LETTERS TO THE EDITOR

MECHANISM OF THE OXIDATIVE DEHYDROGENATION OF 1,3,5-TRIPHENYL-Δ^2-PYRAZOLINE

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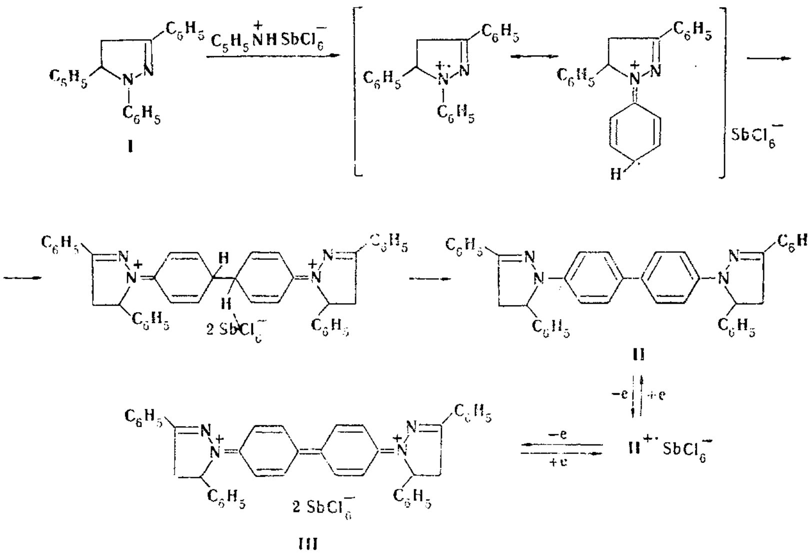
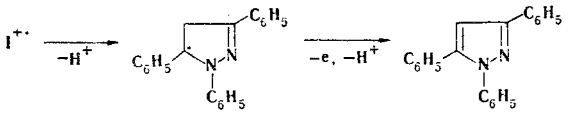
We have obtained indirect evidence in favor of the intermediate formation of the cation radical of the substrate in the course of the dehydrogenation of dihydro aromatic systems in the case of 1,3,5-triphenyl-Δ^2-pyrazoline (I). Thus 4,4'-bis(3,5-diphenyl-Δ^2-pyrazolin-1-yl)-diphenyl (II), with mp 241-244°C [from dimethylformamide (DMF)], was obtained in 50% yield by the action of pyridinium hexachloroantimonate in chloroform on pyrazoline I with subsequent treatment with zinc dust. PMR spectrum (in CF_3COOH), δ: 1.45 (4H) and 3.83 (2H), broad singlets (protons of the CH_2 and CH groups, respectively); 6.5-8.1 ppm, multiplet of aromatic protons. No melting-point depression was observed for a mixture of this product with a genuine sample [1]. The formation of II is the result of successive oxidation of pyrazoline I to a cation radical and dimerization of the latter. The same compound (II) was obtained by reduction of salt III with zinc in acetonitrile or chloroform. Salt III was obtained by oxidation of I or II with a solution of antimony pentachloride in acetonitrile.



An EPR signal related to the cation radical of II (broad singlet) appears when equimolar amounts of II and III in acetonitrile solutions are mixed.

As in the preparation of II, 4,4'-bis(3,5-diphenyl-5-methyl-Δ^2-pyrazolin-1-yl)diphenyl (IV), with mp 249-254°C (from benzene), was obtained from 1,3,5-triphenyl-5-methyl-Δ^2-pyrazoline. Found: M (by meausrement of the heat effects of condensation in chloroform) 590. Calculated: M 622.4.

1,3,5-Triphenyl-Δ^2-pyrazoline derivatives that contain substituents (CH_3, COOH, NO_2) in the para position of the N-phenyl group do not undergo oxidative dimerization under the influence of pyridinium hexachloroantimonate or antimony pentachloride.



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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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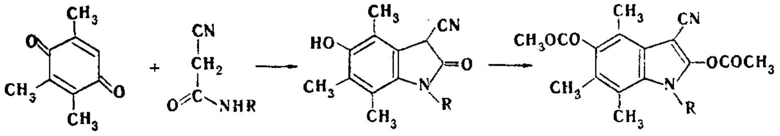
We have found that the reaction of trimethylbenzoquinone (I) with cyanoacetamide (IIa) in the presence of sodium methoxide leads to 3-cyano-4,6,7-trimethyl-5-hydroxyoxindole (IIIa), with mp 242-246°C (dec., from dioxane), in 78% yield rather than to a 2-amino-3-cyanobenzofuran system, as was previously 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 II a,b III a,b IV a,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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