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LETTERS TO THE EDITOR

NOVEL SPIROPYRANS OF THE BENZOXAZINONE SERIES CONTAINING A CONDENSED BENZO RING IN THE HETARENE MOIETY

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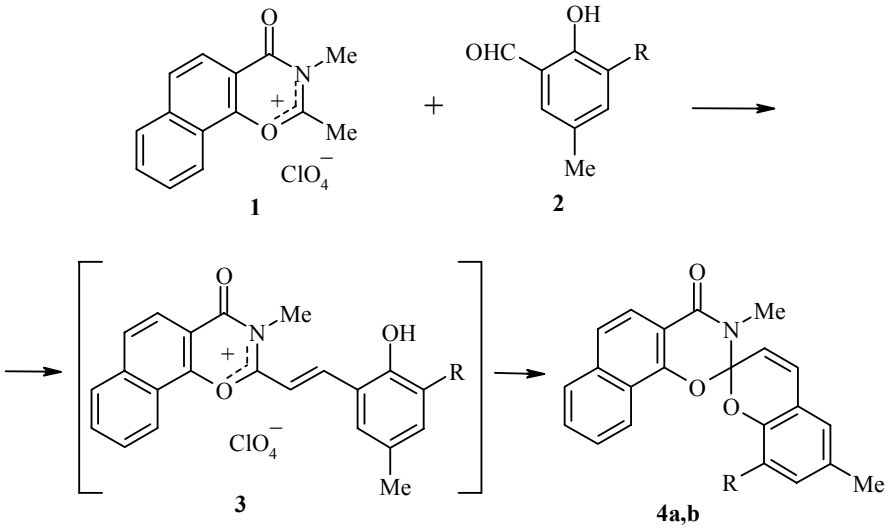
The effect of substituents on the photochromic properties of spiropyrans have been previously studied mainly in compounds containing various substituents on the [2H]-pyran moiety. Spiropyrans of the benzoxazinone series, based on the naphthalene system, have not been successfully obtained until now [1].

Using 1-hydroxy-2-naphthoic acid N-methylamide as the starting compound, we have obtained spiropyrans **4** by brief boiling in acetic acid of equimolar amounts of the perchlorate **1** and the corresponding aldehyde **2**, followed by treatment of the obtained styryl salt **3** by triethylamine in absolute ether.



4 **a** R = H, **b** R = CHO

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3,6'-Dimethylspiro(2,3-dihydronaphtho[2,1-*e*][1,3]oxazin-4-oxo-2,2'-[2H]chromene) (4a). A mixture of aldehyde **2a** (1.36 g, 0.01 mol) and 2,3-dimethyl-2,3-dihydronaphtho[2,1-*e*][1,3]oxazin-4-onium perchlorate (**1**) (3.25 g), obtained by reaction of equimolar amounts of 1-hydroxy-2-naphthoic acid N-methylamide with an equimolar amount of 70% hydrochloric acid in a 6-fold excess of acetic anhydride, was boiled for 3 min in acetic acid (15 ml); the reaction mixture was cooled down, the precipitate of salt **3a** was filtered out, dissolved in absolute ether (50 ml), and then triethylamine (1.5 ml) was added. After 6 h, the ether was decanted and evaporated, the residue of spiropyran **4a** was crystallized from alcohol. Yield 45%; mp 162-164°C (alcohol). Found, %: C 76.89; H 5.03; N 4.01. $C_{22}H_{17}NO_3$. Calculated, %: C 76.97; H 4.97; N 4.08.

8'-Formyl-3,6'-dimethylspiro(2,3-dihydronaphtho[2,1-*e*][1,3]oxazin-4-oxo-2,2'-[2H]chromene (4b) was obtained analogously, using 2,6-diformylphenol as the aldehyde component. Yield 42%; mp 201°C (alcohol). Found, %: C 74.51; H 4.46; N 3.89. $C_{23}H_{17}NO_4$. Calculated, %: C 74.39; H 4.58; N 3.77.

The IR spectra (thin film) contain absorption bands typical of vibrations of the C=C bond of the pyran ring, ν, cm^{-1}: compound **4a**: 1662, 1634, 1567; compound **4b**: 1660, 1633, 1567. In the IR spectrum of spiropyran **4b**, there is a stretching vibration band for the formyl group at 1673 cm^{-1}. The ^1H NMR spectrum [Varian Unity 300 (300 MHz), signals assigned relative to the residual protons of the signal from the deuterated solvent $CDCl_3$, 7.26 ppm], δ, ppm (*J*, Hz): compound **4a**: 2.27 (3H, s, 6'-CH_3); 3.20 (3H, s, N–CH_3); 6.16 (1H, d, $J_{CH=CH}$ = 9.7, H-3'); compound **4b**: 2.35 (3H, s, 6'-CH_3); 3.22 (3H, s, N–CH_3); 6.16 (1H, d, $J_{CH=CH}$ = 10.2, H-3'); 9.88 (1H, s, CHO). UV spectrum (EtOH), λ_{max} (log ε), nm: compound **4a**: 286.5 (3.9), 298 (3.8), 313 (3.58), 328 (3.56), 343 (3.61); compound **4b**: 286 (3.91), 297.5 (3.72), 314 (3.57), 331 (3.82), 342 (3.87). In contrast to spiropyrans of the benzoxazinone series which do not contain a condensed benzo ring in the hetarene moiety [2], the spiropyrans **4** obtained proved to be non-photochromic compounds when they were exposed to a DRSh-250 Hg lamp with 365 nm light filter at -80°C under steady-state conditions.

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