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LETTERS TO THE EDITOR

NOVEL PHOTOCHROMIC INDOLINOSPIROPYRANS CONTAINING A QUINOLINE FRAGMENT CONDENSED WITH A 2H-PYRAN RING

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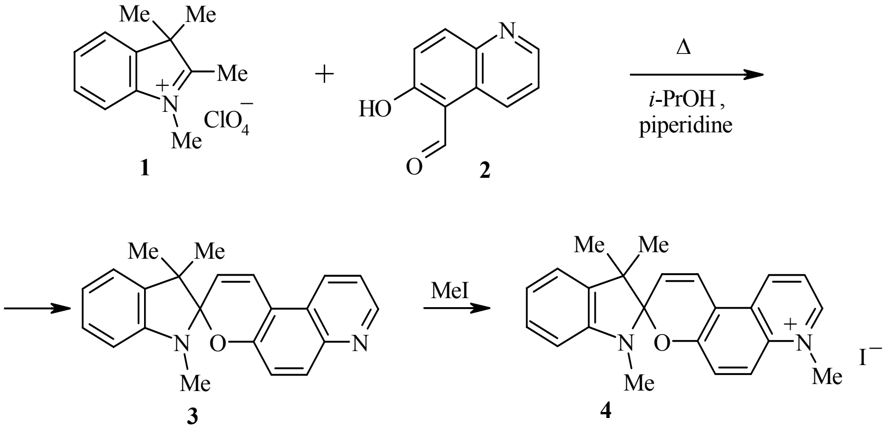
It was reported earlier that the standard methods of synthesis, based on the condensation of methylene bases or their precursors with heterocyclic aldehydes, lead to the formation of only noncyclic isomers [1]. It was demonstrated that the open merocyanine form, the transformation of which into the cyclic (spiropyran) form is only realized as a result of isomerization during thermal vacuum deposition of the merocyanine on a solid substrate (quartz, glass, KBr plates), is isolated during the production of spiropyrans of the indoline series containing 2H-thia- or 2H-selenapyran rings condensed with the heterocyclic pyrazole ring [2].

However, if 6-hydroxyquinoline-5-carbaldehyde (**2**) is used for the synthesis of spiropyrans the cyclic form of indolinospiropyran (**3**), containing a quinoline fragment condensed with the 2H-pyran ring, is formed as a direct result of the reaction. The presence of the basic nitrogen atom in the molecule of **3** makes it possible to obtain the methiodide **4**.



The ^1H NMR spectra were recorded on a Varian Unity-300 instrument (300 MHz), and the signals were assigned with reference to the residual protons of the signal of the deuterated solvent ($CDCl_3$) at 7.26 ppm.

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Spiro(1,3,3-trimethylindolino-2,3'-3H-pyrano[3,2-*f*]quinoline) (3). To a boiling mixture of 1,2,3,3-tetramethylindolenylium perchlorate (2.74 g, 0.01 mol) and the aldehyde **2** (1.90 g, 0.011 mol) [3] in 15 ml of 2-propanol we added dropwise 1.073 g (~1.1 ml, 0.013 mole) of piperidine. The reaction mixture was boiled for 5 min and left for 12 h. The crystals that separated were filtered off and recrystallized. Yield 65%; mp 162°C (hexane). IR spectrum (thin layer), ν, cm^{-1}: 1593-1673 (C=C). UV spectrum (ethanol), λ_{max}, nm (ε): 247 (48390), 289 (11060), 317 sh (4450), 336 sh (4000), 352 (4440), 367 sh (3660). ^{1}H spectrum, δ, ppm (*J*, Hz): 1.20 [3H, s, gem. $(CH_3)_2$]; 1.32 [3H, s, *gem*-$(CH_3)_2$]; 2.73 (3H, s, N–CH_3); 5.83 (1H, d, *J* = 10.4, H-2'); 6.53 (1H, d, *J* = 8.1, H-6'); 6.85 (1H, t, *J* = 7.3, H-5); 7.09 (1H, d, *J* = 6.1, H-7); 7.16-7.22 (2H, m, H-6,4); 7.39 (1H, q, *J* = 8.5, H-9'); 7.5 (1H, d, *J* = 10.4, H-1'); 7.86 (1H, d, *J* = 9.3, H-10'); 8.34 (1H, d, *J* = 8.1, H-5'); 8.74 (1H, d, *J* = 4.2, H-8'). Found, %: C 80.4; H 6.23; N 8.47. $C_{22}H_{20}N_2O$. Calculated, %: C 80.46; H 6.14; N 8.53.

Spiro(1,3,3,7'-trimethylindolino-2,3'-3H-pyrano[3,2-*f*]quinolinium) Iodide (4). A mixture of compound **3** (328 mg, 1 mmol) and methyl iodide (213 mg, ~0.09 ml, 5 mmol) in absolute acetone (11 ml) was boiled for 3 h. The reaction mixture was left for 20 h for the precipitate to separate. The precipitate was filtered off and washed with absolute acetone. Yield 80%; mp >250°C (acetone). IR spectrum (thin layer), ν, cm^{-1}: 1527-1600 (C=C). UV spectrum (ethanol), λ_{max}, nm (ε): 271 (42090), 321 (4090), 334 (3870), 399 (3490).

^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.23 [3H, s, *gem*-$(CH_3)_2$]; 2.74 (3H, s, $N_{(1)}$–CH_3); 4.83 (3H, s, $N_{(7')}$–CH_3); 6.1 (1H, d, *J* = 10.6, H-2'); 6.57 (1H, d, *J* = 7.8, H-7); 6.91 (1H, t, *J* = 7.4, H-5); 7.12-7.22 (2H, m, H-6,4); 7.61 (1H, d, *J* = 9.6, H-6'); 7.72 (1H, d, *J* = 10.7, H-1'); 8.12 (1H, d, *J* = 9.6, H-5'); 8.17 (1H, m, 8.8, H-9'); 9.35 (1H, d, *J* = 8.8, H-10'); 10.08 (1H, d, *J* = 5.6, H-8'). Found, %: C 58.74; H 4.85; N 6.03. $C_{23}H_{23}N_2O$. Calculated, %: C 58.73; H 4.93; N 5.96.

The maxima of the long-wave absorption bands of the photoinduced forms [DRSh-250 Hg lamp with a 365-nm light filter in a stationary regime (T = 297 K, c ~$5 \cdot 10^{-5}$ M in ethanol)] were detected in the electronic spectra at 527, 562, and 434, 564 nm for compounds **3** and **4** respectively.

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