

Reactions of 1-Halo-4-nitroanthraquinones with C-Nucleophiles

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Abstract—1-Fluoro-4-nitroanthraquinone reacts with C-nucleophiles, yielding the corresponding fluorine replacement products. Reactions of 1-chloro-4-nitroanthraquinone with the same nucleophiles result in formation of mixtures of dechlorination and denitration products whose ratio is determined by both charge and orbital interactions. Steric structure of the nucleophile can also affect the regioselectivity of substitution.

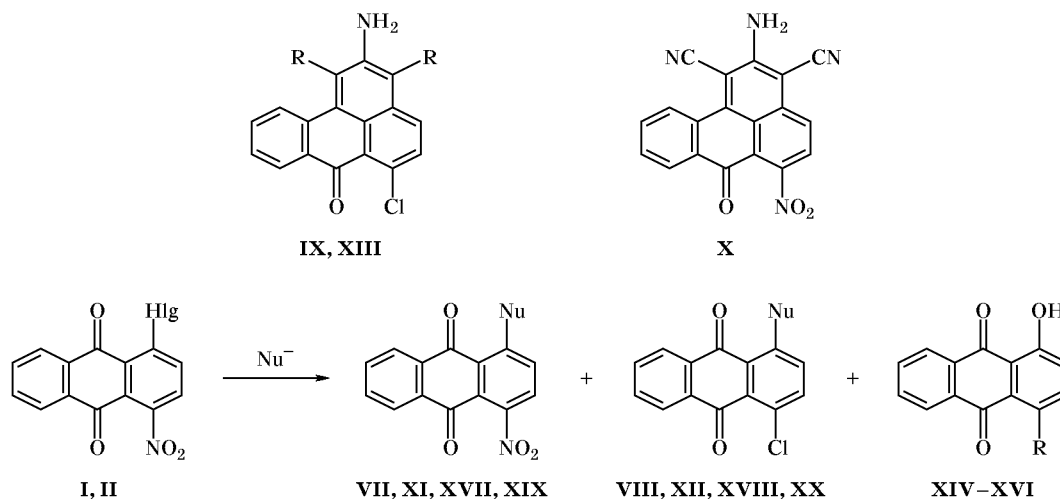
It is known that the chlorine atom and nitro group in 1-chloro-4-nitroanthraquinone (**I**) exhibit similar reactivities in nucleophilic substitution reactions with amines; as a result, mixtures of aminodechlorination and aminodenitration products are formed [1, 2]. An analogous behavior was observed for compound **I** in the reaction with phenylacetonitrile anion [3]. Our studies on the reactions of **I** with phenoxide and benzenethiolate ions showed that the selectivity of substitution is determined by the nucleophile: hard nucleophiles (phenoxide ions) preferentially replace the chlorine atom, while reactions with soft S-nucleophiles result mainly in replacement of the nitro group [4]. On the other hand, 1-fluoro-4-nitroanthraquinone (**II**) reacts with various nucleophiles, exclusively yielding fluorine replacement products [5]. Such behavior of fluoroanthraquinone **II** was explained [4] by high electronegativity of the fluorine atom which induces a considerable positive charge on the adjacent carbon atom (+0.26), and nucleophilic attack by anionic species occurs mainly at that carbon atom. In chloronitroanthraquinone **I** the charge on the carbon atom attached to chlorine is small (+0.09). Therefore, charge-controlled reactions with O-anions lead to preferential replacement of chlorine, whereas reactions with soft, readily polarizable S-nucleophiles are orbital-controlled, and nucleophilic attack is directed at the carbon atom attached to the nitro group, whose contribution to the lowest unoccupied molecular orbital (LUMO) is considerably greater. In order to elucidate whether orbital control is general for nucleophilic reactions of chloronitroanthraquinone **I** and can it determine the regioselectivity of substitution in fluoronitro derivative **II** it was necessary to extend

the series of nucleophiles. Of specific interest was to compare the behavior of substrates **I** and **II** in reactions with carbanions having the same kind of anionic center but differing in charge localization and contribution of the active atom to the highest occupied molecular orbital (HOMO), so that both charge and orbital control of the reaction would be favored.

It should be kept in mind that reactions of substituted anthraquinones with anions derived from CH acids are often complicated by the presence of other functional groups in the nucleophile and that primary substitution products can be unstable in both basic and acidic media [6]. Moreover, the released nitrite ion or hydroxide ion present in the reaction mixture could promote formation of hydroxyanthraquinones [4, 5]. As a result, complex mixtures of products are formed, and isolation of individual components and their purification are not always successful. Naturally, the presence in molecule **I** of two substituents with comparable nucleophilic reactivities implies that the reaction will take at least two pathways, and multi-component reaction mixtures should inevitably be obtained.

As C-nucleophiles we used anions derived from the following CH acids: malonodinitrile (**III**), pentafluorophenylacetonitrile (**IV**), and ethyl cyanoacetate (**V**). Also, the anion derived from 2,6-di-*tert*-butylphenol (**VI**) was used, in which the nucleophilic center is located on C⁴ [7]. The reaction of substrate **I** with 1 equiv of malonodinitrile (**III**) in the presence of sodium hydride, alkali metal hydroxides, or potassium carbonate as a base gave a complex mixture of products. According to the mass spectrometric data,

Scheme 1.



I, Hlg = Cl; **II**, Hlg = F; **VII**, **VIII**, Nu = CH(CN)₂; **XI**, **XII**, **XIV**, Nu = CH(CN)C₆F₅; **XVII**, **XVIII**, Nu = CH(CN)CO₂Et; **XIX**, **XX**, Nu = 4-HO-3,5-(*t*-Bu)₂C₆H₂; **IX**, R = CN; **XIII**, R = C₆F₅; **XIV**, R = CH(CN)C₆F₅; **XV**, R = Cl; **XVI**, R = NO₂.

the mixture contained both products of replacement of chlorine or nitro group by dicyanomethyl fragment (compounds **VII** and **VIII**; m/z 317 and 306) and those with molecular weights of 329 and 340. In addition, the mass spectrum always contained the molecular ion peak of the initial compound.

Gorelik *et al.* [6] studied replacement of chlorine or nitro group in chloro- and nitroanthraquinones by the action of various C-anions and found that dicyanomethylantraquinones in the presence of bases readily react with the second malonodinitrile molecule to give 2-amino-1,3-dicyanobenzanthrones. Probably, in our case primary nucleophilic substitution products are also converted into the corresponding 6-chloro- and 6-nitrobenzanthrones with molecular weights of 329 and 340. In fact, the reaction of anthraquinone **I** with a 4–8-fold excess of malonodinitrile in the presence of potassium hydroxide, followed by heating of the dilute aqueous solution under reflux [7], gave almost exclusively a product with m/z 329, namely 2-amino-6-chloro-1,3-dicyanobenzanthrone (**IX**). In agreement with structure **IX**, in the ¹H NMR spectrum of the product (Table 1) we observed a considerable downfield shift of the signal from one α -proton of the unsubstituted aromatic ring. The IR spectrum of **IX** contained a strong absorption band from aromatic C \equiv N group, and a long-wave absorption maximum appeared in the UV spectrum.

From 1-fluoro-4-nitroanthraquinone (**II**) and an equimolar amount of malonodinitrile in the presence of potassium carbonate in 30 min at room temperature we obtained 1-dicyanomethyl-4-nitro

derivative **VII** (Table 1). However, our attempt to purify this product gave a complex mixture. Reactions of anthraquinones **II** and **VII** with excess malonodinitrile under the conditions ensuring the transformation of **I** into **IX** gave 2-amino-1,3-dicyano-6-nitrobenzanthrone (**X**) which showed in the mass spectrum ion peak with m/z 340; in the IR spectrum a strong aromatic C \equiv N absorption band appeared instead of weak aliphatic C \equiv N band; also, bands due to N–H stretching vibrations were observed.

A conclusion can be drawn that malonodinitrile anion replaces in substrate **II** exclusively the fluorine atom, whereas in anthraquinone **I** the nitro group is replaced preferentially by the action of the same reagent. Minor chlorine substitution products **VII** and **X** can be detected only by mass spectrometry; the substitution ratio Cl/NO₂ is less than 0.1.

The reaction of anthraquinone **I** with pentafluorophenylacetonitrile anion, generated from **IV** by the action of sodium hydride, at room temperature led to formation of compounds **XI** and **XII** as the major products and 2-amino-6-chloro-1,3-bis(pentafluorophenyl)benzanthrone (**XIII**). The latter arises from the reaction of primary nitro-group substitution product **XII** with the second nucleophile molecule. In addition, we isolated two hydroxy-substituted compounds, 1-hydroxy-4-(α -cyanopentafluorobenzyl)anthraquinone (**XIV**) and 1-chloro-4-hydroxyanthraquinone (**XV**). When the reaction was performed at room temperature using potassium hydroxide as a base, no by-products **XIII**–**XV** were formed, and we obtained a mixture of anthraquinones **XI** and **XII** at a ratio

Table 1. ^1H (CDCl_3 , δ , ppm) and ^{19}F NMR (δ_{F} , ppm), IR (ν , cm^{-1}), and UV (λ_{max} , nm) spectra of anthraquinones **VII**, **XI**, **XII**, **XIV**, and **XVIII–XX** and benzanthrones **IX**, **X**, and **XIII**

Comp. no.	^1H NMR spectrum	IR, UV, and ^{19}F NMR spectra
VII	6.35 s [$\text{CH}(\text{CN})_2$], 7.97 m (2H, 6-H, 7-H), 8.15–8.26 m (2H, 5-H, 8-H), 8.18 d and 8.31 d (2-H and 3-H, $J = 8.5$ Hz)	IR: 1360 and 1540 (NO_2), 2200 w (CN), 1675 s (CO)
IX	7.78 m (2H, 9-H, 10-H), 7.83 d, 8.13 d (4-H, 5-H, $J = 8.5$ Hz), 8.44 d.d and 9.03 d.d (8-H, 11-H, $J = 8.0, 2.0$ Hz)	IR: 1630 s (CO); 2220 s (CN); 3240, 3350, 3400 (NH_2) UV (DMF): 380
X		IR: 1625 (CO); 2220 s (CN); 3230, 3350 (NH_2) UV: 534
XI	6.96 s (CHCN), 7.83 m (2H, 6-H, 7-H), 7.86 d, 8.43 d (2-H, 3-H, $J = 8.5$ Hz), 8.19 m (2H, 5-H, 8-H)	^{19}F NMR: 2.04 (2F), 11.00, 23.22 (2F)
XII	6.85 s (CHCN), 7.78 m (2H, 6-H, 7-H), 7.90 d and 8.14 d (2-H, 3-H, $J = 8.5$ Hz), 8.07–8.23 m (2H, 5-H, 8-H)	^{19}F NMR: 1.67 (2F), 10.37 and 23.02 (2F)
XIII	7.08 d and 7.61 d (4-H, 5-H, $J = 9.0$ Hz), 7.49 d.d and 8.37 d.d (7-H, 11-H, $J = 7.5, 2.0$ Hz), 7.30–7.40 m (2H, 9-H, 10-H)	^{19}F NMR: 2.77 and 3.66 (2F each), 10.45 and 11.49 (1F each), 24.74 and 25.10 (2F each)
XIV	7.41d and 7.66 d (2-H, 3-H, $J = 8.5$ Hz), 7.83 m (2H, 6-H, 7-H), 8.12 d and 8.29 d (5-H, 8-H, $J = 8.0$ Hz), 12.92 s (OH)	^{19}F NMR: 0.82 (2F), 13.16 and 22.46 (2F, each)
XVIII	1.35 t (3H, CH_3), 4.32 q (2H, CH_2), 5.94 br.s (CHCN), 7.87 m (2H, 6-H, 7-H), 7.68 d and 7.80 d (2-H, 3-H, $J = 8.5$ Hz), 8.21 d.d and 8.42 d.d (5-H, 8-H, $J = 7.5, 2.0$ Hz)	
XIX	1.46 s [$18\text{H}, 3',5'-(t\text{-Bu})_2$], 5.38 s (OH), 7.08 s (2H, 2'-H, 6'-H), 7.66 d and 7.73 d (2-H, 3-H, $J = 8.5$ Hz), 7.78 m (2H, 6-H, 7-H), 8.08 m and 8.20 m (5-H, 8-H)	
XX	1.45 s [$18\text{H}, 3',5'-(t\text{-Bu})_2$], 5.30 s (OH), 7.05 s (2H, 2'-H, 6'-H), 7.50 d and 7.70 d (2-H, 3-H, $J = 8.5$ Hz), 7.82 m (2H, 6-H, 7-H), 7.99 m and 8.21 m (5-H, 8-H)	

of 7:10. Apart from the products of nucleophilic substitution by pentafluorophenylacetonitrile anion, the mixture contained 10–15 mol% of 1-hydroxy-4-nitroanthraquinone (**XVI**). The formation of hydroxy derivatives may be explained by participation of the released nitrite ion and hydroxide ion of the base catalyst. Under similar conditions anthraquinone **II** is converted into product **XI** as a result of exclusive replacement of the fluorine atom.

The reaction of chloronitroanthraquinone **I** with ethyl cyanoacetate (**V**) in the presence of alkali metal hydroxide or potassium carbonate both at room temperature and at 45°C yields approximately equal amounts of products **XVII** and **XVIII** as a result of replacement of the chlorine atom and nitro group, respectively. 1-[(Cyano)ethoxycarbonylmethyl]-4-nitroanthraquinone (**XVII**) was obtained previously as the sole product of the reaction of fluoronitroanthraquinone **II** with the same nucleophile [4].

Mixtures containing both chlorine and nitro group substitution products were also obtained by reactions of anthraquinone **I** with the anion derived from 2,6-di-*tert*-butylphenol (**VI**). In this case, the replacement of chlorine was the predominant reaction pathway: the ratio of 4-nitro- and 4-chloroanthraquinones **XIX** and **XX** in the reaction mixtures was (5–6):1. The reaction was always accompanied by formation of hydroxynitroanthraquinone **XVI** (12–15 mol %).

The reaction of fluoronitroanthraquinone **II** with an equimolar amount of phenol **VI** in the presence of potassium hydroxide at $20\text{--}45^\circ\text{C}$ afforded a mixture of products, in which we identified by ^1H NMR spectroscopy compounds **XIX** and **XVI** and also initial reagent **VI**. No denitration product was detected, for ion peak with m/z 430 was not found in the mass spectrum and the ^1H NMR spectrum lacked signals from OH proton and 2-H and 6-H of hydroxyphenyl fragment, belonging to a compound other than **XIX**.

Presumably, the formation of product **XVI** in the reactions of **I** and **II** with anions derived from CH acids **IV** and **VI** is not the result of transformations of products **XI** and **XIX**; therefore, it does not affect the reactivity ratio of the chlorine atom and the nitro group in these processes.

Table 2 contains the ratios of products formed by replacement of the chlorine atom and the nitro group in 1-chloro-4-nitroanthraquinone, determined from the ^1H or ^{19}F NMR spectra, and the calculated HOMO energies, charges on the donor centers, and the corresponding orbital coefficients for carbanions. The results obtained previously for the reactions of anthraquinone **I** with phenylacetonitrile anion [3] and phenoxide and benzenethiolate ions [4] are also given for comparison. It is seen that the calculated parameters of malonodinitrile anion $(\text{CN})_2\text{CH}^-$, such as orbital coefficient c and others, are very similar to those of benzenethiolate ion PhS^- . Both these nucleophiles exhibit very high selectivity for replacement of the nitro group in **I**. On the other hand, the anion derived from 2,6-di-*tert*-butylphenol (**VI**) has the lowest (among those considered) orbital coefficient of the C^4 atom, and it preferentially replaces the chlorine atom in **I** (as in the case of PhO^- ion).

The highest selectivity for replacement of chlorine was observed for 4-nitrophenoxide ion which is characterized by low orbital coefficient of the oxygen atom in the HOMO and large energy difference between its HOMO and LUMO of substrate **I** (–1.78 eV) [4]. These parameters are unfavorable for orbital control of the reaction. However, the results obtained for $\text{C}_6\text{F}_5(\text{CN})\text{CH}^-$ (Table 2) contradict the above relation. Pentafluorophenylacetonitrile anion is characterized by a low orbital coefficient of the anionic center and low HOMO energy. Therefore, the reaction should be charge-controlled, and replacement of chlorine should predominate. Nevertheless, the selectivity of the reaction with $\text{C}_6\text{F}_5(\text{CN})\text{CH}^-$ is low: the ratio of substitution products Cl/NO_2 is 0.7. Probably, in this case other factors are responsible for the reaction output. One of these may be difference in steric requirements of carbanions. It is known that the cyano group is characterized by minimal steric requirements and that its effective size is similar to the size of CO_2R [8]. Then, the ratios of substitution products given in Table 2 for carbanions derived from malonodinitrile (**III**) and ethyl cyanoacetate (**V**) properly reflect the contribution of orbital interaction to the reaction with substrate **I**. The reactions with bulky $\text{C}_6\text{F}_5(\text{CN})\text{CH}^-$, $\text{Ph}(\text{CN})\text{CH}^-$, and probably 2,6-(*t*-Bu) $_2\text{C}_6\text{H}_3\text{O}^-$ ions involve some steric hindrances while accessing the reactive centers in

Table 2. Charges on the anionic centers (q), their orbital coefficients in the HOMO (c), and HOMO energies of nucleophiles (E_{HOMO} , eV) and Cl/NO_2 substitution ratios in reactions with anthraquinone **I**

Nucleophile	q	c	E_{HOMO}	Cl/NO_2
$(\text{CN})_2\text{CH}^-$	–0.51	0.80	–2.83	0.1
$\text{C}_6\text{F}_5\text{CH}(\text{CN})^-$	–0.36	0.58	–3.58	0.7
$\text{PhCH}(\text{CN})^-$	–0.38	0.67	–2.54	0.5 [3]
$\text{EtOCOCH}(\text{CN})^-$	–0.50	0.83	–3.26	1.0
2,6-(<i>t</i> -Bu) $_2\text{C}_6\text{H}_3\text{O}^-$	–0.30 ^a	0.56 ^a	–2.90	5.5
PhO^-	–0.53	0.44	–2.52	4.3 [4]
4- $\text{NO}_2\text{C}_6\text{H}_4\text{O}^-$	–0.45	0.34	–3.86	~10 [4]
PhS^-	–0.54	0.75	–2.63	0.15 [4]

^a C^4 atom.

anthraquinone **I**, and the product ratio changes. In particular, strong steric requirements for pentafluorophenylacetonitrile anion hinder its approach to the substrate to a distance ensuring effective Coulomb interaction with the C^4 atom attached to chlorine. On the other hand, orbital interaction with C^1 can occur at a longer distance; as a result, the nitro group is replaced mainly in the reaction with 2,6-di-*tert*-butylphenoxide ion.

We can conclude that nucleophilic substitution of the halogen or nitro group in 1,4-halonitroanthraquinones **I** and **II** is controlled by charge or orbital interactions, depending on the nucleophile structure. Naturally, a combination of steric and electronic factors could vary the type of predominant interaction and hence the predominant $\text{S}_{\text{N}}\text{Ar}$ reaction pathway of

Table 3. Melting points and molecular weights of compounds **VII**, **IX–XIV**, and **XVIII–XX**

Comp. no.	mp, °C	Formula	M	
			found	calculated
VII	200–203	$\text{C}_{17}\text{H}_7\text{N}_3\text{O}_4$	317.0430	317.0436
IX	>350	$\text{C}_{19}\text{H}_8\text{ClN}_3\text{O}_3$	329.0375	329.0356
X	>350	$\text{C}_{19}\text{H}_8\text{N}_4\text{O}_3$	340.0591	340.0596
XI	228–230	$\text{C}_{22}\text{H}_7\text{F}_5\text{N}_2\text{O}_4$	458.0325	458.0326
XII	193–195	$\text{C}_{22}\text{H}_7\text{ClF}_5\text{NO}_2$	447.0076	447.0085
XIII	>340	$\text{C}_{29}\text{H}_8\text{ClF}_{10}\text{NO}$	611.0127	611.0135
XIV	247–249	$\text{C}_{22}\text{H}_8\text{F}_5\text{NO}_3$	429.0436	429.0424
XVIII	57–59	$\text{C}_{19}\text{H}_{12}\text{ClNO}_4$	353.0458	353.0455
XIX	266–269	$\text{C}_{28}\text{H}_{27}\text{NO}_5$	457.1886	457.1889
XX	213–216	$\text{C}_{28}\text{H}_{27}\text{ClO}_3$	446.1653	446.1649

aromatic compounds with several possible leaving groups. An example can be obtained by comparing the mobilities of the *para*-chlorine and *meta*-fluorine atoms in substituted nitrobenzenes under the action of benzenethiolate and methoxide ions [9]. Reactions of 4-chloro-3-fluoro-5-X-nitrobenzenes with sodium benzenethiolate result exclusively in chlorine replacement, whereas charge-controlled reaction with hard methoxide ion involves both chlorine and fluorine atoms at a ratio depending on the 5-substituent. One more example of the nucleophile effect on the direction of fluorine replacement in perfluoroquinoline and perfluoroisquinoline is given in [10]: soft S-anions replace fluorine atoms in positions 4 and 6, while hard O-anions attack *ortho*-positions with respect to the nitrogen atom.

EXPERIMENTAL

The ^1H and ^{19}F NMR spectra of solutions in CDCl_3 were recorded on Bruker WP 200-SY and AC-200 spectrometers (200 MHz). The IR spectra were obtained in KBr on a UR-20 instrument. The UV spectra were measured on a Specord UV-Vis spectrophotometer. The elemental compositions were determined from the exact m/z values in the high-resolution mass spectra which were obtained on a Finnigan MAT spectrometer. The compositions of the reaction mixtures (mol %) were determined from the ^1H and ^{19}F NMR spectra.

Quantum-chemical calculations with full geometry optimization of planar structures were performed by the MNDO method (MNDO-92 program [11]).

Dimethylformamide of pure grade was dried over zeolite, DMSO of chemically pure grade was dried over zeolite and distilled under reduced pressure at 50–60°C. Compounds **III**–**VI** were commercial products which were used without additional purification. The synthesis of anthraquinones **I** and **II** was reported in [4, 5]. The spectra of hydroxyanthraquinones **XIV** and **XVI** were given in [12]. Table 3 contains the melting points and molecular weights of the newly synthesized compounds.

2-Amino-6-chloro-1,3-dicyanobenzanthrone (IX). To a solution of 0.45 mmol of anthraquinone **I** in 7 ml of DMSO we added 3.5 mmol of malonodinitrile (**III**) and 4.3 mmol of powdered potassium hydroxide. The mixture was stirred for 0.5 h at 50°C, diluted with 25 ml of water, refluxed for 1 h, cooled, and acidified with dilute hydrochloric acid. The precipitate was filtered off, washed with water, dried, and recrystallized from acetic acid. Yield 73%.

1-Dicyanomethyl-4-nitroanthraquinone (VII) and 2-amino-2,3-dicyano-6-nitrobenzanthrone (X). To a solution of 0.3–0.4 mmol of compound **II** and an equimolar amount of malonodinitrile in 6–10 ml of DMF we added excess (0.7–1.2 mmol) of freshly calcined potassium carbonate or powdered potassium hydroxide. The mixture was stirred for 2 or 0.5 h, respectively, at room temperature and poured into dilute hydrochloric acid. The precipitate, mp 200–203°C, was compound **VII**. An attempt to purify it by chromatography on silica gel resulted in formation of a complex mixture of products, which we failed to separate. The reaction of fluoronitroanthraquinone **II** with excess malonodinitrile under the conditions for synthesis of benzanthrones gave compound **X**. Found, %: N 16.47. $\text{C}_{19}\text{H}_8\text{N}_4\text{O}_3$. Calculated, %: N 16.46.

1-(α -Cyanopentafluorobenzyl)-4-nitroanthraquinone (XI). A mixture of anthraquinone **II** and pentafluorophenylacetonitrile (**IV**) (0.33 mmol each) in 4 ml of DMSO containing 2 mmol of potassium hydroxide was stirred for 30 min at room temperature and was then treated as described above for the synthesis of **VII**. We isolated 126 mg of almost pure compound **XI**. Tables 1 and 3 give the parameters of product **XI** after additional chromatographic purification on silica gel using benzene as eluent.

Reaction of anthraquinone I with pentafluorophenylacetonitrile (IV). Following the procedure described above for the reaction with anthraquinone **II**, from 0.68 mmol of **I** and 0.68 mmol of **IV** in the presence of excess KOH (3.3 mmol) we obtained 294 mg of a mixture containing (according to the ^1H and ^{19}F NMR data) compounds **XI** and **XII** at a ratio of 7:10. The products were separated by chromatography on silica gel. In some cases, the reaction mixture contained up to 10 mol % of 1-hydroxy-4-nitroanthraquinone (**XVI**). The reaction of equimolar amounts of **I** and **IV** in DMSO in the presence of sodium hydride in 5 h gave a complex mixture of products from which, apart from the major components, compounds **XIII**–**XV** were isolated.

4-Nitro- and 4-chloro-1-[cyano(ethoxycarbonyl)-methyl]anthraquinones XVII and XVIII obtained by reaction of **I** with ethyl cyanoacetate in DMF with potassium carbonate as a base (20 min, 45°C; yield 0.42 mmol) were separated first by column and then by thin-layer chromatography on silica gel using benzene as eluent.

1-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-4-nitroanthraquinone (XIX) and 1-chloro-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)anthraquinone (XX) obtained by reaction of equimolar amounts of anthraquinone **I** and phenol **VI** in the presence of potassium

hydroxide (1 h at room temperature or 20 min at 50°C) were separated by chromatography on silica gel using chloroform as eluent. Under the same conditions, the reaction of anthraquinone **II** with phenol gave 62% of compound **XIX**.

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