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The products of the condensation of quaternary salts of α - and γ -methyl derivatives of pyridine and quinoline with aromatic o-hydroxy aldehydes exist only in the merocyanine form and are incapable of intra-molecular cyclization with the formation of spiropyrans [1-3]. In contrast to this, the intensively colored merocyanines (Ia-c) that we obtained by the reaction of 1,2-dimethylisoquinolinium iodide with the same aldehydes readily transform into the colorless spiropyrans (IIa-c) on heating in aprotic solvents of low polarity. In polar protonic solvents, these colorless forms (IIa-c) give colored solutions identical with the solutions of the corresponding merocyanines (Ia-c). Colorless forms were obtained for derivatives both with donor (Ia, b) and with acceptor (Ic) substituents in the chromene ring. We explain the specific behavior of the o-hydroxystyryl derivatives of isoquinoline by the increased electrophilicity of position 1 of the isoquinoline as compared with the α and γ positions of pyridine and quinoline, and also by the steric influence of the hydrogen atom in position 8.

II a $R = 6' - OCH_3$; II b $R = 8' - OCH_3$; II c R = 6' - Br

 $\frac{1-(2-\text{Hydroxy-5-methoxystyryl})-2-\text{methylisoquinolinium Iodide (IIIa).}}{\text{mmoles) of 1,2-dimethylisoquinolium iodide in 2 ml of ethanol were added 0.38 g (2.5 mmoles) of 5-methoxysalicylaldehyde and 0.03 g (0.35 mmole) of piperidine, and the mixture was boiled for 15-20 min and was then evaporated in vacuum. The dark-brown viscous residue was triturated with 30-40 ml of chloroform, and 0.74 g (70%) of (IIIa) was filtered off. Orange crystals with mp 204-206°C (from butanol). Found: I 30.3; N 3.6%. C₁₉H₁₈INO₂. Calculated: I 30.3; N 3.3%.$

 $\frac{2-\text{Methyl-1,2-dihydroisoquinoline-1-spiro-2'-(6'-methoxy-2'H-chromene)}{\text{IIIa}}. \text{ With heating, 0.36 g}}{(1.25\text{ mmole}) \text{ of (IIIa)}} \text{ was dissolved in 10-12 ml} \text{ of water, the solution was cooled, an aqueous solution of ammonia was added, and 0.2 g of a red precipitate of (Ia) was filtered off. It was dissolved with heating in 20 ml of benzene, the solution was filtered and evaporated in vacuum to 3-5 ml, 25-30 ml of hexane was added, and the resulting mixture was evaporated in vacuum to dryness. This gave 0.1 g (50%) of (IIa) in the form of slightly colored crystals which, on recrystallization from hexane (1:100), separated in the form of colorless needles with mp 122-123°C. Solutions of (IIa) in benzene and hexane are colorless, in chloroform blue, and in ethanol violet. Found: C 78.1; H 6.1; N 4.8%. C₁₉H₁₇NO₂. Calculated: C 78.3; H 5.8; N 4.8%.$

 $\frac{2\text{-Methyl-1,2-dihydroisoquinoline-1-spiro-2'-(8'-methoxy-2'H-chromene) (IIb), colorless crystals}{\text{mp }116\text{-}118°C \text{ (from hexane, }1:100\text{)}.} \\ \text{Solutions of (IIb) had the same colors as solutions of (IIa).} \\ \text{Found: C }78.5; \text{ H }6.2; \text{ N }5.1\%. \\ \text{C }_{19}\text{H}_{17}\text{NO}_2. \\ \text{Calculated: C }78.3; \text{ H }5.8; \text{ N }4.8\%.}$

 $\frac{2\text{-Methyl-1,2-dihydroisoquinoline-1-spiro-2'-(6'-bromo-2'H-chromene) (IIc), colorless crystals with mp 142-144°C (from hexane, 1:150). A solution in ethanol was pink, and a solution in chloroform blue. Found: Br 23.3; N 4.2%. C₁₈H₁₄BrNO. Calculated: Br 23.5; N 4.1%.$

Compounds (IIb and c) were obtained in a similar manner to (IIa) with yields of 60-65%.

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LITERATURE CITED

- 1. E. B. Knott, J. Chem. Soc., 3038 (1951).
- 2. C. Schiele, D. Staudacher, D. Hendriks, and G. Arnold, Tetrahedron, 5017, 5023 (1968).
- 3. V. P. Martynova, N. E. Shelepin, N. S. Loseva, É. R. Zakhs, L. E. Nivorozhkin, V. I. Minkin, and L. S. Éfros, Khim. Geterotsikl. Soedin., 167 (1971).