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NOVEL INDOLINOSPIROPYRANS CONTAINING A CONDENSED FURAN MOIETY

B. S. Luk'yanov, E. N. Shepelenko, V. A. Bren', and A. O. Bulanov

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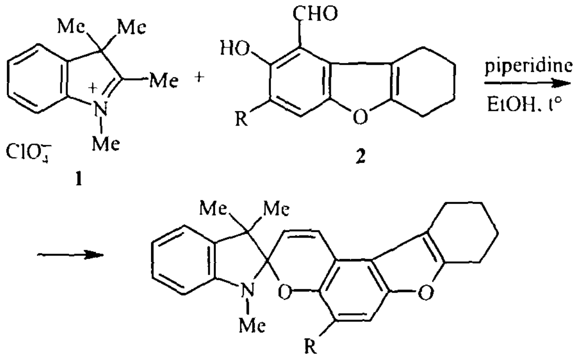
The effect of substituents on photochromic properties of spiropyrans have been mainly studied in compounds containing various π-acceptor substituents [1]. It is certainly of interest to study the effect of π-donor substituents which are not so diverse, since 1,3,3-trimethyl-6'-hydroxyspiro(indolino-2,2'-[2H]benzopyran) [2] and also indolinospiropyrans containing a methoxy group on the 2H-chromene moiety [3] exhibit photochromic properties in the solid phase.

A novel replacement for a π-donor methoxy group in the 6' position of spiropyran is a condensed furan moiety:



3a R = H, 3b R = Br

Spiropyrans **3** are obtained by briefly boiling in alcohol equimolecular amounts of 1,2,3,3-tetramethylindolenylium perchlorate, the corresponding aldehyde **2**, and piperidine.

Compound 3a. Yield 74%; mp 164-165°C (alcohol). Found, %: C 80.71; H 6.82; N 3.68. $C_{25}H_{25}NO_2$. Calculated, %: C 80.83; H 6.73; N 3.77.

Compound 3b. Yield 81%; mp 158°C (alcohol). Found, %: C 66.5; H 5.46; Br 17.43; N 2.94. $C_{25}H_{24}BrNO_2$. Calculated, %: C 66.67; H 5.33; Br 17.74; N 3.11.

The IR spectra (thin layer), ν, cm^{-1} contain absorption bands characteristic for vibrations of the C=C bond of the pyran ring: **3a** – 1647, 1627, 1600; and **3b** – 1644, 1616, 1600. In the ^{1}H NMR spectra ($CDCl_3$) of spirochromenes **3**, we separately observe signals from the *gem*-dimethyl groups of the indoline moiety because of the non-coplanarity of the molecule (1.18 and 1.33 ppm for compound **3a**; 1.19 and 1.33 ppm for compound **3b**). The doublet signal from the proton in the 3' position of the pyran ring (5.68 ppm, $J_{CH=CH}$ = 8.5 Hz for compound **3a** and 5.70 ppm, $J_{CH=CH}$ = 8.2 Hz for compound **3b**) corresponds to a *cis* configuration for the vinyl moiety (Varian

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Scientific-Research Institute of Physical and Organic Chemistry, Rostov State University, Rostov-on-Don 344090, Russia; e-mail: bluk@ipoc.rsu.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 987-988, July, 2000. Original article submitted May 23, 2000.

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Unity 300 spectrometer). UV spectra (toluene), λ_{max}, nm (log ε): **3a** – 304 (4.26), 352 (3.50); **3b** – 301 (4.28), 385 (3.71). Maxima for the long-wavelength absorption bands of the photo-induced forms (irradiation by a DRSh-250 lamp with 365 nm light filter under steady-state conditions, 77 K, $C \sim 5 \cdot 10^{-5}$ mol/l in a 5:2 isopentane–isopropanol mixture) were recorded in the electronic spectra at 546, 587, 627 nm (compound **3a**) and 483, 592, 625 nm (compound **3b**).

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