SYNTHESIS OF SPIROTHIAPYRANS WITH A CONDENSED QUINOLINE FRAGMENT

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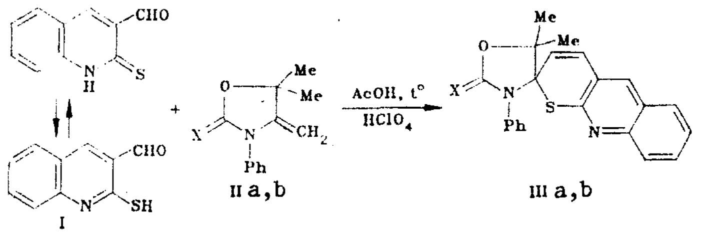
In contrast to spiropyrans [1], their sulfur isologs — spirothipyrans — are difficult to obtain; this is associated with the instability of the starting thiosalicylaldehydes. Only representatives of the 6'-nitroindolinespirothiapyran class are known [2-4]; this is due to the stabilizing effect of the π-acceptor nitro group on the starting thiosalicylaldehydes.

We were able to obtain new spirothiapyrans III with a quinoline fragment condensed with the thiapyran ring by refluxing 2-mercapto-3-formylquinoline (I) [5] and methylene bases II [6, 7] in glacial acetic acid in the presence of catalytic amounts of perchloric acid:



II, III a X=O, b X=S

The spirocyclic structure of III was confirmed by IR, UV, and PMR spectroscopic data. Separate signals of anisochronic methyl groups in the 5 position are observed in the PMR spectra; this is associated with the presence of an asymmetric spiro carbon atom in the molecule.

It should be noted that spirothiapyrans III are among the few representatives of the extremely difficult-to-obtain spiropyrans with a heterocyclic fragment condensed with the pyran ring, attempts at the synthesis of which have been unsuccessful [1].

Compound IIIa. This compound had mp 173-174°C (from ethanol). IR spectrum (mineral oil): 1740 ($\nu_{C=O}$); 1646, 1606, 1586 cm^{-1} ($\nu_{C=C}$). UV spectrum (in isopropyl alcohol), λ_{max} (log ε): 271 (4.83), 349 (3.65), 362 (3.62). PMR spectrum (CDCl$_3$): 1.57 and 1.62 (3H each, s, CH$_3$), 5.96 (1H, d, $^3J_{3',4'}$ = 10.2 Hz, 3'-H), 6.74 (1H, d, $^3J_{3',4'}$ = 10.2 Hz, 4'-H), 7.02-8.00 ppm (10H, m, arom.). The yield was 79%.

Compound IIIb. This compound had mp 224-225°C (from ethanol). IR spectrum (mineral oil): 1606, 1580 cm^{-1} ($\nu_{C=C}$). UV spectrum (in isopropyl alcohol), λ_{max}, nm (log ε): 270 (4.78), 347 (318), 361 (3.14). PMR spectrum (CDCl$_3$): 1.65 and 1.72 (3H each, s, CH$_3$), 6.02 (1H, d, $^3J_{3',4'}$ = 10.8 Hz, 3'-H), 6.72 (1H, d, $^3J_{3',4'}$ = 10.8 Hz, 4'-H), 7.00-7.40 ppm (10H, m, arom.). The yield was 72%.

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