dissolved in a small amount of benzene—methanol (9:1). The solution was filtered through a layer of aluminum oxide, the filtrate was vacuum evaporated, and the residue was recrystallized from benzene containing a small amount of methanol to give 0.5 g (41%) of ester IX with mp 225-226° and R_f 0.43. IR spectrum: 1630 (CO), 1710 ($COOCH_3$), and 3170 cm^{-1} (NH). PMR spectrum (in CF_3COOH): singlet at 2.80 ($2\text{-}CH_3$), singlet at 3.85 (CH_3COO), doublets at 6.92 and 8.03 (olefinic protons, J 16 Hz), multiplet at 7.80 (4-H), and multiplet at 7.33 ppm (the remaining aromatic protons). Found, %: C 69.1; H 5.5. $C_{14}H_{13}NO_3$. Calculated, %: C 69.1; H 5.4.

Methyl 3-(3-Indolyl)acrylate (VIII). As in the preceding experiment, 0.3 g (35%) of ester VIII with mp 184-185° and R_f 0.41 was obtained from 0.7 g (0.003 mole) of 3-(3-indoyl)-acrylic acid in 30 ml of methanol. IR spectrum: 1655 (CO), 1735 (CH_3COO), and 3175 cm^{-1} (NH). Found, %: C 68.2; H 5.0. $C_{13}H_{11}NO_3$. Calculated, %: C 68.1; H 4.8.

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SYNTHESIS AND SPECTRAL CHARACTERISTICS OF PHOTOCHROMIC 1',3',3'-TRIMETHYL-6-NITRO-7-PHENYL-2H-CHROMENE-2-SPIRO-2'-INDOLINE

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5-Nitro-4-phenylsalicylaldehyde, from which the corresponding photochromic indolinespirochromene was obtained, was synthesized. The introduction of a phenyl substituent in the 7 position brings about a substantially smaller change in the longwave band in the electronic absorption spectrum of the merocyanine form than introduction of this substituent in the 8 position.

Continuing our study of the structural factors that affect the spectral characteristics of the colored form of spirochromenes [1], in order to compare the effect of a phenyl substituent in the 7 and 8 positions we attempted to synthesize a photochromic spiran (VII) with a phenyl substituent in the 7 position.

We obtained 4-phenylsalicylaldehyde (II) in low yield by formylation of 3-hydroxydiphenyl (I) [2] by the Duff method [3]; the structure of II was confirmed by oxidation to 4-phenylsalicylic acid (III) [4], which has been distinguished from 2-phenylsalicylic acid (IV) [5]. Thus the formyl group enters the 4 position in the formylation of 3-hydroxydiphenyl by the Duff method.

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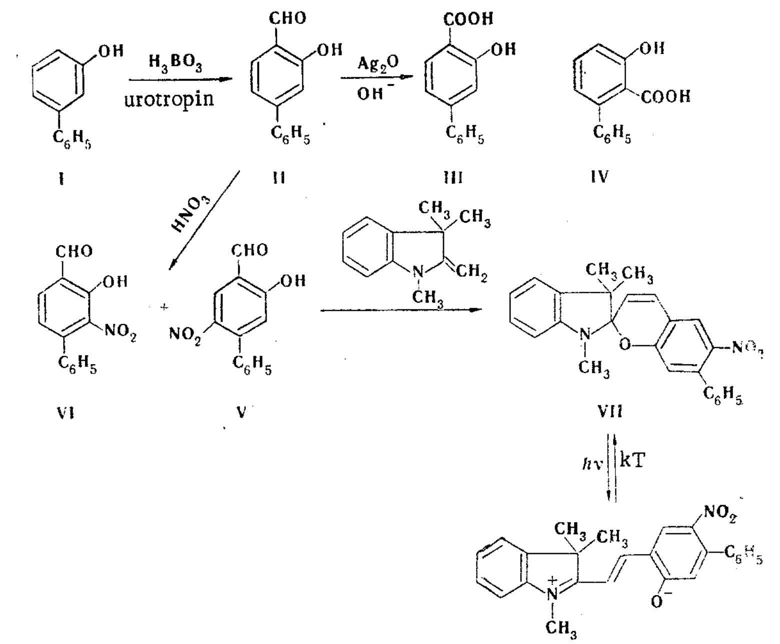

The nitration of aldehyde II gave a mixture of two nitrophenylsalicylaldehydes. Taking into account the fact that nitration of phenylsalicylaldehydes is directed to the ring containing hydroxyl and formyl groups [1], we assumed that the nitration products are 4-phenyl-5-nitro- and 3-nitro-4-phenylsalicylaldehydes (V and VI). We compared the UV spectra of these substances (Fig. 1) with the UV spectra of four pairs of 3- and 5-nitro-substituted salicylaldehydes (Figs. 2 and 3). In all cases the longwave band of the 3-nitro-substituted salicylaldehydes is shifted bathochromically by 40-60 nm as compared with the analogous band of the corresponding 5-nitro-substituted compounds. It is known that the longwave band of o-nitrophenol (λ_{max} 346 nm), which is the band of charge transfer from the hydroxyl group to the o-nitro group (the $\pi_{OH}\rightarrow\pi^*_{o\text{-}NO_2}$ band), is shifted bathochromically by 60 nm as compared with the longwave band of p-nitrophenol (λ_{max} 286 nm, the $\pi_{OH}\rightarrow\pi_{p\text{-}NO_2}$ band [6-8]). This

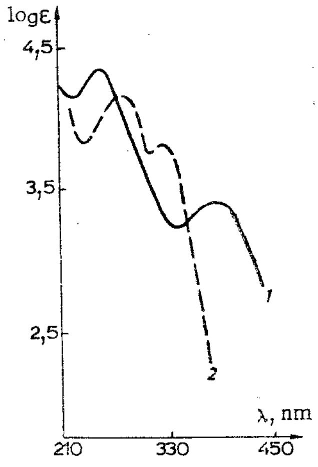

Fig. 1

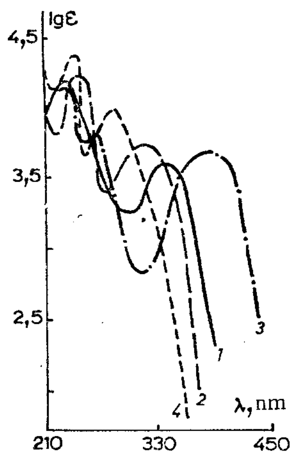

Fig. 2

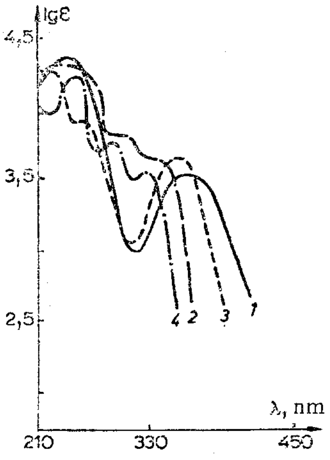

Fig. 3

Fig. 1. Absorption spectra in octane: 1) 3-nitro-4-phenylsalicylaldehyde; 2) 5-nitro-4-phenylsalicylaldehyde.

Fig. 2. Absorption spectra in octane: 1) 3-nitrosalicylaldehyde; 2) 3-methoxy-5-nitrosalicylaldehyde; 3) 3-nitro-5-methoxysalicylaldehyde; 4) 5-nitrosalicylaldehyde.

Fig. 3. Absorption spectra in octane: 1) 3-nitro-5-phenylsalicylaldehyde; 2) 5-nitro-3-phenylsalicylaldehyde; 3) 3-nitro-5-bromosalicylaldehyde; 4) 5-nitro-3-bromosalicylaldehyde.

principle is also characteristic for the correspondingly substituted salicylaldehydes, and 5-nitro-4-phenylsalicylaldehyde (V) with admixed 3-nitro-4-phenylsalicylaldehyde (VI) is consequently formed in the nitration of 4-phenylsalicylaldehyde.

This is in agreement with the principle used in [9]: In the case of salicylaldehydes with ortho-oriented hydroxyl and nitro groups, the melting points are lower than the melting points of compounds with hydroxyl and nitro groups that are para-oriented. Data illustrating this principle in the case of the five pairs of salicylaldehydes that we used in this research are presented in the experimental section.

We obtained spirochromene VII, which has photochromic properties at room temperature, by reaction of aldehyde V with 1,3,3-trimethyl-2-methyleneindoline. Colorless solutions of VII in toluene and dioxane take on a dark blue to azure coloration on irradiation with UV light; this color gradually vanishes after irradiation is discontinued. The intensity of the red-violet color of an alcohol solution of the spiran increases under the influence of UV irradiation.

Using the method in [10], we determined the parameters of the absorption spectra of the merocyanine form of spiran VII. The results are presented in Table 1, in which data for 1',3',3'-trimethyl-6-nitro-2H-chromene-2-spiro-2'-indoline (VIII) and 1',3',3'-trimethyl-6-nitro-8-phenyl-2H-chromene-2-spiro-2'-indoline (IX), previously obtained in [1], are also presented for comparison. The introduction of a phenyl substituent in the 7 position brings about a substantially lower change in the parameters of the first absorption band of the merocyanine form than introduction in the 8 position; at the same time, the second absorption band experiences an appreciable bathochromic shift of 20-30 nm. The oscillator forces of the bands evidently do not change substantially. The negative solvatochromism characteristic for most merocyanine forms of spiropyrans [10] is observed for the colored form of spiran VII.

EXPERIMENTAL

The UV spectra of 0.5-1•10^{-4} M solutions of the salicylaldehydes were recorded with a VSU-2 spectrophotometer; salicylaldehydes with the following physical characteristics were used: 5-nitro-, mp 125-126° [11]; 3-nitro-, mp 108.5-109° [11]; 3-bromo-5-nitro-, mp 149-150° [9]; 5-bromo-3-nitro, mp 125-126° [9]; 3-phenyl-5-nitro-, mp 144-145° [1]; and 5-phenyl-3-nitro-, mp 114-115° [1]. The IR spectra of KBr pellets of the compounds were measured with a UR-20 spectrometer. The absorption spectra of the starting solutions of spirochromenes in the photochemical steady state, the calculation of the extinction coefficients of the colorless and colored forms of the spirochromene at various wavelengths, and the approximation of the results by Gaussian curves by means of an M-220 computer were accomplished as described in [10]; the experimental data were obtained by means of an improved apparatus with recording of the optical densities of the test solutions simultaneously at two different wavelengths.

4-Phenylsalicylaldehyde (II). A mixture of 300 g of glycerol and 70 g of boric acid was heated at 170° for 1 h with removal of the water by distillation, and the mixture was then heated at 200° until water evolution had ceased completely, after which 50 g (0.36 mole) of urotropin and 50 g (0.29 mole) of m-hydroxydiphenyl (mp 78° [2]) were added. At the end of the exothermic reaction, the mixture was heated at 160° for 1 h. It was then cooled to 110°, 80 ml of 70% H_2SO_4 was added, and the mixture was refluxed for 2 h. It was then sub-

TABLE 1. Characteristics of the Electronic Absorption Spectra of the Merocyanine Forms of the Spirans

Compound	Solvent	I band			II band		
		λ_{max}, nm	ε_{max}	f	λ_{max}, nm	ε_{max}	f
VII	Alcohol	547	32000	0,45	384	19000	0,29
	Dioxane	583	58000	0,68	391	25000	0,38
	Toluene	589	93000	1,41	397	38500	0,63
VIII	Alcohol	523	26000	0,42	358	17000	0,45
	Dioxane	582	49000	0,61	375	27000	0,55
	Toluene	596	53000	0,75	373	20000	0,34
IX	Alcohol	554	40000	0,60	379	26000	0,59
	Dioxane	592	53000	0,67	389	32000	0,59
	Toluene	602	46000	0,65	389	29000	0,48

jected to steam distillation with superheated steam. The distillate was extracted with ether, the extract was dried with $MgSO_4$, the solvent was removed by distillation, and the residue was vacuum distilled to give 3.2 g (6%) of aldehyde III with bp 153-154° (1 mm) and mp 79-80° (after two recyrstallizations from ethanol). IR spectrum: 1670 cm^{-1} (C=O). Found, %: C 78.9 H 5.2. $C_{13}H_{10}O_2$. Calculated, %: C 78.8 H 5.0.

4-Phenylsalicylic Acid (III). A solution of 0.4 g (10 mmole) of NaOH in 30 ml of water was added to a solution of 0.85 g (5 mmole) of silver nitrate in 20 ml of water, and the precipitated silver oxide was removed by filtration and suspended in 50 ml of 1% NaOH. The suspension was heated to 70° and treated with a solution obtained by heating 0.5 g (2.5 mmole) of 4-phenylsalicylaldehyde II in 100 ml of 20% NaOH. The reaction mixture was stirred for 1 h, after which it was filtered, and the filtrate was acidified with 10% HCl. The resulting precipitate was dissolved in dilute $NaHCO_3$, the solution was acidified with 10% HCl, and the precipitate was crystallized successively from water and methanol to give 0.12 g (22%) of acid III with mp 205-206° (mp 207-208° [4]). Found, %: C 73.0 H 5.0. $C_{13}H_{10}O_3$. Calculated, %: C 72.9; H 4.7.

4-Phenyl-5-nitrosalicylaldehyde (V) and 3-Nitro-4-phenylsalicylaldehyde (VI). A mixture of 1.6 ml of fuming HNO_3 (sp. gr. 1.5) and 8 ml of glacial CH_3COOH was added in the course of 45 min at 10° to a solution of 1 g (5 mmole) of 4-phenylsalicylaldehyde II in 32 ml of glacial acetic acid, after which the mixture was stirred for 2 h and poured over 10 g of ice. The resulting precipitate was removed by filtration, washed with water, and recrystallized from 45% ethanol. The crystallized product (0.55 g) was dissolved in 10 ml of chloroform and chromatographed with a column filled with 50 g of silica gel with elution with 200 ml of petroleum ether—benzene (1:1) and 500 ml of benzene (100-ml fractions were selected). Each fraction was analyzed by TLC on Silufol in a benzene—hexane—ethyl acetate system (15:26:15). The fractions containing one component with R_f 0.26 were combined, the solvent was removed, and the residue was crystallized three times from ethanol to give 0.2 g (16%) of aldehyde V with mp 152-153°. IR spectrum: 1670 cm^{-1} (C=O). Found, %: C 64.1; H 3.9; N 5.9. $C_{13}H_9NO_4$. Calculated, %: C 64.2; H 3.7; N 5.8.

The fractions containing one component with R_f 0.39 were combined, the solvent was removed, and the residue was crystallized from alcohol to give 70 mg (6%) of aldehyde VI with mp 102-104°. IR spectrum: 1665 cm^{-1} (C=O). Found, %: C 64.2; H 4.2. $C_{13}H_9NO_4$. Calculated, %: C 64.2; H 3.7.

1',3',3'-Trimethyl-6-nitro-7-phenyl-2H-chromene-2-spiro-2'-indoline (VII). A solution of 0.67 g (3.8 mmole) of freshly distilled 1,3,3-trimethyl-2-methyleneindoline in 10 ml of alcohol was added to a hot solution of 0.55 g (2.3 mmole) of 4-phenyl-5-nitrosalicylaldehyde V in 20 ml of ethanol in the course of 30 min, after which the mixture was refluxed for 2 h, and the resulting precipitate was separated and crystallized successively from alcohol and benzene—hexane (1:20) to give 164 mg (18%) of spiran VII with mp 152-153°. UV spectrum in octane, λ_{max}, nm (ε): 237 (28,800) and 277 (14,300). Found, %: C 75.0; H 5.8; N 6.8. $C_{25}H_{22}N_2O_3$. Calculated, %: C 75.4; H 5.6; N 7.0.

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