SPIROPYRANS OF THE 3,4-DIHYDROISOQUINOLINE SERIES

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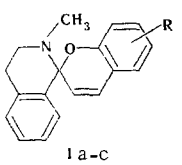
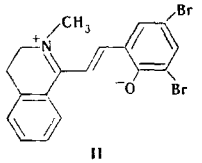
The intensely colored 1-(2-oxidostyryl)-2-methylisoquinolinium ions are capable of undergoing conversion to colorless spiropyrans [1]. We have found that 1,2-dimethyl-3,4-dihydroisoquinolinium iodide undergoes condensation in the cold with o-hydroxy aldehydes, during which colorless spiropyrans (Ia, b) may be immediately obtained in the presence of excess piperidine. The pyran ring of Ia, b is opened only when an alcohol solution of the compound is heated. The product of the reaction with 3,5-dibromosalicylaldehyde, in contrast to the corresponding derivative of the isoquinoline series, can be isolated not only in the merocyanine form (II) but also in the spiropyran form (Ic), which is converted to the merocyanine form on dissolving in alcohol, as confirmed by the absorption spectra. The ease of formation and the greater stability of spiropyrans Ia-c as compared with the derivatives of the isoquinoline series is explained by the increased charge concentration on the nitrogen atom because of the decrease in its conjugation with the benzene ring.



Ia-c



II

Ia R=6'-OCH_3; b R=8'-OCH_3; c R=6',8'-Br_2

EXPERIMENTAL

2-Methyl-6'-methoxyspiro(1,2,3,4-tetrahydroisoquinoline-1,2'-[2H]chromene) (Ia). A 0.33-ml (2.5 mmole) sample of 5-methoxysalicylaldehyde and 0.45 ml (5 mmole) of piperidine were added to a suspension of 0.72 g (2.5 mmole) of 1,2-dimethyl-3,4-dihydroisoquinolinium iodide in 2 ml of isopropyl alcohol, whereupon the resulting solution warmed up and took on a dark-lilac color. After 5-7 min, 0.7 g (84%) of colorless needles of Ia with mp 125-126° [from hexane (1:20)] precipitated. Found: C 77.5; H 6.8; N 4.4%. $C_{19}H_{19}NO_2$. Calculated: C 77.8; H 6.5; N 4.8%.

2-Methyl-8'-methoxyspiro(1,2,3,4-tetrahydroisoquinoline-1,2'-[2H]chromene) (Ib). This compound was similarly obtained in 80% yield (condensation in ethanol) as colorless crystals with mp 114-115° [from hexane (1:15)]. Found: C 77.8; H 7.0; N 4.6%. $C_{19}H_{19}NO_2$. Calculated: C 77.8; H 6.5; N 4.8%.

2-Methyl-6',8'-dibromospiro(1,2,3,4-tetrahydroisoquinoline-1,2'[2H]chromene) (Ic) and 2-Methyl-1-(2-oxido-3,5-dibromostyryl)-3,4-dihydroisoquinolinium (II). The condensation with 3,5-dibromosalicylaldehyde was carried out as in the preceding experiment. Water (20 ml) was added to the resulting suspension, and the dark-brown crystals of II were removed by filtration and crystallization from 25% aqueous isopropyl alcohol to give crimson crystals of II with mp 167-168° in 60% yield. UV spectrum in alcohol, λ_{max}, nm (log ε): 237 (4.43), 335 (3.71), 525 (3.64). Found: Br 38.2%. $C_{18}H_{15}Br_2NO$. Calculated: Br 38.0%. A 0.6-g sample of merocyanine II was dissolved in 6 ml of benzene, and the solution was filtered.

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The filtrate was vacuum evaporated to dryness and the residue was crystallized from petroleum ether (1:10) to give 0.4 g of colorless crystals of Ic with mp 97-98°. UV spectrum in hexane, λ_{max}, nm (log ε): 237 (4.50), 330 (3.41). The absorption spectrum in alcohol was identical to the spectrum of merocyanine II. Found: Br 37.9%. $C_{18}H_{15}Br_2NO$. Calculated: Br 38.0%.

LITERATURE CITED

1. E. V. Bashut-skaya, É. R. Zakhs, and L. S. Éfros, Khim. Geterotsikl. Soedin., 1580 (1973).