SPIRO-2H-OXOCINES

O. M. Babeshko, E. A. Medyantseva,
L. E. Nivorozhkin, and V. I. Minkin

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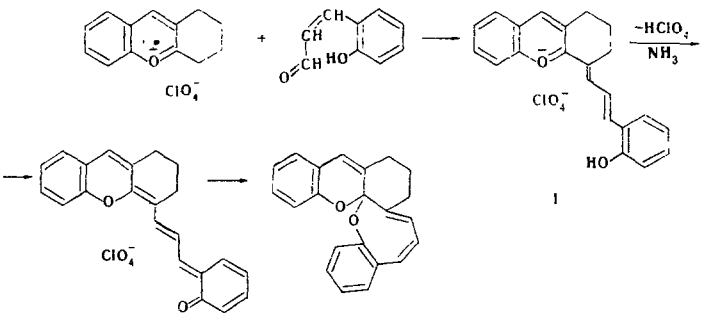
The use of o-hydroxycinnamaldehyde as the aldehyde component in spiran synthesis in the case of condensation with the 2,3-trimethyleno-1-benzopyrylium salt led to the production of the first spiran with a conjugated eight-membered ring – spiro(2H-1-benzopyran-3,3'-trimethyleno-2,2'-2'H-7',8'-benzooxocine). The reaction of o-hydroxycinnamaldehyde and its 5-nitro derivative with 1,3,3-trimethyl-2-methyleneindoline leads to spiro-2H-oxocines in which an additional molecule of the indoline base is connected to the 2H-oxocine ring.

At present an enormous number of diverse (with respect to structure and properties) spirans containing a six-membered 2H-chromene ring have been studied [1]. The general method for their preparation consists in the cocondensation of aromatic o-hydroxy aldehydes with heterocyclic derivatives having an active methylene group.

By subjecting o-hydroxycinnamaldehyde and its 5-nitro derivative to this reaction we obtained the first representative of heterocyclic spirans with an eight-membered 2H-oxocine ring.



I

II

Spiran structure II is extremely stable: II does not display thermochromic, solvatochromic, or photochromic properties; this is generally characteristic of spirans with substituents in the 3,3' position (see [1]).

The reaction of o-hydroxycinnamaldehydes with 1,3-dimethyl-2-methyleneindoline, as a result of which a product of condensation of two molecules of the methylene base with one molecule of the hydroxy aldehyde is formed, proceeds in a somewhat more complex manner. It is known that active methylene bases of the 1,3-dimethyl-2-methyleneindoline type [1, 2] and 1,1-diarylethylenes [3, 4] are inclined to react with salicylaldehydes to give 2 : 1 reaction products, which can be considered to be the result of the addition of a molecule of the methylene base to the double bond of the 2H-chromene ring – III. The following scheme for the formation of spirans from two molecules of methyleneindoline and o-hydroxycinnamaldehydes can be proposed.

In contrast to II, the IR spectrum of III contains only one intense band in the region of C=C stretching vibrations at 1650 cm^{-1}; this band appears in the spectra of various methyleneindoline derivatives [1] and is related to the vibrations of the exocyclic C=C bonds.

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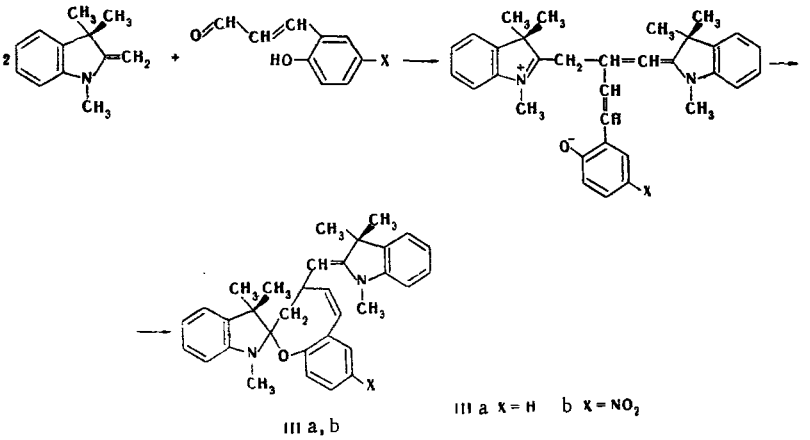

III a, b

III a X = H b X = NO_2

The PMR spectra of III contain signals of the C- and N-methyl groups of two indoline fragments, and diastereotopy of the C-methyl groups shows up distinctly for one of them (included in a spiran system). This result can be explained only by a spiran structure of the III type.

Structure III is one of the possible structures and is probably the most stable tautomer. The other tautomeric forms may arise when a proton is transferred from the 3 position of the oxocine ring to the exocyclic carbon or from the 4 position to the 6 position. However, judging from the PMR and UV spectra, variations in the temperature and solvent do not affect the position of the tautomeric equilibrium.

Attempts to eliminate one molecule of the methyleneindoline base from III in order to convert it to the spiro-2H-7,8-benzooxocine derivative or to obtain it by carrying out the reaction with excess o-hydroxycinnamaldehyde were unsuccessful.

EXPERIMENTAL

The PMR spectra of 10-15% solutions of the compounds in $CDCl_3$ were recorded with a Tesla BS-487-C radiospectrometer. The IR spectra of mineral-oil suspensions of the compounds were recorded with a UR-20 spectrometer. The UV spectra were measured with a VSU-2P spectrophotometer.

The o-hydroxycinnamaldehyde and 2-hydroxy-5-nitrocinnamaldehyde were obtained by the method in [5, 6].

1-(o-Hydroxycinnamylidene)-1,2,3,4-tetrahydro-9-oxaanthracenium Perchlorate (I). This compound was synthesized by refluxing 0.01 mole of 2,3-trimethyleno-1-benzopyrylium perchlorate with excess o-hydroxy-

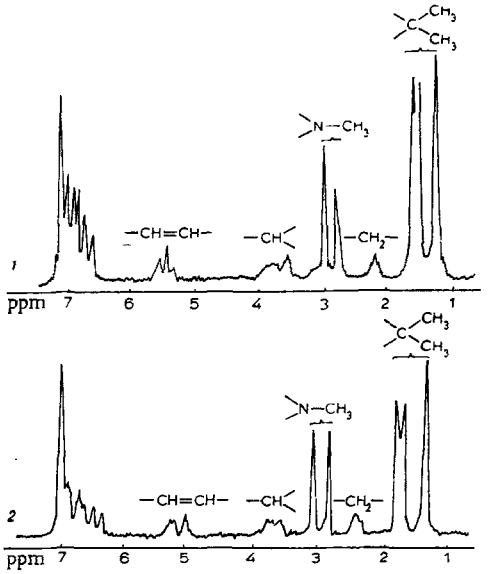

Fig. 1. PMR spectra: 1) IIIa; 2) IIIb.

cinnamaldehyde in glacial acetic acid in the presence of 0.1 ml of perchloric acid for 10-15 min. Workup gave black crystals with mp 196° (from glacial acetic acid). Found: C 63.3; H 4.7; Cl 8.6%. $C_{22}H_{19}ClO_6$. Calculated: C 63.6; H 4.6; Cl 8.8%.

Spiro(2H-1-benzopyran-3,3'-trimethylene-2,2'-2'H-7',8'-benzooxocine (II). This compound was obtained by treatment of salt I in dry ether with ammonia and subsequent removal of the ether by distillation. Crystallization from benzene–alcohol gave bright-yellow crystals with mp 155°. Electronic spectra, λ_{max}, nm ($\varepsilon \cdot 10^{-3}$): in hexane, 212 (51.0), 258 (32.0), and 296 (9.6); in dioxane, 230 (51.6), 258 (48.2), and 296 (12.7); in dimethyl sulfoxide (DMSO), 263 (47.0) and 296 (15.6). IR spectrum: $\nu_{C=C}$ 1670, 1650, and 1630 cm^{-1}. PMR spectrum, ppm: 6.57-7.12 (Ar, CH=CH, m); 2.41, 1.71 (CH_2, m). Found: C 83.0; H 5.7%; M 300 ± 10. $C_{22}H_{18}O_2$. Calculated: C 82.6; H 5.7%; M 314.

Spiro[2H-7,8-benzo-3,4-dihydro-4-(2-methylidine-1,3,3-trimethylindolino)oxocine-2,2'-1',3',3'-trimethylindoline] (IIIa). This compound was synthesized by condensation of equimolar amounts of 1,3,3-trimethyl-2-methyleneindoline and o-hydroxycinnamaldehyde. The reaction was carried out in a sealed ampul by heating on a boiling-water bath for 5 h. The precipitated crystals were removed by filtration and washed with ethanol. Recrystallization from benzene–alcohol (1 : 1) gave a white crystalline substance with mp 184°. Electronic spectra, λ_{max}, nm ($\varepsilon \cdot 10^{-3}$): in hexane, 211 (39.0), 315 (24.2); in dioxane, 229 (44.4) and 316 (45.0); in DMSO, 320 (39.4). IR spectrum: $\nu_{C=C}$ 1650 cm^{-1} (vanished on bromination). See Fig. 1 for the PMR spectrum. Found: C 82.6; H 7.4; N 5.2%; M 466 ± 10. $C_{33}H_{36}N_2O$. Calculated: C 83.3; H 7.3; N 5.9%; M 476.

Spiro[2H-7,8-(5-nitrobenzo)-3,4-dihydro-4-(2-methylidine-1,3,3-trimethylindolino)oxocine-2,2'-1',3',3'-trimethylindoline] (IIIb). This compound was similarly obtained from 1,3,3-trimethyl-2-methyleneindoline and 2-hydroxy-5-nitrocinnamaldehyde. Recrystallization from benzene–alcohol (1 : 1) gave orange-yellow crystals with mp 162°. Electronic spectra, λ_{max}, nm ($\varepsilon \cdot 10^{-3}$): in hexane, 210 (28.8), 315 (31.1); in dioxane, 316 (20.8); in methanol, 315 (23.7), 570 (2.9); in DMSO, 318 (35.4), 420 (1.6). IR spectrum: $\nu_{C=C}$ 1650, $\nu_{NO_2(as)}$ 1520, and $\nu_{NO_2(s)}$ 1345 cm^{-1}. See Fig. 1 for the PMR spectrum. Found: C 74.6; H 6.9; N 8.1%; M 535 ± 10. $C_{33}H_{35}N_3O_3$. Calculated: C 76.1; H 6.6; N 8.1%; M 521.

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