

2-BENZOPYRYLIUM SALTS.

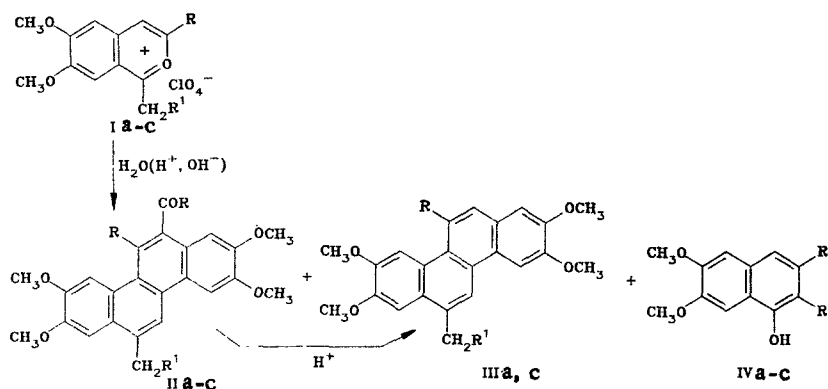
27.* FORMATION OF SUBSTITUTED CHRYSENES
FROM 1-METHYL-2-BENZOPYRYLIUM SALTSI. V. Korobka, A. I. Voloshina,
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1-Methyl-2-benzopyrylium salts with a free β position of the heteroring primarily form substituted chrysenes. In alkaline media this process does not proceed through the intermediate formation of 1,5-diketones.

A characteristic property of α -alkyl-substituted pyrylium salts is their ability to undergo recyclization to phenols in alkaline media [2, 3]. 2-Benzopyrylium salts that contain a methylene group in the 1 position of the heteroring, such as indeno[1,2-c]-2-benzopyrylium salts [5], under similar conditions form annelated analogs of phenols — α -naphthols. It was recently observed that a similar process is also realized in acidic media for 1-methylene-substituted 2-benzopyrylium salts [1].

In the present research we have shown that 1-methyl-2-benzopyrylium salts (Ia-c) with a free β position of the heteroring, regardless of the pH of the solution, primarily undergo the previously unobserved (in the pyrylium series and other heteroaromatic cations) intermolecular self-condensation to give substituted chrysenes (IIa-c and IIIa, c).



I—IV a R=CH₃, R¹=H; b R=C₆H₅, R¹=H; c R=3,4-(OCH₃)₂C₆H₃, R¹=H

The reactions were carried out by heating salts Ia-c in aqueous alcohol containing sodium hydroxide or hydrochloric acid. The reaction times and the products are given in Table 1.

At pH < 7 salts Ia-c reacted considerably more slowly than their 1-methylene-substituted analogs (I, R¹ ≠ H), which are converted to naphthols in 75–90% yields after 1.5–2 h [1]. Only in the case of salt Ia were we able, by thin-layer chromatography (TLC), to detect the formation of naphthol IVa (from the characteristic yellow-green coloration characteristic for α -naphthols in the case of development in iodine vapors [1]), and, using gas-liquid chromatography (GLC),† we were able to determine its yield (>1%).

*For Communication 26, see [1].

†Because of the low volatility of the other naphthols and substituted chrysenes, we were unable to determine their yields by this method.

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TABLE 1. Products of the Transformations of 2-Benzopyrylium Salts Ia-c and Diketones Va-c in Acetic and Alkaline Media

Compound	Acidic media		Alkaline media	
	time, h	products (yields, %)	time, h	products (yields, %)
Ia	9	IIa (67), IIIa (32)	3	IIa (45), IVa (4)
Ib	15*	IIb (41)	6	IIb (60), IVb (12)
Ic	30*	IIIc (56)	6	IIC (63), IVc (34)
Va	3	IIa (58), IIIa (31), IVa (5)	3	IVa (27)
Vb			3	IVb (54)
Vc	12	IIIc (71)	3	IVc (79)

*The salts did not react completely during the indicated times, and the yields were therefore determined from the amount of unchanged product.

The principal reaction products in acidic media were substituted chrysenes IIb and IIIa, c, i.e., intermolecular self-condensation proved to be the dominant process.

The formation of chrysenes IIIa, c under these conditions is probably explained by deacetylation of the primarily formed IIa, c by the liberated perchloric acid. This assumption is confirmed by the formation of IIIa when IIa is heated in acetic acid in the presence of 70% HClO₄ or when it is treated with CF₃COOH in the cold.

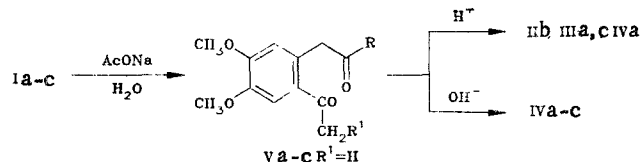
The ease of ipso protonation of acylchrysenes IIa-c should be determined by the nature of the substituent in the ring undergoing attack. In fact, the deacylation of IIC proceeds considerably more readily when the reaction is carried out in the presence of weaker hydrochloric acid. The retention of the benzoyl group in IIb under all of the enumerated conditions is a consequence of the lower nucleophilicity of the phenyl group as compared with the methyl and dimethoxyphenyl groups.

In alkaline media, in which the reactions were complete after 3-6 h (salt Ia, R¹ = Ar, was converted under these conditions to α -naphthols in no higher than 40% yields after 8-10 h [4]), and the formation of α -naphthols IVa-c occurred in all cases; their yields increased with an increase in the size of the substituent in the 3 position of the heteroring of salts Ia-c. However, even here, the principal reaction products were chrysenes IIa-c.

1,5-Diketones (Va-c), which were verified intermediates in the formation of α -naphthols from 1-methylene-substituted 2-benzopyrylium salts [1, 4] and are the most likely intermediates in the formation of chrysenes from salts Ia-c, were obtained by treatment of these salts with an aqueous solution of sodium acetate.

In acidic media they formed the same product in approximately the same ratios as salts Ia-c; to be sure, the yield of naphthol IVa increases to 5%, although we were unable to detect the formation of other naphthols, as in the case of starting salts Ib, c.

In alkaline media the yields of naphthols[†] from diketones increased sharply; however, chrysenes are not formed at all.



1. If R¹ = H, regardless of the pH of the medium, salts Ia-c react primarily intermolecularly; diketones Va-c also react at pH < 7.

2. If R¹ ≠ H, at pH < 7 salts Ia-c and diketones Va-c react intramolecularly.

3. At pH > 7, regardless of the nature of R¹, diketones Va-c form only naphthols, i.e., they react intramolecularly.

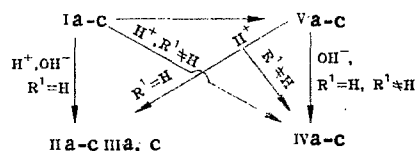
In accordance with these results, the most likely version of the formation of chrysenes from 2-benzopyrylium salts through 1,5-diketones proves to be unfounded, at least for alkaline media.

[†]As in the case of salt Ia, resinification is observed in the acidification of the reaction mixture in the case of diketone Va.

TABLE 2. Characteristics of Diketones Va-c, the Corresponding Naphthols IVa-c, and Substituted Chrysenes IIa-c and IIIa, c

Compound	mp, °C	R _f	IR spectrum, cm ⁻¹	Found, %		Empirical formula	Calc., %	
				C	H		C	H
IIa [6]		0,60	1690, 1625, 1170	—	—	—	—	—
IIb	250	0,78	1665, 1615, 1280	79,4	5,3	C ₃₆ H ₃₀ O ₅	79,7	5,5
IIc	232	0,46	1660, 1610, 1180	72,1	5,5	C ₄₀ H ₃₈ O ₉	72,5	5,7
IIIa [6]		0,83	1620, 1600, 1170	—	—	—	—	—
IIIc	256	0,50	1615, 1600, 1175	74,4	5,9	C ₃₁ H ₃₀ O ₆	74,7	6,1
IVa	142	0,37	3270, 1620, 1180	71,2	6,1	C ₁₉ H ₁₄ O ₃	71,6	6,4
IVb	148	0,36	3250, 1630, 1160	76,8	5,5	C ₁₈ H ₁₆ O ₃	77,1	5,7
IVc	190	0,20	3280, 1615, 1180	70,1	5,2	C ₂₀ H ₂₀ O ₅	70,6	5,7
Va	122	0,43	1705, 1665, 1600, 1170	65,7	6,2	C ₁₃ H ₁₆ O ₄	66,1	6,8
Vb	162	0,63	1680, 1660, 1600, 1175	72,2	5,9	C ₁₈ H ₁₈ O ₄	72,4	6,1
Vc	182	0,35	1670, 1665, 1600, 1160	67,3	5,9	C ₂₀ H ₂₂ O ₆	67,1	6,2

*The compounds were crystallized: IIb, IIIc, Va, c from alcohol, IIc, IVb, c, and Vb from benzene, and IVa from hexane.



EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a Specord 71 IR spectrophotometer. The PMR spectra of solutions of the compounds in CDCl₃ were recorded at 20°C with Tesla BS-467 (60 MHz) and Tesla BS-478C (80 MHz) spectrometers with hexamethyldisiloxane (HMDS) as the internal standard.

The quantitative determination of naphthol Va in the reaction mixtures was carried out by the method of absolute calibration (pure Va was used as the standard) by gas chromatography with a Chrom-42 chromatograph with a flame-ionization detector; the vaporizer temperature was 270°C, the carrier gas was helium, and the flow rate was 55 ml/min. The temperature of the stainless-steel column (1000 × 3.5 mm) packed with silanized N-AW Chromaton was 210°C, and the solvent for the stationary phase was chloroform.

The mass spectra were recorded with a Varian MAT-112 spectrometer with an ionizing-radiation energy of 70 eV with direct introduction of the samples into the source.

The purity of the compounds obtained was monitored by means of TLC on aluminum oxide in a CHCl₃-n-C₆H₁₄ system (1:1). The R_f values and other characteristics of the synthesized compounds are presented in Table 2.

3,4-Dimethoxy-6-acetylphenylacetone (Va). A suspension of 2 g (6 mmole) of salt Ia and 2.5 g of sodium acetate in 50 ml of water was stirred at 20°C for 1 h, after which the precipitate was removed by filtration and washed with water, and the filtrate was extracted with chloroform (three 5-ml portions). Evaporation of the chloroform solution gave 0.45 g (40%) of Va. PMR spectrum (80 MHz): 2.18 (s, CH₃), 2.42 (s, CH₃), 3.85 (s, two OCH₃), 3.88 (s, CH₂), 6.52 (s, 1H), and 7.25 ppm (s, 1H).

3,4-Dimethoxy-6-acetyldeoxybenzoin (Vb). A suspension of 2 g (5 mmole) of salt Ib and 2 g of sodium acetate in 50 ml of water was refluxed for 5 h, after which the solution was cooled, and the precipitate was separated and crystallized with hot filtration from benzene. A 0.9-g sample of unchanged salt Ib remained on the filter, and 0.52 g (61%) of Vb precipitated from the filtrate.

3,3,4,4-Tetramethoxy-6-acetyldeoxybenzoin (Vc). This compound was obtained in 68% yield from salt Ic by a similar method. PMR spectrum (60 MHz): 2.43 (s, CH₃), 3.85 (s, four OCH₃), 4.52 (s, CH₂), and 6.65-8.02 ppm (m, aromatic 5H).

3-Methyl-6,7-dimethoxy-1-naphthol (IVa). A solution of 0.5 g (2 mmole) of diketone Va and 0.5 g of sodium hydroxide in 6 ml of alcohol and 2 ml of water was refluxed for 3 h. The

solution was cooled and poured into 20 ml of water, the aqueous mixture was filtered, and 3 ml of 36% HCl was added. The resulting precipitate was removed by separation, washed with water and dried. Naphthol VIa was isolated by means of preparative column chromatography on Al₂O₃ by elution with ether - hexane (1:1) with dry packing of the column. The retention time of naphthol IVa with a Chrom-42 chromatograph was 7 h 5 min. PMR spectrum (80 MHz): 2.25 (s, CH₃), 3.85 (s, two OCH₃), 6.43 (s, 1H), 6.95 (d, 2H), and 7.38 ppm (s, 1H). Using a similar method, from diketones Vb and Vc, after acidification of the filtrates with hydrochloric acid and purification by crystallization (Table 2), we obtained, respectively, 3-phenyl-6,7-dimethoxy-1-naphthol (Vb) with a PMR spectrum (80 MHz) containing bands at 3.82 (s, two OCH₃) and 6.80-7.35 ppm (m, 9H, aromatic), as well as 3-(3,4-dimethoxyphenyl)-6,7-dimethoxy-1-naphthol (Vc) with a PMR spectrum (60 MHz) containing bands at 3.75 (s, two OCH₃), 3.90 (s, two OCH₃), and 6.75-7.38 ppm (m, aromatic 7H).

6,11-Dimethyl-12-acetyl-2,3,8,9-tetramethoxychrysene (IIa) and 3-Methyl-6,7-dimethoxy-1-naphthol (IVa). A 3.2-g (10 mmole) sample of salt Ia was added to a solution of 2.5 g of sodium hydroxide in 15 ml of alcohol and 5 ml of water, and the mixture was refluxed for 3 h. The solution was cooled, and the resulting precipitate was removed by filtration, washed with water, and dried to give 0.35 g of IIa. The filtrate was diluted with 50 ml of water, and the resulting precipitate was separated. Recrystallization of the latter from alcohol gave another 0.6 g of IIa for an overall yield of 0.95 g of IIa. M⁺ 418. The aqueous alcohol solution was neutralized with hydrochloric acid, and the amount of naphthol IVa in the precipitate was determined by gas chromatography.

We used a similar method to obtain the following compounds: from salt Ib, 6-methyl-11-phenyl-12-benzoyl-2,3,8,9-tetramethoxychrysene (IIb) [PMR spectrum (60 MHz): 2.70 (s, CH₃), 3.02 (s, OCH₃), 3.72 (s, OCH₃), 3.88 (s, OCH₃), 4.05 (s, OCH₃), 6.72-7.50 (m, 13H, aromatic), and 8.02 (s, 1H) and 8.25 ppm (s, 1H)] and 3-phenyl-6,7-dimethoxy-1-naphthol (IVb), as well as from salt Ic, 6-methyl-11-(3,4-dimethoxyphenyl)-12-(3,4-dimethoxybenzoyl)-2,3,8,9-tetramethoxychrysene (IIc) [PMR spectrum (80 MHz): 2.80 (s, CH₃), 3.25 (s, two OCH₃); 3.75, 3.88, 3.92 (three s, five OCH₃), 4.15 (s, OCH₃), 6.45-7.40 (m, aromatic 9H), 8.02 (s, 1H), and 8.40 ppm (s, 1H)] and 3-(3,4-dimethoxyphenyl)-6,7-dimethoxy-1-naphthol (IVa).

6,11-Dimethyl-12-acetyl-2,3,8,9-tetramethoxychrysene (IIa) and 6,11-Dimethyl-2,3,8,9-tetramethoxychrysene (IIIa). A suspension of 1 g (3 mmole) of salt Ia in 20 ml of alcohol containing two drops of 36% HCl was refluxed for 9 h. The solution was then cooled, and the resulting precipitate, which was identified as a mixture of IIa and IIIa, was removed by filtration and washed on the filter with 3 ml of acetone. The residue consisted of 0.19 g of IIIa. M⁺ 376.

The filtrate was diluted with 50 ml of water, and the resulting precipitate was removed by filtration and combined with the precipitate formed after evaporation of the acetone solution and recrystallized from alcohol to give 0.44 g of IIa.

B) A similar method was used to synthesize, from 0.4 g of diketone Va, 0.2 g IIa and 0.1 g of IIIa. The yield of naphthol IVa was determined in the precipitate obtained after dilution of the reaction mixture with water by gas chromatography (see Table 1).

The same method was used to obtain, from 0.6 g of diketone Vc, 0.3 g of 6-methyl-11-(3,4-dimethoxyphenyl)-2,3,8,9-tetramethoxychrysene (IIIc). PMR spectrum (60 MHz): 2.80 (s, CH₃); 3.62, 3.70, 3.80, 4.02 (four s, six OCH₃); 6.70-8.42 ppm (m, aromatic 9H).

6-Methyl-11-phenyl-12-benzoyl-2,3,8,9-tetramethoxychrysene (IIb). A suspension of 2 g (5 mmole) of salt Ib in 50 ml of alcohol containing five drops of 36% HCl was refluxed for 15 h. After hot filtration, during which 1.25 g of unchanged salt Ib separated, the filtrate was cooled and diluted with 100 ml of water. The resulting precipitate was removed by filtration, dried, and recrystallized from alcohol to give 0.22 g of IIb.

A similar method was used to obtain, from 1.5 g of salt Ic after refluxing for 30 h, 0.31 g of IIIc; in this case 0.5 g of unchanged salt Ic remained.

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EPR SPECTRA AND π -ELECTRONIC STRUCTURES OF ANION
RADICALS OF A NITRO-SUBSTITUTED INDOLINE SPIROPYRAN

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547.754'814

Electrochemical generation was used to obtain anion radicals of 1,3,3-trimethyl-5-nitrospiro(indoline-2,2'-[2H]chromene), and their EPR spectra in acetonitrile, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were recorded. On the basis of an analysis of the hyperfine structure (hfs) of the EPR spectra it was concluded that, as a consequence of the relatively weak interaction of the π -systems of the indoline and benzopyran fragments, cleavage of the bond between the spiro carbon atom and the oxygen atom in the pyran ring does not occur in the formation of the anion radical, and the additional unpaired electron is delocalized in the π -system of the indoline fragment of the molecule.

The utilization in science and technology of materials based on spiropyrans is due mainly to the capacity of many of them to form colored products under the influence of UV light and ionizing radiation [1]. From the photochromic transformations of spiropyrans, the accumulated experimental data make it possible to draw rather convincing conclusions regarding the processes that take place under the influence of UV light, which are due to cleavage of the bond between the spiro C(2) carbon atom and the oxygen atom in the pyran ring and lead to the formation of the merocyanine form, which absorbs in the longer-wave region as compared with the starting spiropyran [2].

Individual communications, on the basis of which it is difficult to create a complete representation of the mechanism of the formation of colored compounds, are available regarding the transformation of spiropyrans under the influence of ionizing radiation. Researchers have noted that the colored products that develop during the radiolysis of spiropyrans have absorption spectra that differ from the spectra of the corresponding merocyanine forms [3]. In this connection, a question arises as to whether the development of colored products that differ from the merocyanine forms is due to interaction of the latter with the products of radiolysis of the matrix or whether the transformation of the spiropyran under radiolysis proceeds through a step that bypasses the formation of the merocyanine form. Pulse radiolysis has established [4, 5] that anion radicals of spiropyrans, which are subsequently protonated, are formed in the case of irradiation of indoline spiropyrans in ethanol solution with an electron beam. The data obtained in an investigation by EPR of the radiolysis of an unsubstituted indoline spiropyran - 1,3,3-trimethylspiro(indoline-2,2'-[2H]chromene) (I) - in a vitreous ethanol solution at 77°K [6] also constitute evidence for the formation of anion radicals of a spiropyran and their subsequent protonation, which leads to the formation of free radicals. The EPR spectra of free radicals were obtained in the solid phase and had a resolution that did not make it possible with absolute certainty to establish the structures of the radicals. Attempts to obtain anion radicals of unsubstituted spiropyran I by electrochemical generation in the liquid phase in aprotic solvents were unsuccessful. Polarographic investigations established that its first reduction wave ($E_{1/2} = -2.49 \pm 0.01$ V) is irreversible, in connection with which, we were unable, by using a stationary method, to accumulate anion radicals in concentrations necessary for recording of the EPR spectra.

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