The reaction of pyrazoline I with pyridinium hexachloroantimonate proceeds in a different manner in a proton-acceptor medium (pyridine). The initially formed pyrazoline cation radical is rapidly deprotonated, and 1,3,5-triphenylpyrazole, with mp 136-138°C (from alcohol), is formed in 67% yield as a result of oxidation of the neutral pyrazolinyl radical. No melting-point depression was observed for a mixture of this product with a genuine sample [2], and the IR spectra of the two samples were identical.

The results of elementary analysis of II-IV were in agreement with the empirical formulas.

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ELUCIDATION OF THE DIRECTION OF THE REACTION OF TRIMETHYL-1,4-BENZOQUINONE WITH CYANOACETAMIDES

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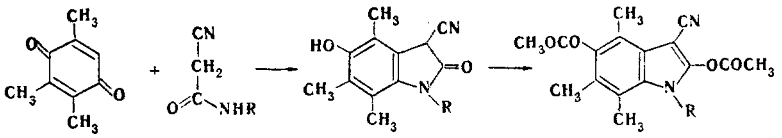
We have found that the reaction of trimethylbenzoquinone (I) with cyanoacetamide (IIa) in the presence of sodium methoxide leads to 3-cyano-4,6,7-trimethyl-5-hydroxyoxindole (IIIa), with mp 242-246°C (dec., from dioxane), in 78% yield rather than to a 2-amino-3-cyanobenzofuran system, as was previously assumed in [1] without, however, completely excluding the possibility of the formation of oxindole IIIa. N-Methylcyanoacetamide (IIb) also reacts similarly with quinone I to give IIIb, with mp 212-215°C (dec., from dioxane), in 71% yield. The IR spectrum of IIIa contains $\nu_{C=O}$ vibrations at 1708 cm^{-1} and indole ν_{NH} vibrations at 3170-3200 cm^{-1}. In the case of IIIb the $\nu_{C=O}$ vibrations appear at 1693 cm^{-1}.



I IIa,b IIIa,b IVa,b

II-IV a R=H; b R=CH$_3$

Compounds III exist in the form of mixtures of enol and oxo tautomeric forms: two bands of $\nu_{C\equiv N}$ vibrations (2262 and 2224 cm^{-1} for IIIa, and 2259 and 2210 cm^{-1} for IIIb) are observed; the long-wave band corresponds to the vibrations of a conjugated C≡N group in the enol form, and the shorter-wave band corresponds to the keto form. Treatment of IIIa,b with acetic anhydride gave diacetoxy derivatives IVa, with mp 227°C (from isopropyl alcohol) (see [1]) in 63% yield and IVb, with mp 202°C (from propanol), in 62% yield.

Two singlet signals of protons of acetyl groups appear in the PMR spectra of IVa,b and only one $\nu_{C\equiv N}$ band at 2230 cm^{-1} for IVa and at 2220 cm^{-1} for IVb remains in the IR spectra. The compounds obtained were characterized by elementary analysis.

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