BROMINATION OF SPIROPYRANS AND REDUCTION OF THEIR NITRO DERIVATIVES

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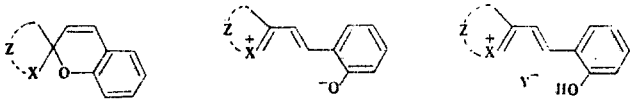
Depending on the nature of the nitrogen heteroring, either substitution only in the chromene ring (phenanthridine derivatives) or in both fragments of the molecule (indoline derivatives) occurs in the bromination of spiropyrans of the phenanthridine and indoline series with N-bromosuccinimide in low-polarity solvents, in which they are found in the cyclic form. The activity of the chromene fragment in both types of spiropyrans is approximately the same. The corresponding amino derivatives are formed in the catalytic reduction of spiropyran derivatives with a nitro group in the chromene ring in benzene solution. In alcohol solutions the nitro group and the 3'–4' double bond of the chromene ring are hydrogenated simultaneously.

A large amount of research has been devoted to the synthesis of substituted spiropyrans. As a rule, they are obtained by condensation of aromatic o-hydroxy aldehydes with quaternary salts of various heterocyclic compounds that contain an active methyl or methylene group or with their methylene bases [1]. All of the substituents that should be found in the spiropyran are usually introduced into the indicated starting compounds beforehand. In a number of cases another method for the preparation of substituted spiropyrans based on the reaction of the parent spiropyrans with various reagents is more efficient. However, up until now the chemical properties of the spiropyrans themselves have remained virtually uninvestigated. The preparation of photochromic monomers by acylation of the β-hydroxyethyl groups bonded to the nitrogen atom of the indoline ring by means of unsaturated acid chlorides [2, 3] and by alkylation of 5-carboxy derivatives of indoline spiropyrans with (chloromethyl)styrene [4] is described in some papers and patents. The alkylation of indoline benzo- and naphthospiropyrans with N-hydroxymethylamides and N-hydroxymethylimides in the presence of acid catalysts has also been reported in patents, but the structures of the reaction products were not established [5]. Some electrophilic substitution reactions in the case of 1,3,3-trimethyl-6'-nitrospiro(indoline-2,2'-[2H]chromene) have been studied only in research by Gal'bershtam and co-workers [6, 7]. However, the presence of a nitro group in the starting compound deactivates the chromene fragment. The conclusions regarding the direction of the substitution reactions drawn in this case therefore cannot be used to evaluate the behavior of the parent compounds.

In the study of the chemical properties of spiropyrans one must take into account the possibility of simultaneous presence of cyclic (A) and merocyanine (B) forms, the position of the equilibrium between which depends on the conditions. In addition, in acidic solutions spiropyrans are converted to salts of the C type as a result of the addition of a proton.



A B C

The chemical properties of these forms will undoubtedly be different. However, it may be assumed that in form A of various spiropyrans the reactivity of the chromene ring will be approximately the same, while the activity of the second fragment may differ very markedly for derivatives of different heterorings.

We studied the behavior of 5-methylspiro(5,6-dihydrophenanthridine-6,2'-[2H]chromene) (I) and 1,3,3-trimethylspiro(indoline-2,2'-[2H]chromene) (II) in the case of bromination. The bromination of I and II was

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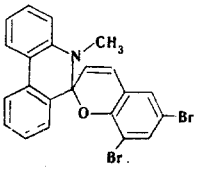
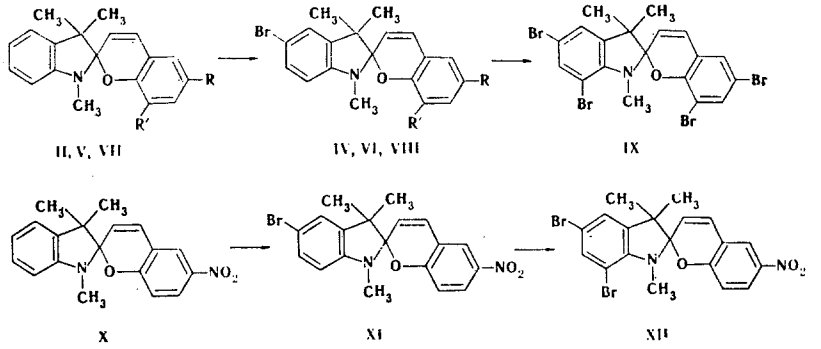
carried out in low-polarity solvents, in which they exist practically completely in the A form. In this case each of the heteroatoms (O and N) has an activating effect only on one of the two fragments of the molecule. N-Bromosuccinimide (NBS) was used as the brominating agent in order to exclude the formation of acids and the conversion of the spiropyrans to salts of the C type during the reaction.



III

It was established that I reacts readily with NBS in chloroform to give 6',8'-dibromo derivative (III). In this case a second bromine atom enters the chromene ring with the same ease as the first. We were unable to obtain a monobromo derivative even when we used equimolar amounts of reagents. The dihydrophenanthridine fragment of the starting molecule remains unchanged in this case. The structure of III was established by comparison of its properties with the properties of authentic samples of 6',8'-dibromo- [8] and 2-bromo- and 2,6'-dibromo-5-methylspiro(5,6-dihydrophenanthridine-6,2'-[2H]chromenes). The 2-bromo derivatives were obtained by the usual methods with the aid of the previously described 2-bromo-6-methylphenanthridine [9].

In contrast to I, the indoline fragment in 1,3,3-trimethylspiro(indoline-2,2'-[2H]chromene) (II) was found to be more active than the chromene fragment. A monobromination product (IV) was obtained when an equimolar amount of NBS was used. Monosubstitution under the same conditions also occurs in the bromination of 6'-bromo- and 6',8'-dibromo derivatives II (V, VII). This constituted evidence for the incorporation of bromine in the indoline ring. Since the 5 position is the most active position in the electrophilic substitution of indoline [10], the structures of 5-bromo derivatives were assumed for IV, VI, and VIII. In the further bromination of IV, in which the 5 position is occupied, it is found that the 7 position of indoline and the 6' and 8' positions of chromene have identical activities and readily form a tetrabromo derivative (IX).



II, V, VII — IV, VI, VIII — IX

X — XI — XII

II, IV R = R' = H; V, VI R = Br, R' = H; VII, VIII R = R' = Br

Thus either 5-bromo or 5,7,6',8'-tetrabromo derivatives can be obtained by bromination of II with NBS in nonpolar solvents. To obtain derivatives with two or three bromine atoms one must use the corresponding mono- and dibromo-substituted II, as shown in the scheme above.

Since the 6'-nitro derivatives have the most valuable photochromic properties among the indoline spiropyrans, we carried out the bromination of 6'-nitro-1,3,3-trimethylspiro(indoline-2,2'-[2H]chromene) (X). In this case also a monobromination product (XI) – 5-bromo-6'-nitro-1,3,3-trimethylspiro(indoline-2,2'-[2H]-chromene) – which was previously obtained by authentic synthesis [11] and by bromination of X under other conditions [6], is readily formed by reaction with an equimolar amount of NBS. Only the 5,7-dibromo derivative of X (XII) is formed with two or more equivalents of NBS. As a result of deactivation of the chromene ring by a nitro group, bromination in the 8' position does not take place under the conditions used.

The structures of IV, V, VII, VIII, X, and XI were proved on the basis of the IR, UV, and PMR spectra and by comparison with authentic samples of the compounds. The IR spectra of all of the compounds contain absorption bands characteristic for the double bond of chromene (1640-1650 cm^{-1}) and the $C_{spiro}-O$ bond (960-980 cm^{-1}) [12]; this provides evidence for retention of the 3'–4' double bond. The characteristic singlet signals of geminal methyl groups in the 3 position and of an N-methyl group and the doublet of the proton of the

TABLE 1. PMR Spectra of VIII, IX, XI, and XII in CCl_4[a]

Compound	3-CH_3	N-CH_3	4-H	6-H	3'-H	4'-H	5'-H	7'-H
VIII	1,15, 1,27	2,64	7,09 (d, 2)	7,22 (q, 2; 8)	5,70 (d, 10)	6,74 (d, 10)	~7,1 b	7,45 (d, 2)
IX	1,08, 1,22	3,02	6,93 (d, 2)	7,33 (d, 2)	5,59 (d, 10)	6,69 (d, 10)	7,02 (d, 2)	7,38 (d, 2)
XI[d]	1,12, 1,20	2,63	7,00 (d, 2)	7,12 (q, 2; 8)	5,72 (d, 10,5)	6,83 (d, 10,5)	7,86 (d, 2,5)	7,95 (q, 2,5; 8)
XII[c]	1,12, 1,21	3,06	6,99 (d, 2)	7,36 (d, 2)	5,72 (d, 10)	6,92 (d, 10)	7,91 (br. s)	8,00 (q, 2,5; 8)

[a]The chemical shifts are presented on the δ scale. The multiplicity of the signal and the spin–spin coupling constants (in Hertz) are indicated in parentheses. [b]Overlapped with the 4-H signal and partially with the 6-H signal. For 7-H, δ 6.32 ppm (d, 8 Hz). [c]For 7-H, δ 6.28 ppm (d, 8 Hz); for 8'-H, δ 6.65 ppm (d, 8 Hz). The 8'-H and 4'-H, 7'-H and 5'-H, and 6-H and 4-H signals are partially overlapped. [d]For 8'-H, δ 6.75 ppm (d, 8 Hz). The 8'-H, and 4'-H and 4-H, 5'-H, and 7'-H signals are partially overlapped.

double bond of the chromene ring in the 3' position are observed in the PMR spectra of the bromo derivatives of the spiropyrans (Table 1) (see [11]). It is interesting to note that the bromine atom in the 5 position of the indoline ring and the substituents in the chromene ring, including the nitro group, have almost no effect on the δ value of the protons of the N-methyl group (see [11] for the PMR spectra of II, V, and VII). At the same time, the presence of bromine in the 7 position causes a shift of this signal to weak field of up to 0.4 ppm. The signals of the other protons depend on the character and position of the substituent and make it possible to unambiguously determine the structures of the compounds. The assignment of these signals is given in Table 1.

The electronic spectra of the compounds obtained (Table 2) are also in agreement with the adopted structures.

The accumulation of bromine atoms in the chromene ring leads to stabilization of the colored merocyanine forms, as revealed from the appearance of coloration and an increase in its intensity in alcohol solutions. At the same time, the bromine atoms in the indoline ring stabilize the colorless spiropyran form (A). This is apparent from a comparison of the spectra of X, XI, and XII, as well as VI and VIII, with the spectra of V [λ_{max} 581 nm (log ε 1.16)] and VII [λ_{max} 582 nm (log ε 2.29)].

Thus as one might have expected, the activities of the chromene portions of the molecules were found to be almost identical when there is a large difference in the reactivities of the nitrogen-containing fragments of spiropyrans based on various heterorings.

In an investigation of the chemical properties of the spiropyrans we attempted to use them for the synthesis of derivatives that are inaccessible by the usual method of condensation. Compounds of this type include derivatives with an amino group in the chromene ring, since the aminosalicylaldehydes necessary for their synthesis are very labile and readily undergo polymerization. These compounds are attracting attention not only in connection with the elucidation of the effect of an amino group on the photochromic and thermochromic properties but also as possible intermediates for the preparation of various derivatives through reactions with the participation of amino groups. Up until now, not one compound of this type has been described. At the same time spiropyran derivatives with a nitro group in the chromene ring are readily accessible; they are usually formed in high yields in the condensation of quaternary salts or methylene bases of heterocycles with nitrosalicylaldehydes. In this connection we investigated the possibility of the preparation of amino-substituted spiropyrans by reduction of the corresponding nitro derivatives.

The reduction of 6'-nitro derivatives of II and I (X and XIII, XIV) was carried out with hydrogen in the presence of Raney nickel in both a nonpolar solvent, in which the starting spiropyran exists in solution in the A form, and in alcohol, i.e., when both forms (A and B) are present. In the case of the reduction of 6'-nitro derivatives of II and I (X and XIII) and the 6'-nitro-8'-methoxy derivative of I (XIV) in benzene the nitro group is primarily reduced, and the corresponding amino derivatives (XV-XVII) are formed in high yields. If hydrogenation is continued after reduction of the nitro group, in the case of XV and XVII hydrogen adds to the double bond of the pyran ring to give amino derivatives of spirodihydropyrans (XVIII, XIX). In the case of XVI this is

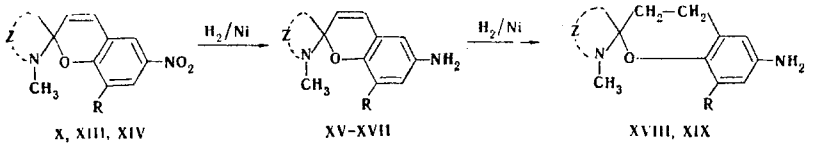
TABLE 2. Bromo Derivatives of Indoline Spiropyrans

Compound	mp, °C	Empirical formula[a]	Br, % found	Br, % calc.	In alcohol, λ_{max}, nm (log ε)[b]	Yield, %[c]
IV	137—138	$C_{19}H_{18}BrNO$	22,8	22,5	255, 307 (4,27; 3,80)	77
VI	135—137	$C_{19}H_{17}Br_2NO$	36,5	36,7	223, 253, 307, 330* (4,62; 4,35; 3,81; 3,46)	93
VIII	135—136	$C_{19}H_{16}Br_3NO$	46,3	46,7	232, 245*, 308 (4,56; 4,40; 3,73)	77
IX	171—172	$C_{19}H_{15}Br_4NO$	54,2	53,9	231, 257, 313 (4,65; 4,38; 3,82)	60 (from II), 97 (from VII)
XI	159—160	$C_{19}H_{17}BrN_2O_3$	20,0	20,0	260, 312, 324—338*, 545 (4,40; 4,00; 3,98; 2,48)	80
XII	156—157	$C_{19}H_{16}Br_2N_2O_3$	34,0	33,3	262, 318 (4,46; 4,08)	83

[a]The compositions of XI and XII were also confirmed by determination of the nitrogen content. [b]The shoulders and inflection points are indicated by an asterisk in this column. [c]The yields of the crude compounds are indicated.

evidently prevented by its precipitation from solution because of its low solubility in benzene. Reduction to the aminospiropyrans can also be carried out in dioxane. An acetyl derivative was obtained from XVI by the action of acetic anhydride.

However, if the reduction is carried out in alcohol, in which the merocyanine form (B) is also present, simultaneous hydrogenation of the 3'—4' double bond and the nitro group is observed.



X, XIII, XIV XV-XVII XVIII, XIX

X, XV, XVIII — indoline derivatives; XIII, XIV, XVI, XVII, XIX — phenanthridine derivatives; XIV, XVII, XIX R=OCH_3, R=H for the rest

The structure of 6'-amino derivatives XV-XIX were proved by their IR, UV, and PMR spectra and the results of elementary analysis. The IR spectra of XV-XIX do not contain the absorption bands at 1530 and 1350 cm^{-1} that are characteristic for nitro groups, and two bands of stretching vibrations of amino group N—H bonds (3250-3400 cm^{-1}) appear. In the case of XV-XVII the bands at 1650-1660 and 950-980 cm^{-1} that are characteristic for spiropyrans are retained, whereas they are absent in the spectra of XVIII and XIX.

The UV spectra of XV-XVII are similar to the spectra of the corresponding spiropyrans. In contrast to them, the spectrum of XVIII is similar to the spectrum of p-anisidine. The spectrum of an alcohol solution of this compound contains absorption maxima at 240 and 300 nm, and only one absorption band with a maximum at 275 nm remains in the spectrum of a solution of the compound in 10% sulfuric acid. This indicates the absence of a 3'—4' double bond and the conjugation of the entire system that is observed when the pyran ring in spiropyrans is opened to give salts of the cyanine type (C).

One-proton 3'-H and 4'-H doublets are observed in the PMR spectra of XVI in CF_3COOH at 6.25 ppm (J = 9 Hz) and 6.77 ppm (J = 9 Hz); a one-proton 3'-H doublet is also observed for XVII in $CHCl_3$ at 5.79 ppm (J = 10 Hz), and a one-proton 3'-H doublet is observed for XV (in CF_3COOH) at 6.35 ppm (J = 13 Hz). The 4'-H signals are overlapped by signals of aromatic protons. The spectrum of XIX (in $CDCl_3$) does not contain signals of protons attached to a double bond, and one clearly sees two one-proton doublets of protons in the ortho positions relative to an amino group at 5.85 and 6.05 ppm (J = 2.5 Hz) and singlets of N—CH_3 (2.95 ppm) and O—CH_3 (3.71 ppm) groups. Two-proton multiplets of CH_2 groups are found in the spectrum of XVIII (in CF_3COOH) at 2.0 and 2.6 ppm. It is interesting to note that the signal of the dihydropyran ring is evidently not overlapped in the spectrum of XVIII in CF_3COOH. This can be judged from the retention of the nonequivalence of the C-methyl groups (singlets at 0.97 and 1.23 ppm) and the splitting of the signal of the N-methyl group as a result of addition of a proton to the indoline nitrogen atom [3.08 ppm (J = 5 Hz)]. At the same time, the signals of the C- and N-methyl groups in the spectrum of spiropyran XV in CF_3COOH are singlets.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were measured with IKS-22 and UR-20 spectrometers. The electronic spectra were recorded with an SF-8 spectrophotometer. The PMR spectra were recorded with an RYa-2305 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard.

Compounds II, V, VII, and X were synthesized by described methods.

2-Bromo-6-methylphenanthridine. A mixture of 2.5 g (8.6 mmole) of 5-bromo-2-acetamidodiphenyl and 5 ml of phosphorus oxychloride was refluxed for 2 h, after which the excess $POCl_3$ was removed by vacuum distillation, and the residue was dissolved in 50 ml of refluxing 1 M HCl. The solution was treated with charcoal and cooled, and the resulting light-yellow acicular crystals were removed by filtration and washed with acetone and ether to give 1.5 g (57%) of 2-bromo-6-methylphenanthridine hydrochloride. The latter was dissolved in 30 ml of hot water, and the solution was neutralized with 40% NaOH solution. The precipitated light-yellow base was removed by filtration and washed with water to give 1.23 g (52%) of 2-bromo-6-methylphenanthridine with mp 128-129°C [9].

2-Bromo-5,6-dimethylphenthridinium Methylsulfate. A 0.4-ml (4 mmole) sample of dimethyl sulfate was added with stirring to a refluxing solution of 0.54 g (2 mmole) of 2-bromo-6-methylphenanthridine in 4 ml of xylene. A yellow precipitate of the quaternary salt began to precipitate almost immediately. The mixture was refluxed for 2 h, after which it was cooled, and the resulting precipitate was separated and washed with ether to give 0.65 g (81%) of light-yellow acicular crystals with mp 280-283°C (dec.). Found: Br 20.0; S 8.1%. $C_{16}H_{16}BrNO_4S$. Calculated: Br 20.1; S 8.0%.

2-Bromo-5-methylspiro(5,6-dihydrophenanthridine-6,2'-[2H]chromene). This compound was obtained by condensation of 0.28 g (0.7 mmole) of 2-bromo-5,6-dimethylphenanthridinium methylsulfate and 0.10 ml (0.7 mmole) of salicylaldehyde in 14 ml of alcohol in the presence of 0.14 ml (1.4 mmole) of piperidine by the method in [8]. The resulting precipitate was separated and washed with alcohol to give 0.15 g (55%) of spiropyran with mp 213-214°C. Crystallization from 9 ml of alcohol–benzene (1 : 2) gave 0.08 g of colorless crystals with mp 215 °C. UV spectrum in alcohol [λ_{max} (log ε)]: 244, 265*, 320, 345 nm (4.67; 4.30; 3.70; 3.73). Found: Br 20.7%. $C_{22}H_{16}BrNO$. Calculated: Br 20.5%.

2,6-Dibromo-5-methylspiro(5,6-dihydrophenanthridine-6,2'-[2H]chromene). This compound was similarly obtained in 67% yield by condensation with 5-bromosalicylaldehyde. After crystallization from xylene the yield of spiropyran, with mp 234-235° (darkens beginning at 220°C), was 42%. UV spectrum in alcohol [λ_{max} (log ε)]: 245, 265*, 335 nm (4.73; 4.01; 3.77). Found: Br 34.1%. $C_{22}H_{15}Br_2NO$. Calculated: Br 34.1%.

5-Methyl-6',8'-dibromospiro(5,6-dihydrophenanthridine-6,2'-[2H]chromene) (III). A solution of 0.24 g (1.3 mmole) of N-bromosuccinimide (NBS) in 12 ml of chloroform was added to a solution of 0.2 g (0.66 mmole) of I in 15 ml of chloroform, and the mixture was refluxed for 1 h. The green solution was washed with water (four 20-ml portions) and dried with sodium sulfate, and the chloroform was removed by distillation to give 0.29 g (97%) of III, which was purified by reprecipitation from alcohol solutions by the addition of water and recrystallized from petroleum ether (1 : 100) to give colorless crystals with mp 170-171°C.† UV spectrum in hexane [λ_{max} (log ε)]: 238, 272*, 328 (4.74; 4.35; 3.99); in alcohol: 240, 260-270*, 328, 380*, 540 nm (4.68; –; 3.98; 3.49; 3.47). Found: M 464. $C_{22}H_{15}Br_2NO$. Calculated: M 469.

Bromination of Indoline Spiropyrans. The appropriate amount of a 0.1-0.15 M solution of NBS was added in 30-60 min with stirring to a refluxing solution of the spiropyran in chloroform (0.2-0.4 mole/liter), and the mixture was refluxed for another 30-60 min. It was then washed three times with water and dried with sodium sulfate. The chloroform was removed by distillation, and the residual spiropyran was crystallized from alcohol. Compound IX was initially chromatographed with a column filled with activity II-III aluminum oxide with elution by chloroform–hexane (1 : 2), after which it was crystallized from alcohol and petroleum ether. The properties of the compounds thus obtained are presented in Table 2.

*The shoulders and inflection points are indicated by asterisks.

†A melting point of 98°C was indicated erroneously in [8] for III. In the preparation of III by the method in [8] the molar ratio of 5,6-dimethylphenanthridinium methylsulfate, 3,5-dibromosalicylaldehyde, and piperidine should be 1 : 1 : 1.1. In the case of a large excess of piperidine difficult-to-remove impurities that lower the melting point of the preparation are formed.

1,3,3-Trimethyl-6'-aminospiro(indoline-2,2'-[2H]chromene) (XV). A 0.5-g sample of aqueous W-4 Raney nickel paste was washed with alcohol and benzene and added to a solution of 0.32 g (1 mmole) of X in 30 ml of benzene, and hydrogenation was carried out under the usual conditions until the calculated amount of hydrogen has been absorbed (~ 2 h). The solution was filtered and vacuum evaporated, and the residual oil crystallized to give 0.28 g (97%) of XV. Two crystallizations (1 : 20) from benzene–petroleum ether (1 : 1) gave 0.14 g of light-colored crystals with mp 140-141°C. UV spectrum in alcohol [λ_{max} (log ε)]: 242, 265‡, 295, 345 nm (4.56; 3.92; 3.77; 3.51); in 10% H_2SO_4: 234, 255-262, 307*, 318, 370* nm (3.91; 3.72; 3.95; 3.98; 3.92). PMR spectrum in CF_3COOH, δ: 1.34 (3-CH_3, s), 3.13 (N-CH_3, s), 6.35 (3'-H, d, 13 Hz) ppm; in $CHCl_3$: 1.12 and 1.27 (3-CH_3, s), 2.67 ppm. (N-CH_3, s). IR spectrum: 3390, 3310, 2930, 2890, 2840, 1650, 1630, 1605, 1590, 1490, 1465, 1367, 1310, 1250, 1190, 1105, 1025, 965-975, 940, 825, 760‡ cm^{-1}. R_f 0.23 (on activity III aluminum oxide, elution with chloroform: bright crimson spot some time after chromatography). Found: 9.8%; M 304 (in benzene)**. $C_{19}H_{20}N_2O$. Calculated: N 9.6%; M 292.

1,3,3-Trimethyl-3',4'-dihydro-6'-aminospiro(indoline-2,2-[2H]chromene) (XVIII). A 0.5-ml sample of alcoholic Raney nickel paste was added to 0.48 g (1.5 mmole) of X in 30 ml of alcohol, and the compound was hydrogenated until hydrogen absorption was complete (140 ml after 2 h 30 min). Only a small admixture of aminospiropyran XV in the dihydro derivative was visible on the chromatogram (elution with chloroform) (R_f of XVIII 0.12; the spot becomes blue when the chromatogram is allowed to stand). The mixture was filtered to remove the catalyst, and the filtrate was evaporated to dryness to give 0.4 g (91%) of a dark viscous mass, which by trituration with 3 ml of benzene–petroleum ether (1 : 1) was converted to a light-colored powder. Two crystallizations from the same mixture (1 : 50-1 : 80) gave 0.2 g of XVIII with mp 134-135°C. Additional purification from chloroform (1 : 30) and the same mixture gave a product with mp 136-137°C. An identical compound was obtained by prolonged hydrogenation of XV in benzene. UV spectrum in alcohol [λ_{max} (log ε)]: 242, 300 nm (4.09; 3.73); in 10% H_2SO_4: 275 nm (3.30). PMR spectrum in $CHCl_3$, δ: 1.15 and 1.38 (3-CH_3), 2.70 ppm (N-CH_3); in CF_3COOH: 0.97 and 1.23 (3-CH_3), 3.08 ppm (N-CH_3, d, 5 Hz). IR spectrum: 3320, 3245, 3000, 2930, 2935, 2780, 1608, 1510, 1490, 1460, 1390, 1300, 1285, 1265, 1220, 1125, 1030, 930, 810, 800, 790, 750 cm^{-1}. Found: N 9.7%. $C_{19}H_{22}N_2O$. Calculated: N 9.5%.

5-Methyl-6'-aminospiro(5,6-dihydrophenanthridine-6,2'-[2H]chromene) (XVI). This compound was obtained by the method used to prepare XV. The reaction mixture was refluxed until the product dissolved completely, after which the solution was filtered to remove the catalyst, and the latter was washed with hot benzene. The solution was evaporated to one-third of its original volume, and the resulting precipitate was removed by filtration to give amine XVI (in 67% yield), which was purified by crystallization from benzene (1 : 200). The light-yellow acicular crystals had mp 298-299°. UV spectrum in alcohol [λ_{max} (log ε)]: 245, 265*, 335 nm (4.66; 4.34; 3.95); in 50% CH_3COOH: 253, 316, 375 nm (4.72; 4.16, 3.78). PMR spectrum in CF_3COOH, δ: 4.3 (N-CH_3, s), 6.25 (3'-H, d, 9 Hz), 6.77 ppm (4'-H, d, 9 Hz). IR spectrum: 3335, 3235, 3150, 1645, 1625, 1605, 1580, 1490, 1470, 1460, 1440, 1425, 1382, 1335, 1320, 1245, 1095, 978, 960, 930, 887, 850, 820, 780, 770, 750, 740, 720 cm^{-1}. Found: C 80.7; H 5.9; N 8.5%; M 333 (in $CHCl_3$). $C_{22}H_{18}N_2O$. Calculated: C 81.0; H 5.6; N 8.6%; M 326.4.

5-Methyl-6'-acetamidospiro(5,6-dihydrophenanthridine-6,2'-[2H]chromene). After separation of the catalyst in the preparation of amine XVI, 3 equivalents of acetic anhydride were added, and the mixture was refluxed for 1 h. An orange precipitate formed when the mixture was cooled. The reaction mixture was washed with two 20-ml portions of 2% NaOH and three 20-ml portions of water, and the benzene solution was dried with sodium sulfate. Light-colored needles formed when the benzene soltuion was allowed to stand. The mixture was heated and filtered to remove the sodium sulfate, and the filtrate was treated with charcoal and evaporated to one-third of its original volume. The filtrate was cooled to give light-colored crystals (28% yield) with mp 205-208°C. Crystallization from chlorobenzene (1 : 100) gave colorless needles with mp 208-209°C. UV spectrum in 20% CH_3COOH [λ_{max} (log ε)]: 251, 317, 377 nm (4.57; 3.94; 3.75). IR spectrum: 3300-3400 (br), 1665 (br, C = O), 1610, 1530, 1490, 1450, 1460, 1380, 1340, 1320, 1270, 1250, 1125, 1100, 985, 950, 910, 880, 825, 770, 755, 735 cm^{-1}. Found: N 7.3%. $C_{24}H_{20}N_2O_2$. Calculated: N 7.6%.

5-Methyl-6'-amino-8'-methoxyspiro(5,6-dihydrophenanthridine-6,2'-[2H]chromene) (XVII). This compound, with mp 135-136°C (dec., from benzene–petroleum ether), was obtained in 74% yield by the method used to prepare XVI. UV spectrum in alcohol [λ_{max} (log ε)]: 245, 338 nm (4.57; 3.86); in 50% CH_3COOH: 250,

*The shoulders and inflection points are indicated by asterisks.

‡The most intense and characteristic bands are underlined.

**The molecular weights were determined by reverse ebullioscopy with an osmometer.

325, 370 nm (4.57, 3.92; 3.79). PMR spectrum in $CHCl_3$, δ: 3.07 (N-CH_3, s), 3.40 (OCH_3, s), 5.79 (3'-H, d, 10 Hz), 6.1 ppm (br. s, 5'-H + 7'-H). IR spectrum: 3400, 3320, 3215, 3075, 3040, 2935, 1660, 1630, 1615 br, 1595, 1490 br, 1450, 1400, 1340, 1310, 1240, 1160, 1120, 1100, 1080, 1040, 1010, 990, 920, 865, 850, 825, 770, 750 cm^{-1}. Found: C 77.7; H 6.1; N 7.7%. $C_{23}H_{20}N_2O_2$. Calculated: C 77.5; H 5.7; N 7.9%.

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SYNTHESIS OF DIHYDROTHIENO[3,4-b]INDOLES

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A new heterocyclic system – 3-imino-4-methyldihydrothieno[3,4-b]indole – was obtained by treatment of 1-methylindole-2-carboxylic acid thioamide with aldehydes or ketones in the presence of hydrogen chloride. Reactions involving saponification and acetylation of the imino group of the thieno ring and opening of the thieno ring by the action of $LiAlH_4$ to give a bis(indolylphenylmethyl) sulfide were carried out. A scheme is proposed in which the SH group of the thioamide adds to the carbonyl compound in the first step, after which the product undergoes intramolecular cyclization in the 3 position of indole.

An attempt to obtain dihydrothieno[3,4-b]indole by the Fischer reaction from 3-thiophanone and phenylhydrazine was unsuccessful and led exclusively to the formation of 2,3-dihydrothieno[3,2-b]indole [1]. Using the previously proposed principle of construction of three-ring indole-containing structures [2] we obtained dihydrothieno[3,4-b]indoles (II-XXI) by reaction of 1-methylindole-2-carboxylic acid thioamide in the presence of hydrogen chloride in alcohol, ether, or acetic acid at room temperature with aldehydes or ketones.

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