In a repeat experiment the reaction of 6.23 g (0.037 mole) of 1-vinyl-2-phenylpyrrole and 4.7 g of ethanethiol in the presence of an initiator (in an ampule at 70°C for 24 h) gave 7.9 g (92.7%) of phenylpyrrole XI with bp 144-145°C (1 mm), n_D^{20} 1.5955, and d_4^{20} 1.0766. The PMR spectra of the undistilled mixture and the distillate are shown in Fig. 2.

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PHOTOCHROMIC PROPERTIES OF SOME N-SUBSTITUTED 3,3-DIMETHYL-6'-NITROINDOLINE-2-SPIRO-2'-2H-CHROMENES

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543.422.6

A number of photochromic 1-carbethoxymethyl-3,3-dimethyl-6'-nitroindoline-2-spiro-2'-2H-chromenes were synthesized. The introduction of a carbethoxymethyl substituent at the nitrogen atom instead of a methyl group somewhat increases the rate of dark decolorization of the photomerocyanines without appreciably affecting the spectral characteristics. The results are compared with the analogous spectral-kinetic characteristics of 1-phenyl-substituted compounds.

The interest in indolinespirochromenes as a class of photochromic compounds is due to the extensive possibilities of variation of the structure; this makes it possible to change their spectral-kinetic properties in a desired direction. From the point of view of the most widely accepted concepts, the rate of decolorization of spirochromenes is determined by the charges on the reaction centers [1], the magnitudes of which are particularly strongly affected by the substituents attached to the nitrogen atom. In this connection, it seemed of interest to compare the effect of a phenyl substituent attached to the nitrogen atom and of a substituent similar to it with respect to its inductive effect on the spectral-kinetic properties of spirochromenes in order to draw a conclusion regarding the effect of structural factors on the individual steps in the thermal decolorization of photomerocyanine molecules.

We synthesized the unstable 1-carbethoxymethyl-3,3-dimethyl-2-methyleneindoline by alkylation of 2,3,3-trimethylindolenine [2] with ethyl bromoacetate and subsequent treatment of the resulting 1-carbethoxymethyl-2,2,3-trimethylindoleninium bromide with sodium hydroxide; reaction of the product with 5-nitro-, 3-methoxy-5-nitro-, 3-bromo-5-nitro-, and 3,5-dinitrosalicylaldehydes gave the corresponding spirochomenes I-IV.

We investigated the kinetics of dark decolorization and the spectral properties of the compounds obtained and the corresponding series of N-phenyl-substituted spirochromenes V-VIII by the methods described in [3, 4]. The results are presented in Tables 1 and 2.

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TABLE 1. Kinetic Parameters of the Dark Decolorization of Spirochromenes

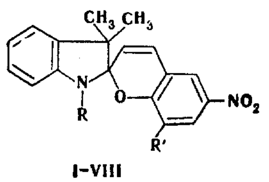
Compound	Solvent	$k \cdot 10^2$, sec^{-1} at					$\Delta H^{\neq}$, kJ/mole	$\Delta S^{\neq}$, J/mole·deg
		10°*	20°	25°	30°	40°		
I	Toluene	2,47	6,70	12,2	22,0	41,3	86,9	17,6
	Dioxane	1,84	5,32	7,97	17,5	32,0	76,6	15,9
II	Toluene	2,20	6,55	13,0	23,4	63,6	83,3	10,5
	Dioxane	0,92	2,96	6,04	10,7	29,0	91,2	30,1
III	Toluene	2,52	9,69	13,8	36,2	61,9	80,3	2,1
	Dioxane	1,10	4,69	7,72	18,8	35,5	92,5	36,8
IV	Toluene	0,106	0,368	1,05	1,78	5,45	98,3	38,5
	Dioxane	0,0374	0,140	0,302	0,550	1,65	99,6	33,9
V	Toluene	4,62	17,7	32,2	62,1	—	91,6	46,4
	Dioxane	2,83	5,60	10,6	27,3	—	87,9	25,1
VI	Toluene	11,8	36,5†	54,0	114,5	—	78,2	48,1
	Dioxane	4,78	14,2	22,5	53,8	—	93,3	49,8
VII	Toluene	0,89	3,17	5,80	11,0	—	90,8	22,6
	Dioxane	0,68	1,42	2,55	4,86	—	77,4	22,6
VIII	Toluene	0,60	2,90	4,75	11,5	—	102,4	66,9
	Dioxane	0,240	1,00	1,80	3,10	—	102,0	56,1

*In the case of dioxane the measurements were made at 12°C.
†At 30-40°C [14].

TABLE 2. Spectral Characteristics of the Merocyanine Forms of the Spirochromenes

Compound	λ_{max}, nm		Position of center of band, nm	
	toluene	alcohol	toluene	alcohol
I	595	550	584	543
II	610	575	598	573
III	605	550	589	541
IV	587	535	577	522
V	610[a]	560[b]	609	549
VI	615[c]	580	610	565
VII	615	560	605	551
VIII	595[d]	540[e]	587	529

a) At 610 nm according to [1]. b) At 559 nm according to [1]. c) At 620 nm according to [14]. d) At 602 nm according to [1]. e) At 537 nm according to [1].



I-VIII

I $R=CH_2COOC_2H_5$, $R'=H$; II $R=CH_2COOC_2H_5$, $R'=OCH_3$; III $R=CH_2COOC_2H_5$, $R'=Br$; IV $R=CH_2COOC_2H_5$, $R'=NO_2$; V $R=C_6H_5$, $R'=H$; VI $R=C_6H_5$, $R'=OCH_3$; VII $R=C_6H_5$, $R'=Br$; VIII $R=C_6H_5$, $R'=NO_2$

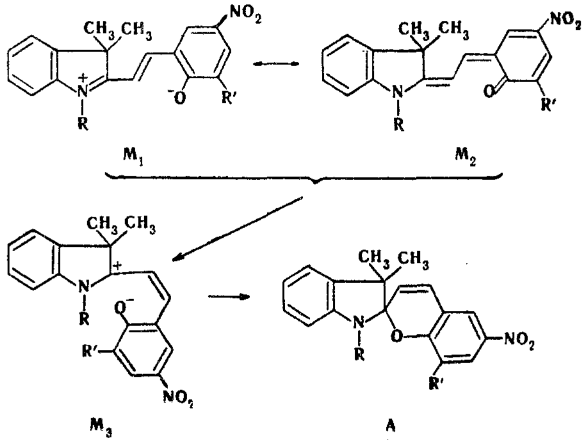
In the series of N-carbethoxymethyl-substituted I-IV (Table 1) the rate of dark decolorization increases somewhat as compared with the corresponding N-methyl-substituted compounds; the effect of substituents in the 8' position is not manifested appreciably (except in the case of the nitro group). Transition from toluene to dioxane slows down the reaction.

In the case of N-phenyl-substituted spirochromenes (V-VIII) the dark decolorization reaction is accelerated appreciably as compared with the series of N-methyl-substituted compounds (except for spirochromene VII); the effect of the substituent in the 8' position on the reaction rate is manifested more distinctly. Transition from toluene to dioxane somewhat slows down the reaction somewhat uniformly for the entire series, in contrast to N-methyl-substituted compounds [5], for which this effect is substantial only for the 8-bromo-substituted spirochromene.

The measurement of the absorption spectra of the colored merocyanine forms of the examined spirochromenes and the subsequent treatment of the experimental data (Table 2) were accomplished as described in [4]. In addition to the position of the center of the absorption band, which, as in preceding studies [4, 5], was determined by an approximation method, we also present the position of the maximum on the experimental curve. The certain difference between these values is associated with the asymmetry of the spectral curves.

The spectral characteristics of the N-carbethoxymethylspirochromenes (I-IV) practically coincide with the characteristics of the N-methyl compounds [5]. A bathochromic shift of the absorption band (5-10 nm in alcohol and up to 25 nm in toluene) is observed in the case of N-phenylspirochromenes (V-VIII). The effect of substituents in the 8' position on the spectral characteristics is subject to the principles that we noted in [6]: a methoxy group gives rise to an appreciable bathochromic shift, whereas a nitro group causes a hypsochromic shift of the absorption band.

According to [7], the thermal decolorization of photomerocyanines includes two successive steps: isomerization of the trans-merocyanine (which can be represented by superposition of the polar M_1 and quinoid M_2 mesomeric structures) to cis isomer M_3 and cyclization of isomer M_3 to spirochromene A. During the isomerization parts of the merocyanine molecule undergo rotation relative to the bond between the carbon atoms in the 3' and 4' positions, and the ease of rotation increases as the contribution of quinoid form M_2 to the resulting structure of the molecule increases [8]. In addition, isomerization should be accompanied by transfer of positive charge from the nitrogen atom to the carbon atom in the 2 position since, as a consequence of considerable steric hindrance in the M_3 structure, this carbon atom cannot exist in the sp^2 hybridization state [7]. This sort of charge transfer will evidently be realized with greater ease, the lower the basicity of the nitrogen atom. Cyclization of cis isomer M_3 to spirochromene A will in turn take place more rapidly, the higher the charges on the reaction centers [9].



It follows from the data obtained that the substituents attached to the nitrogen atom accelerate the decolorization of the photomerocyanine in the order C_6H_5 > $CH_2COOC_2H_5$ > CH_3. A phenyl substituent, which has an inductive effect similar to that of the carbethoxymethyl group [10], reduces the basicity of the nitrogen atom to a great degree (the pK_a values in water are 4.85 for N-methylaniline [11], 2.08 for phenylglycine ethyl ester [12], and 0.9 for diphenylamine [11]). Thus the data obtained confirm the previously expressed assumption [7] that the stabilities of photomerocyanines increase as their basicities increase.

The decrease in the order of the central bond in merocyanine systems that have negative solvatochromism is associated with a bathochromic shift of the long-wave absorption band [13]. On the basis of the spectral characteristics of N-phenyl-substituted photomerocyanines,

TABLE 3. Characteristics of the Spirochromenes Obtained

Spirochromene	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	N		C	H	N	
I	160—163	66,5	5,5	7,5	$C_{22}H_{22}N_2O_5$	67,0	5,6	7,1	15
II	134—136	65,0	5,6	7,2	$C_{23}H_{24}N_2O_6$	65,1	5,7	6,6	20
III	128—132	55,5	4,5	5,7	$C_{22}H_{21}BrN_2O_5$*	55,8	4,5	5,9	10
IV	202	59,9	5,0	10,1	$C_{22}H_{21}N_3O_7$	60,1	4,8	9,6	28

*Found: Br 16.3%. Calculated: Br 16.9%.

in the spectra of which a bathochromic shift is observed as compared with N-carbethoxymethyl-substituted (Table 2) and N-methyl-substituted compounds [5]. It can be concluded that the electronic structure of N-phenyl-substituted merocyanines is characterized by a lower order of the central bond of the polymethine chain. Thus, because of the large contribution of quinoid structure M_2 and the lower basicity of the heterocyclic nitrogen atom the trans—cis isomerization step should evidently proceed more rapidly than in the case of N-alkyl-substitued compounds. The substantial dependence of the reaction rate on the electronic effect of the substituents in the 8' position may constitute evidence in favor of the assumption that in the case of the dark decolorization of N-phenyl-substituted photomerocyanines in nonpolar solvents the trans—cis isomerization step is accelerated as compared with the step involving cyclization of the cis isomer. On the other hand, the rate of the analogous reaction of N-alkyl-substituted photomerocyanines changes only slightly when the substituents in the 8' position are changed. It is possible that in the latter case the rate of the overall process is controlled by the trans—cis isomerization step.

Thus the data obtained illustrate the difference in the stabilities of the photomerocyanine forms of indolinospirochromenes as a consequence of a change in the ease of the trans—cis transformations associated with the change in the basicity of the heterocyclic nitrogen atom.

EXPERIMENTAL

The measurement of the absorption spectra of solutions of the spirochromenes in the photoelectronic steady state and approximation of the data thus obtained by Gaussian curves with a computer were accomplished as described in [4]. The purification of the solvents, preparation of the solutions, and measurement of the dark decolorization rate constants of the phtomerocycanines were accomplished as described in [3].

An automated spectral-kinetic system connected to a Dnepr-1 control computer was used for the experiments. The description of this system will be presented in a separate paper. As a result of using this system we were able to measure the reaction rates by a nonpulse method with a half-converson period of a few seconds.

The N-phenyl-substituted spirochromenes,* the synthesis of which is described in [15], had the following characteristics: spirochromene V, mp 146-147°C (literature mp 148-149°C); spirochromene VI, mp 181-184°C (literature mp 181.5-181.8°C); spirochromene VII, mp 165-166°C (literature mp 165-166°C); spirochromene VIII, mp 209-211°C (literature mp 213-214°C).

1-Carbethoxymethyl-2-methylene-3,3-dimethylindoline. A mixture of 11 g (70 mmole) of 2,3,3-trimethylindolenine [2] and 13.5 g (80 mmole) of ethyl bromoacetate was heated on a water bath for 1 h, after which 150 ml of a 30% solution of sodium hydroxide was added, and the mixture was extracted with ether. The extract was dried with anhydrous magnesium sulfate, the solvent was removed, and the residue was vacuum distilled to give 8 g (47%) of a fraction with bp 110-115°C (2 mm) and n_D^{20} 1.5450. IR spectrum (film): 1765 (C=O), 1670 (C=C), 1385, 1350 cm^{-1} (geminal CH_3).

1-Carbethoxymethyl-3,3-dimethyl-6'-nitroindoline-2-spiro-2'-2H-chromenes (I-IV). A solution of 5 mmole of 1-carbethoxymethyl-2-methylene-3,3-dimethylindoline in 5 ml of absolute ethanol was added to a solution of 5 mmole of the appropriate salicylaldehyde in 15 ml of absolute ethanol, and the mixture was refluxed for 1 h. The resulting precipitate was separated and recrystallized from ethanol. The properties of the spirochromenes obtained are presented in Table 3.

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*We sincerely thank D. A. Drapkina for providing us with these preparations.

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SOME TRANSFORMATIONS OF 2,3-DIAMINOINDOLE DERIVATIVES.
SYNTHESIS OF INDOLO[2,3-b]QUINOXALINES

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1-Methyl-3-methoxy- and 1-methyl-3-piperidino-3-acetamidooxindole anils, respectively, were obtained by oxidation of 1-methyl-2-arylamino-3-acetamidoindoles with oxygen in the presence of copper acetate in methanol and in a mixture of dimethylformamide and piperidine. When the oxindole anils are heated, they undergo cyclization to indolo[2,3-b]quinoxalines. Indolo[2,3-b]quinoxaline N-oxides were obtained from the latter by the usual method.

We have found that 1-methyl-2-arylamino-3-acetamidoindoles form 1-methyl-3-methoxy-3-acetamidooxindole anils (Ia-f) when they are oxidized with oxygen in the presence of copper acetate in methanol. If the oxidation is carried out in dimethylformamide (DMF) in the presence of piperidine, 1-methyl-3-piperidino-3-acetamidooxindole anils (Ig,h) are formed. The formation of the known [1] 1-methylisatin α-anils as side products is observed in all cases. The PMR spectrum of Ic contains singlets at 1.67 (CH_3Ar), 2.25 ($COCH_3$), 3.01 (OCH_3), 3.15 (NCH_3), and 8.48 ppm (NH), as well as a multiplet signal at 6.63-7.40 ppm (eight aromatic protons). One absorption band at 3250 cm^{-1} (NH) is observed in the IR spectra of derivatives Ia-h.

The reaction probably proceeds through a step involving substituted 1-methylisatin diimine, after which methanol or piperidine add to the C=N bond in the 3 position of the latter to give Ia-h (See scheme on following page).

Compounds Ia,c,e,f,h were cyclized to indolo[2,3-b]quinoxalines (IIa-d) by heating to 200-210°C. The formation of indolo[2,3-b]quinoxalines evidently also proceeds through a

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