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TRANSFORMATIONS OF 5-AMINO-4-(3,4-DIMETHOXYPHENYL)PYRAZOLES IN THE DIAZOTIZATION REACTION

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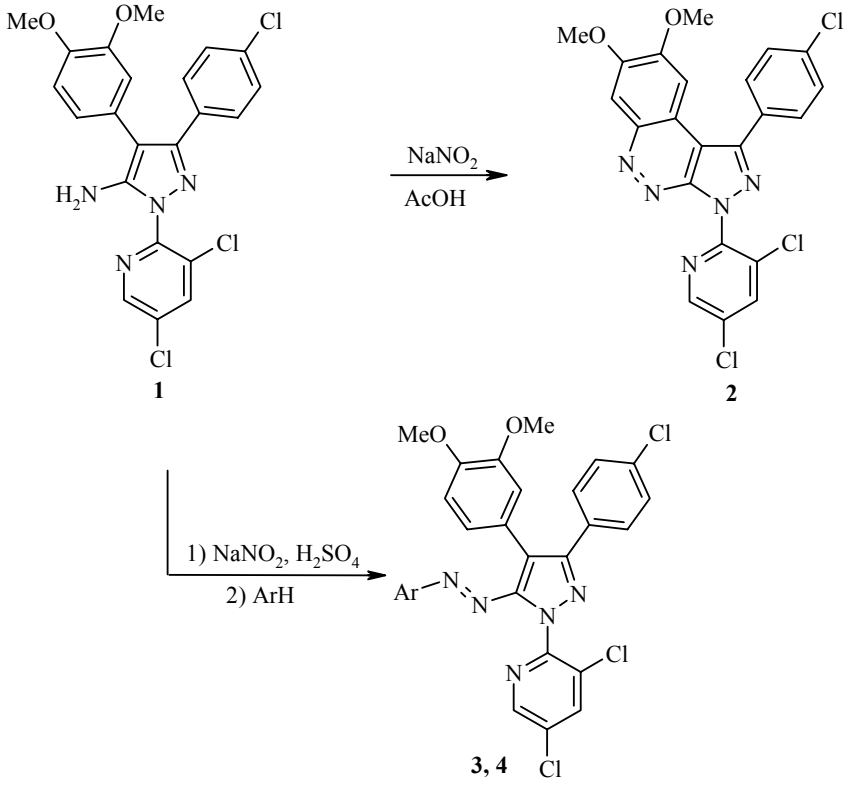
Diazotization reactions of 5-aminopyrazoles, leading to pyrazolyl-5-diazonium salts, are described in the literature [1, 2]. In the case of aminopyrazoles having a 3,4-dimethyloxyphenyl substituent in the position 4 that readily undergoes electrophilic attack, the reaction does not stop at the diazotization step. Upon nitrosation by sodium nitrite in acetic acid, the diazo compound formed as an intermediate undergoes intramolecular azo coupling to form 1,3-disubstituted 7,8-dimethoxypyrazolo[3,4-*c*]cinnolines [3].



3 Ar = 2-hydroxynaphthyl, **4** Ar = *p*-$Me_2NC_6H_4$

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We have established that aminopyrazoles containing the indicated substituent in the position 4, depending on the diazotization reaction conditions, can be converted to either the corresponding cinnoline **2** or to the stable azo compounds **3, 4**. The azo compounds obtained are used for synthesis of hetaryl-substituted azo dyes capable of dying textiles made from natural and synthetic fibers under standard conditions, thereby ensuring high stability parameters of the dyed material relative to washing, dry and wet friction.

1-(4-Chlorophenyl)-3-(3,5-dichloropyridin-2-yl)-7,8-dimethoxy-3H-pyrazolo[3,4-*c*]cinnoline (2). Yield 31%; mp 245-247°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 3.90 (3H, s, OMe); 4.07 (3H, s, OMe); 7.52 (1H, s); 7.75 (2H, d, *J* = 9.6); 8.03 (2H, d, *J* = 9.6); 8.10 (1H, s); 8.75 (1H, d, *J* = 2.8); 8.85 (1H, d, *J* = 2.8). Found, %: C 54.22; H 2.95; N 14.36. $C_{22}H_{14}Cl_3N_5O_2$. Calculated, %: C 54.29; H 2.90; N 14.39.

(*E*)-1-{[3-(4-Chlorophenyl)-1-(3,5-dichloropyridin-2-yl)-4-(3,4-dimethoxyphenyl)]-1H-pyrazol-5-yldiazenyl}naphth-2-ol (3). Yield 70%; mp 170-172°C. UV spectrum (EtOH), λ_{max}, nm (log ε): 349 (3.96), 387 (4.0), 438 (4.0), 456 (4.0), 494 (4.0). Found, %: C 54.22; H 2.95; N 14.36. $C_{22}H_{14}C_3N_5O_2$. Calculated, %: C 54.29; H 2.90; N 14.39.

(*E*)-4-{[3-(4-Chlorophenyl)-1-(3,5-dichloropyridin-2-yl)-4-(3,4-dimethoxyphenyl)]-1H-pyrazol-5-yldiazenyl}-N,N-dimethylaniline (4). Yield 62%; mp 185-186°C (decomp.). UV spectrum (EtOH), λ_{max}, nm (log ε): 237 (4.79), 316 (3.64), 363 (3.78), 443 (3.92), 482 (3.88). Found, %: C 59.22; H 4.22; N 13.76. $C_{30}H_{25}Cl_3N_6O_2$. Calculated, %: C 59.27; H 4.15; N 13.82.

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