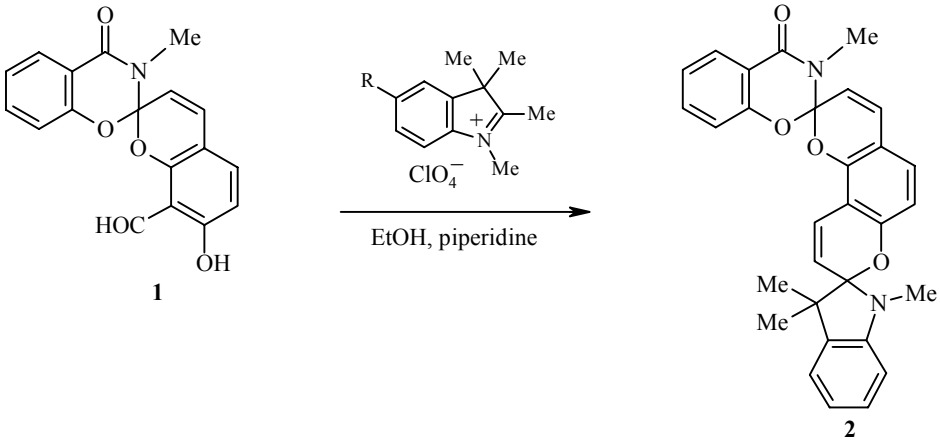
NEW PHOTOCHROMIC BISPIROPYRAN

Yu. S. Alekseenko, A. O. Bulanov, Yu. A. Sayapin, A. S. Alekseenko, B. S. Luk'yanov, and B. B. Safoklov

Keywords: benzoxazinone, bispiropyran, indoline, photochromism.

The photochromic properties of spiropyrans are a function not only of the contribution of the hetarene fragment but also, to a greater extent, to the substituents in the 2H-chromene part of the molecule [1]. We have obtained a new spiropyran **1**, which is a unique salicylaldehyde analog, and used this compound to synthesize spiropyran **2**, containing two different spirocyclic sites and, thus, two asymmetric carbon atoms.



1 **2**

The ^{1}H NMR spectra were taken on a Varian Unity-300 spectrometer at 300 MHz in $CDCl_3$.

8'-Formyl-7'-hydroxy-3-methyl-4-oxo-3,4-dihydro-2H-1,3-benzoxazine-2-spiro-2'-2H-chromene (1) was obtained in 48% yield from N-methylsalicylamide and 2,4-dihydroxy-*iso*-phthalaldehyde according to our previous procedure [2]; mp 155°C (ethanol). IR spectrum (vaseline oil), ν, cm^{-1}: 1673 (C=O), 1633, 1600 (C=C), 984, 954, 921 (C–O). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 3.17 (3H, s, N–CH_3); 5.97 (1H, d, *J* = 9.8, 3'-H); 6.61 (1H, d, *J* = 8.6, 6'-H); 6.88 (1H, d, *J* = 8.3, 8-H); 6.93 (1H, d, *J* = 9.8, 4'-H); 7.37 (1H, d, *J* = 7.8, 5'-H); 7.19 (1H, t, *J* = 7.6, 6-H); 7.47 (1H, t, *J* = 7.4, 7-H); 8.05 (1H, d, *J* = 7.8, 5-H); 10.22 (1H, s, CHO); 11.69 (1H, s, OH). UV spectrum (2-propanol), λ_{max}, nm (log ε): 270 (4.32), 364 (3.48). λ_{max} for the photoinduced form: 510 nm. Found, %: C 67.02; H 3.90; N 4.11. $C_{18}H_{13}NO_5$. Calculated, %: C 66.87; H 4.05; N 4.33.

3-Methyl-4-oxo-3,4-dihydro-2H-1,3-benzoxazine-2-spiro-2'-2H,8H-pyrano[2,3-*f*]chromene-8'-2"-1",3",3"-trimethylindoline (2).A sample of piperidine (0.1 ml, 1.1 mmol) was added dropwise to a heated solution of spiropyran **1** (0.323 g, 1 mmol) and 1,2,3,3-tetramethylindolenylium perchlorate (0.274 g, 1 mmol)

Physical and Organic Chemistry Research Institute, Rostov State University, 344090 Rostov-on-Don, Russia; e-mail: bluk@ipoc.rsu.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1308-1309, September, 2002. Original article submitted June 5, 2002.

 0009-3122/02/3809-1152$27.00

in 2-propanol (5 ml). The reaction mixture was heated at reflux for 10 min and cooled. The precipitate was filtered off and recrystallized to give 0.287 g (60%) **2**; mp 210°C (hexane). IR spectrum (vaseline oil), ν, cm^{-1}: 1673 (C=O), 1633, 1600, 1684 (C=C), 950, 921 (C–O). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 1.08 (3H, s, 3"-H); 1.21 (3H, s, 3"-C<u>H</u>$_3$); 2.64 (3H, s, 1"-C<u>H</u>$_3$); 3.18 (3H, s, 3-C<u>H</u>$_3$); 5.50 (1H, dd, *J* = 8.7, 9'-H); 5.87 (1H, d, *J* = 9.7, 3'-H); 6.30-7.60 (11H, m, arom, 4'-<u>H</u>, 10'-<u>H</u>); 8.08 (1H, d, *J* = 7.8, 8-<u>H</u>). UV spectrum (2-propanol), λ_{max}, nm (log ε): 247 (4.57), 287 sh (4.36), 324 sh (3.49), 340 sh (3.31). λ_{max} of photoinduced form: 418 sh, 434, 520, 560 sh. Found, %: C 75.56; H 5.74; N 5.62. $C_{30}H_{26}N_2O_4$. Calculated, %: C 75.30; H 5.48; N 5.85.

This work was carried out with the financial support of the Russian Basic Research Fund (Grant 02-03-81011 Bel 2002, 00-03-32415) and the Ministry of Education of the Russian Federation (Grant E 00-5.0-111).

REFERENCES

1. H. Duerr and H. Bouas–Laurent (editors), *Photochromism. Molecules and Systems*, Elsevier, Amsterdam (1990).
2. B. S. Luk'yanov, Yu. I. Ryabukhin, G. N. Dorofeenko, L. E. Nivorozhkin, and V. I. Minkin, *Khim. Geterotsikl. Soedin.*, 161 (1978).