STYRYL-SUBSTITUTED SPIROCHROMENES OF THE INDOLINE SERIES

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Styryl-substituted salicylaldehydes were obtained from 5-chloromethylsalicylaldehyde by means of the Wittig reaction, nitration, and several other reactions, and spirochromenes of the indoline series were subsequently synthesized. The possibility of carrying out nitration in the aromatic ring of the benzyl-substituted phosphonium salt and the Wittig reaction at one of the two formyl groups in 5-formylsalicylaldehyde and at the formyl group in the indolinospirochromene molecule is demonstrated. The introduction of a styryl substituent in the chromene part of a photochromic indolinospirochromene gives rise to a significant bathochromic shift of the long-wave absorption band of the photomerocyanine.

The investigation of the structural factors that affect the spectral characteristics of the colored form of spirochromenes is necessary for the subsequent purposeful creation of photochromic materials with the required spectral properties. We have previously established that the introduction of a methoxy or phenyl substituent in the pyran part of indoline nitro-substituted spirochromenes may lead to a 20-30-nm bathochromic shift of the long-wave absorption band of a photomercoyanine [1, 2].

It seemed of interest to ascertain whether one can obtain a more substantial bathochromic shift by introduction into the pyran part of a spirochromene of a substituent that has a larger π system than the phenyl group. With this in mind, we attempted to synthesize indolinospirochromenes that contain styryl substituents in the pyran part.

We obtained the corresponding phosphonium salts III and IV by reaction of 5-chloromethylsalicylaldehyde (I) [3] or its 3-nitro derivative (II) [4] with triphenylphosphine. Nitro-substituted phosphonium salt IV is also formed smoothly by nitration of salt III. This conversion illustrates the possibility of carrying out substitution reactions in the aromatic ring of benzyl-substituted phosphonium salts. It was found that salts III and IV behave substantially differently in the Wittig reaction. While treatment of salt III with sodium ethoxide and subsequent condensation with benzaldehyde or p-nitrobenzaldehyde proceeded in the usual manner and led to the corresponding styryl- or p-nitrostyryl-substituted salicylaldehydes IXa, b in the analogous reaction of salt IV and benzaldehyde we isolated 5-methyl-3-nitrosalicylaldehyde (VII) [5]. Salt IV behaved similarly in attempts to also effect its condensation with other aromatic aldehydes. This difference in the behavior of benzylidenephosphoranes V and VI, which are formed by the action of sodium ethoxide on phosphonium salts III and IV is evidently associated with the presence of a nitro group in phosphorane VI, which, because of its electron-acceptor effect, lowers the reactivity of the phosphorane [6, 7]. Thus, as a consequence of the slow condensation with benzaldehyde, hydrolysis of the phosphorane by traces of moisture [6, 7], which leads to aldehyde VIII, becomes the predominant process. By excluding the presence of moisture and using absolute toluene as the solvent we were able to obtain the desired 3-nitro-5-styrylsalicylaldehyde VII.

We obtained 5-styrylsalicylaldehyde (IXa) by alternative synthesis from 5-formylsalicylaldehyde (X) [3] and triphenylbenzylphosphonium chloride. It is interesting to note in this connection the difference in the reactivity of the formyl groups of dialdehyde X: While the formyl group in the 1 position, which is linked with the hydroxy group by an intramolecular hydrogen bond, does not undergo reaction, the formyl group in the 5 position reacts in the usual manner.

An analysis of the spectral characteristics of aldehyde IXa, b showed that they have a trans structure. The signals of aromatic and ethylene protons in

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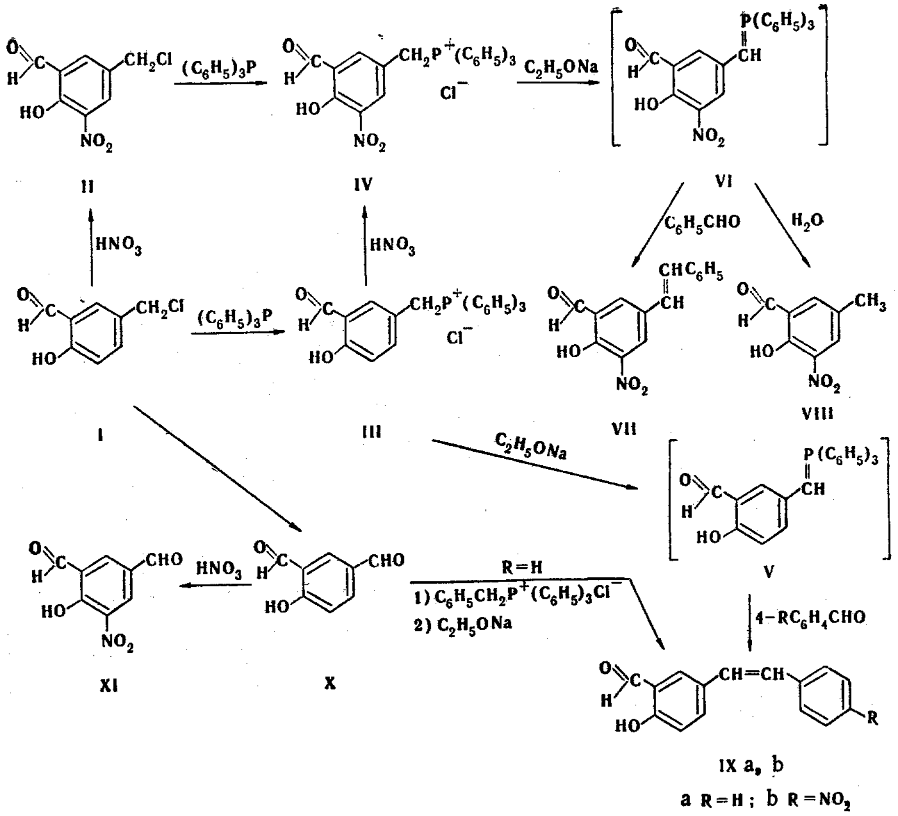
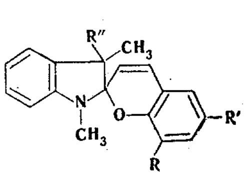


the NMR spectra of these compounds are found at δ = 6.92-7.70 ppm (Va) and 6.97-8.30 ppm (Vb); the absence of signals in the stronger-field region constitutes evidence in favor of the trans structure of aldehydes IXa, b [8, 9]. The same conclusion is confirmed by the presence in the IR spectra of IXa, b of an absorption band at 960-970 cm^{-1}, which is characteristic for the out-of-plane C—H deformation vibrations of trans-ethylene structures [10]. The characteristics of the UV spectra of 5-styrylsalicylaldehyde (IXa) [λ_{max} 309 nm (ε 23400)] and 5-(p-nitrostyryl)salicylaldehyde (IXb) [λ 398 nm (ε 15000)] are considerably closer to the characteristics of the corresponding model trans compounds — trans-4-methoxystilbene [λ_{max} 306 nm (ε 29000) and λ_{max} 310 nm (ε 275000) [11]] and trans-4-methoxy-4'-nitrostilbene [λ_{max} 375 nm (ε 27200) [9]] — than to the characteristics of the analogous cis compounds — cis-4-methoxystilbene [λ_{max} 276 nm (ε 11700) [11]] and cis-4-methoxy-4'-nitrostilbene [λ_{max} 355 nm (ε 9550) [9]].

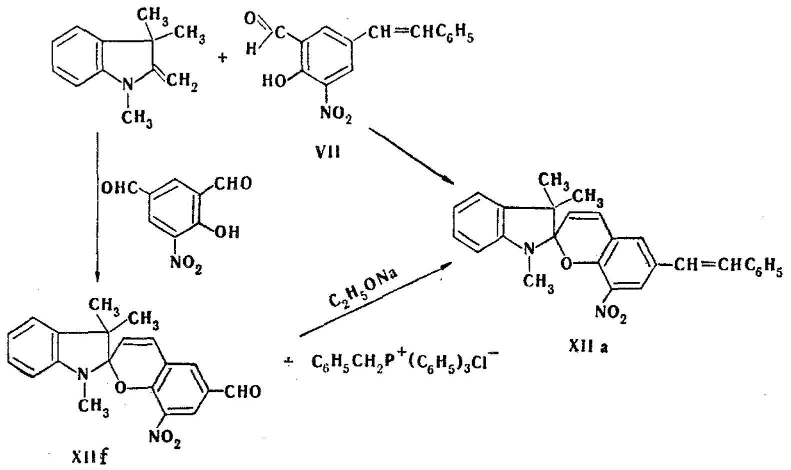
We obtained 3-nitro-5-formylsalicylaldehyde (XI) by nitration of 5-formylsalicylaldehyde (X) [3]. We used styryl-substituted aldehydes VII and IXa, b for the synthesis of styryl-substituted spirochromenes XIIa-c by condensation with the appropriate 2-methyleneindolines



XII

XII **a** R=NO$_2$, R'=C_6H_5CH=CH, R''=CH_3; **b** R=H, R'=C_6H_5CH=CH, R''=CH_3; **c** R=H, R'==4-$NO_2C_6H_4CH$=CH, R''=CH_3; **d** R=H, R'=$CH_2P^+(C_6H_5)_3Cl^-$, R''=CH_3; **e** R=NO$_2$, R'=$CH_2P^+(C_6H_5)_3Cl^-$, R''=C_6H_5; **f** R=NO$_2$, R'=CHO, R''=CH_3

[12]. We also obtained spirochromenes XIId-f from aldehydes III, IV, and XI by a similar method. We also obtained the most interesting 6-styryl-8-nitro-substituted spirochromes (XIIa) by the Wittig reaction from XIIf and benzyltriphenylphosphonium chloride:



The latter reaction is one of the few examples of the conversion of a functional group without involvement of the indolinospirochromene structure.

In alcohol solution spirochromene XIIa has photochromic properties: the original colorless solution turns blue upon irradiation with UV light from a mercury lamp, and when the illumination is discontinued, the blue color gradually vanishes. We used the method in [13] to measure the absorption spectrum of the resulting photomerocyanine in the visible region. When we compared the resulting λ_{max} values (see the experimental section) with the analogous characteristics of some other 8-nitro-substituted spirochromenes [1], we observed that the introduction of a styryl substituent in the pyran part of the spirochromene molecule gives rise to an ∿ 80-nm bathochromic shift of the long-wave absorption band of the photomerocyanine. Let us note that the introduction of an electron-acceptor formyl group, in accordance with the conclusions drawn in [14], gives rise to a hypsochromic shift of the indicated absorption band.

Thus the introduction of a substituent that has an additional system of π electrons on the periphery of the chromophore chain of the merocyanide may give rise to a considerable bathochromic shift of the long-wave absorption band. This shift possibly attests to an increase in the contribution of the quinoid mesomeric structure as a consequence of an increase in the tendency toward "dearomatization" of the phenolate part of the molecule [15].

Owing to the presence of ionic fragments in their structure, spirochromenes XIId, e are capable of dissolving in water. An equilibrium between the colorless spiro form and the colored merocyanine form is established in the resulting intensely colored solutions (λ_{max} 525 nm). This equilibrium is shifted to favor the merocyanine form to a greater extent, the greater the electron-acceptor effect of the substituents in the chromene part and the higher the polarity of the medium [16, 17]. The merocyanine form is usually produced to an appreciable extent in solution only when there is a nitro group in the chromene part of the spirochromene molecule. The ability of XIId to dissolve in water made it possible to establish that in a strongly polar aqueous medium the merocyanine form of the spirochromene may be stabilized to a sufficient degree even when there are no strong electron-acceptor substituents in the pyran part of the molecule.

In conclusion, let us note that colorless solutions of spirochromenes XIIb, c, which do not contain a nitro group in the chromene portion, do not display photochromic properties at room temperature when they are irradiated with the UV light of a mercury lamp; on the other hand, spirochromene XIIf, which contains two electron-acceptor substituents in the chromene portion, in polar solvents forms intensely colored solutions that are readily decolorized by irradiation with light in the visible region of the spectrum; the original color of the solution is restored after irradiation is discontinued (see Fig. 1).

EXPERIMENTAL

The absorption spectra of the compounds in the UV and visible regions of the spectrum were measured with a Unicam SP 8000 spectrophotometer. The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. A Tesla BS-467 spectrometer (60 MHz) was used to measure the PMR spectra. Chromatographic purification was carried out with columns

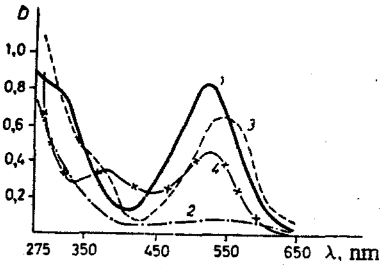


Fig. 1. Absorption spectra of spirochromenes: 1) XIIf in absolute ethanol; 2) the same solution after irradiation for 1 sec with the total light of an incandescent lamp (500 W); 3) XIIe in water; 4) XIId in water.

TABLE 1. Characteristics of the Compounds Obtained

Compound	mp, °C	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	N		C	H	N	
III	290	72,6	5,5	—	$C_{26}H_{22}ClO_2P$	72,1	5,1	—	73,5
IV	~220 (dec)	65,1	4,6	2,7	$C_{26}H_{21}ClNO_4P$	65,3	4,4	2,9	68,0 (A) 97,0 (B)
VII	182—183	67,0	4,2	4,9	$C_{15}H_{11}NO_4$	66,9	4,1	5,2	10,0
VIII	144*	—	—	—	—	—	—	—	44,0
IXa	141—142,5	80,2	5,7	—	$C_{15}H_{12}O_2$	80,4	5,4	—	55,5 (A) 44,5 (B)
IXb	153	67,1	4,2	5,4	$C_{15}H_{11}NO_4$	66,9	4,1	5,2	28,0
XI	147—148	49,6	2,1	7,4	$C_8H_5NO_5$	49,3	2,6	7,2	47,5
XIIa	94—95	76,5	5,4	6,4	$C_{27}H_{24}N_2O_3$	76,4	5,6	6,5	20,0 (A) 14,0 (B)
XIIb	120—121	85,2	6,6	3,5	$C_{27}H_{25}NO$	85,5	6,6	3,7	26,0
XIIc	152	76,5	5,8	6,4	$C_{27}H_{24}N_2O_3$	76,4	5,6	6,5	24,7
XIId	>350	77,5	6,1	2,0	$C_{38}H_{35}ClNOP$	77,6	6,0	2,4	33,6
XIIe	>350	74,2	5,5	4,3	$C_{43}H_{36}ClN_2O_3P$	74,4	5,2	4,0	21,0
XIIf	>350	68,3	5,0	8,0	$C_{20}H_{18}N_2O_4$	68,4	5,2	8,0	22,0

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*According to the data in [5], this compound has mp 143°C.

with a diameter of 25 mm and a height of 120 mm with L-100/25μ silica gel. The characteristics of the compounds obtained are presented in Table 1.

3-Formyl-4-hydroxybenzyltriphenylphosphonium Chloride (III). A 35-g (0.133 mole) sample of triphenylphosphine was added to a solution of 21.9 g (0.128 mole) of 5-chloromethylsalicylaldehyde [3] in 250 ml of toluene, and the mixture was refluxed with stirring for 2 h. It was then allowed to stand overnight, and the resulting precipitate was separated and reprecipitated from solution in chloroform by the addition of ether.

3-Formyl-4-hydroxy-5-nitrobenzyltriphenylphosphonium Chloride (IV). A) A mixture of 10 g (0.046 mole) of 3-nitro-5-chloromethylsalicylaldehyde [4] and 12.5 g (0.048 mole) of triphenylphosphine in 80 ml of dry benzene was refluxed with stirring for 2 h, after which it was allowed to stand overnight. The resulting precipitate was separated and reprecipitated from solution in chloroform by the addition of ether.

B) A solution of 1 ml of nitric acid (sp. gr. 1.49) in 10 ml of acetic anhydride was added to a solution of 1 g (2.4 mmole) of phosphonium salt III in 50 ml of acetic anhydride, and the mixture was stirred at 45°C for 3 h. It was then vacuum evaporated to dryness, and the residue was reprecipitated twice from solution in chloroform by the addition of ether.

3-Nitro-5-styrylsalicylaldehyde (VII). A solution of sodium ethoxide, obtained from 0.46 g (0.02 g-atom) of sodium in 10 ml of absolute ethanol, was added rapidly to a suspension of 4.77 g (0.01 mole) of 3-formyl-4-hydroxy-5-nitrobenzyltriphenylphosphonium chloride III in 70 ml of toluene, a solution of 1.06 g (0.01 mole) of benzaldehyde in 20 ml of dry toluene was added, and the mixture was refluxed for 30 min. It was then cooled and treated with 20 ml of hydrochloric acid (1 : 1), and the mixture was shaken. The organic layer was separated, dried with anhydrous magnesium sulfate, and evaporated, and the residue was chromatographed on silica gel (elution with benzene). The eluate was evaporated, and the residue was crystallized from benzene to give a substance with R_f 0.4 (on Silufol, elution with benzene).

3-Nitro-5-methylsalicylaldehyde (VIII). A 3-g (6.3 mmole) sample of phosphonium salt IV was dissolved in 100 ml of absolute alcohol, a solution of sodium ethoxide, prepared from

0.013 g-atom of sodium in 20 ml of absolute alcohol, was added, 0.97 g (9.1 mmole) of benzaldehyde was added rapidly, and the mixture was refluxed for 30 min. It was then allowed to stand overnight, after which 50 ml of water was added, and the mixture was acidified with hydrochloric acid (1 : 1). The resulting precipitate was separated, the filtrate was evaporated to half its original volume, and 50 ml of water was added. The aqueous mixture was extracted with chloroform, the extract was dried with anhydrous magnesium sulfate and evaporated to dryness, and the residue was combined with the precipitate and dissolved in the minimum amount of chloroform. The chloroform solution was chromatographed on silica gel (elution with benzene — petroleum ether (1 : 1)], and the eluate was evaporated to give a substance with R_f 0.3 [on Silufol, in benzene — petroleum ether (1 : 1)].

trans-5-Styrylsalicylaldehyde (IXa). A) A 4.32-g (0.01 mole) sample of dry phosphonium salt III was added in a nitrogen atmosphere to 40 ml of absolute alcohol, and the mixture was stirred until the solid dissolved completely. A solution of sodium ethoxide, prepared by dissolving 0.46 g (0.02 g-atom) of sodium in 20 ml of absolute alcohol, was added to the mixture. A 1.06-g (0.01 mole) sample of benzaldehyde was added rapidly to the resulting yellow solution of the ylid, and the mixture was refluxed for 30 min. It was then cooled to 20°C and treated with 20 ml of water, and the aqueous mixture was acidified with hydrochloric acid (1 : 1). The resulting precipitate was separated, and the filtrate was vacuum evaporated to half its original volume. Water (50 ml) was added, and the mixture was extracted with ether. The extract was dried with anhydrous magnesium sulfate and evaporated to dryness, and the residue was combined with the precipitate and crystallized twice from cyclohexane. NMR spectrum (deuterochloroform), δ: 6.92-7.70 (multiplet of 10 aromatic and ethylene protons); 9.90 (singlet of the proton of a formyl group); 11.00 ppm (singlet of the proton of a hydroxy group). IR spectrum: 970 cm^{-1} (trans-CH=). UV spectrum (ethanol): λ_{max} 309 nm (ε 23400).

B) A mixture of 5 g (14 mmole) of triphenylbenzylphosphonium chloride [18], 1.95 g (14 mmole) of 5-formylsalicylaldehyde [2], and 100 ml of absolute alcohol was stirred in a nitrogen atmosphere until the solid dissolved completely, after which a solution of sodium ethoxide, prepared from 0.6 g (0.026 g-atom) of sodium in 15 ml of absolute alcohol, was added, and the mixture was stirred for 2 h. Water (40 ml) was added, and the mixture was acidified with hydrochloric acid (1 : 1). It was then evaporated to half of its original volume, 50 ml of water was added, and the mixture was extracted with chloroform. The extract was dried with anhydrous magnesium sulfate and evaporated, and the residue was recrystallized three times from cyclohexane.

trans-5-(p-Nitrostyryl)salicylaldehyde (IXb). A 3-g (7 mmole) sample of phosphonium salt III was dissolved in 50 ml of absolute alcohol in a nitrogen atmosphere, a solution of sodium ethoxide prepared from 0.23 g (0.01 g-atom) of sodium in 10 ml of absolute alcohol was added, a solution of 0.6 g (4 mmole) of p-nitrobenzaldehyde in 30 ml of alcohol was added, and the mixture was refluxed for 30 min and allowed to stand overnight. It was then acidified with hydrochloric acid (1 : 1) and vacuum evaporated to half its original volume. Water (50 ml) was added, and the mixture was extracted with dry anhydrous magnesium sulfate. It was then evaporated, and the residue was crystallized from alcohol to give 0.9 g of aldehyde Vb with mp 147-149°C. For final purification, the product was dissolved in the minimum amount of benzene, and the solution was chromatographed on silica gel (elution with benzene). The eluate was evaporated, and the residue was crystallized twice from benzene to give a product with R_f 0.4 (on Silufol, elution with benzene). NMR spectrum (deuterodimethyl sulfoxide), δ: 6.97-8.30 (multiplet of 9 aromatic and ethylene protons): 10.30 (singlet of the proton of a formyl group); 11.05 ppm (singlet of the proton of a hydroxy group). IR spectrum: 960 cm^{-1} (trans-CH =). UV spectrum (ethanol): λ_{max} 398 nm (ε 15000).

3-Nitro-5-formylsalicylaldehyde (XI). A 0.6-g (4.5 mmole) sample of 5-formylsalicylaldehyde [3] was added in small portions at −5 to −10°C to a mixture of 0.9 g of nitric acid (sp. gr. 1.47) and 10 g of concentrated sulfuric acid, and the mixture was stirred for 2 h. It was then poured over ice, and the precipitate was removed by filtration, washed with cold water, and crystallized from 30% alcohol.

1,3,3-Trimethyl-6'-styryl-8'-nitroindoline-2-spiro-2'-2H-chromene (XIIa). A) A 0.4-g (1.5 mmole) sample of 3-nitro-5-styrylsalicylaldehyde (VII) was dissolved in 20 ml of alcohol, a solution of 0.26 g (1.5 mmole) of 1,3,3-trimethyl-2-methyleneindoline in 10 ml of alcohol was added, and the mixture was refluxed for 2 h and allowed to stand overnight. The resulting precipitate was removed by filtration and crystallized twice from alcohol. UV spectrum: λ_{max} 620 nm (merocyanine form, absolute ethanol).

B) A 5-g (0.014 mole) sample of triphenylbenzylphosphonium chloride [18] was suspended in 70 ml of dry toluene, a solution of sodium ethoxide, obtained from 0.585 g (0.025 g-atom) of sodium in 15 ml of absolute alcohol, was added, a solution of 3.68 g (0.01 mole) of 1,3,3-trimethyl-6'-formyl-8'-nitroindoline-2-spiro-2'-2H-chromene XIIf in 70 ml of dry toluene was added, and the mixture was refluxed for 1 h. It was then cooled and treated with 20 ml of hydrochloric acid (1 : 1). The mixture was shaken, and the organic layer was separated, dried with anhydrous magnesium sulfate, and evaporated. The residue was chromatographed on silica gel (elution with chloroform), and the eluate was evaporated. The residue was crystallized from alcohol to give a product with R_f 0.3 (on Silufol, elution with chloroform).

1,3,3-Trimethyl-6'-styrylindoline-2-spiro-2'-2H-chromene (XIIb). A solution of 0.9 g (3.3 mmole) of 5-styrylsalicylaldehyde IXa and 0.58 g (3.3 mmole) of 1,3,3-trimethyl-2-methyleneindoline in 300 ml of absolute alcohol was refluxed for 2 h, after which it was allowed to stand overnight. The resulting precipitate was separated and crystallized from benzene.

1,3,3-Trimethyl-6'-(p-nitrostyryl)indoline-2'-2H-chromene (XIIc). A mixture of 0.9 g (3.3 mmole) of aldehyde IXb, 0.58 g (3.3 mmole) of 1,3,3-trimethyl-2-methyleneindoline, and 300 ml of absolute alcohol was refluxed for 2 h, after which it was allowed to stand overnight. The precipitate was separated and crystallized three times from benzene.

1,3,3-Trimethyl-6'-triphenylphosphoniamethylindoline-2-spiro-2'-2H-chromene Chloride (XIId). A 1-g (2.3 mmole) sample of phosphonium salt III was dissolved in 30 ml of absolute alcohol, 0.4 g (2.3 mmole) of 1,3,3-trimethyl-2-methyleneindoline was added, and the mixture was refluxed for 3 h and allowed to stand overnight. The oily precipitate was separated, triturated with heptane while cooling, and crystallized three times from methanol to give red crystals of spirochromene XIId, which were quite soluble in water, alcohol, and acetone.

1,3-Dimethyl-3-phenyl-6'-triphenylphosphoniamethyl-8'-nitroindoline-2-spiro-2'-2H-chromene Chloride (XIIe). A solution of 0.5 g (2.1 mmole) of 1,3-dimethyl-3-phenyl-2-methyleneindoline [19] was added to a solution of 1 g (2.1 mmole) of phosphonium salt IV in 40 ml of absolute alcohol, and the mixture was refluxed for 4 h. The precipitate was separated, crystallized twice from methanol, and reprecipitated from a solution in chloroform by the addition of benzene.

1,3,3-Trimethyl-6'-formyl-8'-nitroindoline-2-spiro-2'-2H-chromene (XIIf). A solution of 1.56 g (9 mmole) of 1,3,3-trimethyl-2-methyleneindoline in 10 ml of alcohol was added to a hot solution of 1.75 g (9 mmole) of aldehyde XI in 40 ml of alcohol, and the mixture was refluxed for 2 h. The precipitate was separated, crystallized twice from alcohol, and dissolved in the minimum amount of chloroform. The chloroform solution was chromatographed on silica gel (elution with benzene—chloroform (1 : 1), and the eluate was evaporated. The residue was crystallized twice from alcohol to give spirochromene XIIf in the form of dark-violet crystals with R_f 0.25 (on Silufol, from benzene—chloroform (1 : 1). UV spectrum: λ_{max} 530 nm (merocyanine form, absolute ethanol).

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3-CARBAMIDO-2-INDOLYLURETHANES AND THEIR CYCLIZATION TO PYRIMIDO[4,5-b] INDOLES

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The reaction of isocyanates and isothiocyanates with 2-indolylurethanes takes place primarily in the 3 position of the indole ring to give the corresponding amides and thioamides, which smoothly undergo cyclization when they are heated with sodium ethoxide to give the corresponding quinazoline derivatives.

The high nucleophilicity of the pyrrole ring of the indole grouping makes it possible to directly introduce a carbamido group via the usual scheme of electrophilic substitution. Thus the corresponding amides of indole-3-carboxylic acid are formed by the action of isocyanates on indole and 1- or 2-alkylindoles, and the analogous thioamides are obtained from isothiocyanates under somewhat more severe conditions [1]. Tosyl isocyanate reacts more sluggishly than phenyl isocyanate [2]. The indole anion undergoes carbamidation at the nitrogen atom [1]. Similar processes have been noted in several cases. Thus both the anilide of the acid and 2-methylindole-3-carboxylic acid N,N'-diphenylamidine are formed from 2-methyl-

TABLE 1. 2-(Alkoxycarbonylamino)indole-3-carboxylic Acid Amides

Compound	Reaction time, h	mp, °C*	UV spectrum λ_{max}, nm (log ε)	IR spectrum, ν, cm^{-1}	Found, %			Empirical formula	Calculated, %			Yield, %
					C	H	N		C	H	N	
IIa	2	131—133	237 (4,30), 284 (4,29)	1700, 1720, 3220	67,8	5,9	12,6	$C_{19}H_{19}N_3O_3$	67,6	5,7	12,5	89
IIb	4	101—103	283 (4,28), sh 326 (3,08)	1695, 1710, 3270, 3330	69,7	6,6	11,1	$C_{22}H_{25}N_3O_3$	69,6	6,6	11,1	64
IIc	7	177—178	285 (4,30), 305 (4,26)	1630, 1680, 1720, 3250	71,7	4,8	11,0	$C_{23}H_{19}N_3O_3$	71,7	5,0	10,9	71
IId	5	191—193	285 (4,36), 306 (4,38), sh 313 (4,34), 358 (2,92), 376 (2,76)	1680, 1715, 3320, 3380	65,9	4,5	—	$C_{23}H_{18}ClN_3O_3$ †	65,8	4,3	—	73
IIe	9	187—189	282 (4,36), sh 300 (4,26), 357 (2,65), 375 (2,59)	1630, 1680, 1715, 3330, 3380	72,4	5,4	—	$C_{24}H_{21}N_3O_3$	72,2	5,3	—	62
IIf	8	195—197	sh 242 (4,38), 282 (4,15), 322 (4,21)	1620, 1690, 1750, 3190, 3310, 3340	69,8	4,7	10,2	$C_{24}H_{19}N_3O_4$	69,7	4,6	10,2	21
IIg	6	180—183	244 (4,46), 280 (4,32), 302 (4,25), 385 (3,73)	1650, 1715, 3260, 3380, 3410	64,2	4,4	13,2	$C_{23}H_{18}N_4O_5$	64,2	4,2	13,0	72
IV	5	225—227	283 (4,34), 304 (4,36), sh 312 (4,34), sh 352 (2,08)	1630, 1710, 3380, 3440	66,8	5,4	13,1	$C_{18}H_{17}N_3O_3$	66,9	5,3	13,0	34

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*Amides IIa, b, e and IV were recrystallized from benzene—heptane, and the remaining compounds were recrystallized from benzene.
†Found: Cl 8.4%. Calculated: Cl 8.4%.

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