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NOVEL PHOTOCHROMIC INDOLINOSPIROPYRANS CONTAINING PHENYL SUBSTITUENTS IN THE CONDENSED FURAN MOIETY

B. S. Lukyanov, E. N. Shepelenko, V. A. Bren, M. B. Lukyanova, and S. O. Bezuglyi

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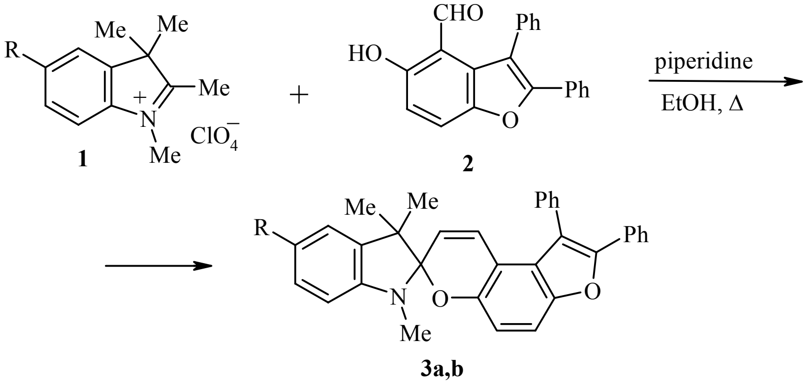
The effect of substituents on the photochromic properties of spiropyrans have mainly been studied in compounds containing various π-acceptor substituents [1], and the studies have been limited by their lack of diversity. However, they are certainly of interest, since 1,3,3-trimethyl-6'-hydroxyspiro(indolino-2,2'-[2H]-benzopyran) [2] and also indolinospiropyrans containing a methoxy group in the 2H chromene moiety [3] exhibit photochromic properties in the solid phase.

An unusual replacement for the π-donor methoxy group at the 6' position of the spiropyran is a condensed furan moiety.

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



3 a R = H, **b** R = Cl

Compound 3a. Yield 72%; mp 179°C (alcohol). Found, %: C 84.32; H 5.92; N 3.09. $C_{33}H_{27}NO_2$. Calculated, %: C 84.41; H 5.80; N 2.98.

Compound 3b. Yield 81%; mp 183°C (alcohol). Found, %: C 78.51; H 5.16; Cl 6.91; N 2.94. $C_{33}H_{26}ClNO_2$. Calculated, %: C 78.64; H 5.20; Cl 7.03; N 2.78.

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. 1, pp. 131-133, January, 2006. Original article submitted October 16, 2005.

The IR spectra (thin film), ν, cm^{-1}, contain absorption bands typical of vibrations of the C=C bond of the pyran ring: **3a**: 1631, 1602, 1576 and **3b**: 1640, 1600, 1573. In the ^1H NMR spectra of spirochromenes **3** (Varian Unity 300 spectrometer (300 MHz) in $CDCl_3$, signals assigned relative to the residual protons of the deuterated solvent signal, $CDCl_3$, 7.26 ppm), the signals from the *gem*-dimethyl groups of the indoline moiety are observed separately due to the non-coplanarity of the molecule (1.10 ppm and 1.32 ppm for compound **3a**; 1.09 and 1.29 ppm for compound **3b**), while the signals from the protons of the $N–CH_3$ group are found at 2.69 ppm and 2.66 ppm for the spiropyrans **3a** and **3b** respectively. The doublet signal from the proton at the 3 position of the pyran ring is observed in compound **3a** at 5.42 ppm ($J_{CH=CH}$ = 10.4 Hz) and at 5.39 ppm ($J_{CH=CH}$ = 10.4 Hz) in compound **3b**, and corresponds to a *cis* configuration of the vinyl moiety. UV spectra (ethanol), λ_{max}, nm (log ε): **3a**: 246 (4.44), 320 (4.59), 364 shoulder (3.70); **3b**: 252 (4.28), 320 (4.60), 364 shoulder (3.67). The maxima of the long-wavelength absorption bands in the electronic spectra for the photoinduced forms (exposure to a DRSh-250 Hg lamp with 365 nm light filter under steady-state conditions, T = 203 K, $c \sim 5 \cdot 10^{-5}$ mol/l in ethanol) were recorded at 475 nm, 583 nm and at 482 nm, 586 nm for compounds **3a** and **3b** respectively.

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