vent was then removed, and the residue was chromatographed with a column filled with silica gel (elution with chloroform). The chloroform was removed from the eluate, and the residue was treated with ethanol and purified on a porous plate in an ether chamber to give 0.07 g (8%) of product.

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REACTION OF o-DIAMINOANTHRAQUINONES WITH MALONIC ESTER

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The reaction of 1,2- and 2,3-diaminoanthraquinones with malonic ester was studied. It was established that the reaction products are N-ethoxymalonyl-o-diaminoanthraquinones and their heterocyclic derivatives – 1H-2-ethoxycarbonylmethylanthraimidazolediones. N-Ethoxymalonyl-2,3-anthraquinone undergoes cyclization to 1H-2,3,4,5-tetrahydroanthra[2,3-b]-1,4-diazepine-2,4,7,12-tetraone when it is heated with sodium methoxide in absolute methanol, whereas 2-N-ethoxymalonyl-1,2-diaminoanthraquinone undergoes cyclization to 1H-2-ethoxycarbonylmethylanthra-1,2-d]imidazole-6,11-dione.

In [1] we showed that a monoacylation product – N-ethoxymalonyl-2,3-diaminonaphthaquinone – rather than a cyclic diamide – naphthoquinonediazepine-2,4-dione [2] – is formed in the reaction of 2,3-diaminonaphthoquinone with malonic ester. In the present research we studied the reaction of 1,2- and 2,3-diaminoanthraquinones (I and II) with malonic ester. The reaction is interesting from a synthetic point of view, since it may open up a pathway to the preparation of new heterocyclic derivatives of anthraquinone.

In contrast to 2,3-diaminonaphthoquinone [1], complex mixtures of products, which can be separated by chromatography on silica gel, are formed when diamines I and II are heated with excess malonic ester. We isolated monoacyl derivative III (30%) and a cyclization product – 2-carbethoxymethylimidazole V (32%) – from the mixture obtained in the reaction of diamine I with malonic ester. In the case of diamine II, in addition to monoacyl derivative IVa and imidazole VI, we observed the formation of appreciable amounts (26%) of diacylation product IVb.

The structures of the compounds obtained are confirmed by the analytical and spectral data (see Table 1). The IR spectra of III-VI contain absorption bands that confirm the presence of carbonyl groups of a quinone, amide (1640-1680 cm^{-1}), and an ester (1720-1740 cm^{-1}), as well as NH_2 and (or) NH groups (3150-3450 cm^{-1}). In addition to signals of protons of an anthraquinone ring at 7-8 ppm and NH groups, the PMR spectra contain a triplet and quartet of an ethyl group (1.20 and 4.00-4.15 ppm); the singlet at 3.55 or 4.00-4.10 ppm (in the case of V and VI) corresponds to the protons of the methylene group of a carbethoxymethyl fragment.

The proof of the structures of 1,2-diaminoanthraquinone derivatives III and V, for which products with isomeric structures is possible, is based on the following analogies. The chemical shifts of the amide

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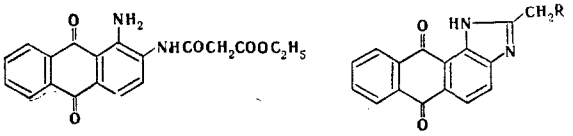
TABLE 1. Characteristics of the Synthesized Anthraquinone Derivatives

Compound	mp (dec.)[a]	Found, %			Empirical formula	Calc., %			PMR spectrum in d_6-DMSO	
		C	H	N		C	H	N	δ(NH), ppm	δ(NH_2), ppm
III	181—183	64,4	4,5	8,0	$C_{19}H_{16}N_2O_5$	64,8	4,5	7,9	9,63	7,3—8,0[b]
IVa	Does not melt up to 360°C	64,9	4,5	8,1					9,33	6,33
IVb	189—191	61,8	4,8	5,0	$C_{24}H_{22}N_2O_8$	61,8	4,7	6,0	9,86	
VII[3]									9,40	7,3—8,3[b]
V[c]	191—193	68,3	4,3	8,4	$C_{19}H_{14}N_2O_4$	68,3	4,2	8,4	12,80	
VI[c]	237—242	68,3	4,1	8,2					<4,20[b]	
VIII	174—176	75,5	5,7	8,8	$C_{20}H_{18}N_2O_2$	75,6	5,7	8,8	12,60	
IX	250—254	75,3	5,6	8,8					<4,20[b]	
XIII[d]	Does not melt up to 360°C	65,9	3,1	9,2	$C_{17}H_{10}N_2O_4$	66,6	3,3	9,1		

[a]Compounds III, VIII, and IX were recrystallized from benzene, IVa,b were recrystallized from chloroform, V was recrystallized from acetone, and VI was recrystallized from methanol. [b]Accurate assignment is impossible because of superimposition of the signals. [c]Found: M 334. Calculated: M 334. [d]Found: M 306. Calculated: M 306.



IV a, XII R=H; IV b R=$COCH_2CO_2C_2H_5$; V, VI R=$CO_2C_2H_5$; VIII, IX R=$(CH_2)_3CH_3$

proton in the PMR spectra of III, IVa, IVb, and 1-amino-2-acetamidoanthraquinone (VII) [3] are close and are found at 9.3-9.8 ppm, whereas the protons of the amino group in III and VII are found at weaker field as compared with the same protons in the spectrum of IVa (see Table 1). These facts constitute evidence that the amino group in quinone III is in the α position and that the ethoxymalonylamino group is in the β position and not vice versa. The structure of the 1H isomer was similarly ascribed to imidazole V, in the PMR spectrum of which the proton of the NH group is shifted considerably to weak field (12.80 ppm) as compared with the formation of an intramolecular hydrogen bond between the NH group and the quinone CO group. The protons of the α-acylamino or α-hydroxy derivatives of anthraquinone, in which chelate formation with the participation of the carbonyl group of the quinone occurs [3, 4], usually resonate in the weak-field region. The presence in the IR spectrum of imidazole V of one quinone $\nu C=O$ band (1670 cm^{-1}) apparently is not a sufficient basis for the assertion that the indicated hydrogen bond is absent (see [5]), since the frequencies of the carbonyl absorption must be interpreted cautiously [6]. For comparison, let us point out that the spectral data for imidazoles V and VI are in good agreement with the data for 2-alkylimidazoles VIII and IX (see Fig. 1 and Table 1), which we obtained by isomerization [7] of the corresponding anthraquinoneimidazolines X and XI.

It is interesting that, in contrast to the naphthoquinone analog [1], ethoxymalonylaminoanthraquinones III and IVa do not have polymorphic forms; samples of quinones III and IVa obtained by recrystallization from solvents with different polarities have identical IR spectra and melting points (this is true for each of the compounds).

It is known that the N-ethoxymalonyl derivatives of 2,3-diaminonaphthoquinone [1] and o-phenylenediamine [8] undergo smooth cyclization in alkaline media to the corresponding diazepine-2,4-dione derivatives. We have found that ethoxymalonylaminoanthraquinones III and IVa remain virtually unchanged in aqueous alco-

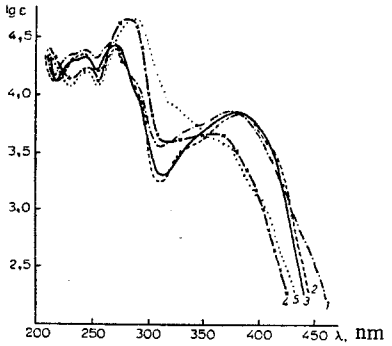


Fig. 1. UV spectra (in alcohol, $c \cdot 10^{-5}$ mole/liter): 1) V; 2) VIII; 3) XII; 4) VI; 5) IX.

holic alkali at room temperature after 24 h; however, transformations do occur in the case of brief refluxing, but the expected cyclization products cannot be isolated. Compound IVa is hydrolyzed in this case to diamine II, and quinone III gives imidazole XII, which, judging from the UV spectrum (see Fig. 1), is the 1H isomer (see [3]), in high yield. However, if the cyclization is carried out in anhydrous media, only IVa is converted to 1H-2,3,4,5-tetrahydroanthra[2,3-b]-1,4-diazepine-2,4,7,12-tetraone (XIII). Under these conditions, quinone III gives imidazole V (in 50% yield), during heating of which in aqueous alcoholic alkali imidazole XII is formed quite rapidly. The formation of imidazole XII is also observed when III is heated in acidic media (in agreement with [8]). The prevailing cyclization to imidazole derivatives is probably due to the peculiarities of the structure of III associated with the possibility of the existence of a hydrogen bond between the hydrogen atom of the amino group and the carbonyl group of the quinone.

The structure of diazepine XIII was confirmed by the analytical and spectral data. Its UV spectrum coincides with the spectrum of N,N'-diacetyl-2,3-diaminoanthraquinone, and absorption bands in the region of the stretching vibrations of the N–H and C=O bonds are present in the IR spectrum.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The UV spectra of solutions of the compounds in ethanol were recorded with an SF-16 spectrophotometer. The PMR spectra of 3-5% solutions in d_6-DMSO were recorded with a Varian A-56/56A spectrometer (60 MHz) with tetramethylsilane as the internal standard (the chemical shifts are presented on the δ scale). The molecular weights were determined by mass spectrometry with an MS-902 spectrometer. Silica gel (the 0-140 mm fraction), which was elutriated and dried at 130°C for 24 h, was used for the chromatography (elution with chloroform).

2-N-Ethoxymalonyl-1,2-diaminoanthraquinone (III) and 1H-2-Ethoxycarbonylmethylanthra[1,2-d]imidazole-6,11-dione (V). A mixture of 2 g (8.4 mmole) of diamine I and 40 ml of malonic ester was placed in a bath heated to 200°C, and the mixture was refluxed for 5 min. It was then cooled and poured into 150 ml of petroleum ether, and the resulting precipitate was removed by filtration, washed with petroleum ether, and dried. Chromatography gave 0.9 g (30%) of red III and 0.9 g (32%) of yellow V. Several unidentified fractions remained in the column.

N-Ethoxymalonyl-2,3-diaminoanthraquinone (IVa), N,N'-Bis(ethoxymalonyl)-2,3-diaminoanthraquinone (IV), and 1H-2-Ethoxycarbonylmethylanthra[2,3-d]imidazole-5,10-dione (VI). A mixture of 2 g (8.4 mmole) of diamine II and 70 ml of malonic ester was placed in a bath heated to 200°C, and the mixture was refluxed for 15 min. It was then cooled, and the orange precipitate was removed by filtration. The filtrate was diluted with 150 ml of petroleum ether, and the yellow precipitate was separated. Both precipitates were washed with petroleum ether and dried. Recrystallization of the orange precipitate from chloroform gave 1 g (33%) of IVa. The yellow precipitate was chromatographed to give 1 g (26%) of IVb and 0.4 g (5%) of VI. Several unidentified fractions remained in the column.

1H-Amylanthra[1,2-d]imidazole-6,11-dione (VIII). A mixture of 0.26 g (0.8 mmole) of 2,2-pentamethyleneanthra[1,2-d]imidazoline-6,11-dione (X) [9] and 5 ml of diphenyl oxide was refluxed for 1 h, after which it was cooled and poured into 50 ml of petroleum ether. The yellow precipitate was separated and chromatographed to give 0.2 g (80%) of VIII. IR spectrum: 1670 (C=O) and 3370 cm^{-1} (N–H). PMR spectrum (in

$CDCl_3$): 0.83 (3H, t, J = 5 Hz, CH_3), 1.06-2.10 (6H, m, $CH_2CH_2CH_2CH_3$), 2.93 (2H, t, J = 7 Hz, CH_2C), 7.50-8.30 (6H, m, protons of the anthraquinone ring), and 10.90 ppm (1H, s, NH).

1H-Amylanthra[2,3-d]imidazole]5,10-dione (IX). A mixture of 0.5 g (1.6 mmole) of 2,2-pentamethyleneanthra[2,3-d]imidazoline-5,10-dione (XI) [9] and 5 ml of diphenyl oxide was refluxed for 1 h, after which it was worked up as in the preceding experiment to give 0.1 g (20%) of IX. IR spectrum: 1670 (C=O) and 3265 cm^{-1} (N-H).

Cyclization of Ethoxymalonylaminoanthraquinones III and IVa. A) A mixture of 0.1 g (0.28 mmole) of quinone III and 0.5 ml of 50% aqueous KOH solution in 30 ml of ethanol was refluxed for 1 h, after which it was neutralized with 10% HCl. The precipitate was separated and chromatographed to give 0.06 g (76%) of 1H-2-methylanthra[1,2-d]imidazole-6,11-dione (XII) with mp 317-320°C. The product was identified by comparison with an authentic sample [3] with respect to the IR spectra and a mixed-melting-point determination.

The experiment was carried out similarly with 0.2 g of quinone IVa, and 0.07 g (50%) of diamine II was obtained.

B) A solution (20 ml) of sodium methoxide in absolute methanol (from ~0.01 g of sodium) was added to a mixture of 0.1 g of quinone III in 20 ml of absolute methanol, and the mixture was refluxed for 30 min. It was then poured into water, and the aqueous mixture was neutralized with 10% HCl and extracted with chloroform. The solvent was removed by evaporation, and the residue was chromatographed to give 0.05 g (50%) of imidazole V with mp 189-193°C.

The experiment was carried out similarly with 0.35 g of quinone IVa, and 0.15 g (50%) of diazepine XIII as yellow crystals from DMSO.

C) A 0.07-g sample of quinone III was heated in 10 ml of glacial acetic acid containing 0.03 ml of concentrated H_2SO_4 at 100°C for 5 h, after which the mixture was poured into water, and the aqueous mixture was extracted with chloroform. The solvent was removed by evaporation, and the residue was crystallized from benzene to give 0.03 g (57%) of imidazole XII with mp 316-319°C.

The characteristics of the synthesized compounds are presented in Table 1.

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