SYNTHESIS OF 3- AND 5-HYDRAZINO-1-METHYL-4-NITROPYRAZOLES

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5-Halo-1-methyl-4-nitropyrazoles enter into a nucleophilic substitution reaction in relatively soft conditions [1, 2]; the mobility of the nitro group in position 3 of the pyrazole ring in 3,4-dinitropyrazoles in ammonolysis was also demonstrated [3].

In continuing the study of nucleophilic substitution reactions in the pyrazole series, we conducted the reaction of 5bromo-1,3-dimethyl-4-nitropyrazole (I) [1] and 1,5-dimethyl-3,4-dinitropyrazole (II) [4] with hydrazine hydrate in boiling in isopropyl alcohol and 5-hydrazino-1,3-dimethyl- (III) and 3-hydrazino-1,5-dimethyl-4-nitropyrazoles (IV), respectively, were obtained.



The UV spectra were made on a Specord M-400 spectrophotometer in ethanol; the PMR spectra were recorded on a Bruker CXP-200 (200 MHz) in DMSO-D₆ with HMDS internal standard. The evolution of the reaction and purity of the compounds obtained were controlled by TLC on Silufol UV-254 plates in chloroform—ethanol system, 10:1.

5-Hydrazino-1,3-dimethyl-4-nitropyrazole (III, $C_5H_9N_5O_2$). Here 1.5 ml (0.03 mole) of hydrazine hydrate was added to a solution of 2.20 g (0.01 mole) of I in 10 ml of isopropyl alcohol, and the mixture was boiled until the reaction ended (TLC control). After cooling, the bright yellow crystals were filtered off, washed with a small amount of isopropyl alcohol, and dried, yielding 1.57 g (92%) of compound III. mp = 175-176°C (from isopropanol). PMR spectrum: 2.26 (3H, s, 3-CH₃); 3.89 (3H, s, 1-CH₃); 4.74 (2H, s, NH₂); 8.33 ppm (1H, s, NH). UV spectrum, λ_{max} (log ε): 283 (3.64), 350 nm (3.748). Found, %: C 35.3; H 5.2; N 40.6. Calculated, %: C 35.1; H 5.3; N 40.9.

5-Hydrazino-1,5-dimethyl-4-nitropyrazole (IV, $C_5H_9N_5O_2$). Similarly, 1.52 g (89%) of compound IV was obtained from 1.86 g (0.01 mole) of II. mp = 152-154°C (from isopropanol). PMR spectrum: 2.43 (3H, s, 5-CH₃); 3.55 (3H, s, 1-CH₃); 3.83 (2H, s, NH₂); 7.10 ppm (1H, s, NH). UV spectrum, λ_{max} (log ε): 284 (3.87), 357 nm (3.61). Found, %: C 35.4; H 5.5; N 40.7. Calculated, %: C 35.1; H 5.3; N 40.9.

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