5H-2-Methylthiazolo[4,3-b]-1,3,4-thiadiazole-5-thione (VIII). A mixture of 0.22 g (1 mmole) of rhodanine Va, 0.22 g (1 mmole) of phosphorus pentasulfide, and 3 ml of dioxane was refluxed for 2 h, after which the dioxane was evaporated, and the residue was crystallized from alcohol to give 0.1 g (53%) of a product with mp 234-235°C (mp 235°C [9]). Found: N 14.7; S 50.9%. $C_5H_4N_2S_3$. Calculated: N 14.8; S 51.1%.

2-Carboxymethylthio-1,3,4-thiadiazole (IX). A solution of 0.22 g (1 mmole) of rhodanine Va in 5 ml of 50% formic acid was heated at 80°C for 2 h, after which it was evaporated to dryness, and the residue was triturated with acetonitrile to give 0.1 g (52%) of a product with mp 158-159°C (from acetonitrile) (mp 156-158°C [9]). Found: N 15.9; S 35.8%. $C_4H_4N_2O_2S_2$. Calculated: N 15.9; S 36.4%.

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REACTION OF A FISCHER BASE AND ITS DERIVATIVES WITH BENZOYLACETALDEHYDES

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The corresponding 2-(3-benzoyl-2-propen-1-ylidene)indolines, which exist in the form of merocyanines and do not display tendencies to undergo intramolecular cyclization to the spiro form, were obtained as a result of the reaction of 1,3,3-trimethyl-2-methyleneindoline and its analogs with p-substituted benzoylacetaldehydes.

Indolinespiropyrans presently constitute one of the most promising classes of photochromic substances [1]. The overwhelming majority of compounds of this type are synthesized by the reaction of a Fischer base and its derivatives with substituted salicylaldehydes and have indoline-2-spiro-2'-[2H]chromene structures. Recently performed quantum-chemical calculations have shown [2] that the photochromic properties of these compounds depend markedly on the electronic structure of the pyran fragment. Thus, for example, the transition from benzopyran derivatives to pyran derivatives sharply increases the stability of the open form, which leads to the loss of photochromic properties. In this connection, it seemed of interest to study the properties of indoline merocyanines in which one might have expected the formation of a closed form with a pyran fragment containing a phenyl substituent. We selected 2-(3-benzoyl-2-propenylidene)indolines as the subjects of this investigation.

It is known [3] that β-dicarbonyl compounds (primarily β-keto aldehydes) react smoothly with primary or secondary amines to give β-aminovinyl ketones. We have established that the reaction of β-keto aldehydes (IVa-g) with Fischer bases (I-III), which can be regarded

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TABLE 1. 2-[3-(p-R-Benzoyl-2-propen-1-ylidene)indolines (V-VII)

Compound	R	mp, °C	Found, %			Empirical formula[a]	Calculated, %			Yield, %
			C	H	N		C	H	N	
Va	H	159—160[b]	82,9	7,0	4,3	$C_{21}H_{21}NO$	83,2	7,0	4,6	41
Vb	NO_2	160—161	72,3	7,9	5,9	$C_{21}H_{20}N_2O_3$	72,4	8,0	5,8	49
Vc	Cl	141—142	75,0	6,0	4,1	$C_{21}H_{20}ClNO$	74,7	6,0	4,2	47
Vd	Br	165—167	66,1	5,2	3,6	$C_{21}H_{20}BrNO$	66,0	5,3	3,7	48
Ve	CH_3	157—158	83,0	7,7	4,5	$C_{22}H_{23}NO$	83,2	7,3	4,4	39
Vf	OCH_3	133—134	79,3	7,0	4,1	$C_{22}H_{23}NO_2$	79,2	7,0	4,2	48
Vg	$N(CH_3)_2$	193—195	79,4	7,4	8,1	$C_{23}H_{26}N_2O$	79,7	7,6	8,1	47
VIf	OCH_3	277—278	69,6	6,0	7,1	$C_{22}H_{22}N_2O_4$	69,8	5,9	7,4	40
VIg	$N(CH_3)_2$	307—308	70,3	6,2	10,6	$C_{23}H_{25}N_3O_3$	70,6	6,4	10,7	20
VIIb	NO_2	162—165	76,4	5,4	6,6	$C_{26}H_{22}N_2O_3$	76,1	5,4	6,8	46
VIIf	OCH_3	169—171	81,6	6,4	3,4	$C_{27}H_{25}NO_2$	82,0	6,4	3,5	41
VIIg	$N(CH_3)_2$	221—223	82,6	6,8	7,1	$C_{28}H_{28}N_2O$	82,3	6,9	6,9	26

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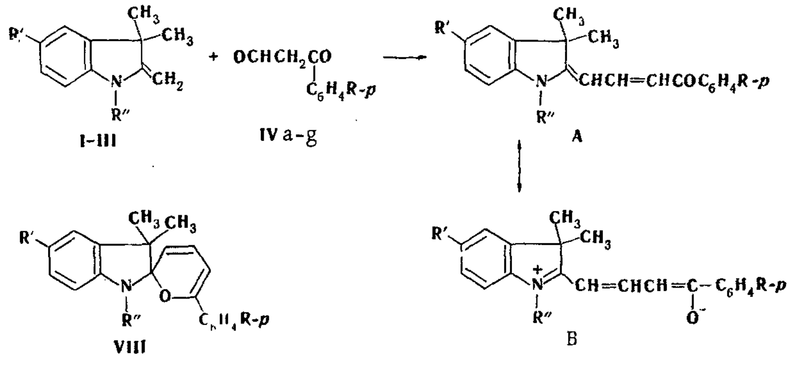
[a] The compositions of Vc, d were also confirmed by determination of the halogen content. [b] This compound had mp 158-159°C [4].

as enamines with an active nucleophilic CH_2 group, proceeds similarly and leads to the corresponding vinylogs of aminovinyl ketones (V-VII, Table 1).

The reaction products, viz., 2-(3-benzoyl-2-propenylidene)indolines (V-VII), are yellow to dark-red crystalline substances. Merocyanine Va was previously obtained by reaction of a Fischer base with benzoylacetylene [4], by reaction of 1,3,3-trimethyl-2-formylmethyleneindoline with acetophenone [5, 6], or by cleavage of a hemicyanine [7]. Solutions of merocyanines V-VII have intense absorption in the visible region (430-490 nm) that does not change as the temperature is changed or when they are irradiated with visible or UV light (Table 2). These data constitute evidence for the absence of conversion to closed spiro form VIII in solutions of V-VII.



Va-g; VIf,g; VIIb,f,g

I, V R'=H, R''=CH_3; II, VI R'=NO_2, R''=CH_3; III, VII R'=H, R''=C_6H_5; a R=H; b R=NO_2; c R=Cl; d R=Br; e R=CH_3; f R=CH_3O; g R=$N(CH_3)_2$

A bathochromic shift (15-29 nm) of the long-wave absorption band is observed for all of the compounds on passing from a nonpolar (toluene) to a polar (ethanol) solvent. The positive solvatochromism constitutes evidence for the primary contribution of nonpolar mesomeric structure A to the ground state of merocyanines V-VII [8].

The long-wave absorption band in the electronic spectra of V is shifted in conformity with the electronic effect of the substituents in the benzene fragment. The position of the band (on the frequency scale) is described satisfactorily by correlation equations with the aid of the σ_p constants:

$$\nu(\text{cm}^{-1}) = 22\,700 - 1390\sigma_p;\ s = 90;\ r = 0.986\ \text{(toluene)};$$

$$\nu(\text{cm}^{-1}) = 21\,800 - 1670\sigma_p;\ s = 140;\ r = 0.976\ \text{(ethanol)}$$

The negative sign of the reaction constants in these correlation equations constitutes evidence for stabilization of zwitterion mesomeric structure B with an increase in the

TABLE 2. Electronic Spectra of Merocyanines V-VII

Compound	Toluene		Ethanol	
	λ_{max}, nm	$\varepsilon_{max} \times 10^{-4}$	λ_{max}, nm	$\varepsilon_{max} \times 10^{-4}$
Va	442	4,91	456	4,88
Vb	462	3,01	491	3,62
Vc	449	4,74	466	5,14
Vd	450	5,03	466	5,27
Ve	439	4,65	456	5,21
Vf	436	5,75	455	5,24
Vg	435	7,56	457	6,31
VIf	443	5,87	457	7,18
VIg	444	5,43	465	6,17
VIIb	469	3,18	485	3,55
VIIf	433	4,17	450	4,27
VIIg	433	5,82	454	5,01

electron-acceptor effect of the substituent in the benzene fragment. Similar stabilization is characteristic for the photomerocyanine forms of indolinespiropyrans [9]. The introduction of a nitro group in the indoline part of the merocyanine molecule (VIf, g as compared with Vf, g) leads to a slight (7-9 nm) bathochromic shift of the long-wave band; this is possibly a consequence of superimposition of two oppositely acting effects, viz., stabilization of nonpolar mesomeric structure A (a hypsochromic shift) and expansion of the chromophore system of the molecules due to inclusion of the π-like electrons of the substituent (a bathochromic shift). Similar superimposition of opposite effects was also observed in [9]. Similarity in the structural effects in merocyanines V-VII and photomerocyanines of the indoline series is also observed when a methyl group is replaced by a phenyl group at the nitrogen atom of the indoline part of the molecule; The hypsochromic shift in the case of the indicated substitution (VII as compared with V) constitutes evidence for an increase in the contribution of nonpolar mesomeric structure A; similar stabilization of the nonpolar structure also occurs in the photomerocyanine series [10].

A band of vibrations of a carbonyl group is found at 1635-1650 cm^{-1} in the IR spectra of merocyanines V-VII; this is very characteristic for conjugated amino ketones that are vinylogs of amides [11]. The PMR spectra of merocyanines V-VII contain characteristic signals of two equivalent methyl groups at δ 1.93-2.20 ppm; this constitutes evidence for coplanarity of the molecules [12, 13]. A singlet signal of protons of the methyl group attached to the nitrogen atom of the indoline part of merocyanines V-VII is observed at 3.43-3.60 ppm, and this makes it possible to conclude that only a weak positive charge is present on the nitrogen atom of the indoline part of the molecule [13], i.e., that nonpolar mesomeric structure A makes the primary contribution to the resulting merocyanine structure.

Thus the corresponding 2-(3-benzoyl-2-propenylidene)indolines, which have properties that are typical for merocyanine structures and do not display a tendency to undergo ring closing to the spiro form, are formed in the condensation of 2-methyleneindoline derivatives with benzoylacetaldehydes. The results obtained in the present research constitute evidence that the introduction of an aryl substituent in the pyran part of indoline-spiro-(2H-pyran) cannot appreciably shift the equilibrium to favor the closed structure and thus confirm the general conclusion of V. I. Minkin and co-workers [2] that benzo annelation is necessary in the 2H-pyran molecule for a substantial increase in the stability of the spiro form.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in carbon tetrachloride were measured with a Tesla BS-467 spectrometer with an operating frequency of 60 MHz. The IR spectra were recorded with a UR-20 spectrometer. The UV spectra of $(1-5) \cdot 10^{-5}$ mole/liter solutions were recorded with a VSU-2P spectrophotometer.

Benzoylacetaldehydes IV. These compounds were obtained by formylation of the corresponding ketones by the methods in [14-16]. For the purification of aldehydes IVc-g, their sodium salts were converted to copper salts, and the aldehydes were liberated from the salts immediately prior to the reaction with the Schiff bases by the action of dilute sulfuric acid. The aldehydes were extracted with ether, and the ether extracts were washed with water and dried with magnesium sulfate. The ether was then removed by distillation, and the residue was used in the reaction. Compounds IVa, b were not converted to copper salts but were stored in the free state.

Copper Salt of p-Dimethylaminobenzoylacetaldehyde (IVg). This compound was obtained by the method in [14] in 82% yield based on the starting p-dimethylaminoacetophenone. The brown-green powder had mp 258-260°C (dec.). Found: C 59.2; H 5.4; Cu 14.7; N 5.9%. $C_{22}H_{24}CuN_2O_4$. Calculated: C 59.4; H 5.4; Cu 14.4; N 6.3%.

1,3,3-Trimethyl-2-(3-benzoyl-2-propen-1-ylidene)indoline (Va). A solution of 2.7 g (16 mmole) of 1,3,3-trimethyl-2-methyleneindoline (I) in 20 ml of absolute ethanol was added to a solution of 2.2 g (15 mmole) of benzoylacetaldehyde (IVa) in 20 ml of alcohol, and the mixture was refluxed for 3.5 h. The precipitated crystals were removed by filtration after 2 days and crystallized from alcohol to give Va in the form of red plates. IR spectrum (CCl_4): 1650, 1600, 1550, 1490, 1470, 1380, 1340, 1310, 1220, 1180, 1160, 1130, and 1120 cm^{-1}. PMR spectrum: 1.93 (6H, s, 3-CH_3), 3.43 (3H, s, 1-CH_3), 5.78 (1H, d, J = 13 Hz, 1'-H), and 6.75-8.50 ppm (11H, m).

1,3,3-Trimethyl-2-[3-(p-nitrobenzoyl)-2-propen-1-ylidene]indoline (Vb). A solution of 0.44 g (2.6 mmole) of indoline I in 10 ml of alcohol was added to a solution of 0.5 g (2.6 mmole) of aldehyde IVb in 15 ml of alcohol, and the mixture was allowed to stand for 2 days. The precipitate was crystallized from alcohol to give dark-red plates. IR spectrum (CCl_4): 1650, 1600, 1550, 1490, 1470, 1380, 1340, 1310, 1180, 1130, and 1120 cm^{-1}. PMR spectrum: 2.00 (6H, s, 3-CH_3), 3.50 (3H, s, 1-CH_3), 5.85 (1H, d, J = 14 Hz, 1'-H), and 6.75-8.60 ppm (10H, m).

1,3,3-Trimethyl-2-[3-(p-chlorobenzoyl)-2-propen-1-ylidene]indoline (Vc). A solution of 0.44 g (2.6 mmole) of indoline I in 10 ml of alcohol was added to a solution of 0.46 g (2.6 mmole) of aldehyde IVc in 10 ml of alcohol, and the mixture was refluxed for 2 h and allowed to stand overnight. The precipitate was crystallized from alcohol to give fine, acicular crimson crystals. IR spectrum (CCl_4): 1650, 1590, 1570, 1555, 1490, 1470, 1385, 1340, 1320, 1180, 1160, 1130, and 1120 cm^{-1}. PMR spectrum: 2.06 (6H, s, 3-CH_3), 3.57 (3H, s, 1-CH_3), 5.80 (1H, d, J = 14 Hz, 1'-H), and 6.63-8.45 ppm (10H, m).

1,3,3-Trimethyl-2-[3-(p-bromobenzoyl)-2-propen-1-ylidene]indoline (Vd). A solution of 0.44 g (2.6 mmole) of indoline I in 10 ml of alcohol was added to a solution of 0.59 g (2.6 mmole) of aldehyde IVd in 10 ml of alcohol, and the mixture was refluxed for 2 h. After 24 h, the precipitate was removed by filtration and crystallized from alcohol to give crimson needles. IR spectrum (CCl_4): 1645, 1580, 1570, 1550, 1490, 1470, 1385, 1340, 1310, 1185, 1160, 1130, 1120 cm^{-1}. PMR spectrum: 2.06 (6H, s, 3-CH_3), 3.60 (3H, s, 1-CH_3), 5.85 (1H, d, J = 13 Hz, 1'-H), and 6.83-8.60 ppm (10H, m).

1,3,3-Trimethyl-2-[3-(p-methylbenzoyl)-2-propen-1-ylidene]indoline (Ve). A solution of 0.44 g (2.6 mmole) of indoline I in 10 ml of alcohol was added to a solution of 0.42 g (2.6 mmole) of aldehyde IVe in 10 ml of alcohol, and the mixture was refluxed for 5 h. It was then cooled, and the precipitate was crystallized from alcohol to give red crystals in the form of long narrow prisms. IR spectrum (CCl_4): 1635, 1575, 1490, 1470, 1385, 1340, 1315, 1185, 1170, 1130, 1120 cm^{-1}. PMR spectrum: 2.00 (6H, s, 3-CH_3), 2.70 (3H, s, CH_3—Ar), 3.47 (3H, s, 1-CH_3), 5.75 (1H, d, J = 14 Hz, 1'-H), and 6.8-8.3 ppm (10H, m).

1,3,3-Trimethyl-2-[3-(p-methoxybenzoyl)-2-propen-1-ylidene]indoline (Vf). A solution of 0.44 g (2.6 mmole) of indoline I and 0.46 g (2.6 mmole) of aldehyde IVf in 20 ml of alcohol was refluxed for 5 h, after which it was maintained at room temperature for 2 days. The precipitated crystals were removed by filtration and crystallized from alcohol to give red-orange plates. IR spectrum (CCl_4): 1642, 1595, 1575, 1550, 1490, 1460, 1385, 1340, 1250, 1185, 1160, 1130, 1120 cm^{-1}. PMR spectrum: 2.10 (6H, s, 3-CH_3), 3.50 (3H, s, 1-CH_3), 4.20 (3H, s, CH_3OAr), 5.90 (1H, d, J = 12 Hz, 1'-H), and 6.85-8.35 ppm (10H, m).

1,3,3-Trimethyl-2-[3-(p-dimethylaminobenzoyl)-2-propen-1-ylidene]indoline (Vg). This compound was obtained by a method similar to that used to prepare merocyanine Vf and was crystallized from alcohol in the form of yellow crystals. IR spectrum (CCl_4): 1640, 1600, 1570, 1490, 1470, 1380, 1360, 1340, 1320, 1290, 1180, 1130, 1120 cm^{-1}. PMR spectrum: 2.00 (6H, s, 3-CH_3), 3.30 [6H, s, $N(CH_3)_2$], 3.50 (3H, s, 1-CH_3), 5.91 (1H, d, J = 14 Hz, 1'-H), and 6.91-8.41 ppm (10H, m).

1,3,3-Trimethyl-5-nitro-2-[3-(p-methoxybenzoyl)-2-propen-1-ylidene]indoline (VIf). A solution of 0.57 g (2.6 mmole) of indoline II in 20 ml of alcohol was added to 10 ml of an alcohol solution of 0.46 g (2.6 mmole) of aldehyde IVf, and the mixture was refluxed for 5 h and allowed to stand at room temperature for 2 days. The oily precipitate was purified by chromatography with a column filled with aluminum oxide by elution with acetone. The substance obtained after evaporation of the solvent was crystallized from alcohol to give dark-cherry-red crystals in the form of fine needles with R_f 0.25 (Silufol UV-254, acetone). IR spectrum (KBr): 1635, 1585, 1535, 1520, 1500, 1425, 1400, 1340, 1310, 1285, 1260, 1180, 1140 cm^{-1}.

1,3,3-Trimethyl-5-nitro-2-[3-(p-dimethylaminobenzoyl)-2-propen-1-ylidene]indoline (VIg). An alcohol solution of 0.36 g (1.9 mmole) of aldehyde IVg and 0.41 g (1.9 mmole) of indoline II was refluxed for 6 h and allowed to stand at room temperature for 2 days. The precipitate was removed by filtration, crystallized from alcohol, and purified by chromatography with a column filled with aluminum oxide by elution with acetone. The precipitate obtained after evaporation of the solvent was crystallized from alcohol to give fine cherry-red needles with R_f 0.2 (Silufol, UV-254, acetone). IR spectrum (KBr): 1650, 1620, 1585, 1565, 1520, 1500, 1455, 1430, 1405, 1345, 1325, 1295, 1275, 1250, 1215, 1180, 1140 cm^{-1}.

1-Phenyl-3,3-dimethyl-2-[3-(p-nitrobenzoyl)-2-propen-1-ylidene]indoline (VIIb). A solution of 0.63 g (2.7 mmole) of indoline III and 0.46 g (2.4 mmole) of aldehyde IVb in 20 ml of alcohol was maintained at room temperature for 3 weeks, after which the red precipitate was removed by filtration and recrystallized three times from alcohol. IR spectrum (CCl_4): 1650, 1600, 1550, 1500, 1480, 1460, 1340, 1305, 1175, 1040 cm^{-1}. PMR spectrum: 2.00 (6H, s, 3-CH_3), 5.50 (1H, d, J = 13 Hz, 1'-H), and 6.5-8.67 ppm (15H, m).

1-Phenyl-3,3-dimethyl-2-[3-(p-methoxybenzoyl)-2-propen-1-ylidene]indoline (VIIf). A solution of 0.61 g (2.6 mmole) of indoline III and 0.46 g (2.6 mmole) of aldehyde IVf in 30 ml of alcohol was refluxed for 5 h, after which it was poured into a beaker and allowed to stand until the alcohol evaporated almost completely. The resulting crystalline mass was chromatographed with a column filled with aluminum oxide by elution with acetone–petroleum ether (1:4). The solvent was evaporated, and the residue was crystallized twice from alcohol to give fine orange acicular crystals with R_f 0.35 [Silufol UV-254, acetone–petroleum ether (1:4)]. IR spectrum (CCl_4): 1650, 1600, 1580, 1560, 1505, 1480, 1465, 1380, 1350, 1330, 1305, 1295, 1280, 1255, 1230, 1180, 1160 cm^{-1}.

1-Phenyl-3,3-dimethyl-2-[3-(p-dimethylaminobenzoyl)-2-propen-1-ylidene]indoline (VIIg). This compound was obtained and chromatographed as in the preparation of VIIf. Recrystallization from acetone gave light-yellow fine crystals with R_f 0.3 [Silufol UV-254, acetone–petroleum ether (1:4)]. IR spectrum (CCl_4): 1645, 1600, 1570, 1505, 1485, 1465, 1350, 1320, 1300, 1285, 1230, 1180, 1160 cm^{-1}.

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