INDOLIZINO[2,3-b]PYRYLIUM SALTS

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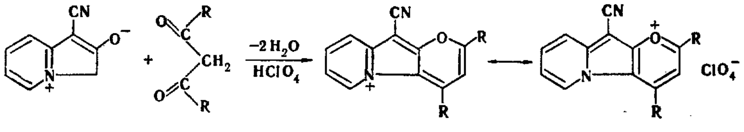
We have found that 1-cyano-2-(3H)-indolizinone (I) reacts with β-diketones (II) in acidic media to give a new heterocyclic system — the indolizino[2,3-b]pyrylium ion (III). The reaction is carried out by heating a mixture of the starting components in acetic acid in the presence of perchloric acid for several hours. In particular, the reaction of I with acetylacetone gives 2,4-dimethyl-10-cyanoindolizino[2,3-b]pyrylium perchlorate [III, $R = CH_3$, 75% yield, mp 251° (from water)].



I II III

The signal of the protons of the methylene group of the starting indolizinone are absent in the PMR spectrum of this compound (in trifluoroacetic acid), but two singlets from the protons of methyl groups with chemical shifts of 3.12 (3H, $2-CH_3$, singlet) and 2.90 ppm (3H, $4-CH_3$, singlet) appear. The signal of the proton in the 3 position, which is found in the region of absorption of aromatic protons [δ_{3-H} 7.0 ppm (1H, singlet)], serves as a confirmation of the formation of a pyrylium ring. It follows from the structure presented above that the methyl groups in the product react with p-dimethylaminobenzaldehyde to give a deeply colored dye. The reaction of indolizinone I with dibenzoylmethane under the conditions presented above gives 2,4-diphenyl-10-cyanoindolizino[2,3-b]pyrylium perchlorate [III, $R = C_7H_5$, 72% yield, mp > 300° (from acetic acid)]. The absorption band of a nitrile group at 2235-2240 cm^{-1} is observed in the IR spectra of the compounds obtained. The empirical formulas of the compounds were confirmed by the results of analysis for chlorine and nitrogen.

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