PHOTO- AND THERMOCHROMIC SPIRANS
18.* INDOLINOSPIROCHROMENES WITH π-ACCEPTOR SUBSTITUENTS IN THE 8′ POSITION

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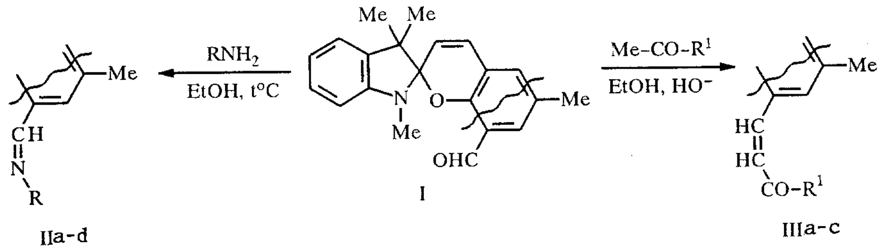
New spiropyrans with π-acceptor azomethine and ketovinyl substituents in the 8′ position were synthesized using the functional possibilities of the carbonyl group. The structures of the compounds obtained and their photochromic properties in 2-propanol at −70°C were studied.

Methods for the creation of spirocyclic structures from compounds that do not have a C_{spiro} atom have been elucidated in quite some detail in the literature. A promising but rarely used method is the functionalization of spirocyclic structures — the halogenation, nitration, and diazo coupling of 1,3,3-trimethylindolinospiropyran in the 6′ position [2]. The use of specific reactions of functional groups has been limited thus far to the reduction of a nitro group to an amino group and acylation of the latter [3].

To partially fill this gap we obtained indolinospirochromene I, with a formyl group in the 8′ position, from 2,6-diformyl-4-cresol and synthesized derivatives involving the formyl group — azomethines II and ketovinyl derivatives III — from it.



IIa-d a) R = 4-MeCOC$_6$H$_4$, b) R = 4-NO$_2$C$_6$H$_4$, c) R = 4-MeC$_6$H$_4$, d) R = CH$_2$Ph; IIIa-d a) R^1 = Me, b) R^1 = Ph, c) R = 2-OHC$_6$H$_4$

The structures of the compounds obtained were confirmed by IR, PMR, and UV spectroscopic data.

The IR spectra of the spiropyrans obtained contain an intense absorption band at 1650-1690 cm^{-1} ($\nu_{C=C}$ or $\nu_{C=N}$) and absorption bands of medium intensity at 1628-1665 cm^{-1} (pyran ring $\nu_{C=C}$), as well as other absorption bands (Table 1) that are characteristic for indolinospirochromenes [4].

In the PMR spectra of spiropyrans II the azomethine proton (in the case of IIc) is characterized by δ = 8.52 ppm and is shifted to stronger field as compared with the signal of formyl proton of starting spiropyran I (δ = 9.99 ppm) (Table 2).

A doublet signal of the 8′-CH=CH proton at 6.1-6.2 ppm with $^3J_{CH=H}$ = 5-8 Hz shows up in the PMR spectra of spiropyrans III; this makes it possible to establish a cis configuration for the vinyl substituent in III.

A comparative study of the photochromic properties of spiropyran I and its azomethine derivatives showed that replacement of the carbonyl group by an imino group leads to disappearance of the photochromic properties that are retained under the experimental conditions (solutions of the spiropyrans in 2-propanol, −70°C, irradiation with UV light with λ_{max} = 365 nm under steady-state conditions) only for IIb — a p-nitroaniline derivative (Table 3).

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*For Communication 17 see [1].

Scientific-Research Institute of Physical and Organic Chemistry, Rostov State University, Rostov-on-Don 344104. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 176-179, February, 1993. Original article submitted July 14, 1992.

TABLE 1. Characteristics of the Synthesized Compounds

Compound	Empirical formula	mp, °C*	IR spectrum, cm^{-1}					Yield, %
			C=O or C=N	Pyran ring C=C	arom.	C-N	C—O	
I	$C_{21}H_{21}NO_2$	105...106	1667	1646	1600...1580	1220	1100, 1020, 969, 920	56
IIa	$C_{28}H_{28}N_2O_2$	173...174	1673	1656	1604...1593	1246	1100, 960, 917	61
IIb	$C_{27}H_{25}N_2O_3$	128...129	1672	1647	1625...1593	1245	1100, 973, 960	52
IIc	$C_{28}H_{28}NO$	195...196	1686	1651	1607...1589	1224	1127, 967, 924	67
IId	$C_{28}H_{28}NO$	155...156	1660	1646	1633...1606	1220	1126, 966	36
IIIa	$C_{24}H_{25}NO_2$	Oil	1680	1665	1590	1250	1100, 985, 930	62
IIIb	$C_{29}H_{27}NO_2$	137...138	1680	1665	1610...1585	1243	1120, 990, 972, 940	76
IIIc	$C_{29}H_{27}NO_3$	105...106	1650	1628	1600...1566	1213	1142, 1010, 966, 922	65

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*The compounds were recrystallized: I, IIc, and IIIb, c from ethanol; IIa, c from benzene—hexane; IIb from octane. Compound IIIa was purified by chromatography.

TABLE 2. PMR Spectra of Spiropyrans I, IId, and IIIa-c

Compound	$C(CH_3)_2$, 3H, s,s	6'-CH_3, 3H, s	N—CH_3, 3H, s	3'-H, 1H, d ($^3J_{CH=CH}$, Hz)	Harom, 4'-H (integral intensity)	—$C\underline{H}$=CH—CO—, 1H, d ($^3J_{CH=CH}$, Hz)	Other protons
I	1,10; 1,25	2,15	2,65	5,68 (11,0)	6,34...7,36 (7H)	—	9,99 (1H), s CHO
IId	1,28; 1, 33	2,20	2,78	6,5 (9,65)	9,70...7,80 (11H)	—	8,52 (1H), s, —CH=H—; 2,26 (3H), s, —CH=N—C $_6H_4$—C $\underline{H}_3$
IIIa	1,09; 1,15	2,09	2,55	5,58 (11,0)	6,30...7,38 (8H)	6,15 (8,0)	1,59 (3H), s, —CO—CH_3
IIIb	1,06; 1,21	2,12	2,64	5,60 (10,5)	6,48...7,45 (8H)	6,15 (8,0)	7,13 (5H), s, CO—Ph
IIIc	1,14; 1,27	2,19	2,71	5,66 (10,5)	6,22...7,90 (12H)	6,09 (5,0)	9,63 (1H), br.s —$C_6H_4O\underline{H}$

TABLE 3. Characteristics of the UV Absorption Spectra of Spiropyrans I-III and Their Photoinduced Forms

Compound	λ_{max}, nm (log ε)	λ_{max}, nm, of the photoinduced form
I	269 (4,14), 298 sh(3,66), 347 (3,60), 370 (3,62)	490 sh, 590
IIa	232 (4,15), 285 (4,14), 326 (4,04), 340 sh (4,01), 381 (4,01)	—
IIb	228 (4,42), 272 sh (3,92), 306 sh (3,97), 379 (4,58)	587
IIc	244 (4,23), 283 (4,42), 340 (3,92)	—
IId	247 (4,28), 282 (4,43), 320 sh (3,54)	—
IIIa	248 (4,33), 267 (4,24), 290 (3,69), 369 (3,75)	628
IIIb	268 (3,99), 297 (3,87) 323 sh (3,75), 369 (3,33)	615
IIIc	255 (4,26); 269 sh (3,65), 335 sh(3,55)	617

In contrast to spiropyrans II with an azomethine group, ketovinyl derivatives III proved to be photoactive compounds. The long-wave absorption bands of their photoinduced forms are shifted bathochromically 25-40 nm as compared with those of starting spiropyran I (Table 3).

EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil were recorded with a Specord IR-75 spectrometer. The PMR spectra of solutions in $CDCl_3$ were obtained with a Tesla BS-487C spectrometer (80 MHz) with hexamethyldisiloxane (HMDS) as the internal standard. A Specord UV-vis spectrophotometer equipped with a special cryostat for recording the spectra of the photoinduced forms of the spiropyrans at low temperatures was used to record the electronic spectra. Irradiation with UV light was carried out with a DRSh-250 mercury lamp with light filters that isolate light with λ_{max} 365 nm.

The characteristics of the compounds obtained are presented in Tables 1-3.

The results of elementary analysis of the synthesized compounds for C, H, and N were in agreement with the calculated values.

1,3,3,6′-Tetramethyl-8′-formylspiro(indoline-2,2′-[2H]chromene) (I). This compound was obtained by brief refluxing in 2-propanol of a mixture of 2,6-diformyl-4-cresol [5] and 1,2,3,3-tetramethylindolenylium perchlorate in a molar ratio of 1.1:1 in the presence of an equimolar amount of piperidine. The reaction mixture was poured into water, and the precipitated product was removed by filtration and purified with a column packed with Al_2O_3 (elution with benzene). The residual I obtained after removal of the solvent by distillation was recrystallized from alcohol.

Azomethines II. An equimolar amount of the corresponding amine was added to 0.36 g (1 mmole) of spiropyran I in 1 ml of hot alcohol, and the reaction mixture was heated to the boiling point and allowed to stand until product II precipitated. The precipitated II was removed by filtration and recrystallized from a suitable solvent.

Ketovinyl Derivatives III. These compounds were obtained by mixing a solution of spiropyran in warm alcohol with a methyl aryl ketone or excess acetone and an aqueous solution of alkali at ≈20-70°C. The mixtures were allowed to stand for 3-24 h. The products were recrystallized (IIIb, c) or purified by chromatography (IIIa).

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