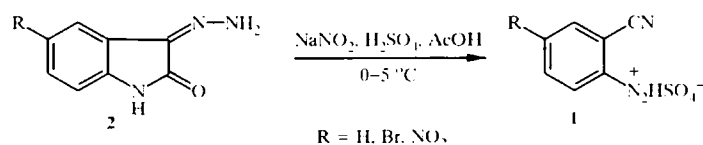


A NEW APPROACH TO THE SYNTHESIS OF 4-ARYLHYDRAZONES OF 1-ARYL- 3-METHYLPYRAZOLE-4,5-DIONES

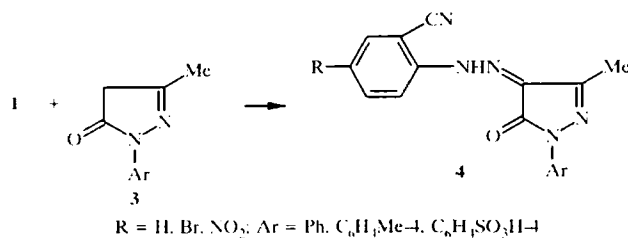
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4-Arylhydrazones of 1-aryl-3-methylpyrazole-4,5-diones are usually obtained by coupling 1-aryl-3-methyl-5-pyrazolones with aryldiazonium salts [1]. The common method for the synthesis of the latter is the diazotization of primary aromatic amines. This method is often restricted by the multistage and complicated syntheses of the initial amines ArNH_2 . This applies in particular to the derivatives of aniline containing a CN group at the *ortho* position and particularly with other substituents. We showed that the reaction of the readily obtainable hydrazones **2** with nitrosylsulfuric acid in acetic acid can be used for the production of such aryldiazonium salts **1** [2]:



Salts **1** were brought *in situ* into coupling with the 5-pyrazolone derivatives **3**; in this way high yields of the previously undescribed compounds **4** were obtained.



3-Methyl-1-phenylpyrazole-4,5-dione 4-(2-Cyanophenyl)hydrazone (4) (R = H, Ar = Ph). A solution of 3-methyl-1-phenyl-5-pyrazolone (1.1 g, 0.0063 mol) in alcohol (10 ml), cooled to 5°C, was gradually added to salt **1** (R = H) [2] with stirring at room temperature. The mixture was stirred for 1 h. The precipitate was filtered off, washed three times with water, and recrystallized from alcohol-DMF mixture. Yield 0.8 g (42.6%); mp 226°C. IR spectrum (KBr), ν , cm^{-1} : 2220 (CN), 1610 (N=N=C), 1720 (CO) UV spectrum, λ_{max} (log ϵ), nm: 205.6 (1.92), 247.6 (1.94), 380.8 (1.91). Found, %: C 67.14; H 4.21; N 22.71. $\text{C}_{17}\text{H}_{11}\text{N}_3\text{O}$. Calculated, %: C 67.31; H 4.32; N 23.09.

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The other compounds **4** were obtained similarly from the corresponding compounds **1** and **3**.

3-Methyl-1-phenylpyrazole-4,5-dione 4-(4-Bromo-2-cyanophenyl)hydrazone (4) (R = Br, Ar = Ph). Yield 50.6%; mp 232°C (alcohol–DMF). IR spectrum (KBr), ν , cm^{-1} : 2224 (CN), 1625 (N=N=C), 1720 (CO). UV spectrum, λ_{max} (log ϵ), nm: 206 (1.78), 246.8 (1.72), 385.6 (1.73). Found, %: C 53.12; H 3.16; N 18.32. $\text{C}_{17}\text{H}_{12}\text{BrN}_4\text{O}$. Calculated, %: C 53.42; H 3.16; N 18.32.

3-Methyl-1-phenylpyrazole-4,5-dione 4-(2-Cyanophenyl-4-nitro)hydrazone (4) (R = NO₂, Ar = Ph). Yield 69.4%; mp 275°C (alcohol–DMF). IR spectrum (KBr), ν , cm^{-1} : 2228 (CN), 1615 (N=N=C), 1735 (CO), 1365, 1540 (NO₂). UV spectrum, λ_{max} (log ϵ), nm: 204.4 (1.59), 246.4 (1.58), 393.6 (1.59). Found, %: C 59.03; H 3.15; N 23.78. $\text{C}_{17}\text{H}_{12}\text{N}_6\text{O}_3$. Calculated, %: C 58.62; H 3.47; N 24.13.

3-Methyl-1-(*p*-tolyl)pyrazole-4,5-dione 4-(2-Cyanophenyl)hydrazone (4) (R = H, Ar = 4-MeC₆H₄). Yield 86.3%; mp 234°C (alcohol–DMF). IR spectrum (KBr), ν , cm^{-1} : 2230 (CN), 1605 (N=N=C), 1670 (CO). UV spectrum, λ_{max} (log ϵ), nm: 205.6 (1.84), 246.8 (1.76), 381.2 (1.69). Found, %: C 69.38; H 4.48; N 22.34. $\text{C}_{18}\text{H}_{15}\text{N}_4\text{O}$. Calculated, %: C 68.12; H 4.76; N 22.07.

3-Methyl-1-(*p*-tolyl)pyrazole-4,5-dione 4-(4-Bromo-2-cyanophenyl)hydrazone (4) (R = Br, Ar = 4-MeC₆H₄). Yield 93.5%; mp 243°C (alcohol–DMF). IR spectrum (KBr), ν , cm^{-1} : 2232 (CN), 1620 (N=N=), 1660 (CO). UV spectrum, λ_{max} (log ϵ), nm: 208.8 (1.84), 247.2 (1.78), 385.2 (1.64). Found, %: C 54.18; H 3.42; N 17.18. $\text{C}_{18}\text{H}_{14}\text{N}_4\text{O}$. Calculated, %: C 54.56; H 3.56; N 17.67.

3-Methyl-1-(*p*-tolyl)pyrazole-4,5-dione 4-(2-Cyano-4-nitrophenyl)hydrazone (4) (R = NO₂, Ar = 4-MeC₆H₄). Yield 83.3%; mp 280°C (alcohol–DMF). IR spectrum (KBr), ν , cm^{-1} : 2234 (CN), 1620 (N=N=), 1705 (CO), 1340, 1515 (NO₂). UV spectrum, λ_{max} (log ϵ), nm: 206.0 (1.73), 244.4 (1.68), 394.2 (1.28). Found, %: C 59.54; H 4.25; N 23.47. $\text{C}_{18}\text{H}_{14}\text{N}_6\text{O}_3$. Calculated, %: C 59.66; H 3.89; N 23.19.

3-Methyl-1-(*p*-sulfohenyl)pyrazole-4,5-dione 4-(2-Cyanophenyl)hydrazone (4) (R = H, Ar = 4-HO₃SC₆H₄). Yield 63%; mp 331°C (water). IR spectrum (KBr), ν , cm^{-1} : 2230 (CN), 1605 (N=N=), 1665 (CO), 1345, 1120 (SO₂OH). UV spectrum, λ_{max} (log ϵ), nm: 205.2 (1.84), 250.0 (1.55), 385.6 (1.62). Found, %: C 53.12; H 3.42; N 18.01. $\text{C}_{17}\text{H}_{11}\text{N}_4\text{O}_4\text{S}$. Calculated, %: C 53.25; H 3.42; N 18.36.

3-Methyl-1-(*p*-sulfohenyl)pyrazole-4,5-dione 4-(4-Bromo-2-cyanophenyl)hydrazone (4) (R = Br, Ar = 4-HO₃SC₆H₄). Yield 73.9%; mp 341°C (alcohol–water). IR spectrum (KBr), ν , cm^{-1} : 2240 (CN), 1615 (N=N=), 1665 (CO), 1335, 1115 (SO₂OH). UV spectrum, λ_{max} (log ϵ), nm: 206.8 (1.67), 250.4 (1.28), 394.0 (1.39). Found, %: C 44.37; H 2.42; N 15.48. $\text{C}_{17}\text{H}_{11}\text{BrN}_4\text{O}_4\text{S}$. Calculated, %: C 44.16; H 2.61; N 15.15.

3-Methyl-1-(*p*-sulfohenyl)pyrazole-4,5-dione 4-(2-Cyano-4-nitrophenyl)hydrazone (4) (R = NO₂, Ar = 4-HO₃SC₆H₄). Yield 71.6%; mp 369°C (alcohol–water). IR spectrum (KBr), ν , cm^{-1} : 2235 (CN), 1625 (N=N=), 1660 (CO), 1330, 1125 (SO₂OH), 1370, 1520 (NO₂). UV spectrum, λ_{max} (log ϵ), nm: 205.2 (1.76), 301.2 (1.41), 400.0 (0.91). Found, %: C 47.28; H 2.98; N 19.09. $\text{C}_{17}\text{H}_{11}\text{N}_6\text{O}_6\text{S}$. Calculated, %: C 47.66; H 2.82; N 19.61.

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