<u>3H,10H-Indeno[1,2-f]indol-10-one (Xa)</u>. This compound was obtained from acid VIIIa by a method similar to that used to prepare IXa. The yield of Xa, with mp 231-232°C, was 0.22 g (49%). IR spectrum: 3341, 3270 (NH); 1692 cm⁻¹ (C=O). UV spectrum, λ_{max} (log ε): 206 (4.28), 243 (4.41), 263 (4.53), and 398 nm (3.71). Found: C 82.9; H 4.2; N 6.4%; M⁺ 219. C₁₅H₉NO. Calculated: C 82.2; H 4.1; N 6.4%; M 219.

<u>1H,9H-Indeno[1,2-f]indol-9-one (Xb).</u> This compound was obtained from acid VIIIb by a method similar to that used to prepare IXa. The yield of Xb, with mp 249-250°C, was 0.15 g (33%). IR spectrum: 3270, 3340 (NH); 1700 cm⁻¹ (C-O). UV spectrum, λ_{max} (log ε): 204 (4.20), 224 (4.17), 254 (4.35), 283 (4.52), and 392 nm (3.84). Found: C 82.2; H 4.2; N 6.3%; M⁺ 219. C₁₅N₉NO. Calculated: C 82.2; H 4.1; N 6.4%; M 219.

LITERATURE CITED

1. W. J. Neis, Rec. Trav. Chim., <u>67</u>, 349 (1948)

2. N. Campbell and W. H. Stafford, J. Chem. Soc., No. 2, 299 (1952).

3. O. Diels, Chem. Ber., <u>34</u>, 1758 (1901).

4. J. H. Weisburger, E. K. Weisburger, and H. P. Morris, J. Am. Chem. Soc., <u>74</u>, 4540 (1952). 5. R. R. Phillips, in: Organic Reactions [Russian translation], Vol. 10, Inostr. Lit.,

Moscow (1963), p. 148.

SYNTHESIS AND PHOTOCHROMIC PROPERTIES OF INDOLINOSPIROCHROMENES WITH BENZYL, ETHYL, AND ACETONYL GROUPS ATTACHED TO THE NITROGEN ATOM

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A number of photochromic indoline spirochromenes with benzyl, acetonyl, and ethyl substituents attached to the nitrogen atom in the indoline part of the molecule were synthesized. The introduction of a benzyl group at the nitrogen atom in place of a methyl group does not change the rate constants of the dark decolorization of the photomerocyanines, whereas an acetonyl group increases them, and an ethyl group decreases them. The introduction of the indicated substituents in the 1 position gives rise to a bathochromic shift (up to 18 nm) of the long-wave absorption band of the merocyanine form of the spirochromene.

Substituents attached to the nitrogen atom have a substantial effect on the photochromic properties of indolinospirochromenes [1]. In the present research we studied this effect for a series of new compounds with benzyl, ethyl, and acetonyl substituents attached to the nitrogen atom.



I $R^1 = H$, $R^2 = CH_2C_6H_5$; II $R^1 = H$, $R^2 = CH_2COCH_3$; III $R^1 = C_6H_5$, $R^2 = C_2H_5$; I--III a $R^3 = NO_2$, $R^4 = H$; b $R^3 = NO_2$, $R^4 = OCH_3$; c $R^3 = NO_2$, $R^4 = Br$; d $R^3 = R^4 = NO_2$; e $R^3 = H$, $R^4 = NO_2$; f $R^3 = OCH_3$, $R^4 = NO_2$; g $R^3 = Br$, $R^4 = NO_2$

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'TABLE 1. Spectral-Kinetic Characteristics of the Photomerocyanines of Spirochromenes I-III

Com-	k•10 ² (20°C)	, șec ⁻¹	λ_{max} , nm			
pound	to l- uene	di- oxane	tol- uene	eth- anol		
la Ib Ic Ida Ila Ilb Ilc Illa Illb Illc Illa Ille Illfa Illg	$\begin{array}{c} 3,45\\ 3,36\\ 6,22\\\\ 6,20\\ 20,0\\ 4,00\\ 2,20\\ 1,50\\ 1,70\\\\ 2,70\\\\ 6,20\end{array}$	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	597 615 597 595 615 600 610 623 610 623 610 620 648	$\begin{array}{c} 550\\ 575\\ 545\\ 530\\ 555\\ 565\\ 540\\ 548\\ 575\\ 545\\ 525\\ 567\\ 628\\ 580\end{array}$		

^aBecause of the extremely low solubilities of these compounds, we were unable to detect photochromic properties upon irradia= tion with UV light.

TABLE 2. Spirochromenes I-III

Com- pound	R²	R ³	R⁴	mp, ℃	Found, %		%	Empirica1	Calc., %			d, %
					с	н	N	formula	с	н	N	Yiel
la lb lc lla llb llc lld llf llia llb lllc llla lllb lllc llld lllc llld lllc	$\begin{array}{c} CH_2C_6H_5\\ CH_2C_6H_5\\ CH_2C_6H_5\\ CH_2C_6H_5\\ CH_2COCH_3\\ CH_5\\ C_2H_5\\ C$	$\begin{array}{c} NO_2\\ NO_2\\ NO_2\\ NO_2\\ NO_2\\ NO_2\\ NO_2\\ OCH_3\\ Br\\ NO_2\\ NO_2\\ NO_2\\ NO_2\\ HO_2\\ HOCH_3\\ Br\\ \end{array}$	H OCH ₃ Br NO ₂ H OCH ₃ Br NO ₂ NO ₂ H OCH ₃ Br NO ₂ NO ₂ NO ₂ NO ₂	$\begin{array}{c} 162\\ 167\\ 120-122\\ 270\\ 232\\ 179\\ 152\\ 192\\ 177\\ 172\\ 211\\ 206\\ 201\\ 285\\ 138\\ 143\\ 201\\ \end{array}$	$\begin{array}{c} 75,5\\72,8\\63,1\\67,1\\69,7\\67,0\\57,1\\61,2\\67,0\\57,3\\75,7\\73,3\\63,0\\67,7\\76,0\\74,0\\63,6\end{array}$	5,8 5,7 4,6 4,8 5,6 4,4,8 5,6 4,5 6,1 6,0 5,1 5,4 5,9 4,5 6,1 5,4 5,9 4,5 5,9 4,5 6,1 5,4 6,1 5,4 5,9 5,9 4,4 5,6 5,10	$\begin{array}{c} 7,0\\ 6,5\\ 6,2\\ 9,3\\ 7,8\\ 7,0\\ 6,2\\ 10,0\\ 7,0\\ 6,3\\ 7,2\\ 6,6\\ 5,4\\ 9,6\\ 7,1\\ 6,1\\ 5,3\end{array}$	$\begin{array}{c} C_{25}H_{22}N_2O_3\\ C_{26}H_{24}N_2O_4\\ C_{25}H_{21}BrN_2O_3\\ C_{27}H_{21}N_3O_5\\ C_{21}H_{20}N_2O_4\\ C_{22}H_{22}N_2O_5\\ C_{21}H_{19}BrN_2O_4\\ C_{21}H_{19}N_3O_6\\ C_{22}H_{22}N_2O_5\\ C_{21}H_{19}BrN_2O_4\\ C_{26}H_{22}N_2O_3\\ C_{27}H_{26}N_2O_4\\ C_{26}H_{23}BrN_2O_3\\ C_{26}H_{23}N_3O_5\\ C_{26}H_{24}N_2O_3\\ C_{27}H_{26}N_2O_4\\ C_{26}H_{23}BrN_2O_3\\ C_{27}H_{26}N_2O_4\\ C_{26}H_{23}BrN_2O_3\\ \end{array}$	$\begin{array}{c} 75,4\\72,9\\62,9\\67,7\\69,2\\67,0\\56,9\\61,6\\67,0\\56,9\\75,7\\73,3\\63,5\\75,7\\73,3\\63,5\\75,7\\73,3\\63,5\end{array}$	5,6 5,6 4,4 5,5 5,6 4,3 5,6 4,3 5,6 4,3 5,9 5,9 4,7 5,9 5,9 4,7 5,9 4,7 5,9 4,7 5,9 4,7 5,9 4,7 5,9 4,7 5,9 4,7 5,9 4,7 5,9 4,7 5,9 4,7 5,9 4,7 5,9 4,7 5,9 4,7 5,9 4,7 5,9 4,7 5,9 4,7 5,9 5,9 4,7 5,9 5,9 4,7 5,9 5,9 4,7 5,9 5,9 4,7 5,9 5,9 4,7 5,9 5,9 4,7 5,9 5,9 4,7 5,9 5,9 4,7 5,9 5,9 4,7 5,9 5,9 4,7 5,9 5,9 4,7 5,9 5,9 4,7 5,9 5,9 4,7 5,9 4,7 5,9 5,9 4,7 5,9 5,9 4,7 5,9 5,9 4,7 5,9 5,9 4,7 5,9 5,9 4,7 5,9 5,9 4,7 5,9 5,9 4,7 5,9 5,9 4,7 5,9 5,9 4,7 5,9 4,7 5,9 4,7 5,9 4,7 5,9 4,7 5,9 4,7 5,9 4,7 5,9 4,7 5,9 4,7 5,9 4,7 5,9 4,7 5,9 4,7 5,9 5,9 4,7 5,9 4,7 5,9 4,7 5,9 4,7 5,9 5,9 4,7 5,9 5,9 4,7 5,9	7,0 6,5 5,9 9,5 7,7 7,1 6,3 10,3 7,1 6,3 6,3 5,7 9,2 6,8 6,3 5,7 9,2 6,8 5,7 5,7	3,9 4,3 2,8 5,0 4,1 14,2 9,0 30,0 20,0 12,3 16,8 15,8 29,0 25,4 18,1 23,6 23,0

 ${}^{a}R^{1} = H$, except for the III series, for which $R^{1} = C_{e}H_{5}$. ^bThe compositions of Ic, IIc, g, and IIIc, g were also confirmed by determination of the bromine content. ^CThe overall yields were calculated on the basis of the starting hydrazine for the I and II series and on the basis of 4-nitrobiphenyl for the III series.

1-Benzyl- and 1-acetonyl-2-methyleneindolines, which were obtained by alkylation of 2,3,3 trimethylindolenine with benzyl chloride or bromoacetone with subsequent treatment of the quaternary salts with an aqueous solution of sodium bicarbonate, react with salicylaldehydes to give the corresponding spirochromenes of the I and II series. The compounds of the III series were obtained by condensation of 5-phenyl-1-ethyl-3,3-dimethyl-2-methyleneindoline with salicylaldehydes.

Most of the spirochromenes obtained have photochromic properties. When colorless solutions in nonpolar or slightly polar solvents are irradiated with UV light, they become blue or blue-green as a consequence of conversion to the merocyanine form. When irradiation is discontinued, the solutions gradually become colorless. Alcohol solutions of the spirochromenes have bright-violet or blue coloration due to partial conversion to the merocyanine form. The intensity of the coloration increases upon irradiation with UV light, whereas it decreases in the case of irradiation with visible light. When irradiation is discontinued, the solutions are gradually restored to their original state. The positions of the maxima of the long-wave absorption bands of the merocyanine forms and the rate constants (k) for the dark decolorization of the photomerocyanines at 20°C for the compounds obtained are presented in Table 1.

The rate constants for dark decolorization for the compounds obtained undergo slight changes when the substituents in the pyran part of the molecule are varied. The character of the effect of the substituents differs in the different series, and no definite relationships between the rate constants for dark decolorization and the peculiarities of the electronic effect of the substituents in the pyran part of the molecule can be established; we have already discussed similar behavior in [1].

The effect of the substituents in the pyran part of the molecule on the position of the long-wave absorption band is in complete agreement with the established principles [2]: The methoxy group gives rise to a substantial bathochromic shift (up to 20 nm in toluene and up to 27 nm in ethanol; spirochromenes Ib, IIb, and IIIb as compared with, respectively, spirochromenes Ia, IIa, and IIIa), whereas the nitro group induces a hypsochromic shift (up to 23 nm in ethanol; spirochromenes Id and IIId as compared with, respectively, spirochromenes Ia and IIIa). The compounds that contain a nitro group in the 8' position are characterized by absorption in a longer-wave region than the isomeric compounds with a nitro group in the 6' position (spirochromenes IIIe, f, g as compared with, respectively, spirochromenes IIIa, b, c).

A comparison of the data that we obtained for the spirochromenes of the I series with the characteristics of the corresponding N-methyl-substituted compounds [3] shows that the introduction of a benzyl substituent in place of a methyl group at the nitrogen atom does not change the rate of dark decolorization substantially; a tendency for a bathochromic shift (up to 18 nm) of the long-wave absorption band of the photomerocyanine is observed, particularly in ethanol. The observed effect is possibly a consequence of an increase in the steric hindrance to solvation of the positively charged nitrogen atom of the photomerocyanine as the volume of the substituent is increased. Similar effects have already been noted [4].

From a comparison of the characteristics of the spirochromenes of the II series and the corresponding N-methyl-substituted [3] and N-carbethoxymethyl-substituted [1] it may be concluded that the introduction of an acetonyl substituent in place of the methyl group increases the rate of dark decolorization of the photomerocyanines several times. This is evidently due to a decrease in the basicity of the nitrogen atom as a consequence of the electron-acceptor effect of the acetyl fragment. The indicated effect is expressed to a smaller degree than the effect of the more electron-acceptor ethoxycarbonyl fragment [1].

Substantial changes in the absorption band of the photomerocyanine in toluene are not observed when the methyl substituent attached to the nitrogen atom is replaced by an acetonyl group; in ethanol the band undergoes a bathochromic shift. A similar shift, which, as in the case of N-benzyl-substituted compounds, may evidently be associated with an increase in the volume of the substituent, was also previously observed in the case of the introduction of a carbethoxymethyl substituent in the 1 position [1].

A comparison of the data for the spirochromenes of the III series with the characteristics of 1-methyl-5-phenyl-substituted compounds [5] makes it possible to conclude that a certain degree of retardation of the rate of dark decolorization of the photomerocyanine is observed in most cases when an ethyl group is introduced in the 1 position in place of the methyl group; this can evidently be regarded as being a consequence of a certain increase in the volume of the substituent and its electron-donor effect. A tendency for a bathochromic shift of the absorption band (12-18 nm) is also observed. Let us note that retardation of the rate of dark decolorization when the volume of the alkyl substituent attached to the nitrogen atoms increases has been previously noted [6].

The confirmed (in the present research for new examples) possibilities of decreasing the rate of dark decolorization of the photomerocyanines when the donor character of the substituent in the 1 position is increased and of increasing the indicatedrates as the acceptor effect of such substituents is intensified, as well as the possibility of achieving a bathochro-

mic shift of the long-wave absorption band of the photomerocyanine as the volume of the substituent attached to the nitrogen atom, can be used in the purposeful development of photochromic systems with predesignated properties.

EXPERIMENTAL

The rate constants of dark decolorization and the absorption spectra of the photomerocyanines were measured by means of an automated spectral-kinetic apparatus as described in [7]. The synthesis of the 1-ethy1-5-pheny1-substituted spirochromenes (IIIa-g, Table 2), was realized by a previously described method [5].

<u>1-Benzyl-3,3-dimethyl-6'-nitroindoline-2-spiro-2'-[2H]chromenes (Ia-d, Table 2).</u> A mixture of 2.5 g (15.8 mmole) of 2,3,3-trimethylindolenine [8] with 16.2 ml (140 mmole) of benzyl chloride was heated on a boiling-water bath for 2 h, after which it was poured into water, and the aqueous mixture was filtered. The aqueous solution of the quaternary salt was washed with benzene and made alkaline with a solution of sodium bicarbonate. The 1-benzyl-3,3-dimethyl-2-methyleneindoline was extracted with ether, and the extract was dried over anhydrous magnesium sulfate. The ether was removed, and the oily red residue [0.4 g (1.6 mmole)] was dissolved in 10 ml of absolute ethanol. The solution was added to 1.6 mmole of the corresponding salicylaldehyde in 10 ml of absolute ethanol, the mixture was refluxed for 20 min, and the precipitate was separated and recrystallized from ethanol or heptane.

<u>1-Acetonyl-3,3-dimethyl-6'(or 8')-nitroindoline-2-spiro-2'-[2H]chromenes (IIa-d, f, g, Table 2).</u> A mixture of 3 g (18.9 mmole) of 2,3,3-trimethylindolenine with 4.9 g (35 mmole) of freshly distilled bromoacetone was heated at 56°C for 10 min, after which 250 ml of hot water was added, and the aqueous mixture was filtered with charcoal. The aqueous mixture was washed with benzene and made alkaline with a solution of sodium bicarbonate. The 1-acetonyl-3,3-dimethyl-2-methyleneindoline was extracted with ether, and the extract was dried over anhydrous magnesium sulfate. The solvent was removed, the residual 1-acetonyl-3,3-dimethyl-2-methyleneindoline [2,37 g(11 mmole)] in the form of an orange oil was dissolved in 20 ml of absolute ethanol, and the solution was added to a solution of 11 mmole of the corresponding salicylaldehyde. The mixture was refluxed for 10 min, and the precipitate was separated and recrystallized from ethanol.

LITERATURE CITED

- 1. M. A. Gal'bershtam, N. M. Przhiyalgovskaya, O. R. Khrolova, I. B. Lazarenko, G. K. Bobyleva, and N. N. Suvorov, Khim. Geterotsikl. Soedin., No. 12, 1640 (1977).
- 2. V. I. Pantsyrnyi and M. A. Gal'bershtam, Khim. Geterotsikl. Soedin., No. 5, 659 (1973).
- 3. M. A. Gal'bershtam, N. M. Przhiyalgovskaya, O. R. Khrolova, I. V. Manakova, G. K. Bobyleva, and N. N. Suvorov, Khim. Geterotsikl. Soedin., No. 8, 1069 (1977).
- 4. M. A. Gal'bershtam, M. V. Loseva, O. R. Khrolova, and G. K. Bobyleva, Khim. Geterotsikl. Soedin., No. 10, 1367 (1979).
- 5. M. A. Gal'bershtam, N. M. Przhiyalgovskaya, I. B. Lazarenko, V. S. Kononova, and N. N. Suvorov, Khim. Geterotsikl. Soedin., No. 4, 497 (1976).
- N. P. Samoilova, G. K. Bobyleva, and M. A. Gal'bershtam, Khim. Geterotsikl. Soedin., No. 1, 51 (1980).
- M. A. Gal'bershtam, O. R. Khrolova, G. K. Bobyleva, Yu. B. Pod'yachev, N. P. Samoilova, V. M. Bulgakov, and Yu. V. Zasukhin, Khim. Vys. Énerg., <u>13</u>, 230 (1979).
- 8. G. Plancher, Chem. Ber., 31, 1488 (1898).