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Synthesis and Photochemical Properties of Phenoxy Derivatives of Anthra[2,3-*b*]furan-5,10-dione

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Abstract—Nucleophilic replacement of the hydroxy groups in ethyl 4,11-dihydroxy-2-methyl-5,10-dioxo-5,10-dihydroanthra[2,3-*b*]furan-3-carboxylate by chlorine upon treatment with phosphorus acid chlorides gave the corresponding 4(11)-chloro derivatives which were converted into photochromic ethyl 4(11)-phenoxy-2-methyl-5,10-dioxo-5,10-dihydroanthra[2,3-*b*]furan-3-carboxylates. Photoinduced decomposition of the latter leads to the formation of phenol and fluorescent hydroxyanthra[2,3-*b*]furandiones.

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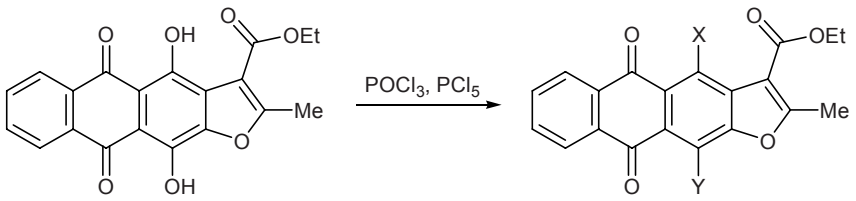
Anthraquinone derivatives are widely used in various fields of chemistry, chemical technology, medicine, technics, etc. [1]. Photochromic α-aryloxy derivatives of anthraquinone and naphthacenequinone [2] are promising materials for nanotechnology, microelectronics, laser technics, and data storage and recording systems. Fusion of a heterocyclic fragment to anthraquinone chromophore could strongly affect spectral and photochemical properties of such compounds [3]. We have developed a scheme for the synthesis and examined photochromic properties of phenoxy-substituted anthra[2,3-*b*]furan-5,10-dione derivatives.

α-Aryloxyanthraquinones are generally synthesized by nucleophilic replacement of halogen atoms by the action of phenoxides. Therefore, the first step in the synthesis of aryloxy derivatives of anthra[2,3-*b*]furan-5,10-dione was preparation of the corresponding halogen-substituted compounds which were not reported previously. As starting material we used accessible ethyl 4,11-dihydroxy-2-methyl-5,10-dioxo-5,10-dihydroanthra[2,3-*b*]furan-3-carboxylate (**I**) prepared in two steps from quinizarin and ethyl acetoacetate [4]. The hydroxy groups in molecule **I** can be replaced by halogen atoms. Heating of ester **I** in $POCl_3$ for 6 h resulted in replacement of one hydroxy group by chlorine atom with formation of a mixture of chloro derivatives **IIa** and **IIb** in an overall yield of 35–40% (Scheme 1). Under analogous conditions, 4,11-dihydroxyanthra[2,3-*b*]thiophene-5,10-dione gives rise to the corresponding 4,11-dichloro derivative [5]; however, we detected no 4,11-dihalo-substituted products even after prolonged heating of dihydroxyanthrafurandione **I** in $POCl_3$. According to the ^1H NMR data, the ratio of isomers **IIa**/**IIb** was about 3 : 1 (after

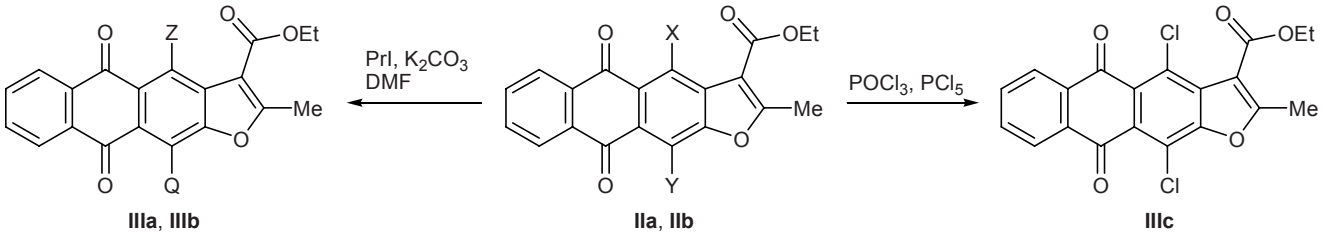
Scheme 1.



I **IIa**, **IIb**

X = OH, Y = Cl (**a**); X = Cl, Y = OH (**b**).

Scheme 2.



Z = OPr, Q = Cl (**a**); Z = Cl, Q = OPr (**b**).

chromatographic purification). By fractional crystallization from toluene we succeeded in isolating individual isomers **IIa** and **IIb**. Their ^{1}H NMR spectra were fairly similar, while the ^{13}C NMR spectra revealed a considerable difference in the positions of the C^4 and C^{11} signals. In the ^{13}C NMR spectrum of the major isomer, the COH signal was located at δ_C 154.71 ppm, while the COH carbon atom in the minor isomer resonated at δ_C 143.92 ppm. The upfield shift of the latter results from the presence of oxygen atom in the *ortho* position [6]; therefore, the minor isomer was assigned structure **IIb**.

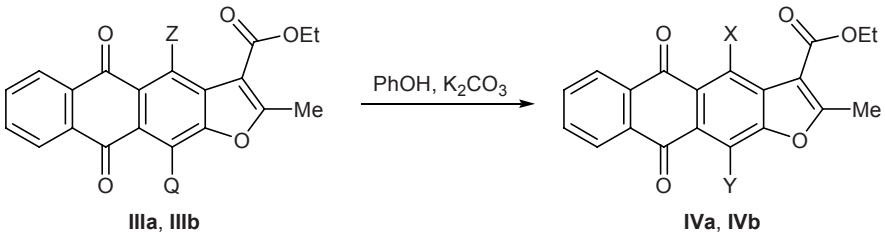
In the reaction of ethyl 4,11-dihydroxy-2-methyl-5,10-dioxo-5,10-dihydroanthra[2,3-*b*]furan-3-carboxylate (**I**) with more active phosphorus pentachloride in a mixture with $POCl_3$, replacement of hydroxy group by chlorine was considerably faster (2–3 h at 40–50°C), and halogen derivatives **IIa** and **IIb** were obtained in a higher yield (50–60%). However, the isomer ratio **IIa**/**IIb** approached 1:4, i.e., 4-chloro derivative **IIb** was the major product. Thus variation of the halogenating agent ensures some regioselectivity in the formation of 4(11)-chloro-11(4)-hydroxy-2-methyl-5,10-dioxo-5,10-dihydroanthra[2,3-*b*]furan-3-carboxylates **IIa** and **IIb**.

The chlorine atom in molecules **IIa** and **IIb** turned out to be weakly reactive, and we failed to replace it by phenoxy group. The reduced reactivity of compounds **IIa** and **IIb** in S_N2_{Ar} processes results from the presence of a hydroxy group in the *para* position with respect to the chlorine atom; ionization of that hydroxy group by the action of base deactivates the halogen atom toward nucleophilic replacement. To prevent ionization of the hydroxy group chloro derivatives **IIa** and **IIb** were subjected to alkylation with propyl iodide in dimethylformamide in the presence of potassium carbonate. We thus obtained 4(11)-chloro-11(4)-propoxy derivatives **IIIa** and **IIIb** (Scheme 2).

The structure of propoxy derivatives **IIIa** and **IIIb** was confirmed by NMR spectra. Compound **IIIa** showed nuclear Overhauser effect between methylene protons of the propoxy group and methylene protons of the ester ethoxy group, indicating their spatial proximity. No analogous effect was observed in the spectrum of **IIIb**; this means that the propoxy group in molecule **IIIb** is attached to C^{11}.

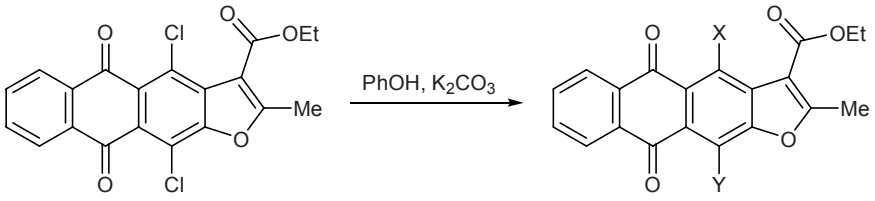
We detected no 4,11-dichloro derivative when compound **I** was heated in a boiling PCl_5–$POCl_3$ mixture; however, heating of monohalo derivatives **IIa** and **IIb** or their mixture in PCl_5–$POCl_3$ at the boiling point gave ethyl 4,11-dichloro-2-methyl-5,10-dioxoanthra-[2,3-*b*]furan-3-carboxylate (**IIIc**) (Scheme 2). The halogen atoms in compounds **IIIa** and **IIIb** are readily replaced by phenoxy group on heating in molten phenol in the presence of potassium carbonate at 70–80°C; as a result, 4(11)-phenoxy-11(4)-propoxy derivatives **IVa** and **IVb** are formed (Scheme 3). In the reaction with 4,11-dichloroanthrafuran **IIIc** it was possible to replace one or both chlorine atoms by phenoxy group, depending on the conditions. The reaction of **IIIc** with

Scheme 3.



X = OPr, Y = OPh (**a**); X = OPh, Y = OPr (**b**).

Scheme 4.



IIIc **IVc**, **IVd**

X = OPh, Y = Cl (**c**); X = Y = OPh (**d**).

phenol in melt at 60°C in the presence of K_2CO_3 gave mainly one monophenoxy derivative **IVc**, whereas at higher temperature ethyl 2-methyl-5,10-dioxo-4,11-bis-(phenoxy)-5,10-dihydroanthra[2,3-*b*]furan-3-carboxylate (**IVd**) was obtained (Scheme 4).

The structure of phenoxy derivatives **IVa**–**IVd** was confirmed by NMR spectra. Unlike initial compounds **IIa**, **IIb**, and **IIIa**–**IIIc** and other ethyl 2-methyl-5,10-dioxo-5,10-dihydroanthra[2,3-*b*]furan-3-carboxylates [3], in the ^{1}H NMR spectra of **IVb**–**IVd** in $CDCl_3$ the triplet signal from the methyl protons in the ester ethyl group is displaced downfield by about 1.07 ppm due to deshielding effect of the magnetically anisotropic phenyl group in position *4* (ASIS effect). No analogous effect was observed in the spectrum of compound **IVa** having a phenoxy group in the 11-position. These findings allowed us to assign compound **IVc** the structure of 4-phenoxy derivative and to confirm once more the structure of initial monochloro-substituted compounds **IIa** and **IIb**.

The electronic absorption spectra of chloroanthra-[2,3-*b*]furan-5,10-diones **IIa** and **IIb** showed that replacement of hydroxy group in anthrafuran **I** by chlorine atom induces a 60–70-nm blue shift of the absorption maximum. Chloro-, propoxy-, and phenoxy-substituted anthra[2,3-*b*]furan-5,10-diones **III** and **IV** absorb in the region λ 370–380 nm. 4(11)-Chloro-11(4)-hydroxy derivatives **IIa** and **IIb** exhibit fluorescence in solution (λ_{fl} = 570 nm), while dichloro-, propoxy-, and phenoxyanthra[2,3-*b*]furan-5,10-diones **III** and **IV** do not possess fluorescent properties.

Like related phenoxy-substituted 5,12-naphthacenequinones [7], phenoxyanthra[2,3-*b*]furan-5,10-diones **IVa**–**IVd** are photochromic compounds. Irradiation of their solutions in toluene with filtered light at λ 380 nm induced an appreciable red shift and increase in intensity of the long-wave absorption maximum (see table). The spectra of the photoinduced forms contained two absorption bands in the region λ 480–510 nm (Fig. 1). The observed photoinduced variations in the spectral pattern are reversible. Irradiation of the photoinduced forms in solution at λ 502 nm restores the initial state. Alternate irradiation at λ 380 and 502 nm causes multiple reversible phototransformations (Fig. 2). However, recycling is accompanied by decrease in the photoinduced optical density as a result of photochemical decomposition (Fig. 2).

As in the case of phenoxynaphthacenequinones, the observed variations in the spectral pattern may be interpreted in terms of photoinduced rearrangement involving isomerization of 4(11)-phenoxyanthra-[2,3-*b*]furan-5,10-diones into the corresponding *ana*-quinone structures, 5(10)-phenoxyanthra[2,3-*b*]furan-4,10(5,11)-diones [2]. The long-wave absorption maxima in the electronic spectra of photochromic phenoxyanthra[2,3-*b*]furan-5,10-diones **IVa**–**IVd** are displaced by 30 nm to the blue region, while the absorption maxima of their photoinduced forms are displaced by 20 nm to the red region relative to the corresponding maxima of analogous naphthacene-5,12-quinone derivatives [7]. Thus the presence of a fused

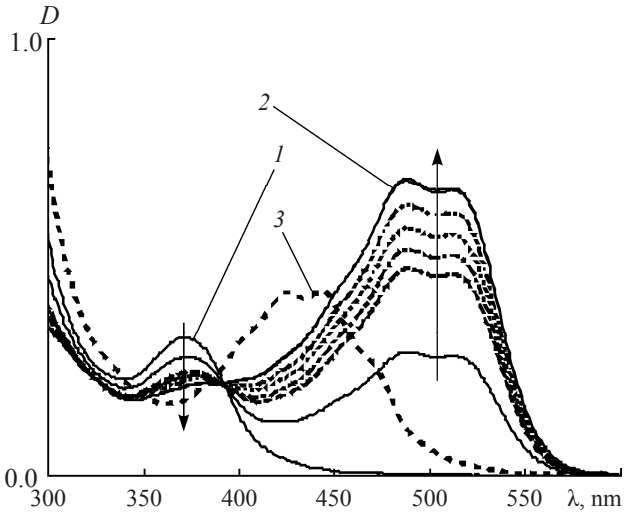


Fig. 1. Electronic absorption spectra of (*1*) anthra[2,3-*b*]-furan-5,10-dione **IVc**, (*2*) its photoinduced form after irradiation at λ 380 nm for 30, 90, 150, 210, and 360 s, and (*3*) photodecomposition product; toluene, $c = 5 \times 10^{-5}$ M.

Electronic absorption spectra of phenoxy-substituted anthra[2,3-*b*]furan-5,10-diones **IVa**–**IVd** and their photoinduced forms and photodecomposition products and photocoloration rate constants (k) in toluene ($c = 5 \times 10^{-5}$ M)

Comp. no.	λ_{max},[a] nm			$k \times 10^2$, s^{-1}
	initial form	photoinduced form	photodecomposition product	
IVa	379	475, 498	(427), 446	1.1
IVb	376	484, 506	(430), 448	1.8
IVc	370	486, 510	(428), 444	1.4
IVd	372	481, 504	422, 442	1.5

[a] Hereinafter, in parentheses are given the positions of inflection points.

heterocyclic fragment considerably affects photochemical properties of such compounds.

Photoinduced isomerization of propoxyphenoxyanthra[2,3-*b*]furan-5,10-diones **IVa** and **IVb** was accompanied by fluorescence in the region λ 560–570 nm. A more detailed examination showed that the observed fluorescence is not related to the formation of the *ana*-quinone isomer: it originates from the photochemical decomposition products. When the photoinduced forms were irradiated at λ 502 or 380 nm, decrease in the intensity of the long-wave absorption maxima was accompanied by increase in the fluorescence intensity at λ 570 nm. The photodecomposition of propoxy derivatives **IVa** and **IVb** was especially fast, whereas toluene solutions of the photoinduced forms of 11-chloro and 11-phenoxy derivatives **IVc** and **IVd** were more stable: their decomposition occurred only under irradiation with unfiltered UV light over a period of 10–15 min (Fig. 3). Photodecomposition of **IVc** and **IVd** also gave fluorescent products. Thus the nature of substituents and their position in the chromophore core strongly affect the rate of photodecomposition of phenoxyanthra[2,3-*b*]furan-5,10-diones. In addition, the rate of photodecomposition strongly depends on the solvent nature. For example, the decomposition of compounds **IVa**–**IVd** in chloroform and alcohols was considerably faster.

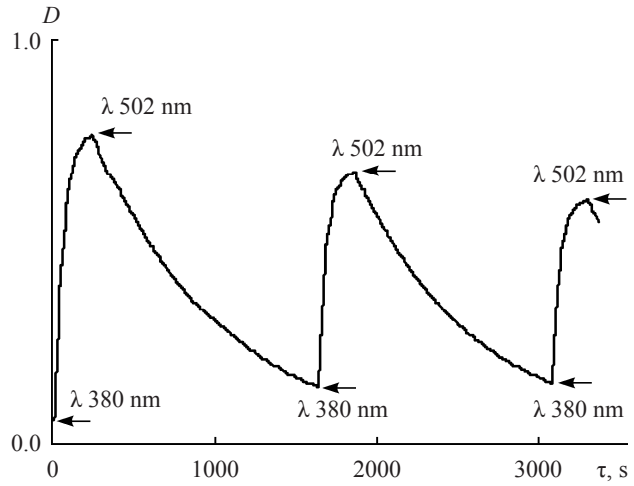


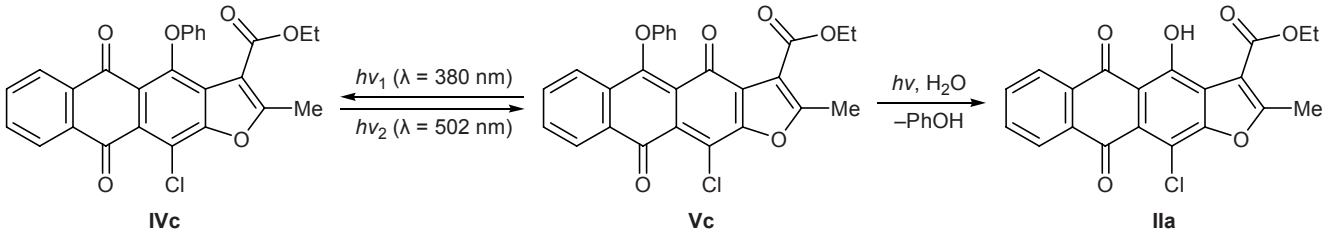
Fig. 2. Kinetics of reversible photochemical transformations of phenoxyanthrafurandione **IVc** in toluene upon alternate irradiation at λ 380 and 502 nm; the optical density was measured at the absorption maximum of **IVc**, λ 485 nm.

Unlike phenoxynaphthacenequinones [2], solutions of the photoinduced forms derived from anthra[2,3-*b*]-furan-5,10-diones **IVa**–**IVd** in toluene or chloroform underwent complete decoloration on storage for 24 h in the dark. The absorption and fluorescence spectra of the products were identical to those of the photodecomposition products. Moreover, addition of protic solvents (e.g., alcohols) to solutions of the photoinduced forms of **IVa**–**IVd** was found to considerably accelerate the decoloration process.

The photochemical transformations of phenoxy derivative **IVc** were studied by ^{1}H NMR spectroscopy. Irradiation of a solution of **IVc** in $CDCl_3$ at λ 380 nm resulted in the formation of equimolar amounts of the corresponding hydroxy compound **IIa** and phenol (Scheme 5) as products of decomposition of the photoinduced form. Compound **IIa** and phenol were identified by thin-layer chromatography using authentic samples and the Pauli reagent as developer. These data are consistent with the previously noted similarity of the emission spectra of the photodecomposition products obtained from phenoxy-5,12-naphthacenequinones and the corresponding hydroxy derivatives [8]. Obviously, the photodecomposition of phenoxy-substituted anthra[2,3-*b*]furan-5,10-diones involves photochemical nucleophilic replacement of the phenoxy group in the photoinduced form by hydroxy group.

We succeeded in recording the ^{1}H NMR spectrum of the photoinduced form derived from compound **IVc** upon irradiation at λ 380 nm in C_6D_6. The spectrum confirmed formation of *ana*-quinone structure **Vc**. The rearrangement of 4-phenoxy derivative **IVc** into 5-phenoxy derivative **Vc** leads to an appreciable upfield shift ($\delta\Delta = 0.25$ ppm) of the triplet signal from the methyl protons of the ester ethyl group and downfield shift ($\delta\Delta = 0.24$ ppm) of the 6-H signal. The observed shifts are related to the deshielding effect of the migrating magnetically anisotropic phenyl group on spatially close groups, CH_3 group in **IVc** and C^6H in **Vc**. The dark decoloration of photoinduced form **Vc** is accompanied by appearance and increase in intensity

Scheme 5.



of signals corresponding to hydroxy derivative **IIa** and phenol.

Our results led us to conclude that, unlike phenoxy-substituted 5,12-naphthacenequinones, photoinduced forms derived from phenoxyanthra[2,3-*b*]furan-5,10-diones are hydrolytically unstable and that they undergo hydrolysis with water present in the solvent to give the corresponding hydroxyanthrafurandiones and phenol. The hydrolysis process is considerably accelerated by irradiation. Taking into account that the hydrolysis and photodecomposition products of the photoinduced forms exhibit fluorescence, such compounds may be interesting as materials for the design of data storage systems. In addition, decomposition of the photoinduced colored forms of phenoxyanthra[2,3-*b*]furan-5,10-diones to the corresponding fluorescent dye and phenol attracts interest from the viewpoint of nanotechnology for creation of photocontrolled compositions. However, practical implementation of the results of the present work requires further study on phenoxyanthra[2,3-*b*]furan-5,10-diones, specifically on the effect of fused heterocyclic fragment and functional groups therein on the photochemical and spectral properties of these compounds.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-400 spectrometer at 400 MHz using tetramethylsilane as internal reference. The mass spectra (electron impact, 70 eV) were obtained on a Finnigan MAT SSQ 710 mass spectrometer with direct sample admission into the ion source (ion source temperature 150°C, batch inlet probe temperature up to 350°C). The electronic absorption spectra were measured on a Varian Cary 50 Bio spectrophotometer. The fluorescence spectra were recorded on a Varian Cary Eclipse spectrofluorimeter. Photochemical studies were performed using a Namamatsu Spot Light Source LC-4. The required wavelengths were isolated using UFS-8 and BS-8 composite glass filters (λ 380 nm) or ZhS-18, SZS-20, and SZS-22 filters (λ 502 nm). Variation of the absorption spectra during phototransformations (see table and Fig. 1) was studied at a half of the maximal light source power. The kinetics of photochromic transformations (Fig. 2) and photodecomposition were studied at the maximal light source power. The progress of reactions and the purity of products were monitored by thin-layer chromatography on Silufol UV-254 and Kieselgel F_{254} (Merck) plates. Kieselgel Merck 60 silica gel was used for preparative chromatography.

Ethyl 11-chloro-4-hydroxy-2-methyl-5,10-dioxo-5,10-dihydroanthra[2,3-*b*]furan-3-carboxylate (IIa). A solution of 400 mg (1.1 mmol) of ester **I** in 15 ml of phosphoryl chloride was heated for 6 h at the boiling point. The mixture was cooled to room temperature and poured onto ice under stirring. After 1 h, the mixture was neutralized to pH 7 by carefully adding sodium carbonate and was stirred overnight.

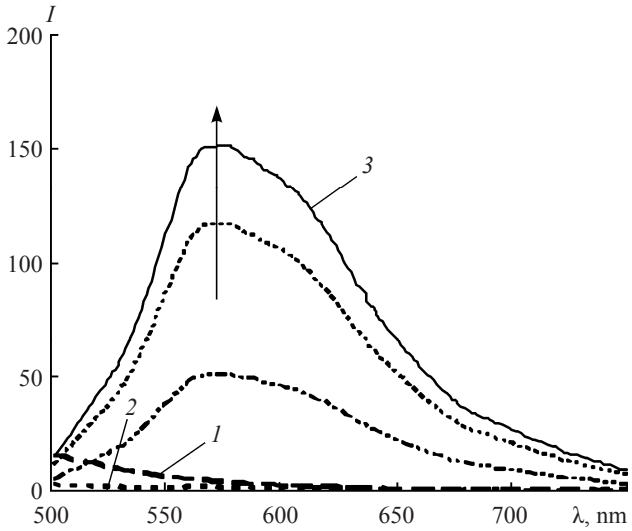


Fig. 3. Fluorescence spectra in toluene ($c = 5 \times 10^{-5}$ M) of (*1*) initial phenoxyanthrafurandione **IVc** (excitation at the absorption maximum at λ 380 nm), (*2*) *ana*-quinoid photoinduced form **Vc** generated by irradiation of compound **IVc** at λ 380 nm over a period of 360 s (excitation at the absorption maximum at λ 502 nm), and (*3*) photodecomposition product obtained by irradiation of **Vc** with unfiltered light for 150, 600, and 900 s (excitation at the absorption maximum at λ 440 nm).

The precipitate containing compounds **IIa** and **IIb** was filtered off and subjected to column chromatography on silica gel using toluene–diethyl ether (1:0 to 10:1) as eluent. The product was recrystallized twice from toluene. Yield 83 mg (19%), orange crystals, mp 220–222°C. UV spectrum (EtOH), λ_{max}, nm (logε): 204 (4.3), (238), 253 (4.5), 265 (4.5), 272 (4.5), (285), 322 (3.5), (401), 420 (3.9), 435 (3.9), (458). ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$: 1.44 t (3H, CH_3, J = 7.1 Hz), 2.77 s (3H, CH_3), 4.42 q (2H, OCH_2, J = 7.1 Hz), 7.77–7.82 m (2H, 7-H, 8-H), 8.22–8.26 m (2H, 6-H, 9-H), 14.63 s (1H, OH); in C_6D_6: 1.13 t (3H, CH_3, J = 7.1 Hz), 2.26 s (3H, CH_3), 4.23 q (2H, OCH_2, J = 7.1 Hz), 7.00–7.05 m (2H, 7-H, 8-H), 8.07–8.18 m (2H, 6-H, 9-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 187.80 (C=O), 180.91 (C=O), 164.37 (COO), 162.09 (C), 158.31 (C), 154.19 (C), 134.22 (C), 124.95 (C), 120.17 (C), 112.73 (C), 112.22 (C), 112.11 (C), 134.58 (CH), 133.80 (CH), 127.37 (CH), 126.56 (CH), 61.41 (CH_2), 14.49 (CH_3), 14.16 (CH_3). Mass spectrum, m/z (I_{rel}, %): 384 (100) $[M]^+$, 356 (18), 339 (85) $[M - OC_2H_5]^+$, 321 (22). Found, %: C 62.43; H 3.41. $C_{20}H_{13}ClO_6$. Calculated, %: C 62.42; H 3.38. M 384.77.

Ethyl 4-chloro-11-hydroxy-2-methyl-5,10-dioxo-5,10-dihydroanthra[2,3-*b*]furan-3-carboxylate (IIb). A mixture of 400 mg (1.1 mmol) of ester **I**, 15 ml of $POCl_3$, and 1.5 g (7.3 mmol) of PCl_5 was heated for 2.5 h at 50°C. The mixture was cooled to room temperature and poured onto ice under stirring. After 1 h, the mixture was neutralized to pH 7 by carefully adding sodium carbonate and was stirred overnight. The precipitate containing compounds **IIa** and **IIb** was filtered off and subjected to column chromatography on silica gel using toluene–diethyl ether (1:0 to 10:1) as eluent. The product was recrystallized from toluene. Yield 156 mg (37%), orange crystals, mp 236–237°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.44 t (3H, CH_3, J = 7.1 Hz), 2.67 s (3H, CH_3), 4.46 q (2H, OCH_2, J = 7.1 Hz), 7.74–7.80 m (2H, 7-H, 8-H), 8.21–8.24 m (2H, 6-H, 9-H), 14.01 s (1H, OH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 188.30 (C=O), 181.13 (C=O), 163.38 (C), 163.14 (COO), 148.81 (C), 143.92 (C), 134.72 (C), 132.93 (C), 132.06 (C), 120.30 (C), 113.52 (C), 113.64 (C), 134.91 (CH), 133.62 (CH), 127.66 (CH), 126.26 (CH), 61.56 (CH_2), 13.40 (CH_3), 13.38 (CH_3). Mass spectrum, m/z (I_{rel}, %): 384 (100) $[M]^+$, 356 (36), 339 (63) $[M - OC_2H_5]^+$, 321 (22), 305 (20), 199 (8), 163 (38), 156 (7), 105 (7), 87 (13), 82 (17), 50 (12), 43 (29). UV spectrum (EtOH), λ_{max}, nm (logε): 204 (4.4), (239), 251 (4.5), (268), 274 (4.5), (289), (320), (395), 410 (3.9), 424 (3.9), 445. Found, %: C 62.40; H 3.42. $C_{20}H_{13}ClO_6$. Calculated, %: C 62.42; H 3.38. M 384.77.

Ethyl 11-chloro-2-methyl-5,10-dioxo-4-propoxy-5,10-dihydroanthra[2,3-*b*]furan-3-carboxylate (IIIa). Powdered potassium carbonate, 0.73 g (5.3 mmol), was added to a solution of 200 mg (0.47 mmol) of ester **IIa** in 10 ml of DMF, 0.4 ml (4.0 mmol) of propyl iodide was then added, and the mixture was stirred for 1.5 h on heating at 100°C. The mixture was cooled to room temperature, the precipitate was filtered off, and the filtrate was acidified with 5% hydrochloric acid and extracted with ethyl acetate. The extract was washed with water, dried, and evaporated, and the residue was purified by column chromatography on silica gel using toluene as eluent, followed by recrystallization from hexane. Yield 150 mg (75%), yellow crystals, mp 157–158°C. UV spectrum (EtOH), λ_{max}, nm (logε): 244 (4.3), 272 (4.5), 374 (3.7). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.02 t (3H, CH_3, J = 7.4 Hz), 1.43 t (3H, CH_3, J = 7.1 Hz), 1.93–2.01 m (2H, CH_2), 2.75 s (3H, CH_3), 4.03 t (2H, OCH_2, J = 7.1 Hz), 4.44 q (2H, OCH_2, J = 7.1 Hz), 7.72–7.77 m (2H, 7-H, 8-H), 8.17–8.21 m (2H, 6-H, 9-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 182.77 (C=O), 182.01 (C=O), 164.03 (COO), 162.61 (C), 154.02 (C), 153.67 (C), 134.32 (C), 127.69 (C), 126.31 (C), 125.89 (C), 123.79 (C), 114.34 (C), 112.07 (C), 133.76 (CH), 133.41 (CH), 126.73 (CH), 126.60 (CH), 78.14 (CH_2), 61.83 (CH_2), 23.11 (CH_2), 14.33 (CH_3), 14.08 (CH_3), 10.27 (CH_3). Mass spectrum, m/z (I_{rel}, %): 426 (10) $[M]^+$, 338 (15) $[M - C_3H_7 - OC_2H_5]^+$, 163 (22), 87 (18), 75 (16), 50 (7), 43 (100) $[C_3H_7]^+$. Found, %: C 64.70; H 4.49. $C_{23}H_{19}ClO_6$. Calculated, %: C 64.71; H 4.45. M 426.85.

Ethyl 4-chloro-2-methyl-5,10-dioxo-11-propoxy-5,10-dihydroanthra[2,3-*b*]furan-3-carboxylate (IIIb) was synthesized as described above for compound **IIIa** using ester **IIb** as initial compound. Yield 80%, yellow crystals, mp 119–121°C. UV spectrum (EtOH), λ_{max}, nm (logε): 244 (4.3), 273 (4.5), 379 (3.7). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.13 t (3H, CH_3, J = 7.4 Hz), 1.45 t (3H, CH_3, J = 7.2 Hz), 1.95–2.01 m (2H, CH_2), 2.67 s (3H, CH_3), 4.35 t (2H, OCH_2, J = 6.7 Hz), 4.47 q (2H, OCH_2, J = 7.2 Hz), 7.71–7.74 m (2H, 7-H, 8-H), 8.13–8.18 m (2H, 6-H, 9-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 182.84 (C=O), 181.95 (C=O), 163.24 (C), 162.59 (COO), 148.47 (C), 144.53 (C), 134.19 (C), 134.05 (C), 131.81 (C), 127.59 (C), 126.56 (C), 123.55 (C), 121.92 (C), 113.05 (C), 133.49 (CH), 133.43 (CH), 126.69 (CH), 126.27 (CH), 76.94 (CH_2), 61.79 (CH_2), 23.41 (CH_2), 14.05 (CH_3),

13.76 (CH_3), 10.26 (CH_3). Mass spectrum, *m*/*z* (I_{rel}, %): 426 (57) $[M]^+$, 397 (11), 384 (12), 356 (7), 339 (10) $[M - C_3H_6 - OC_2H_5]^+$, 191 (8), 163 (29), 87 (9), 76 (14), 50 (6), 43 (100) $[C_3H_7]^+$. Found, %: C 64.73; H 4.44. $C_{23}H_{19}ClO_6$. Calculated, %: C 64.71; H 4.45. *M* 426.85.

Ethyl 4,11-dichloro-2-methyl-5,10-dioxo-5,10-dihydroanthra[2,3-*b*]furan-3-carboxylate (IIIc). Phosphoryl chloride, 12.0 ml, was added to 300 mg (0.78 mmol) of a mixture of compounds **IIa** and **IIb**, 1.0 g (4.8 mmol) of PCl_5 was added, and the mixture was heated for 3 h at the boiling point, cooled to room temperature, and poured onto ice under stirring. After 1 h, the mixture was neutralized to pH 7 by carefully adding sodium carbonate and was stirred overnight. The precipitate was filtered off and subjected to column chromatography on silica gel using toluene–diethyl ether (1:0 to 10:1) as eluent. The product was recrystallized from toluene–heptane (1:1). Yield 172 mg (55%), mp 173–174°C. UV spectrum (EtOH), λ_{max}, nm (log ε): 243 (4.1), 274 (4.5), 367 (3.6). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.44 t (3H, CH_3, *J* = 7.1 Hz), 2.71 s (3H, CH_3), 4.48 q (2H, OCH_2, *J* = 7.1 Hz), 7.75–7.79 m (2H, 7-H, 8-H), 8.18–8.21 m (2H, 6-H, 9-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 182.09 (C=O), 181.98 (C=O), 164.06 (COO), 162.83 (C), 152.15 (C), 134.21 (C), 133.79 (C), 130.46 (C), 128.42 (C), 128.03 (C), 126.84 (C), 117.91 (C), 113.37 (C), 134.06 (CH), 133.80 (CH), 126.91 (CH), 126.70 (CH), 117.91 (CH), 61.99 (CH_2), 14.11 (CH_3), 13.96 (CH_3). Mass spectrum, *m*/*z* (I_{rel}, %): 402 (10) $[M]^+$, 357 (7) $[M - OC_2H_5]^+$, 238 (9), 210 (54), 174 (100), 164 (22), 151 (26), 133 (28), 122 (20), 105 (76), 98 (42), 92 (10), 87 (52), 76 (82), 63 (10), 50 (50), 43 (84). Found, %: C 59.57; H 3.01. $C_{20}H_{12}Cl_2O_5$. Calculated, %: C 59.55; H 2.98. *M* 403.21.

Ethyl 2-methyl-5,10-dioxo-11-phenoxy-4-propoxy-5,10-dihydroanthra[2,3-*b*]furan-3-carboxylate (IVa). A mixture of 100 mg (0.23 mmol) of ester **IIIa**, 3.0 g (31.9 mmol) of phenol, and 150 mg (1.1 mmol) of potassium carbonate was heated for 30–60 min at 80–90°C. When the reaction was complete (TLC), the mixture was diluted with toluene and poured into water. The product was extracted into warm toluene, the extract was washed with a 5% solution of sodium hydroxide, water, and a saturated solution of sodium chloride, dried, and evaporated. The dry residue was purified by column chromatography on silica gel using toluene as eluent, followed by recrystallization from hexane. Yield 65 mg (58%), light yellow crystals, mp 122–123°C. UV spectrum (EtOH), λ_{max}, nm (log ε): 201 (4.5), (210), 245 (4.4), 271 (4.5), 379 (3.8). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.06 t (3H, CH_3, *J* = 7.5 Hz), 1.41 t (3H, CH_3, *J* = 7.1 Hz), 1.90–2.02 m (2H, CH_2), 2.60 s (3H, CH_3), 4.07 t (2H, OCH_2, *J* = 7.3 Hz), 4.44 q (2H, OCH_2, *J* = 7.1 Hz), 6.82 d (2H, H_{arom}, *J* = 8.8 Hz), 7.06 t (1H, H_{arom}, *J* = 7.3 Hz), 7.26–7.3 m (2H, H_{arom}), 7.64–7.71 m (2H, 7-H, 8-H), 8.20–8.25 m (2H, 6-H, 9-H). Mass spectrum, *m*/*z* (I_{rel}, %): 484 (15) $[M]^+$, 442 (30) $[M - C_3H_6]^+$, 409 (10), 396 (53), 339 (8), 319 (15), 283 (8), 255 (9), 226 (8), 198 (10), 163 (13), 151 (11), 128 (10), 105 (15), 87 (9), 77 (75) $[Ph]^+$, 51 (30), 43 (100) $[C_3H_7]^+$. Found, %: C 71.89; H 4.99. $C_{29}H_{24}O_7$. Calculated, %: C 71.90; H 4.96. *M* 484.50.

Compounds **IVb–IVd** were synthesized in a similar way.

Ethyl 2-methyl-5,10-dioxo-4-phenoxy-11-propoxy-5,10-dihydroanthra[2,3-*b*]furan-3-carboxylate (IVb) was synthesized from ester **IIIb**. Yield 62%, light yellow crystals, mp 126–127°C. UV spectrum (EtOH), λ_{max}, nm (log ε): 202 (4.3), (211), 244 (4.4), 271 (4.5), 377 (3.8). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.07 t (3H, CH_3, *J* = 6.8 Hz), 1.16 t (3H, CH_3, *J* = 7.2 Hz), 2.00–2.07 m (2H, CH_2), 2.73 s (3H, CH_3), 4.07 q (2H, OCH_2, *J* = 7.2 Hz), 4.40 t (2H, OCH_2, *J* = 6.8 Hz), 6.80 d (2H, H_{arom}, *J* = 8.8 Hz), 6.94 t (1H, H_{arom}, *J* = 7.2 Hz), 7.21–7.27 m (2H, H_{arom}), 7.65–7.72 m (2H, 7-H, 8-H), 8.05–8.22 m (2H, 6-H, 9-H). Mass spectrum, *m*/*z* (I_{rel}, %): 484 (8) $[M]^+$, 442 (7) $[M - C_3H_6]^+$, 396 (7) $[M - C_3H_7 - OC_2H_5]^+$, 163 (7), 105 (8), 77 (45) $[Ph]^+$, 51 (24), 43 (100) $[C_3H_7]^+$. Found, %: C 71.92; H 4.98. $C_{29}H_{24}O_7$. Calculated, %: C 71.90; H 4.96. *M* 484.50.

Ethyl 11-chloro-2-methyl-5,10-dioxo-4-phenoxy-5,10-dihydroanthra[2,3-*b*]furan-3-carboxylate (IVc) was synthesized from ester **IIIc**; the mixture was heated at 60°C. Yield 64%, light yellow crystals, mp 228–229°C. UV spectrum (EtOH), λ_{max}, nm (log ε): 202 (4.4), (212), 244 (4.2), 272 (4.5), 369 (3.7). ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$: 1.07 t (3H, CH_3, *J* = 7.1 Hz), 2.77 s (3H, CH_3), 4.08 q (2H, OCH_2, *J* = 7.1 Hz), 6.81 d (2H, H_{arom}, *J* = 7.8 Hz), 7.01 t (1H, H_{arom}, *J* = 7.3 Hz), 7.23–7.28 m (2H, H_{arom}), 7.62–7.69 m (2H, 7-H, 8-H), 8.18–8.21 m (2H, 6-H, 9-H); in C_6D_6: 0.79 t (3H, CH_3, *J* = 7.1 Hz), 2.21 s (3H, CH_3), 3.88 q (2H, OCH_2, *J* = 7.1 Hz), 6.80–7.09 m (7H, C_6H_5, 7-H, 8-H), 7.91 d (1H, 6-H, *J* = 7.5 Hz), 8.12 d (1H, 9-H, *J* = 7.7 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 182.31 (C=O), 180.83 (C=O), 165.88 (COO), 162.27 (C), 158.90 (C), 153.82 (C), 146.91 (C), 133.98 (C), 133.81 (C), 127.80 (C), 126.13 (C), 124.36 (C),

116.14 (C), 111.96 (C), 133.89 (CH), 133.55 (CH), 129.47 (2CH), 126.82 (CH), 126.69 (CH), 121.81 (CH), 114.66 (2CH), 61.48 (CH_2), 14.45 (CH_3), 13.79 (CH_3). Mass spectrum, *m*/*z* (I_{rel}, %): 460 (20) $[M]^+$, 415 (13) $[M - OC_2H_5]^+$, 387 (9) $[M - CO_2C_2H_5]^+$, 339 (8), 311 (7), 283 (7), 239 (15), 207 (7), 199 (10), 175 (11), 163 (25), 149 (12), 105 (14), 98 (7), 87 (8), 77 (100) $[Ph]^+$, 65 (9), 51 (58), 43 (53). Found, %: C 67.73; H 3.66. $C_{26}H_{17}ClO_6$. Calculated, %: C 67.75; H 3.69. *M* 460.86.

Ethyl 2-methyl-5,10-dioxo-4,11-diphenoxyanthra[2,3-*b*]furan-3-carboxylate (IVd) was synthesized from ester **IIIc**. Yield 53%, light yellow crystals, mp 225–227°C. UV spectrum (EtOH), λ_{max}, nm (log ε): 205 (4.5), (213), 243 (4.3), 270 (4.5), 372 (3.6). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.08 t (3H, CH_3, *J* = 7.1 Hz), 2.63 s (3H, CH_3), 4.06 q (2H, OCH_2, *J* = 7.1 Hz), 6.87 d (2H, H_{arom}, *J* = 8.8 Hz), 6.98 d (2H, H_{arom}, *J* = 8.7 Hz), 7.01 t (1H, H_{arom}, *J* = 7.3 Hz), 7.09 t (1H, H_{arom}, *J* = 7.3 Hz), 7.25–7.36 m (4H, H_{arom}), 7.64–7.68 m (2H, 7-H, 8-H), 8.03–8.11 m (2H, 6-H, 9-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 181.73 (C=O), 180.39 (C=O), 165.85 (COO), 162.50 (C), 158.99 (C), 158.01 (C), 150.54 (C), 145.23 (C), 137.28 (C), 134.11 (C), 128.00 (C), 124.09 (C), 123.54 (C), 111.83 (C), 97.66 (C), 133.76 (CH), 133.54 (CH), 129.70 (2CH), 129.53 (2CH), 126.95 (CH), 126.61 (CH), 122.65 (CH), 121.86 (CH), 115.07 (2CH), 114.66 (2CH), 61.52 (CH_2), 14.42 (CH_3), 13.82 (CH_3). Mass spectrum, *m*/*z* (I_{rel}, %): 518 (7) $[M]^+$, 105 (11), 77 (100) $[Ph]^+$, 65 (7), 51 (43), 43 (30). Found, %: C 74.10; H 4.24. $C_{32}H_{22}O_7$. Calculated, %: C 74.13; H 4.25. *M* 518.51.

Ethyl 11-chloro-2-methyl-4,10-dioxo-5-phenoxy-4,10-dihydroanthra[2,3-*b*]furan-3-carboxylate (Vc). A solution of 3 mg (0.007 mmol) of ester **IVc** in 1.0 ml of C_6D_6 was irradiated at λ 380 nm (filtered light) over a period of 1.5 h, and ^{1}H NMR spectrum of the solution was recorded, δ, ppm: 1.03 t (3H, CH_3, *J* = 7.1 Hz), 2.11 s (3H, CH_3), 4.08 q (2H, OCH_2, *J* = 7.1 Hz), 6.80–7.06 m (7H, Ph, 7-H, 8-H), 7.67 d (1H, 6-H, *J* = 7.3 Hz), 8.32 d (1H, 9-H, *J* = 7.7 Hz).

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