CYCLIZATION OF ACETYLENIC DERIVATIVES OF AROMATIC CARBOXYLIC ACIDS

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The Cu(I)-catalyzed intramolecular cyclization of 1-phenylethynyl- and 1-hexyn-1-yl-anthraquinone-2-carboxylic acid is a 6-endo-dig-addition, whereas the reaction for 1-(3-phenoxypropyn-1-yl)anthraquinone-2-carboxylic acid proceeds in a directionally nonspecific way. It is shown that the cyclization of vicinal acetylenic derivatives of aromatic carboxylic acids leads to the formation of the more stable of the possible cyclic structures.

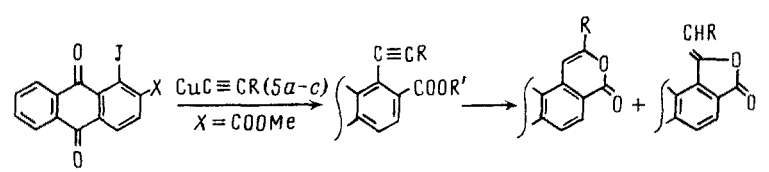
Keywords: *1-phenylethynylanthraquinone-2-carboxylic acid, 1-hexyn-1-yl-anthraquinone-2-carboxylic acid, 1-(3-phenoxypropyn-1-yl)anthraquinone-2-carboxylic acid, intramolecular cyclization, MNDO calculation method.*

Vicinal acetylenic derivatives of carbo- and heteroaromatic carboxylic acids undergo intramolecular cyclization in weakly acid media [1, 2], under acid hydration conditions [3], and in the presence of Cu(I) salts in basic or neutral media [4-7]. The reaction catalyzed by Cu(I) seems to be of the greatest general importance. It is significant also that, just as with the carboxyl group, intramolecular addition of other nucleophilic groups (NHR, OH, SH, etc.) at the triple bond can be catalyzed by Cu(I) [4, 8, 9]. Although the synthetic importance of these cyclizations is not in doubt [10], up to now their mechanisms have remained uncertain.

According to the classification of results in [11], in the cyclization of acetylenic derivatives of aromatic carboxylic acids, 5-exo-dig- and 6-endo-dig-addition is possible, leading to the formation of γ- and δ-lactones. For acids of the five-membered heterocycle series, in the presence of compounds of Cu(I), 6-endo-dig-addition is typical [6, 7, 12], while *ortho*-acetylenylbenzoic acids show a tendency to close to a γ-lactone ring [4]. No other rules linking the structure of the compounds and the course of their cyclization have been developed.

In this work we have studied features of the intramolecular cyclization of 1-acetylenylanthraquinone-2-carboxylic acid (**1**), assisted by Cu(I), and have attempted, using our own results and literature data, to identify the basic factors determining the directional behavior of this reaction in the general series of vicinal acetylenic derivatives of various aromatic carboxylic acids.

To obtain the initial materials **1a-c** 2-hydroxymethyl-1-iodoanthraquinone (**2**) [13] was oxidized by $K_2Cr_2O_7$ in H_2SO_4–AcOH at 20-60°C to the acid (**3**), which was subsequently esterified with MeOH–H_2SO_4. The ester (**4**) was condensed with acetylenides of Cu(I) (**5a-c**) in pyridine at 45-50°C (15-30 min) (Table 1). It should be noted that (**4**), while showing a high reactivity in condensation with (**5**), reacts with terminal acetylenes in the presence of $Pd(PPh_3)_2Cl_2$–CuI slowly and with formation of tar [14], probably on account of steric hindrance to the formation of three-dimensional organopalladium complexes. The compounds **6a-c** were hydrolyzed to **1a-c** in a water–dioxane solution of KOH at 20°C.



X=CH_2OH(2), COOH(3), COOMe(4). R¹=Me(6a-c), H(1a-c); R=Bu(a), Ph(b), CH_2OPh(c). (7a-c) (8c)

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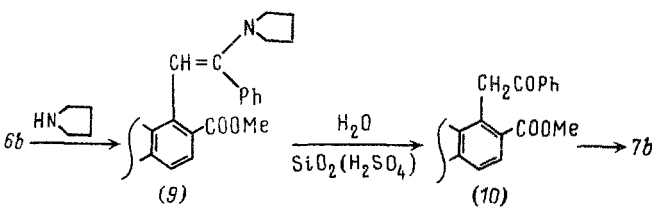
TABLE 1. Synthesis of Esters of the Acetylenylanthraquinonecarboxylic Acids (**6**) and Cyclization of the Acids (**1**)

Compound	Yield, %	mp, °C (benzene–hexane)	Found/Calculated, %		Empirical formula	PMR spectrum, δ, ppm	IR spectrum ν, cm^{-1}
			C	H			
6a	86.3	69–70	76.15 / 76.29	5.18 / 5.24	$C_{22}H_{16}O_4$	0.99 t (CH_3); 1.45—1.75 m (β- and γ-CH_2); 2.62 t (α-CH_2); 3.97 ($COOCH_3$); 7.7—7.9 m ($H^{6,7}$); 7.91 d 8.28 d ($H^{3,4}$); 8.2—8.35 m ($H^{5,8}$)	2230 (C≡C); 1740, 1680 (C=O)
6b	95.5	129–131	78.65 / 78.76	3.79 / 3.70	$C_{24}H_{14}O_4$	4.02 ($COOCH_3$); 7.3—7.45 m (3H Ph); 7.6—7.9m (2HPh, $H^{6,7}$); 8.04d, 8.34d ($H^{3,4}$); 8.2—8.4 m ($H^{5,8}$)	2215, sh 2220 (C≡C); 1735, 1680 (C=O)
6c	94.1	121–121.5	75.82 / 75.75	4.11 / 4.07	$C_{25}H_{16}O_5$	3.75 ($COOCH_3$); 5.10 (CH_2); 6.9—7.45 m (Ph); 7.7—7.9 m ($H^{6,7}$); 7.98 d ($H^{3(4)}$); 8.2—8.4 m ($H^{4(3),5,8}$)	2240 (C≡C) 1735, 1680 (C=O)
7a	91.2	141.5–142	75.96 / 75.89	4.78 / 4.85	$C_{21}H_{16}O_4$	0.96 t (CH_3); 1.25—1.75 m (β- and γ-CH_2); 2.61 t (α-CH_2); 7.75—7.85 m ($H^{9,10}$); 8.19 (H^1); 8.2—8.3 m ($H^{8,11}$); 8.34 d, 8.63 d ($H^{5,6}$)	1730, 1670, 1645 (C=O)
7b	79.5	272–273 (benzene)	78.33 / 78.40	3.44 / 3.43	$C_{23}H_{12}O_4$	—	
7c	44.4	223.5–224.5 (benzene)	75.42 / 75.39	3.65 / 3.69	$C_{24}H_{14}O_5$	(DMSO-d_6) 5.05 (CH_2); 7.0—7.4 m (Ph); 7.85—7.95 m ($H^{9,10}$); 8.15—8.2 m ($H^{8,11}$); 8.34d, 8.59 d ($H^{5,6}$); 8.40 (H^1)	
8c	32.9	199–200	75.43 / 75.39	3.57 / 3.69	$C_{24}H_{14}O_5$	5.15d (CH_2); 6.95—7.4 m (Ph); 7.8—7.9 m ($H^{6,9}$); 7.97 t (=CH); 8.25—8.35 m ($H^{4(5),7,10}$); 8.62 d ($H^{5(4)}$)	1680, 1780, sh 1790 (C=O)

The acetylenic acids **1a-c** were cyclized in the presence of **5b** (1.2 moles/mole) in pyridine under Ar at 20°C. The cyclization of **1a** and **1c** took 35-40 min, but the reaction for **1b**, which contains phenylethynyl groups, took 2.5 h. In this case, as was established, **1a** and **1b**, in contrast to the analogous acetylenic derivatives of benzoic acid, give essentially on the products of 6-endo-dig-addition — the δ-lactones (**7a, b**), whereas the acid **1c**, which has a heteroatom in the unsaturated side chain, forms a mixture of comparable quantities of δ- (**7c**) and γ-lactones (**8c**) (Table 1).

The size of the heterocycle in **7a, c** and in **8c** is established from the multiplicity of the PMR signals due to the endo- or exocyclic CH groups formed in the reaction, and to the α-CH_2 group of the substituent R.

In order to elucidate the structure of **7b**, pyrrolidine was added to the ester **6b**, and the pyrrolidinovinyl compound (**9**) obtained was hydrolyzed over SiO_2 [15]. After a brief hydrolysis the methoxycarbonyl group in **9** was scarcely affected, the yield of the phenacylanthraquinone (**10**) amounting to 63%. The position assigned for the carbonyl group in the side chain of **10** is in this case secured by the directional specificity of the nucleophilic addition of the amine [15]. Confirmation of the position is provided by the PMR spectrum of **10**, in which the signals due to the *ortho*-H-phenyl group are shifted toward the region of $\delta > 8$ ppm. Prolonged exposure of **9** or **10** over SiO_2, as with acid hydrolysis of **9**, led to **7b** (73-82%). All this clearly demonstrates that **7b** is a δ-lactone.



It is useful to note that, as we have found, 1-phenylethynylanthraquinone (**11**), like its 2-isomer [9], is hydrolyzed in the presence of $HgSO_4-H_2SO_4$ to the corresponding phenacylanthraquinone (**12**), whereas **6b** and **1b** give the δ-lactone **7b**. This appears to indicate that the specified course of the acid hydration of the phenylethynyl derivatives of anthraquinone is of very general applicability.

Thus, 1-acetylenic derivatives of anthraquinone-2-carboxylic acid are cyclized in the presence of Cu(I) either exclusively to six-membered lactone rings, or to a mixture of five- and six-membered rings, whereas in contrast, under the same conditions the analogous *ortho*-substituted benzoic acids show a greater tendency to form five-membered rings [4].

In the absence of any data on the mechanism of the reaction it is extremely difficult to attempt to establish the connection between the course of the cyclization and the composition of the acids. We have tried to discover the main factors controlling the local directivity of the process, by comparing available experimental information with quantum chemical calculations of the energetic characteristics of the simplest hypothetical reaction model and the distribution of charge in the molecules of the starting compounds.

It is very probable that a heterocycle of either size is formed by nucleophilic attack on the triple bond by the neighboring functional group. In basic media (pyridine) carboxylic acids are to an appreciable degree dissociated, and it can be taken that the anions formed undergo intramolecular cyclization directly. The cyclization of acid anions has therefore been taken as a reaction model for the purposes mentioned. In the initial stage, the effect on its mechanism of Cu(I), which is instrumental in promoting the cyclization to a practicable degree, was disregarded.

To clarify in this instance the effect of the constitution of the aromatic nucleus of the compound and the acetylenic substituent on the course of the reaction we carried out quantum chemical calculations on the energetic characteristics of the gas-phase cyclization of a series of anions (in view of the uniformity of the changes solvation effects are unlikely to be able to alter the course of the cyclization). For the calculations we used the MNDO method [16], with the AMPAC program [17]. Preliminary consideration of a model assuming direct addition of an undissociated carboxyl group at the triple bond had shown such a mechanism to be impossible because of the instability of the initial products of the reaction.

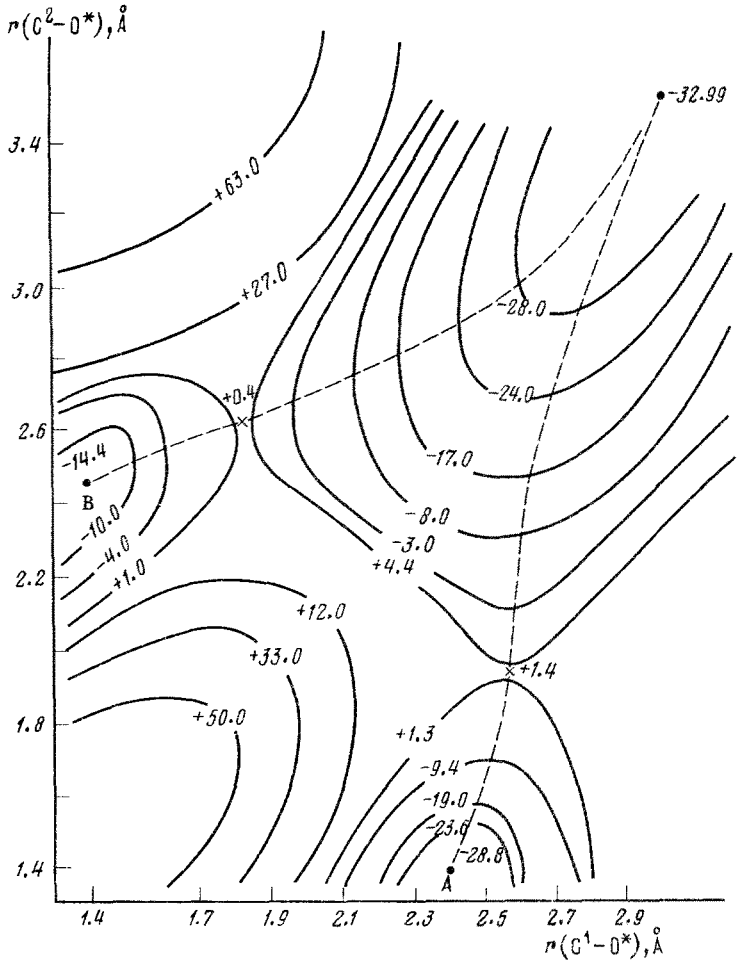
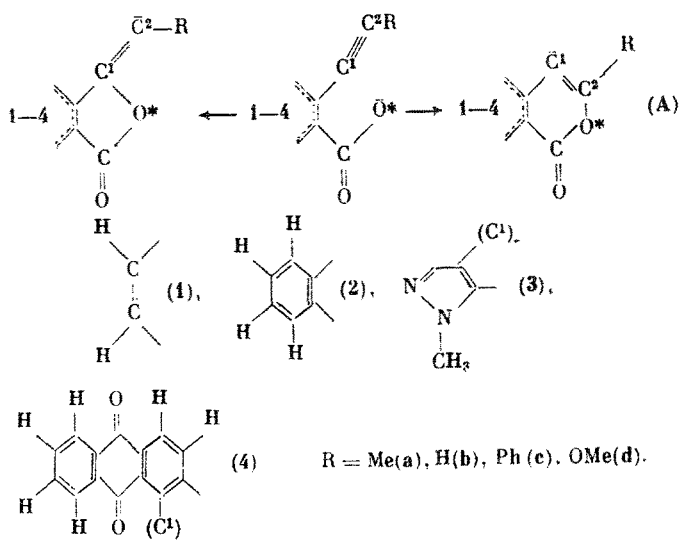


Fig. 1. Profile of the potential energy surface for the anionic cyclization of compound **1b** (transition states are indicated by a small cross, and minimum energy paths by a broken line; the numbers at the line gaps give the energy levels, kcal/mole).



The energy profile of the reaction was obtained by the method of reaction coordinates, taking the distances $r_{O^*-C^2}$ for **A** and r_{O-C^1} for **B**. For given values of the reaction coordinates the geometric parameters which control the position of the C^1 and C^2 atoms and the R and CO_2^- groups were optimized.

The energetics of the cyclization of the anions is considered in detail for the case of **1b**. Figure 1 gives the potential energy surface as a function of the coordinates $r_{O^*-C^1}$ and $r_{O^*-C^2}$. Starting from a wide valley, which develops into a hill,

TABLE 2. Changes on Atoms C^1 and C^2 and Energetic Features of the Cyclization of Anions (2)-(4) (calculation) and Course of the Reaction

Compound	1			2			3		Experiment
	q_{C^1}	q_{C^2}	Theory	$E_a^{(A)*}$	$E_a^{(B)*}$	Theory	$\Delta Q = Q_A^* - Q_B^*$	Theory	
2a	−0.02	−0.21	B	33.8	21.2	B	0.0	A, B	A, B
2b	−0.06	−0.17	B	29.1	23.8	B	−9.0	A	B
2c	0.00	−0.16	B	37.5	20.04	B	2.0	B	B
2d	–	–	–	28.5	21.4	B	7.2	B	–
3a	0.03	−0.25	B	45.4	42.4	B	−11.5	A	A
3b	−0.01	−0.22	B	40.1	45.4	A	−22.1	A	A
3c	0.06	−0.21	B	48.4	41.7	B	−8.9	A	A
4a	−0.07	−0.13	B	–	–	–	−41.4	A	A
4b	−0.11	−0.09	A, B	–	–	–	−80.4	A	–
4c	−0.05	−0.09	A, B	–	–	–	−38.6	A	–

*kcal/mole.

the reaction path later divides and may emerge by one of two cols of similar height, $E_a^A = 34.4$ and $E_a^B = 33.4$ kcal/mole. The energies of the initial cyclic products differ more noticeably: the six-membered cycle (**A**) is more stable than the five-membered (**B**) by 14.4 kcal/mole. The height of the barrier is determined mainly by interactions during the contact of O* with the triple bond (with $r_{O^*-C^1,C^2}$ = 2-2.5 Å). The product **A** is only insignificantly higher in energy (~4 kcal/mole) than the starting reagent **1b**, which indicates that intramolecular cyclization in the gas phase is thermodynamically possible. Calculations of correlation energy according to the MNDO method of limited configuration interaction lead to an insignificant reduction of the energy barriers. This is connected with the fact that in the course of the reaction the number of correlated electron pairs does not change. We therefore confined ourselves to less unwieldy calculations using the Hartree–Fock approximation.

For compounds **2-4** the following characteristics were calculated: 1) the charges q on atoms C^1 and C^2 in the parent anion; 2) the cyclization activation energies E_a; 3) the heats of reaction $Q = E_{fin} - E_{init}$. The results are given in Table 2.

In accordance with electrostatics the attack of the nucleophile should be directed toward the C atom of the acetylenic group carrying the smallest negative or the largest positive charge. As can be seen from Table 2, it is only for the compounds **2** that predictions based on estimates from this index conform with experiment to a reasonable extent, although for **2a**, judging from the magnitude of q_{C^1} and q_{C^2}, only a five-membered ring closure would be expected, and not five- and six-membered closures at comparable rates, as takes place for *ortho*-alkynylbenzoic acids [4]. It is clear that this simple index is not directly related to the observed mechanisms.

The activation energies for the formation of five- and six-membered rings given in Table 2 for **2** and **3**, in contrast to the corresponding values of E_a for **1**, differ appreciably from one another by up to 17 kcal/mole. The effect of the composition of the acetylenic substituent on E_a is comparatively small — up to 8 kcal/mole. Predictions of the course of the cyclization based on calculated values of E_a are not entirely in keeping with the experimental data. The observable discrepancies could be explained as being due to the relative crudeness of the quantum chemical method, or to neglecting to take account of the effect of the medium, but they are more likely to be an indication that the actual intermediate compounds in the reaction are more complex.

The heat of reaction may be considered as a thermodynamic indication of the stability of the products under reversible reaction conditions or as a characteristic of the unknown transition state, accepting as correct the frequently used assumption regarding the linear correlation between activation energy and heat of reaction for chemical changes of the same type. Table 2 gives the difference between the heats of reaction for the formation of the products **A** and **B**. Optimization of the geometry of the initial cyclic products **A** and **B** for compound **4** was not carried out completely, and this may possibly account for the excessively high values of ΔQ.

For the reactions studied in all the compounds except **2b** the computed values of ΔQ correctly indicated the type of cyclization which, as is evident from the data in Table 2, is determined mainly by the composition of the aromatic nucleus in the starting compound. For **2a**, $\Delta Q \approx 0$, which is in agreement with the experimental data showing that in this case a mixture of comparable quantities of γ- and δ-lactones is formed. In [18] it was noted that MNDO calculations for anions on which the negative charge is localized on an atom linked to a hydrogen atom (HO^-, H_3C^-, etc.), yield substantially underestimated

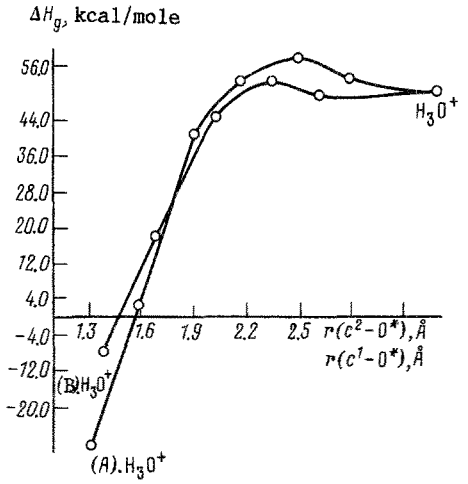


Fig. 2. Energy profile for the anionic cyclization of compound **1b** coordinated with $[H_3O]^+$ at the triple bond.

values for the bond energies (by ~20 kcal/mole). It cannot therefore be ruled out that for all the ethynyl anions (R=H) are values of ΔQ are too high, since atom C^2 in the anions of γ-lactones (**B**) carries a large negative charge [for example, in (**B**) from (**2b**) $q_{C^2} = -0.355$].

Quantum chemical analysis has been carried out on a model of the intramolecular nucleophilic addition reaction of CO_2^- groups to the triple bond in acid anions, and a comparison of the results with the experimental data on the course of the cyclization of these acids in the presence of Cu(I) apparently indicates that the directional behavior of such a reaction is determined by the stability of the cyclic structures which are formed. The actual transition state probably includes Cu(I), whose influence is primarily related to its positive charge. The results of a model calculation for the anionic cyclization of **1b**, π-coordinated at the triple bond with the H_3O^+ cation, are presented in Fig. 2. Coordination leads to a reduction in $E_a^{(A)}$ of about 5.3 kcal/mole, and in $E_a^{(B)}$ of about 2.9 kcal/mole, this reaction becoming exothermic. Coordination with a proton gives an even greater effect: the reaction becomes barrierless, and there is a significant rise in the heat of reaction. From all this it can be suggested that in the cyclization process under consideration Cu(I) forms a reaction complex through the coordination of Cu(I) at the triple bond of the parent carboxylic acid anions, as a result of which the energetic prohibitions on the reaction are removed.

EXPERIMENTAL

PMR spectra were obtained on JEOL FX-90Q and Varian XL-200 spectrometers in $CDCl_3$, and the IR spectra on a UR-20 instrument, in $CHCl_3$.

1-Iodoanthraquinone-2-carboxylic Acid (3). To a solution of 0.36 g (1.0 mmole) of **2** [13] in 75 ml AcOH over a period of 10 min at 25-35°C we added 1.00 g (3.4 mmoles) $K_2Cr_2O_7$ in dilute H_2SO_4 (2 ml concentrated H_2SO_4 and 15 ml water), stirred for 4 h at 20-25°C and then heated to 60°C. After holding at this temperature for 15-20 min the solvent was distilled off in vacuum, then we added 150 ml water and extracted **3** with $CHCl_3$; yield 0.34 g (91%), mp 263-264°C (dioxane) [19]. **2**, obtained from 1-amino-2-hydroxymethylanthraquinone [13] and containing 1-amino-2-methylanthraquinone and possibly other by-products, was oxidized without purification to **3** by the same process.

Methyl Ester of 1-Iodoanthraquinone-2-carboxylic Acid (4). 3 g (7.9 mmoles) of **3** in 375 ml MeOH and 57 ml concentrated H_2SO_4 were boiled for 15-17 h (TCX-control: silufol; $CHCl_3$–ether, 4:1), poured off into 500 ml $CHCl_3$ and 200 ml water, the chloroform extract separated, washed with aqueous Na_2CO_3, water, and dried over $MgSO_4$. Obtained 2.8 g (90%) of **4**, mp 169-170°C (benzene–hexane) [19].

Methyl Ester of 1-(Hexyn-1-yl)anthraquinone-2-carboxylic Acid (6). 1.57 g (4.0 mmoles) of **4** and 0.87 g (6.0 mmoles) of **5a** in 70 ml pyridine were heated at 45-47°C in an atmosphere of Ar for 25 min (TCX-control: silufol, benzene), diluted to 300 ml with $CHCl_3$, washed with 400 ml dilute HCl (1:3) and water. Chromatographic separation on SiO_2 with benzene yielded 1.20 g **6a** (Table 1).

6b, c were synthesized in an analogous manner (Table 1).

1-(Hexyn-1-yl)anthraquinone-2-carboxylic Acid (1a). To 1.2 g (3.5 mmoles) of **6a** in 32 ml dioxane we added 2.4 g KOH in 16 ml water, stirring at 20°C for 4 h (TCX-control:silufol; $CHCl_3$–ether, 4:1), the dioxane was removed by extraction with ether, the remainder diluted with water and on cooling acidified with concentrated HCl. The **1a** was filtered off, washed with water, and dried; yield 1.0 g (87%), mp 120-121°C (decomp.; dioxane–hexane). Found, %: C 75.77; H 4.87. $C_{21}H_{16}O_4$. Calculated, %: C 75.89; H 4.85.

6b was hydrolyzed to **1b** in the same way, yield 88.6%, mp 148-150°C (decomp., dioxane–hexane). Found, %: C 78.34; H 3.42. $C_{23}H_{12}O_4$. Calculated, %: C 78.40; H 3.43; **6c** to **1c**, yield 77.1%, mp 175-176°C (decomp.) (not obtained in analytically pure state).

2-Butyl-4H-anthra[2,1-c]pyran-4,7,12-trione (7a). 0.68 g (2.1 mmoles) of **1a** and 0.40 g (2.4 mmoles) of **5b** in 30 ml pyridine were stirred under Ar at 20°C for 35 min (TCX-control: silufol; $CHCl_3$–ether 4:1), diluted to 250 ml with $CHCl_3$, washed with dilute HCl, water, and dried with $MgSO_4$. Chromatographic separation on SiO_2 in benzene yielded 0.62 g of **7a** (Table 1). Similarly, **7b** was obtained from **1b** (reaction time 2.5 h), and **7c** and **8c** from **1c** (Table 1).

Methyl Ester of 1-(2-N-Pyrrolidino-2-phenylethenyl)anthraquinone-2-carboxylic Acid (9). 0.85 g (2.3 mmoles) **6b** and 0.38 g (0.44 ml; 5.3 mmoles) of pyrrolidine in 10 ml dioxane were stirred at 20°C for 50 h, diluted to 15 ml with toluene and the solvent and excess amine distilled off in vacuum; the residue was recrystallized from a mixture of benzene and hexane (1:3). Obtained 0.85 g (83.7%) of **9**, mp 140-141°C. Found, %: C 76.82; H 5.42; N 3.18. $C_{28}H_{23}NO_4$. Calculated, %: C 76.87; H 5.30; N 3.20. PMR spectrum (δ, ppm): 1.8-2.1 m (4H, β,β'-CH_2CH_2–); 3.0-3.4 m (4H, CH_2NCH_2); 3.72 (3H, $COOCH_3$); 6.54 (1H, CH=); 7.0 w (5H, Ph); 7.65 d, 7.93 d (2H, $H^{3,4}$); 7.65-7.85 m (2H, $H^{6,7}$); 8.1-8.3 m (2H, $H^{5,8}$). IR spectrum (ν, cm^{-1}): 1735, 1680 (C=O).

Methyl Ester of 1-Phenacylanthraquinone-2-carboxylic Acid (10). 0.40 g (0.9 mmole) of **9** in 50 ml of $CHCl_3$ were applied to 300 ml SiO_2, inserted into a column of diameter 50 mm, then in 30 min (after change of color to light yellow) eluted with $CHCl_3$, the solvent separated under vacuum, the residue crystallized in ether on cooling; yield of **10** 0.22 g (62.9%), mp 168-169°C (benzene–hexane). Found, %: C 75.16; H 4.13. $C_{24}H_{16}O_5$. Calculated, %: C 74.99; H 4.20. PMR spectrum (δ, ppm): 3.87 (3H, $COOCH_3$); 5.42 (2H, CH_2); 7.40-7.85 m (2H, $H^{6,7}$, 3H, Ph); 8.0-8.5 m (4H, $H^{3-5,8}$, 2H, Ph). IR spectrum (ν, cm^{-1}): 1730, 1680 w (C=O).

Production of Lactone 7 from the Esters of Carboxylic Acids (6b), (9), and (10). a. 0.18 g (0.5 mmole of **10** in benzene was applied to 150 ml SiO_2 and left for 3 days; 0.12 g (78.7%) of **7b** was obtained. In a similar way from 0.35 g (0.8 mmole) of **9** (solvent — $CHCl_3$) 0.23 g (81.6%) of **7b** was obtained.

b. 0.10 g (0.2 mmole) of **9**, 0.12 ml water, and 0.10 g concentrated H_2SO_4 ion 10 ml dioxane were heated at 80°C for 23 h, diluted to 250 ml with $CHCl_3$, washed repeatedly with water, and dried with $MgSO_4$; yield of **7b** 0.06 g (74.5%).

c. 0.37 g (1.0 mmole) of **6b**, 0.22 ml water, 0.20 g concentrated H_2SO_4, and 0.08 g $HgSO_4$ in 15 ml dioxane were stirred at 80°C for 7.5 h; 0.32 g of **7b** (89.9%) were separated out. Under the same conditions, **11** gave 89.0% of **12**, mp 239-240°C (benzene). Found, %: C 81.08; H 4.35. $C_{22}H_{14}O_3$. Calculated, %: C 80.97; H 4.32. PMR spectrum (δ, ppm): 4.94 (2H, CH_2); 7.45-7.85 m (4H, $H^{2,3,6,7}$, 3H, Ph); 8.05-8.45 m (3H, $H^{4,5,8}$, 2H, Ph). IR spectrum (ν, cm^{-1}): 1675, sh 1690 (C=O).

1-Phenacylanthraquinone-2-carboxylic Acid (13). 0.18 g (0.5 mmole) of **7b** in 18 ml dioxane on stirring with 1.26 g KOH in 9 ml water (20°C, 25 min) was hydrolyzed to **13**; yield 0.15 g (79.4%); on heating this cyclizes to **7b**. Found, %: C 74.49; H 3.93. $C_{23}H_{14}O_5$. Calculated, %: C 74.59; H 3.81.

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