,5-diaminopyrazole (1) (R = Br). Yield 65.4%; mp 195-196°C (propanol). IR spectrum (KBr), ν, cm^{-1}: 2220 (CN), 1412 (N=N), for NH_2, 3488 (N–H), 1636 (C–N), 3312 (N–H). UV spectrum (EtOH), λ_{max}, nm (log ε): 208.0 (2.12), 232.2 (1.316) (inflection point), 276.2 (1.77), 328.8 (1.57), 400.8 (1.63). Found, %: C 39.29; H 2.41; N 32.43. $C_{10}H_8BrN_7$. Calculated, %: C 39.29; H 2.41; N 32.41.

4-(2-Cyano-4-nitrophenyl)azo-3,5-diaminopyrazole (1) (R = NO_2). Yield 78%; mp 235-237°C (propanol). IR spectrum (KBr), ν, cm^{-1}: 2228 (CN), 1426 (N=N), for NH_2, 3360 (N–H), 1626 (C–N), 3312 (N–H), 1520, 1370 (NO_2). UV spectrum (EtOH), λ_{max}, nm (log ε): 203.2 (2.03), 223.2 (2.04), 261.6 (1.81), 323.2 (2.05). Found, %: C 44.13; H 2.87; N 40.61. $C_{10}H_8N_8O_2$. Calculated, %: C 44.12; H 2.96; N 41.16.

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