REACTION OF 3(5)-AMINO-5(3)-METHYLYRAZOLE WITH 1-NITRO- AND 1-CHLOROANTHRAQUINONES

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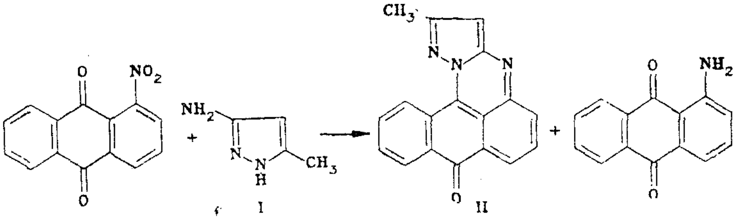
UDC 547.773.547.673.1:54.057

We have previously established that 3(5)-methylpyrazole reacts with 1-nitroanthraquinone (30 h at 150°C) to give 1-(3-methyl-1-pyrazolyl)anthraquinone [1].

We have observed that the reaction of 1-nitroanthraquinone with 3(5)-amino-5(3)-methylpyrazole (I) in sulfolane or N-methylpyrrolidone at 150°C is complete after 9 h. However, 2-methyl-8H-pyrazolo[5,1-b]benzo[e]perimidin-8-one (II, M^+ 285) and admixed 1-aminoanthraquinone, which were separated with a chromatographic column, are formed instead of the possible 1-(3-methyl-5-pyrazolylamino)anthraquinone.



Only one band of stretching vibrations of a C=O group at higher frequencies (1675 cm^{-1}) as compared with the spectrum of anthraquinone [2] is observed in the IR spectrum of II. The PMR spectrum of II was interpreted using the method of homonuclear resonance, which made it possible to reveal the protons in the unsubstituted ring of the "anthraquinone" fragment, and also by comparison with the PMR spectrum of 9-methylacridine [3]. The differences between the chemical shifts for the 5-H and 6-H protons and for the corresponding protons of the model compound are virtually identical, which made it possible to assign the indicated structure to II.

Only II is formed in the reaction with 1-chloroanthraquinone.

2-Methyl-8H-pyrazolo[5,1-b]benzo[e]perimidin-8-one (II, $C_{18}H_{11}N_3O$). A 0.2-g sample of K_2CO_3 and 0.27 g of amine I were added at 110°C to a solution of 0.63 g of 1-nitroanthraquinone in 6 ml of sulfolane (or N-methylpyrrolidone), and the mixture was heated for 9 h at 150°C (with monitoring by TLC). It was then cooled and diluted with water, and the precipitate was separated, washed with water, and dried. The product was separated with a column [silica gel 100/400 μ, elution with chloroform—ethanol (20:1)] to give 0.22 g (13%) of 1-aminoanthraquinone (R_f 0.73; the melting point and UV spectrum were in agreement with those obtained for the standard) and 0.54 g (77%) of II [R_f 0.51, mp 226-266. PMR spectrum ($CDCl_3$): 2.60 (3H, s, 2-CH_3), 7.70 (1H, t, 11-H), 7.82 (1H, t, 10-H), 8.02 (1H, t, 6-H), 8.39 (1H, d, 9-H), 8.42 (1H, d, 7-H), 8.67 (1H, d, 5-H), and 8.79 ppm (1H, d, 12-H)].

Compound II was formed in 54% yield in the reaction of amine I with 1-chloroanthraquinone for 30 h at 150°C in the presence of copper and copper(II) acetate; the starting 1-chloroanthraquinone (32%) was also isolated.

LITERATURE CITED

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