PHOTOCHROMIC AND THERMOCHROMIC SPIROPYRANS.

10.* PHOTOCHROMIC SPIROPYRANS OF THE DITHIOLANE SERIES

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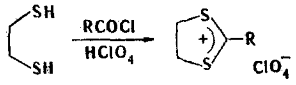
The preparation of 1,3-dithiolanium salts from 1,2-ethanedithiol and carboxylic acid chlorides, the subsequent condensation of which with aromatic o-hydroxy aldehydes leads to spiropyrans of the dithiolane series, is described. The PMR spectra were studied, and the photochromic properties are discussed.

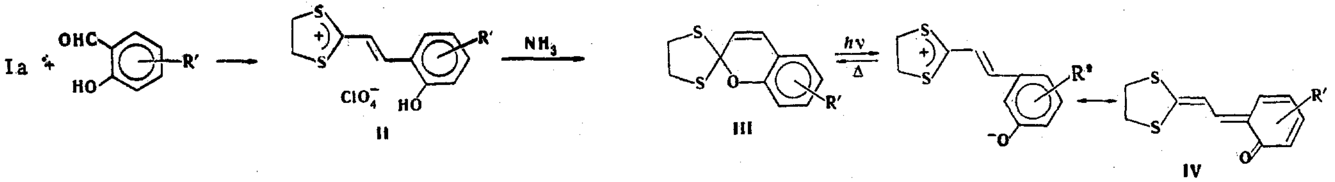
Photochromic spiropyrans of the benzodithiol [2, 3] and dithiol [4] series were previously obtained for a number of 1,3-dithiaheterocyclic compounds. In the present paper we describe the synthesis and spectral characteristics of the cyclic and open forms of spiropyrans of the dithiolane series, as well as the photochromic properties of the spiropyrans obtained. The starting 1,3-dithiolanium salts (Ia-d, Table 1) were obtained from ethanedithiol via the scheme



Ia-d

I a R=CH$_3$; b R=C$_2$H$_5$; c R=CH$_2$Cl; d R=C$_6$H$_5$

o-Hydroxystyryl derivatives of dithiolanium salts (II, Table 2), which were obtained by condensation of salt Ia with substituted aromatic o-hydroxy aldehydes under the usual conditions [2], readily split out the elements of perchloric acid to give spiropyrans (III). In order to increase the yields of II, in a number of cases we used the corresponding cyclic ethyleneacetals in place of the o-hydroxy aldehydes.



Spiropyrans III (Table 3) exist in the colorless cyclic form in the solid phase and in solutions in polar and nonpolar solvents. Absorption bands at 1640 cm^{-1} ($\nu_{C=C}$), which are characteristic for the C=C bond of chromenes, at 1590 cm^{-1} ($\nu_{C=C}$), which correspond to an aromatic system with a conjugated unsaturated group, and at 930-950 cm^{-1} (ν_{C-O}) are present in the IR spectra of these compounds. The typical PMR spectrum of 6'-methylspiro(1,3-dithiolane-2,2'-[2H]chromene) is presented in Fig. 1. The signals of the protons in the 3' and 4' positions of the pyran ring show up in the form of the characteristic quartet of an AB system at ~5.74-6.48 ppm with a spin-spin coupling constant (SSCC) of 10.4 Hz. The four aliphatic protons of the dithiolane ring (an AA'BB' system) give a complex multiplet at 3.0-3.5 ppm. The signal of the methyl group in the 6' position is found at 2.08 ppm.

When alcohol solutions of spiropyrans III are irradiated at −100°C, a complex structural band with a long-wave edge up to 670 nm (Table 4) develops in the absorption band of the spirocyclic form (λ_{max} 313 and 365 nm) in the visible region of the spectrum. As established for spiropyrans [5], the origin of this band is associated with electrocyclic opening of the benzopyran ring in the electronically excited state and the formation of o-quinoid structure

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*See [1] for Communication 9.

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TABLE 1. 1,3-Dithiolanium Perchlorates (Ia-d)

Compound	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	Cl		C	H	Cl	
Ia	194 (dec.)	22,2	3,3	15,9	$C_4H_7ClO_4S_2$	22,0	3,2	16,0	60
Ib	90	26,1	4,0	27,4	$C_5H_9ClO_4S_2$	25,9	3,9	27,6	56
Ic	122	19,2	2,3	25,3	$C_4H_6Cl_2O_4S_2$	19,0	2,3	25,3	62
Id	139	38,4	3,8	22,8	$C_9H_{11}ClO_4S_2$	38,3	3,9	22,7	51

TABLE 2. 2-(2'-Hydroxystyryl)-1,3-dithiolanium Perchlorates (II)

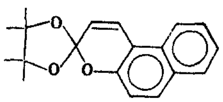
R'	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	Cl		C	H	Cl	
H	155	41,1	3,6	11,2	$C_{11}H_{11}ClO_5S_2$	40,8	3,4	11,3	80
5-Br	159	33,0	2,5	31,1	$C_{11}H_{10}BrClO_5S_2$	32,8	2,5	31,3	76
5-CH_3	153	43,0	4,1	10,5	$C_{12}H_{13}ClO_5S_2$	42,7	3,8	10,7	69
3-CH_3	165	43,0	3,9	10,6	$C_{12}H_{13}ClO_5S_2$	42,7	3,8	10,7	74
3-NO_2	160	36,0	2,6	9,6	$C_{11}H_{10}ClNO_7S_2$	35,8	2,7	9,7	82
4-OCH_2Ph	159	52,8	4,0	8,4	$C_{18}H_{17}ClO_6S_2$	52,6	3,9	8,3	84
3-NO_2-5-OCH_3	154	36,3	3,1	9,2	$C_{12}H_{12}ClNO_8S_2$	36,2	3,0	9,0	73
3-NO_2-5-Br	183	29,2	2,2	27,9	$C_{11}H_9BrClNO_7S_2$	29,5	2,1	28,1	76
3,5-Br_2	158	27,6	1,6	40,2	$C_{11}H_9Br_2ClO_5S_2$	27,4	1,6	40,1	68
5,6-C_4H_4	190 (dec.)	40,9	3,4	9,4	$C_{15}H_{13}ClO_5S_2$	40,7	3,5	9,5	81

TABLE 3. R'-Spiro(1,3-dithiolane-2,2'-[2H]chromenes) (III)

R'	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	S		C	H	S	
H	157	59,2	4,4	28,3	$C_{11}H_{10}OS_2$	59,0	4,5	28,8	68
6-Br	110	44,0	3,1	22,0	$C_{11}H_9BrOS_2$	43,8	3,0	21,7	76
6-CH_3	187	61,3	4,9	27,0	$C_{12}H_{12}OS_2$	61,0	5,0	27,1	65
8-CH_3	152	59,8	4,9	27,4	$C_{12}H_{12}OS_2$	61,0	5,0	27,1	72
8-NO_2	290	49,1	3,4	24,1	$C_{11}H_9NO_3S_2$	49,4	3,4	24,0	70
7-OCH_2Ph	125	65,5	5,0	20,0	$C_{18}H_{16}O_2S_2$	65,8	4,8	19,5	72
6-OCH_3—8-NO_2	192	48,5	3,6	21,2	$C_{12}H_{11}NO_4S_2$	48,5	3,7	21,5	68
6-Br—8-NO_2	218	38,3	2,4	18,4	$C_{11}H_8BrNO_3S_2$	38,1	2,3	18,5	64
6,8-Br_2	153	34,9	2,0	17,0	$C_{11}H_8Br_2OS_2$	34,7	2,1	16,8	73
5,6-C_4H_4	112	66,2	4,7	24,0	$C_{15}H_{12}OS_2$	66,2	4,4	23,5	67
6-OCH_3	202	57,5	4,9	25,4	$C_{12}H_{12}O_2S_2$	57,1	4,7	25,4	81
6-Cl	212	51,6	3,4	25,1	$C_{11}H_9ClOS_2$	51,4	3,5	24,9	78
6-NO_2	194	49,6	3,3	23,8	$C_{11}H_9NO_3S_2$	49,4	3,4	24,0	65
8-NO_2-**benzo[f]**	192	56,4	3,7	19,6	$C_{15}H_{11}NO_3S_2$	56,7	3,4	20,2	65

IV. The reverse conversion of the open form to the spirocyclic form occurs when solutions are heated or irradiated with visible light. The typical electronic absorption spectrum of photochromic spiropyran III (R' = 7'-$OCH_2C_6H_5$) is presented in Fig. 2. The data in Table 4 show that the introduction of a donor substituent ($OCH_2C_6H_5$) and annelation of the benzene ring lead to a 50-70 nm hypsochromic shift of the long-wave absorption band. This result is in agreement with the results of calculations [1].

A comparison of the positions of the absorption maxima of the open forms of benzo[f]-chromenes of the benzodithiol (570 nm [1, 2]), benzoxathiol (530 nm [6]), and dithiolane (530 nm) series and of 4,4,5,5-tetramethylspiro(1,3-dioxolane-2,2'-[2H]-benzo[f]chromene) (V, 480 nm) shows that deannelation of the heterene part of the molecule and replacement of the sulfur atom by an oxygen atom give rise to an approximately identical hypsochromic shift (∿40 nm) of the long-wave absorption band. When both of these factors operate together, they lead to a 90-nm hypsochromic shift of the long-wave band for spiropyran V of the dioxolane series.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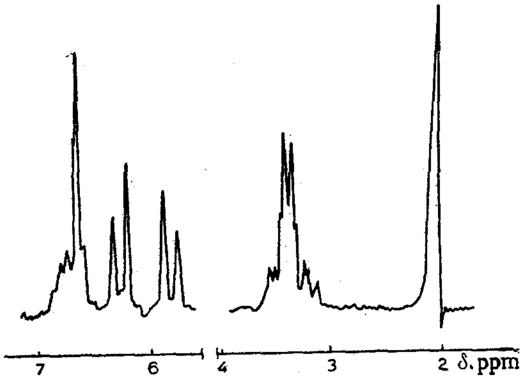

Fig. 1

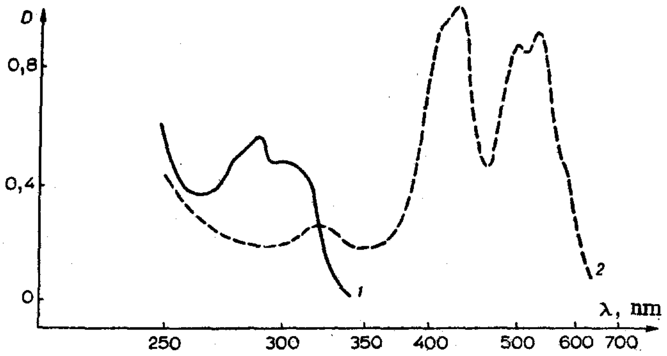

Fig. 2

Fig. 1. PMR spectrum of 6'-methylspiro(1,3-dithiolane-2,2'-[2H]chromene) in hexachlorobutadiene.

Fig. 2. Electronic absorption spectrum of 7'-benzyloxyspiro(1,3-dithiolane-2,2'-[2H]chromene) (in ethanol, c $1.3 \cdot 10^{-5}$ mole/liter, −100°C): 1) cyclic form; 2) photocolored form.

TABLE 4. Absorption Spectra of Spiropyrans III in Ethanol

R'	λ_{max}, nm	
	spiro form (III)	open form (IV)
H	230, 285	410, 570, 615
6-CH_3	240, 285, 295	410, 570, 610
7-OCH_2Ph	245, 290, 310	435, 515, 538
5,6-C_4H_4	232, 320	435, 510, 530
8-NO_2-benzo[f]	225, 308	380, 540, 600

EXPERIMENTAL

The electronic spectra of alcohol solutions of spiropyrans III and their photocolored isomers (at −100°C) were recorded with a Specord UV-vis spectrophotometer with a cryostat for low-temperature measurements. The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of 10-15% solutions of the spiropyrans in hexachlorobutadiene were recorded with a Tesla BS-487 spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard.

2-Methyl-1,3-dithiolanium Perchlorate (Ia). A 28-ml (0.5 mole) sample of 72% perchloric acid was added carefully with stirring to an ice-cooled mixture of 16 ml (0.17 mole) of ethanediol [7] and 72 ml (1 mole) of acetyl chloride. The acid was added in 15-20 min to avoid, as far as possible, pronounced coloration of the solution. The precipitated salt was removed by filtration, washed with ethyl acetate and ether, and recrystallized from glacial acetic acid to give 22 g (60%) of a colorless or slightly colored substance with mp 194°C.

Salts Ib-d (Table 1) were similarly obtained.

2-(2'-Hydroxystyryl)-1,3-dithiolanium Perchlorates (II, Table 2). A 0.011-mole sample of substituted o-hydroxybenzaldehyde or o-hydroxynaphthaldehyde and one to two drops of 72% perchloric acid were added to a solution of 2.18 g (0.01 mole) of perchlorate Ia in 10 ml of glacial acetic acid, and the mixture was heated at 100°C for 3-5 min until the o-hydroxystyryl derivative began to crystallize. The colored precipitate was removed by filtration, washed with ethyl acetate and ether, and recrystallized from glacial acetic acid.

The condensation of 0.01 mole of perchlorate Ia with 0.012 mole of hydroxybenzaldehyde ethyleneacetal in 10 ml of a mixture of glacial acetic acid with acetic anhydride (1:1) led to the corresponding o-hydroxystyryl derivatives in higher yields.

Spiro(1,3-dithiolane-2,2'-[2H]chromenes) (III, Table 3). A stream of dry ammonia was passed into a suspension of 0.01 mole of the corresponding perchlorate II in 20 ml of benzene until the solid material became colorless and dissolved. The resulting benzene solution was filtered, and the filtrate was chromatographed with a column filled with Al_2O_3 (with benzene as the mobile phase). The fraction with R_f 0.9 was collected, and the benzene was removed by distillation at reduced pressure. Recyrstallization of the residue from isopropyl alcohol—benzene gave the spiropyrans in the form of colorless or slightly colored crystalline substances.

4,4,5,5-Tetramethylspiro(1,3-dioxolane-2,2'-[2H]benzo[f]chromene) (V). This compound was synthesized from 2,4,4,5,5-pentamethyl-1,3-dioxolanium perchlorate [8] and 2-hydroxynaphthaldehyde by a method similar to that used to obtain spiropyrans III. The product, with mp 98-99°C (from glacial acetic acid), was obtained in 56% yield. Found: C 77.2; H 6.6%. $C_{19}H_{20}O_3$. Calculated: C 77.0; H 6.7%.

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1-OCTADECYL- AND 3,3-DIPHENYL-SUBSTITUTED PHOTOCHROMIC INDOLINOSPIROCHROMENES

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A number of photochromic indolinospirochromenes that contain an octadecyl substituent in the 1 position were synthesized. The introduction of an octadecyl group in place of a methyl group increases the stability of the merocyanine form in solution but does not change its spectral characteristics. On the other hand, the introduction of phenyl groups in place of methyl groups in the 3 position does not change the stability of the merocyanine but gives rise to a bathochromic shift of the long-wave absorption band.

The modification of the structures of photochromic indolinospirochromenes through the introduction of substituents that increase the possibility of steric interactions in the molecule is of interest in the development of photochromic compositions with predesignated properties. The introduction of bulky substituents may lead both to an increase in the stability of the colored photomerocyanine form by hindering its isomerization to the cisoid isomer and subsequent cyclization to the colorless spirochromene and to a decrease in the efficiency of the photocoloration process by hindering cis-trans isomerization of the photomerocyanine [1].

It has been recently shown that the introduction of a hexadecyl substituent in the 1 position of the photochromic spirochromene increases the stability of the photomerocyanine form in solution [2]. We have confirmed this interesting principle in a new case. We ob-

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