SYNTHESIS OF 3'-ACYL-SUBSTITUTED INDOLINE SPIROPYRANS

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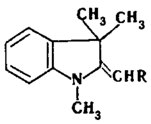
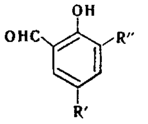
The reaction of 1,3,3-trimethyl-ω-formyl-2-methyleneindoline with substituted salicylaldehydes in most organic solvents is accompanied by decarbonylation and gives known spiropyrans that do not contain a formyl group; however, 3'-formyl-substituted spiropyrans can be obtained in low yields in dimethyl sulfoxide. The reaction of 1,3,3-trimethyl-ω-acetyl-2-methyleneindoline with 3-bromo-5-nitrosalicylaldehyde gave a 3'-acetyl-substituted compound in the open merocyanine form with a branched chromophore chain. 3'-Acyl-substituted indoline spiropyrans can be obtained by acylation of the appropriate compounds that do not contain substituents in the 3' position. Indoline spiropyrans with 3'-acyl substitutents do not have photochromic properties.

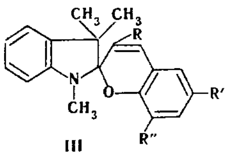
It is well known that the corresponding indoline spiropyrans (III, R = H) are formed **smoothly** in the reaction of 1,3,3-trimethyl-2-methyleneindoline (I, R = H) with substituted salicylaldehydes (II) [1]. The reaction of ω-alkyl-substituted or ω-aryl-substituted 1,3,3-trimethyl-2-methyleneindolines (I, R = alkyl or aryl) with substituted salicylaldehydes also gives the corresponding indoline spiropyrans (III, R = alkyl or aryl) [2-4].



I



II



III

We attempted to use a similar reaction for the preparation of indoline spiropyrans with acyl substituents in the 3' position (III, R = acyl) from ω-acyl-methyleneindolines (I, R = acyl). However, ω-acetyl- (I, R = $COCH_3$) [5] and ω-benzoyl-1,3,3-trimethyl-2-methyleneindoline (I, R = COC_6H_5) [6] do not react with 5-nitrosalicylaldehyde, despite extensive variation of the solvent, temperature, and catalyst; this is apparently a consequence of the reduced activity of the β-carbon atom of an enamine with an electron-acceptor substituent in nucleophilic addition reactions [4, 7, 8].

When we heated ω-formyl-1,3,3-trimethyl-2-methyleneindoline (I, R = CHO) [5] with 5-nitro-, 3-bromo-5-nitro-, and 3-methoxy-5-nitrosalicylaldehydes in ethanol we isolated the corresponding photochromic 6',8'-disubstituted indoline spiropyrans, which, however, did not contain a formyl group in the 3' position (III, R - H). The structures of these spiropyrans were confirmed by comparison with authentic samples.

It is known that ω-formyl-2-methyleneindoline (I, R = CHO) undergoes decarbonylation when it is heated in the presence of sulfuric acid to give 1,3,3-trimethyl-2-methyleneindoline (I, R = H) [9]; a similar reaction apparently takes place in our case, and the resulting methyleneindoline (I, R = H) then condenses with the substituted salicylaldehydes to give the corresponding spiropyrans.

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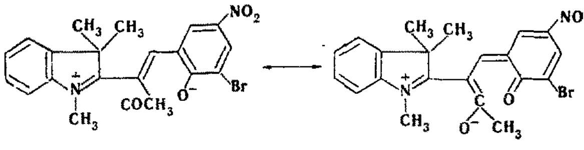
The decarbonylation of ω-formyl-1,3,3-trimethyl-2-methyleneindoline proceeds efficiently in alcohol dimethylformamide (DMFA), tetrahydrofuran (THF), N-methylpyrrolidone, and hexametapol. Only in dimethyl sulfoxide (DMSO) does heating of ω-formylmethyleneindoline (I, R = CHO) with 5-nitrosalicylaldehyde (II, R' = NO_2, R" = H) and 3-bromo-5-nitrosalicylaldehyde (II, R' = NO_2, R" = Br) give low yields of condensation products containing a formyl group. The IR spectra of the indicated compounds contain intense absorption bands of the stretching vibrations of a carbonyl group at 1695 and 1700 cm^{-1}, respectively, and weak-intensity bands at 2720 and 2740 cm^{-1}, respectively, which correspond to the stretching vibrations of the C–H bond of the formyl groups. Intense absorption at 950 and 980 cm^{-1}, respectively, which is characteristic for C_{spiro}–O vibrations [10], is also observed. Thus the indicated data provide evidence that the compounds obtained have the 1,3,3-trimethyl-3'-formyl-6'-nitrospiro(indoline-2,2'-[2H-1]benzopyran) (IIIa, R = CHO, R' = NO_2, and R" = H) and 1,3,3-trimethyl-3'-formyl-6'-nitro-8'-bromospiro(indoline-2,2'-[2H-1] benzopyran) (IIIb, R = CHO, R' = NO_2, and R" = Br) structures, respectively. In addition to the peaks corresponding to the molecular ions, the mass spectra of spiropyrans IIIa, b contain characteristic intense peaks at m/e 159, which correspond to the 1,3,3-trimethylindoline fragment of the molecule [4], and intense peaks of fragments formed upon splitting out of a CHO group from the molecular ion. Less intense peaks of fragments formed as a result of successive splitting out of a formyl group and, successively, one, two, and three methyl groups from the molecular ion are also observed.

The PMR spectrum of IIIa is in complete agreement with the proposed structure. The gem-dimethyl group shows up in the spectrum as two singlets at δ 1.00 and 1.18 ppm, the relative intensity of each of which corresponds to three protons; the nonequivalence of the methyl groups attests to the fact that the compound exists in a closed spiro form [4, 11]. No signals whatsoever are present at 4.8-6.2 ppm, and this constitutes evidence for the absence of a proton in the 3' position in the IIIa molecule [4]; the singlet one-proton signal at 9.82 ppm (the proton of an aldehyde group) confirms the presence of a formyl group in the IIIa molecule.

A yellow crystalline substance, the results of the elementary analysis and mass spectrum of which corresponded to the empirical formula $C_{21}H_{19}N_2BrO_4$, was obtained in low yield when ω-acetyl-2-methyleneindoline (I, R = $COCH_3$) was heated with 5-nitro-3-bromosalicylaldehyde (II, R' = NO_2, R" = Br) in DMSO. The yellow alcohol solution of this compound has an absorption band in the visible region with a maximum at 418 nm. The PMR data are in good agreement with structure IV, which is the open merocyanine form of the corresponding spiropyran containing an acetyl group in the 3' position. In fact, the signal at 1.88 ppm apparently corresponds to the protons of two equivalent methyl groups of the indoline portion in the 3 position (according to the data in [12, the singlet signals of these methyl groups are found at 1.80 ppm) and to the protons of the acetyl groups. The signal at 5.95 ppm can apparently be assigned to the ethylene proton adjacent to the acetyl group; the protons of the methyl group attached to the positively charged nitrogen atom and the aromatic protons give a multiplet signal at 7.0-8.75 ppm.



IVa IVb

The absorption of a carbonyl group is absent in the IR spectrum of IV, but the spectrum contains two intense peaks at 1518 and 1533 cm^{-1}, which are characteristic for C–O vibrations in merocyanine molecules [13]. This fact may apparently constitute evidence that, in addition to mesomeric phenoxide form IVa, mesomeric quinoid-enolate structure IVb makes an appreciable contribution to the real structure. Thus IV has a dipolar structure with a single branched merocyanine chromophore. The absorption spectra of such systems in the visible region contain one maximum [14]; in contrast to this, if there are two interacting chromophores in the molecule, their absorption bands are split [15]. Branching of the polymethine chromophone chain evidently brings about a significant decrease in the uniformity of the π-electron density distribution, and this may be the reason for the considerable hypsochromic shift of the absorption of the branched chromophore chain as compared with the unbranched chain [16, 17]. These considerations make it possible to understand the reasons for the strong hypsochromic shift of the absorption band of IV as compared with the absorption of the corresponding merocyanine forms that do not contain an acetyl group, which is found at 524 nm [18].

In our investigation of the reactivities of indoline spiropyrans we unexpectedly found that a compound with a formyl group, which proved to be identical to the above-described 3'-formyl-substituted spiropyran

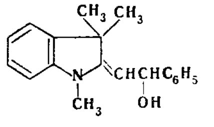
IIIa, is formed in the formylation of 1,3,3-trimethyl-6'-nitrospiro(indoline-2,2'-[2H-1]benzopyran) (IIIc, R = R" = H, R' = NO_2) by means of a dimethylformamide-phosphorus oxychloride complex.

Acetylation of spiropyran IIIc by means of acetic anhydride in the presence of boron trifluoride etherate in chloroform gave $C_{21}H_{20}N_2O_4$ (mass spectrum), which has intense absorption in its IR spectrum at 1670 (C = O) and 940 cm^{-1} ($C_{spiro}-O$). Singlets from the protons of two nonequivalent methyl groups at 0.90 and 1.08 ppm are observed in the PMR spectrum of this compound, whereas signals are absent at 4.8-6.2 ppm. The mass spectrum of the compound is characterized by intense peaks corresponding to splitting out of an acetyl group from the molecular ion and by the peak of a trimethylindoline fragment at m/e 159. The indicated spectral data constitute unambiguous evidence that the compound contains an acetyl group in the 3' position and has the IIId (R = $COCH_3$, R' = NO_2, R" = H) structure.

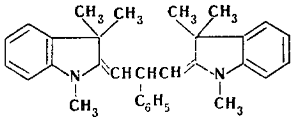
We obtained $C_{26}H_{22}N_2O_4$ (mass spectrum) by benzoylation of spiropyran IIIc with benzoyl chloride in carbon disulfide in the presence of aluminum bromide and also by the action of benzoyl chloride in dimethylaniline; the IR spectrum of this compound contains intense absorption at 1658 (C = O) and 958 cm^{-1} (C_{spiro} $-O$). Signals at 4.8-6.2 ppm are absent in the PMR spectrum of this compound, but singlet signals of the protons of two nonequivalent methyl groups are present at 1.02 ppm and 1.30 ppm. The mass spectrum contains peaks of fragments formed by splitting out of benzoyl and various numbers of methyl groups from the molecular ions and a peak at m/e 159, which is characteristic for the trimethylindoline fragment. On the basis of the spectral data, we assigned a spiropyran structure (IIIe, R = COC_6H_5, R' = NO_2, R" = H) with a benzoyl group in the 3' position to this compound.

Colorless solutions that do not display photochromic properties on irradiation with the UV light of a mercury lamp are formed with IIIa, b, d, e are dissolved in alcohol, chloroform, benzene, and other organic solvents.

In the course of our investigation of the possibility of the synthesis of indoline spiropyrans with various substituents in the 3' position from the corresponding ω-substituted 1,3,3-trimethyl-2-methyleneindolines, we carried out the reaction of ω-formylmethyleneindoline (I, R = CHO) with phenylmagnesium bromide; however, instead of the expected carbinol (V), we obtained 2-phenyl-1,3-bis(1,3,3-trimethyl-2-indolinylidene)propane (VI) [19, 20]. Heating VI with 5-nitrosalicylaldehyde in alcohol gave a known spiropyran (IIIc, R = R" = H, R' = NO_2), which does not contain a substituent in the 3' position.



V



VI

EXPERIMENTAL

The melting points were determined with a Boetius microheater stage. The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The mass spectra were measured with an MKh-1303 spectrometer at an ionization potential of 30 eV.* The UV spectra of absolute ethanol solutions of the compounds were measured with a Unicam-SP-8000 spectrophotometer. The PMR spectra were measured with a Perkin–Elmer R-12 spectrometer at 60 MHz. The compounds were purified by preparative chromatography in a thin layer on 15 × 15 cm Silufol plates; a narrow band of the starting solution was applied to the plate, the zone containing the principal component was cut out after development of the chromatogram, and the pure substance was extracted by heating the cut-out portion of the plate in a suitable solvent. The identical character of the compounds and genuine samples was established by comparison of the IR spectra and mixed-melting-point determinations.

1,3,3-Trimethyl-6'-nitrospiro(indoline-2,2'-[2H-1]benzopyran) (IIIc, R = R" = H, R' = NO_2). A) A solution of 2 g (0.01 mole) of 1,3,3-trimethyl-ω-formyl-2-methyleneindoline (I, R = CHO) [5] was added to a solution of (0.01 mole) of 5-nitrosalicylaldehyde in 17 ml of ethanol at 70°, after which the mixture was refluxed for 2 h and allowed to stand overnight. The resulting precipitate was separated and crystallized from heptane to give 1.35 g (42%) of spiropyran IIIc with mp 177-179° (mp 179-180° [1]); the product was identical to the compound obtained from 1,3,3-trimethyl-2-methyleneindoline and 5-nitrosalicylaldehyde.

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*We sincerely thank A. D. Vasil'eva and I. A. Rotermel' for measuring the mass spectra.

B) A solution of 0.5 g (1.1 mmole) of 2-phenyl-1,3-bis(1,3,3-trimethyl-2-indolinylidene)propane (VI) in 40 ml of ethanol was added to a solution of 0.3 g (1.8 mmole) of 5-nitrosalicylaldehyde in 7 ml of ethanol, and the mixture was refluxed for 2 h. It was then cooled, and the resulting precipitate was separated and crystallized from heptane to give 0.22 g (31 %) of spiropyran IIIc with mp 176-179°. The product was identical to a sample of known structure [1].

1,3,3-Trimethyl-6'-nitro-8'-bromospiro(indoline-2,2'-[2H-1]benzopyran) (IIIf, R = H, R' = NO_2, R" = Br). A solution of 0.5 g (2.5 mmole) of 1,3,3-trimethyl-ω-formyl-2-methyleneindoline (I, R = CHO) in 5 ml of ethanol was added dropwise at 70° to a solution of 0.61 g (2.5 mmole) of 3-bromo-5-nitrosalicylaldehyde in 6.5 ml of ethanol, after which the mixture was refluxed for 20 min and allowed to stand overnight. The resulting dark-green precipitate was separated and crystallized from alcohol to give 0.49 g (49 %) of spiropyran IIIf with mp 252-255° (mp 255-256° [21]).

Spiropyran IIIf was identical to a compound of known structure obtained [21] from 1,3,3-trimethyl-2-methyleneindoline and 3-bromo-5-nitrosalicylaldehyde.

1,3,3-trimethyl-6'-nitro-8'-methoxyspiro(indoline-2,2'-[2H-1]benzopyran) (IIIg, R = H, R' = NO_2, R" = OCH_3). Spiropyran IIIg [0.15 g (24 %)], with mp 159-161.5° (from ethanol), was obtained as described above from 0.35 g (1.8 mmole) of 3-methoxy-5-nitrosalicylaldehyde and 0.36 g (1.8 mmole) of 1,3,3-trimethyl-ω-formyl-2-methyleneindoline (I, R = CHO) in 10 ml of ethanol. The product was identical to a compound of known structure obtained [21] from 1,3,3-trimethyl-2-methyleneindoline and 3-methoxy-5-nitrosalicylaldehyde (mp 152.5-153.5° [21] and 165-166° [22]).

1,3,3-Trimethyl-3'-formyl-6'-nitrospiro(indoline-2,2'-[2H-1]benzopyran) (IIIa, R = CHO, R' = NO_2, R" = H). A) A solution of 1 g (5 mmole) of indoline I (R = CHO) and 0.84 g (5 mmole) of 5-nitrosalicylaldehyde in 15 ml of dimethyl sulfoxide (DMSO) was stirred at 115-120° for 6 h, after which it was cooled and poured into 100 ml of water. The aqueous mixture was saturated with sodium chloride, and the resulting precipitate was separated and dissolved in a small amount of benzene. The solution was chromatographed with a column filled with silica gel with successive elution by benzene and ethyl acetate. The fraction obtained by elution with ethyl acetate was evaporated, and the residue was crystallized from alcohol to give 0.20 g (11 %) of spiropyran IIIa with mp 175-177° (from alcohol). Mass spectrum, m/e (I/I_{max}, %: 350 (86), 321 (100), 306 (75), 291 (14), 276 (12), 260 (45), 246 (17), 159 (99), and 158 (65). UV spectrum, λ_{max}, nm (log ε): 239 (4.37), 284 (4.58), and 340 (4.16). Found: N 7.6 %. $C_{20}H_{18}N_2O_4$. Calculated: N 8.0 %.

B) A 0.5-ml sample of freshly distilled phosphorus oxychloride and a solution of 1.32 g (4 mmole) of IIIc in 20 ml of dimethylformamide (DMFA) were added successively to 5 ml of DMFA at 0°, after which the mixture was stirred at 70-80° for 3 h and allowed to stand overnight. The mixture was then treated with 100 ml of a 10 % sodium carbonate solution and extracted with chloroform. The extract was washed with water, the solvent was removed, and the residue was chromatographed in a thin layer of silica gel with elution by benzene. The zone of the principal component was extracted with chloroform, the extract was evaporated, and the residue was crystallized from heptane to give 0.31 g (22 %) of spiropyran IIIa with mp 175-177°; the product was identical to the sample described above.

1,3,3-Trimethyl-3-formyl-6'-nitro-8'-bromospiro(indoline-2,2'-[2H-b]-benzopyran) (IIIb, R = CHO, R' = NO_2, R" = Br). A mixture of 1 g (5 mmole) of methylenindoline I (R = CHO), 1,3 g (5.3 mmole) of 3-nitro-5-bromosalicylaldehyde, and 20 ml of DMFA was stirred at 95-100° for 2 h, after which it was cooled and poured into 50 ml of water. The aqueous mixture was saturated with sodium chloride, and the resulting precipitate was separated, washed with a small amount of ethyl acetate, and dissolved in acetone. The acetone solution was filtered through a layer of silica gel, and the filtrate was worked up to give 0.12 g (5.6 %) of spiropyran IIIb with mp 171-173° (dec., from ethanol). Mass spectrum, m/e (I/I_{max}, %): 430 (5.9), 428 (5.9), 401 (20.6), 399 (19.8), 386 (8.3), 384 (7.8), 371 (2.8), 369 (2.3), 356 (2.0), 354 (1.4), 340 (4.6), 338 (4.9), 326 (1.4), 324 (1.3), 259 (4.6), 230 (4.2), 217 (4.8), 159 (100), 158 (40.8). UV spectrum, λ_{max}, nm (log ε): 242 (4.33), 291 (4.37), and 340 (4.20). Found: C 55.9; H 4.2; N 6.3 %. $C_{20}H_{17}BrN_2O_4$. Calculated: C 55.9; H 4.0; N 6.5 %.

2-Bromo-4-nitro-6-[2-(1,3,3-trimethyl-2-indolenio)-2-acetylvinyl] Phenoxide (IV). A mixture of 1.2 g (5.6 mmole) of indoline I (R = $COCH_3$), 1.38 g (5.6 mmole) of 3-bromo-5-nitrosalicylaldehyde, and 25 ml of DMSO was stirred at 95-100° for 3 h, after which it was cooled and poured into 50 ml of water. The aqueous mixture was saturated with sodium chloride, and the resulting resinous precipitate was washed with a small amount of ethyl acetate and dissolved in chloroform. The chloroform solution was chromatographed with a column filled with silica gel; the unchanged aldehyde was initially eluted with benzene, after which the reaction product was eluted with hexane-ethyl acetate (1 : 1). The eluate was evaporated, and the residue was crystallized from alcohol to give 0.20 g (8 %) of merocyanine IV with mp 189.5-190.5°. Mass spectrum, m/e (I/I_{max}, %): 445 (53), 443 (51), 430 (12), 428 (24), 415 (2.4), 413 (2.2), 402 (9.7), 400 (7.3), 159 (100). UV spectrum (ethanol), λ_{max}, nm (log ε): 268 (4.17), 290 (4.08), and 418 (4.59). Found: C 56.9; H 4.5; N 6.1 %. $C_{21}H_{19}N_2BrO_4$. Calculated: C 56.8; H 4.5; N 6.3 %.

1,3,3-Trimethyl-3'-acetyl-6'-nitrospiro(indoline-2,2'-[2H-1]benzopyran) (IIId, R = $COCH_3$, R' = NO_2, R" = H). Acetic anhydride (2 ml) and 1 ml of boron trifluoride etherate were added with stirring to a solution of 0.66 g (0.021 mole) of spiropyran IIIc in 20 ml of chloroform, and the mixture was heated at 60-65° for 2 h. It was then cooled, 15 g of sodium carbonate, 60 ml of chloroform, and 75 ml of water were added, and the mixture was stirred at 70° for 40 min. It was then cooled and extracted with chloroform. The extract was washed with water, evaporated to a small volume, and chromatographed on aluminum oxide with elution by chloroform. The eluate was concentrated and chromatographed in a thin layer of silica gel with elution by benzene. The zone of the principal component was extracted with chloroform, the extract was evaporated, and the residue was crystallized from hexane to give 0.43 g (56 %) of spiropyran IIId with mp 203°. Mass spectrum, m/e (I/I_{max}, %): 364 (41), 349 (5), 334 (4), 322 (59), 321 (100), 307 (32), 306 (72), 260 (41), 159 (39), 158 (40). Found: C 69.6; H 5.4 %. $C_{21}H_{20}N_2O_4$. Calculated: C 69.2; H 5.5 %.

1,3,3-Trimethyl-3'-benzoyl-6'-nitrospiro(indoline-2,2'-[2H-1]benzopyran) (IIIe, R = COC_6H_5, R' = NO_2, R" = H). A) A 3.22-g (0.01 mole) sample of spiropyran IIIc and 1.4 g (0.01 mole) of benzoyl chloride were added successively with stirring to 5.3 g (0.02 mole) of aluminum bromide in 70 ml of carbon disulfide, and the mixture was refluxed with stirring until hydrogen chloride evolution ceased (3.5 h). The mixture was then poured into 150 ml of 20 % sodium carbonate solution, the carbon disulfide was removed by distillation on a water bath, and the residue was extracted with chloroform. The solvent was removed from the extract by distillation to give a crude product, which was chromatographed with a column filled with aluminum oxide with successive elution with benzene–heptane (1 : 1) and chloroform. The chloroform fraction was evaporated, and the residue was dissolved in 100 ml of octane and irradiated with UV light. The precipitated blue form that had not undergone reaction with the starting spiropyran was removed by filtration, the filtrate was evaporated, and the residue was crystallized from benzene–heptane to give 1.12 g (26.3 %) of spiropyran IIIe with mp 183-185°. Mass spectrum, m e: 426, 411, 396, 321, 306, 291, 159, 158. Found: C 73.7; H 5.5 %. $C_{26}H_{22}N_2O_4$. Calculated: C 73.2; H 5.2 %.

B) A 0.42-g (3 mmole) sample of benzoyl chloride was added to 0.5 g (1.6 mmole) of spiropyran IIIc in 15 ml of dimethylaniline at 150°, during which a precipitate formed; the precipitate then gradually dissolved. After all of the benzoyl chloride had been added, the mixture was stirred at 150° for 15 min. The dimethylaniline was then removed by vacuum distillation, 20 ml of 20 % sodium carbonate solution was added to the residue, and the mixture was extracted with benzene. The solvent was removed from the extract by distillation, and the residue was chromatographed with a column filled with silica gel with elution by benzene. The eluate was evaporated to give 0.40 g (60.5 %) of spiropyran IIIe with mp 183-185°. The product was identical to the compound obtained by method A.

2-Phenyl-1,3-bis(1,3,3-trimethyl-2-indolinylidene)propane (VI). A solution of 6.03 g (0.03 mole) of indoline I (R = CHO) in 30 ml of dry benzene was added dropwise to a solution of phenylmagnesium bromide obtained from 6.28 g (0.04 mole) of bromobenzene and 1.09 g (0.044 g-atom of magnesium in 20 ml of absolute ether, after which the mixture was refluxed for 30 min. It was then cooled, 10 ml of a satured ammonium chloride solution was added, and the organic layer was separated and evaporated. The resulting solid was crystallized from hexane with the addition of activated charcoal to give 2 g (30.6 %) of VI with mp 145-146° (mp 142-144° [19]). The molecular weight of VI was determined by potentiometric titration of an aqueous acetone solution of the compound with 0.1 N hydrochloric acid. Found: C 85.6; H 7.7; N 6.8 %. $C_{31}H_{34}N_2$. Calculated: C 85.7; H 4.9; N 6.4 %.

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