The combined mother liquors were evaporated, and indole XII with mp 110-111° (from alcohol) and R_f 0.36 (activity II Al_2O_3), was isolated from the residue by preparative chromatography on a loose layer of aluminum oxide. PMR spectrum (in CCl_4): δ 1.7-2.2 (2-CH_2 and 3-CH_2), 2.4 (6-CH_3, s), and 3.8 ppm (4'-CH_3O, s). Found: C 82.2; H 7.4; N 5.2%. $C_{20}H_{21}NO$. Calculated: C 82.5; H 7.3; N 4.8%.

Indole XII was also synthesized by reaction of 6-methyl-1,2,3,4-tetrahydrocarbazole with p-bromoanisole; the product had mp 110-111°. No melting-point depression was observed for a mixture of a sample of this product with a sample of indole XII obtained as indicated above, and their PMR spectra were identical.

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THERMOLYSIS OF 1-DIALKYLAMINOANTHRAQUINONES — NEW METHOD FOR THE SYNTHESIS OF ANTHRA[1,9-bc]PYRROLE DERIVATIVES

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1-Dialkylaminoanthraquinones undergo cyclization to give anthra[1,9-bc]pyrrole derivatives on thermolysis in pyridine and other polar solvents. The cyclization proceeds through intramolecular rearrangement of 1-dialkylaminoanthraquinones to anthra[1,9-de]-1,3-oxazine derivatives and through subsequent contraction of the 1,3-oxazine ring to a pyrrole ring.

Heterocyclic systems containing an anthracene ring condensed in the 1,9 position with a heterocyclic ring are the basis of many vat and acid dyes and dyes for synthetic materials [1]. One such system is anthra[1,9]bc]pyrrole.*

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*This system can also considered to be naphth[1,2,3-cd]indole (see [2]). We have adopted the anthra[1,9-bc]pyrrole designation in order to emphasize the relationship to anthracene derivatives, on the basis of which the synthesis of the system under consideration is usually realized.

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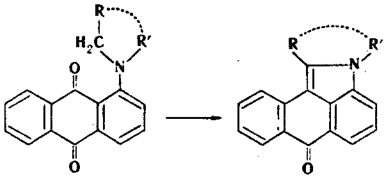
The parent compound itself has not been described in the literature, but a number of methods for the synthesis of substituted anthra[1,9-bc]pyrroles are known. According to the method in [3], anthra[1,9-bc]pyrrole derivatives are obtained by reaction of 1-amino-10-anthrone with carboxylic acids or their derivatives in the presence of acidic condensing agents. According to the data in [4], 1-phenyl-6-H-anthra[1,9-bc]pyrrole is formed in the cyclization of 9-benzoyl-9,10-dihydroanthracene oxime. The method for the synthesis of antra[1,9-bc]pyrrole that has found most extensive application is cyclization of N-alkyl-substituted 1-aminoanthraquinones that contain an active α-methylene group [5-9]. Activation of the latter is achieved by introduction of an electron-acceptor group (for example, a carboxyl group [5]) in the alkyl chain.

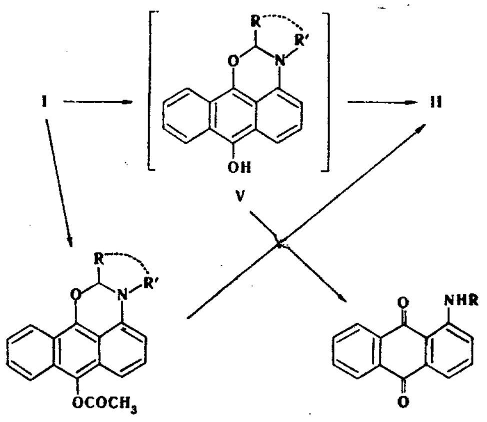
We have found that anthra[1,9]bc]pyrrole derivatives are formed by thermolysis of 1-dialkylaminoanthraquinones. This transformation, which proceeds without additional activation of the α-methylene group, makes it possible to obtain anthra[1,9-bc]pyrroles from 1-substituted anthraquinones containing a cyclic amine (for example, piperidine) or a dialkylamine with long alkyl chains as a substituent; this substantially expands the synthetic possibilities of the method.


I II

I, II a $R+R'=(CH_2)_4$; b $R=CH_3$, $R'=C_2H_5$; c $R=H$, $R'=CH_3$

When 1-piperidinoanthraquinone is heated in pyridine (at 250°C for 10 h), anthrapyrrole IIa is obtained in 40% yield; in addition, N-(1-anthraquinonyl)-δ-aminovaleraldehyde (III) was isolated from the reaction mixture. Under the same conditions, IIb was obtained along with 1-monoethylaminoanthraquinone (IV) from 1-diethylaminoanthraquinone. Closing of the pyrrole ring also occurs when I and Ib are heated in alcohol or in acetic acid. The addition of substances that tie up water such as BaO, CaO, KOH, and acetic anhydride promotes the reaction.

The structure of IIa-c was established on the basis of analytical and spectral data. Thus the triplet and quartet of the protons of the ethyl group at 1.25 and 4.16 ppm ($J_{H-H}=7$ Hz), respectively, the singlet of the protons of a methyl group at 2.78 ppm, and the signals of seven aromatic protons at 7.02-8.18 ppm are observed in the PMR spectrum of IIb.



VI III, IV

VI a $R+R'=(CH_2)_4$; b $R=CH_3$, $R'=C_2H_5$; III $R=(CH_2)_4CHO$;
IV $R=C_2H_5$

The most probable pathway for the conversion of 1-dialkylanthraquinones to anthra[1,9-bc]pyrroles seems to us to be one involving the intermediate formation of anthra[1,9-de]-1,3-oxazine derivatives (V) with subsequent contraction of the 1,3-oxazine ring to a pyrrole ring.

It is known [10] that 1-dialkylaminoanthraquinones are smoothly rearranged on heating in pyridine (140-170°) and other polar solvents to V; the latter are readily hydrolyzed with opening of the 1,3-oxazine ring, but they can be isolated in the form of the relatively stable acetates. The fact that III and IV — typical

TABLE 1. Thermolysis of Anthraquinone Ia

Solvent	Condensing reagent (7% of weight of Ia)	Reaction time, h	Yield of IIa, %
Acetic acid	—	5	15
n-Butyl alcohol	—	2,5	25
n-Butyl alcohol	KOH	2,5	71
n-Butyl alcohol	CaO	3,5	65
n-Butyl alcohol	BaO	3,5	68

TABLE 2. Thermolysis of Acetates VIa, b

Starting compound	Solvent	Condensing reagent (7% of the weight of starting compound)	Reaction time, h	Yield of anthrapyrrole, %
VIa	Pyridine	—	10	20
VIa	n-Butyl alcohol	KOH	5	57
VIa	n-Propyl alcohol	p-PrONa	5	70
VIb	n-Butyl alcohol	KOH	5	49

products of decomposition of the corresponding anthra[1,9-de]-1,3-oxazines — were isolated along with anthrapyrroles from the reaction mixture indicates the formation of oxazines V under the reaction conditions that we selected.

The possibility of contraction of the 1,3-oxazine ring to a pyrrole ring was shown in [11] in the case of benzoxazine. This sort of transformation was previously unknown for anthra[1,9-de]-1,3-oxazines. In order to confirm the conclusion that these compounds are capable of contraction of the oxazine ring, we synthesized oxazine acetates VIa and VIb by the method in [10] and subjected them to thermolysis. Oxazine VIa gave the expected anthrapyrrole IIa in 20% yield when it was heated in pyridine (at 250° for 10 h). Higher yields of the anthrapyrroles (50-70%) were observed in the thermolysis of VIa and VIb in n-propyl alcohol or n-butyl alcohol in the presence of basic reagents (alkali and alkoxides).

EXPERIMENTAL*

The electronic absorption spectra of ethanol solutions of the compounds were recorded with a Unicam SP 700c spectrophotometer. The PMR spectra of trifluoroacetic acid solutions were recorded with a Varian A 56/60A spectrometer with hexamethyldisiloxane as the internal standard.

1-Piperidinoanthraquinone (Ia) was obtained by heating 1-chloroanthraquinone with piperidine at (100° for 10 h) to give red crystals with mp 120° (methanol)(mp 121° [12]). Compound Ib was obtained by the method in [13], and VIa and VIb were obtained by the method in [10]; the melting points of the products were in agreement with the literature values. Compound Ic was synthesized by heating 1-chloroanthraquinone with dimethylamine in pyridine (at 100° for 8 h) to give dark red needles with mp 137-138° (from ethanol)(mp 138° [14]).

9-Oxo-1,2,3,4-tetrahydro-9H-anthra[1,9-bc]pyrido]2,1-e]pyrrole (IIa). A mixture of 0.5 g of Ia and 5 ml of absolute pyridine was heated in a sealed glass ampul at 250° for 10 h, after which the ampul was cooled and opened, and the reaction mixture was poured into water (50 ml). The aqueous mixture was acidified with 5 ml of concentrated hydrochloric acid, and the resulting precipitate was removed by filtration and washed with water. The dried solid product was chromatographed with a column filled with activity II aluminum oxide with elution by benzene. Elution of the red zone and subsequent evaporation of the eluate gave 0.08 g (15%) of aldehyde III, which was identified by comparison with an authentic sample [10]. Work-up of the bright-yellow zone gave 0.19 g (40%) of yellow needles of II with mp 218.5-220.5° (from benzene). Found: C 83.9; H 5.5; N 4.7%; M 273 (mass spectrometrically). $C_{19}H_{15}NO$. Calculated: C 83.5; H 5.5; N 5.1%; M 273. λ_{max} nm (log ε): 205 (4.59); 238 (4.28); 245 (4.27); 256 (4.20); 279 (4.37); 357 (3.34); 446 (4.06). Signals at 1.70, 2.67, and 3.13 ppm with an intensity ratio of 4 : 2 : 2, which corresponds to an α,α-disubstituted piperidine ring, and signals of seven aromatic ring protons at 7.10-8.05 ppm are observed in the PMR spectrum. Data on the thermolysis of anthraquinone Ia in various solvents and in the presence of various condensing agents (0.5 g of Ia, 5 ml of solvent, 250°) are presented in Table 1.

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*A. L. Samarodov participated in the experimental work.

1-Methyl-2-ethyl-6-oxo-6H-anthra[1,9-bc]pyrrole (IIb). The thermolysis of Ib (0.5 g) and the isolation of the reaction products were carried out as described above to give 0.14 g (31%) of 1-ethylaminoanthraquinone (IV) [15] and 0.20 g (43%) of anthrapyrrole IIb as yellow needles with mp 145-147° [benzene–petroleum ether (1 : 4)]. Found: C 82.6; H 5.6; N 5.6%. $C_{18}H_{15}NO$. Calculated: C 82.7; H 5.7; N 5.4%. λ_{max}, nm (log ε): 204 (4.61); 238 (4.32); 244 (4.31); 254 (4.25); 227 (4.39); 352 (3.49); 437 (4.06).

2-Methyl-6-oxo-6H-anthra[1,9-bc]pyrrole (IIc). A 0.7-g sample of quinone Ic was heated in a mixture of 5.6 ml of acetic acid and 1.4 ml of acetic anhydride in a sealed glass ampul at 190° for 4 h, after which the mixture was poured into water (150 ml). The resulting precipitate was removed by filtration and washed with water. Chromatography of the dried solid product on aluminum oxide (elution with benzene) gave 0.28 g (40%) of yellow needles of IIc with mp 196-198° (from benzene). Found: C 82.4; H 4.9; N 5.9%. $C_{16}H_{11}NO$. Calculated: C 82.4; H 4.7; N 6.0%. λ_{max}, nm (log ε): 211 (4.42); 2.37 (4.31); 243 (4.26); 253 (4.20); 276 (4.29); 304 (4.02); 347 (3.8); 417 (4.08). A singlet of protons of a methyl group at 3.78 ppm and signals of seven aromatic ring protons at 7.0-8.4 ppm were observed in the PMR spectrum.

Thermolysis of Anthra[1,9-de]-1,3-oxazine Acetate. Acetates VIa and VIb (0.5 g of the acetate in 5 ml of solvent) were subjected to thermolysis in sealed glass ampuls at 250°. The reaction mixtures were separated chromatographically on aluminum oxide (elution with benzene). The experimental results are presented in Table 2.

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