SPIROPYRANS OF THE QUINOLINE SERIES

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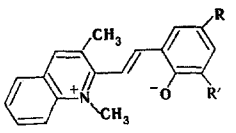
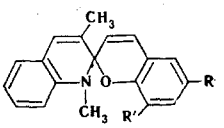
It has frequently been noted that 2-(o-oxidostyryl)quinolinium derivatives are incapable of intramolecular cyclization. We have found that this sort of cyclization to give spiropyrans becomes possible when one uses the steric effect of a substituent introduced in the 3 position of the quinoline ring. Condensation of 1,2,3-trimethylquinolinium iodide (I) with substituted salicylaldehydes in the presence of piperidine gave 1,3-dimethyl-2-(o-oxidostyryl)quinoliniums (IIa-c), two of which were converted to the corresponding spiropyrans (IIIa, b). When the acceptor properties of the substituents in the styryl ring are reinforced (IIc), almost complete conversion to the spiropyran (IIIc) occurs only in nonpolar solvents, and the crystalline preparation has an intense color. Isomeric 1,3-dimethyl-4-(o-oxidostyryl)-quinoliniums and, probably, derivatives of β-substituted α- and γ-picoliniums should behave like IIa-c.

The condensation of salts I with aldehydes was carried out by refluxing them for 30 min in alcohol with a catalytic amount of piperidine. Compounds II were isolated from the resulting hydroxystyrylquinolinium iodides by the action of ammonium hydroxide.



II a-c



III a, b

II, III a R = H, R′ = OCH_3; b R = Br, R′ = H; c R = R′ = Br

Spiropyrans IIIa and IIIb were obtained by treatment of the corresponding merocyanines (IIa, b) with benzene and hexane (IIc from benzene). The yields with respect to I were 40-50%. The compositions of the compounds were confirmed by the results of elementary analysis.

TABLE 1

Compound	Empirical formula	mp, °C	λ_{max}, nm (log ε)	
			in octane (IIc in benzene	in alcohol
IIIa	$C_{20}H_{19}NO_2$	145—148	240, 320 (4,47, 3,57)	244, 305, 380, 580 (4,44; 3,83; 4,05; 3,42)
IIIб	$C_{19}H_{16}BrNO$	135—136	230, 320 (4,66; 3,67)	243, 340, 540 (4,54; 4,05; 3,68)
IIв	$C_{19}H_{15}Br_2NO$	165—168	325, 530, 690 (3,72; 2,23; 2,65)	243, 355, 530 (4,51; 4,09; 4,06)

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