REACTION OF 1-ALKYL-3-ARYL-2-BENZOPYRYLIUM SALTS WITH AMMONIA

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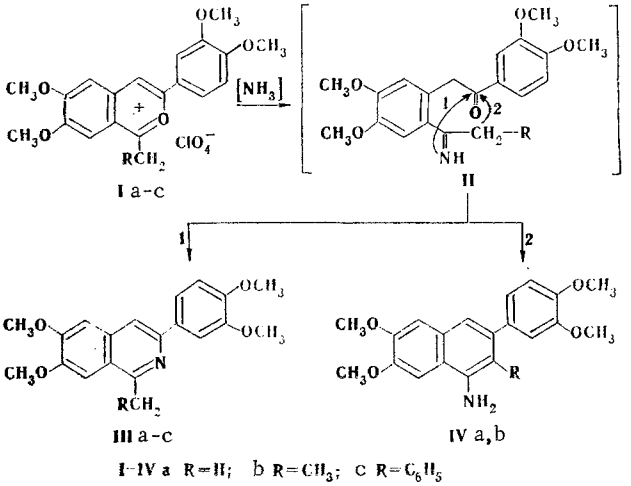
It has been previously shown that 2-benzopyrylium salts react with ammonia under various conditions to give either isoquinolines [1] or their precursors — 3-hydroxy-3,4-dihydroisoquinolines [2] or 1,5-dicarbonyl compounds [3] — i.e., only one reaction pathway was established.

We have observed that 3-aryl-2-benzopyrylium salts I, depending on the conditions, can be converted to products of different pathways (1 or 2) of recyclization of the heteroring, i.e., not only to isoquinolines III but also to α-naphthylamines IV; the latter are primarily formed under more severe conditions.



I–IV a R=H; b R=CH_3; c R=C_6H_5

Thus, isoquinoline IIIa was obtained in 52% yield when salt Ia was refluxed for a long time in glacial acetic acid with excess ammonium acetate [1]. PMR spectrum (CF_3COOH), δ: 2.77 (s, CH_3), 3.57 (s, two OCH_3), 3.73 (s, two OCH_3), 6.80-7.67 (m, 6H, aromatic), and 12.00 ppm (broad s, H—N^+).

However, a mixture of IIIa and IVa, which was separated by means of preparative column chromatography [$Al_2O_3/CHCl_3$, R_f (IIIa) > R_f (IVa)], was formed when salt Ia was heated in an autoclave with a saturated (in the cold) alcohol solution of ammonia. Isoquinoline IIIa [1] was obtained in 30% yield, while α-naphthylamine IVa was obtained in 70% yield and had mp 194°C. IR spectrum: 3200, 1640, and 1600 cm^{-1}. PMR spectrum, δ: 3.53 (s, OCH_3), 3.57 (s, OCH_3), 3.63 (s, two OCH_3), 6.77-7.67 (m, 7H, aromatic), and 8.89 ppm (broad s, $-N^+H_3$).

1-Ethyl-substituted salt Ib behaved similarly under the same conditions to give isoquinoline IIIb [in 35% yield with mp 165°C. IR spectrum: 1620 and 1570 cm^{-1}. PMR spectrum, δ: 1.25 (t, CH_3), 3.25 (q, CH_2), 3.63 (s, two OCH_3), 3.80 (s, two OCH_3), 6.90-7.75 (m, 6H, aromatic), and 12.10 ppm (broad s, H—N^+)] and α-naphthylamine IVb [in 60% yield with mp 150°C. IR spectrum: 3200, 1642, and 1590 cm^{-1}. PMR spectrum, δ: 2.13 (s, CH_3), 3.58 (s, OCH_3), 3.60 (s, OCH_3), 3.68 (s, two OCH_3), 6.58-7.40 (m, 6H, aromatic), and 8.55 ppm (broad s, $-N^+H_3$)].

The formation of naphthylamines does not proceed via the pathway of the Kost—Sagitullin rearrangement [4], since isoquinoline IIIa itself under the described conditions does not undergo any transformations. The structure of the final product is probably determined by the geometry of intermediate II, which is formed by opening of the heteroring. This is evidently the reason why 1-benzyl-substituted salt Ic under various conditions forms only corresponding isoquinoline IIIc, with mp 167°C, in 70% yield. IR spectrum: 1610 and 1570 cm^{-1}. PMR spectrum, δ: 3.58 (s, two OCH_3), 3.70 (s, OCH_3), 3.80 (s, OCH_3), 4.60 (s, CH_2), 6.83-

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7.83 (m, 11H, aromatic), and 12.00 ppm (broad s, H—N^+). The absence in the reaction mixture of the alternative product, viz., β-phenyl-α-naphthylamine (IV, R = Ph), can also be explained by the inhibiting effect of the atropoisomerism that is mandatory for this compound.

The results of elementary analysis of the substances obtained for their C, H, and N content were in agreement with the calculated values.

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AROMATIZATION OF 1-SUBSTITUTED ISOCHROMENES UNDER THE INFLUENCE OF 1-OXO-2,2,6,6-TETRAMETHYLPIPERIDINIUM PERCHLORATE

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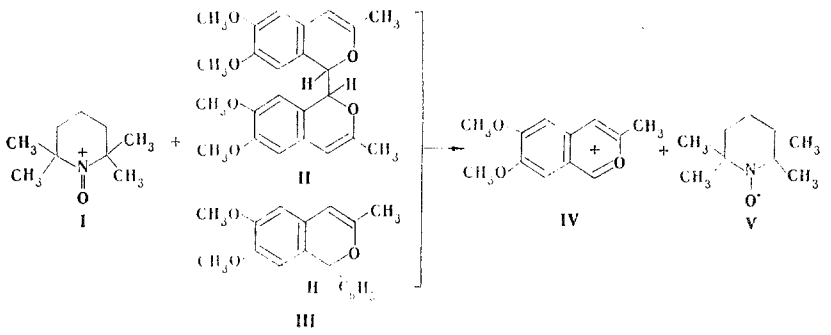
1-Oxo-2,2,6,6-tetramethylpiperidinium perchlorate (I) is an effective dehydrogenating agent in reactions involving the aromatization of partially hydrogenated heterocyclic compounds [1]. However, examples in which cleavage of the C—C bond would occur under the influence of the I cation in such reactions were heretofore unknown. We have found that in the reaction of the I cation with bis(3-methyl-6,7-dimethoxy-1H-isochromene) (II) or 1-phenyl-3-methyl-6,7-dimethoxy-1H-isochromene (III) in an inert atmosphere in anhydrous acetonitrile, as in the case of aromatization of these compounds under the influence of acetyl- or triphenylmethyl perchlorates [2] or in the case of electrochemical oxidation [3], the substituent in the 1 position is split out with cleavage of the C—C bond and the formation in both cases of 3-methyl-6,7-dimethoxy-2-benzopyrylium perchlorate (IV); the formation of the 2,2,6,6-tetramethylpiperidine 1-oxyl radical (V) was observed:



Products IV and V were obtained in quantitative yields. Iminoxyl radical V was identified by means of the EPR spectra (a_N = 15.6 Oe) [4], while the III cation was identified from the UV spectra and by polarography [3, 5].

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