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Cycloaddition of 1-Aryl-3-trimethylsiloxy-1,3-butadienes in the Synthesis of Natural Quinone Analogs*

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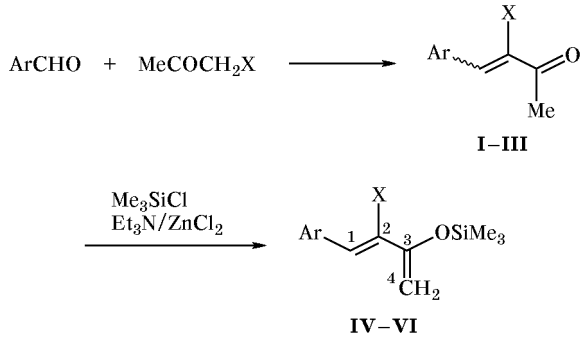
Abstract—7-Hydroxy-5-(2-methoxyphenyl)-2-methyl-6-R-1,4-naphthoquinones, 8-hydroxy-1-(2-methoxyphenyl)-3-oxo-1,2,3,4-tetrahydro-9,10-anthraquinone, and 2-ethoxycarbonyl-8-hydroxy-1-(2-methoxyphenyl)-3-trimethylsiloxy-1,1a,4,4a-tetrahydro-9,10-anthraquinone were synthesized by reactions of 1-(2-methoxyphenyl)-2-R-3-trimethylsiloxy-1,3-butadienes with 2-bromo-5-methyl-1,4-benzoquinone and juglone. 1-Aryl-2-ethoxycarbonyl-3-trimethylsiloxy-1,3-butadienes reacted with 1,4-naphthoquinone to afford 1-aryl-2-ethoxycarbonyl-3-hydroxy-9,10-anthraquinones and their 4,4a-dihydro derivatives.

Diversity of structures and accessibility of siloxybutadienes in combination with their high reactivity and regioselectivity toward various dienophiles in the Diels–Alder reaction make them important synthons [1, 2]. Of particular interest is the use of siloxybutadienes in the synthesis of natural quinones and their analogs exhibiting important biological activity [1, 3, 4].

The present communication is an extension of our studies on the synthesis of quinoid compounds which are potential antiviral and cytostatic agents. As previously [5, 6], the synthesis of such compounds is based on the Diels–Alder reaction of 1-substituted 3-trimethylsiloxy-1,3-butadienes with quinones. The structure of the diene component allowed us to introduce into the target products 2-$MeOC_6H_4$ and 2,3-$(MeO)_2C_6H_3$ fragments which are intrinsic to a number of naturally occurring compounds of the phenol and quinone series [3]. The initial siloxydienes were obtained by the known procedure [5, 6]. Crotonization of acetone and ethyl acetoacetate with benzaldehydes [7] gave 74–78% of α,β-unsaturated ketones **I**–**III** (Scheme 1). Ketones **II** and **III** were isolated as mixtures of *Z* and *E* isomers at a ratio of 1.6:1. Ketones **I**–**III** were treated with chlorotrimethylsilane in the presence of anhydrous zinc(II) chloride and triethylamine under argon to obtain 1-aryl-3-trimethylsiloxy-1,3-butadienes **IV**–**VI** in 55, 50, and 28% yield, respectively. Dienes **IV**–**VI** are high-boiling liquids which are stable under argon but undergo fast hydrolysis on exposure to atmospheric moisture. Table 1 contains the ^1H and ^{13}C NMR spectra of compounds **I**–**VI**.

Scheme 1.



I, **IV**, Ar = 2-$MeOC_6H_4$, X = H; **II**, **V**, Ar = 2-$MeOC_6H_4$, X = CO_2Et; **III**, **VI**, Ar = 2,3-$(MeO)_2C_6H_3$, X = CO_2Et.

In the reactions of siloxybutadienes **IV** and **V** with 2-bromo-5-methyl-1,4-benzoquinone in boiling benzene the only products were naphthoquinones **VII** and **VIII** which were isolated in 35–40% yield (Scheme 2). Under similar conditions diene **IV** reacted with juglone **IX** with formation of tetrahydroanthraquinone **X** in 47% yield (Scheme 3). In contrast to

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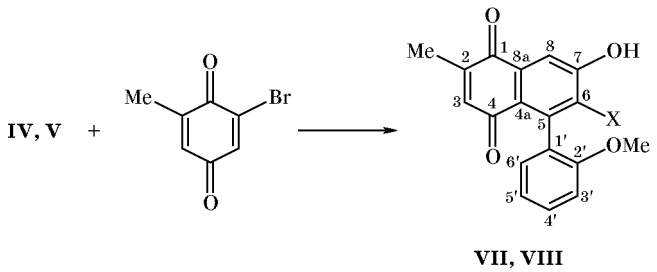
Scheme 2.



VII, VIII

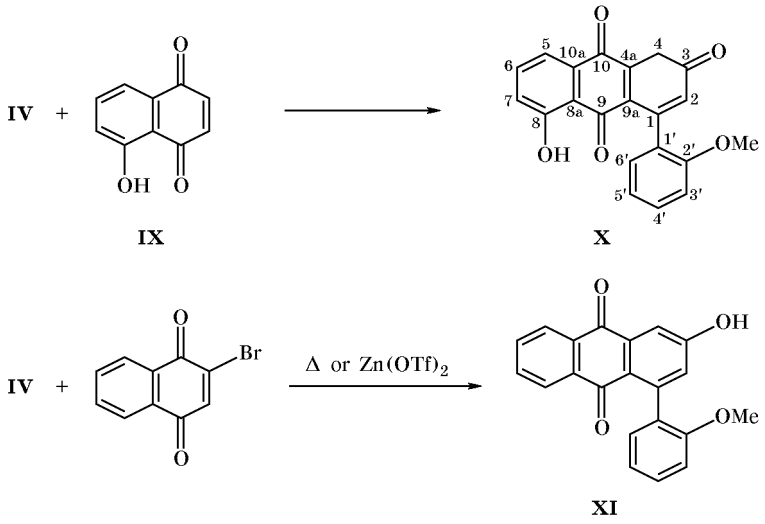
VII, X = H; **VIII**, X = CO_2Et.

our previous data [5], we failed to isolate the primary adduct. Dehydrogenation is possible both by the action of atmospheric oxygen and by the action of juglone. The reaction of 2-bromonaphthoquinone with diene **IV** is accompanied by dehydrobromination and yields 36% of the expected arylanthraquinone **XI**. When the reaction was performed at room temperature in the presence of 0.5 equiv of $Zn(OTf)_2$ (Tf = trifluoromethylsulfonyl) [8], anthraquinone **XI** was isolated in 44% yield by column chromatography.

Diene **V** reacted with juglone (**IX**) in benzene under reflux (Scheme 4). The reaction was regioselective; unlike preceding experiment, we succeeded in isolating primary adduct **XII** in 66% yield. By column chromatography of the residue on silica gel we isolated anthraquinone derivatives **XIII** and **XIV** in 10 and 7% yield, respectively. In boiling benzene in the presence of $Eu(fod)_3$ (fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octadionate) as catalyst anthraquinone **XIV** becomes the predominant product (yield 51%). In this case dihydroanthraquinone **XIII** is formed in 19% yield. Treatment of siloxy ester **XII** with methanol leads to formation of enol **XV** which was detected by ^1H NMR spectroscopy. The reaction of **XII** with potassium carbonate in methanol (reaction time 2 h) results in dehydrogenation with formation of 85% of dihydroanthraquinone **XIII**. We also failed to isolate primary adduct of diene **V** and naphthoquinone **XVI** (in benzene under reflux); by column chromatography on silica gel we isolated compounds **XVII** and **XVIII** in 18 and 25% yield, respectively. By addition of diene **VI** to naphthoquinone **XVI** we succeeded in isolating anthraquinone derivatives **XIX** and **XX** in 32 and 8% yield, respectively. Previously [6], we detected neither primary siloxy adduct nor tetrahydroanthraquinone in the reactions of 2-ethoxycarbonyl-1-(4-methoxyphenyl)-3-trimethylsiloxy-1,3-butadiene with 1,4-quinones. The yields, IR and UV spectra, and elemental analyses of naphthoquinones **VII** and **VIII** and anthraquinones **X**–**XIV** and **XVII**–**XX** are given in Table 2.

The structure of the newly synthesized naphtho- and anthraquinone derivatives was deduced from the ^1H and ^{13}C NMR spectra (Tables 3, 4). Mutual arrangement of the aryl substituent and methyl group (in compounds **VII** and **VIII**) or hydroxy group (in **XIV**) was determined on the basis of multiplicities of signals from the carbonyl carbon atoms in the ^{13}C NMR spectra. The following data were obtained for naphthoquinone **VIII**: C^1, δ_C 183.5 ppm, d.d, $^3J(C^1–3\text{-H})$ = 5.4, $^3J(C^1–8\text{-H})$ = 3.5 Hz; C^4, δ_C 183.9 ppm, d, $^2J(C^4–3\text{-H})$ = 4.4 Hz. It is known that the constant $^3J(C^1–3\text{-H})$ in naphthoquinone fragment is the greatest, as compared to $^3J(C^1–8\text{-H})$ and $^2J(C^4–3\text{-H})$; it ranges from 6 to 7.5 Hz [9]. These

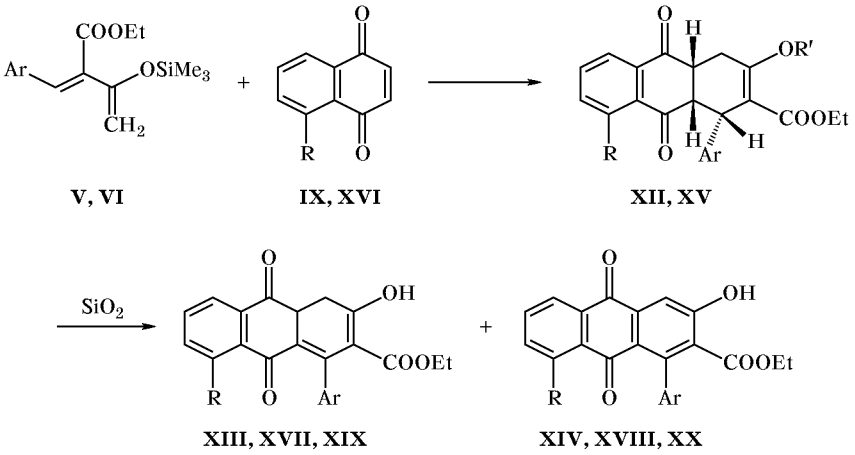
Scheme 3.



IX **X**

XI

Scheme 4.



V, VI **IX, XVI** **XII, XV**

XIII, XVII, XIX **XIV, XVIII, XX**

V, **XII**, **XIII**, **XIV**, **XV**, Ar = 2-$MeOC_6H_4$; **VI**, **XIX**, **XX**, Ar = 2,3-$(MeO)_2C_6H_3$; **IX**, **XII**, **XIII**, **XIV**, **XV**, R = OH; **XVI**, **XVII**, **XVIII**, **XIX**, **XX**, R = H; **XII**, R′ = $SiMe_3$; **XV**, R′ = H.

findings indicate that the methyl group in naphthoquinone **VIII** occupies position *2* rather than *3*.

In the ^{13}C NMR spectrum of anthraquinone **XIV** the carbonyl carbon signal (C^9) is displaced downfield (δ_C 187.5 ppm), and the C^{10} atom gives a signal at δ_C 182.1 ppm. The downfield shift of the C^9 signal is caused by the effect of the hydroxy group in position *8* ($\Delta\delta_C$ 5.4 ppm for C^9 and –0.7 ppm for C^{10}) [10]. The signal at δ_C 187.5 ppm (C^9) is a singlet, and that at δ_C 182.1 ppm (C^{10}) is a triplet with the coupling constants $^3J(C^{10}$–4-H) = 3.4 Hz and $^3J(C^{10}$–5-H) = 3.4 Hz. The ^3J values coincide with the known data (3–4.5 Hz [9]), and the signal multiplicities indicate that the OH and Ar substituents occupy positions *1* and *8*. Likewise, the carbonyl carbon (C^9) signal in the spectrum of tetrahydroanthraquinone **X** is displaced downfield (δ_C 190.1 ppm), the C^{10} signal is observed at δ_C 184.0 ppm, and unconjugated carbonyl group (C^3) is characterized by a chemical shift δ_C of 204.8 ppm. In the monoresonance spectrum of **X** the signal at δ_C 184.0 ppm (C^{10}) is split due to coupling with 5-H, 4α-H, and 4β-H; it appears as a broadened multiplet with a more complex structure than that of the multiplet signal at δ_C 190.1 ppm (C^9). These data allowed us to locate the OH and Ar substituents at positions *1* and *8*, respectively.

The ^{13}C NMR spectra of dihydroanthraquinones **XVII** and **XIX** should be characterized by more upfield signal from the conjugated carbonyl group (C^9, δ_C 182.4–182.9 ppm), as compared to the C^{10} signal (δ_C 184.0–185.2 ppm). Using the increments for hydroxy group (see above), we obtained with a good accuracy the experimental chemical shifts of C^9 and C^{10} in compounds **XIII** and **XIV**. In keeping with the monoresonance spectrum of **XI**, the downfield signal belongs to the carbonyl carbon atom C^{10}, and the upfield signal, to C^9. The signal at δ_C 183.8 ppm is a triplet with the coupling constants $^3J(C^{10}$–4-H) = 3.7 and $^3J(C^{10}$–5-H) = 3.7 Hz; it corresponds to C^{10}. The signal at δ_C 182.2 ppm (C^9) is a doublet with $^3J(C^9$–8-H) = 3.4 Hz.

EXPERIMENTAL

The IR spectra were recorded on a Specord M-80 spectrometer in KBr. The UV spectra were measured from solution in ethanol ($c = 10^{-4}$ M) using a Specord UV-Vis spectrophotometer. The ^1H NMR spectra were obtained on a Bruker WP-200SY instrument at 200.2 MHz. The ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer (50.323 MHz) in the JMOD and monoresonance modes; samples were prepared as 5–10% solutions in $CDCl_3$ or $(CD_3)_2CO$. The solvent signal was used as reference. The progress of reactions was monitored by TLC on Silufol UV-254 plates in the system chloroform–methanol (20 : 1); spots were visualized in UV light or with ammonia vapor. Column chromatography was performed on KSK silica gel (0–140) using chloroform and chloroform–methanol (100 : 1, 50 : 1, and 20 : 1) as eluent. Zinc(II) trifluoromethanesulfonate was synthesized by the procedure described in [11].

4-Aryl-3-buten-2-ones I–III. Ketone **I** was synthesized from acetone and 2-methoxybenzaldehyde under conditions corresponding to aldol condensation

Table 1. ^1H and ^{13}C NMR spectra of ketones **I**–**III** and siloxydienes **IV**–**VI** in $CDCl_3$

Comp. no.	^1H NMR spectrum, δ, ppm (*J*, Hz)	^{13}C NMR spectrum, δ_C, ppm
I	2.28 s (3H, MeCO), 3.89 s (3H, OMe), 6.57 d (1H, CH=, 16.5), 6.84 d (1H, 3′-H, 8), 6.84 d (1H, 4′-H, 8), 7.26 t.d (1H, 5′-H, 8, 1.5), 7.49 d.d (1H, 6′-H, 8, 1.5), 7.70 d (1H, CH=, 16.5)	
II[a]	1.19 t (*Z*-Me), 1.33 t (*E*-Me), 2.17 s (*E*-MeCO), 2.32 s (*Z*-MeCO), 3.86 s (3H, OMe), 4.18 q (*Z*-CH_2), 4.25 q (*E*-CH_2), 6.84 m (2H, H_{arom}), 7.27 m (2H, H_{arom}), 7.75 br.s (1H, CH=)	13.9 q (*Z*-Me), 14.2 q (*E*-Me), 26.4 q (*Z*-C^1), 30.6 q (*E*-C^1), 55.0 q (*E*-OMe), 55.2 q (*Z*-OMe), 60.7 t (CH_2), 110.5 d ($C^{3'}$), 120.4 d (*Z*-$C^{6'}$), 120.5 d (*E*-$C^{6'}$), 122.5 s (*E*-C^3), 122.7 s (*Z*-C^3), 129.2 d and 131.6 d (*Z*-$C^{4'}$, $C^{5'}$), 130.2 d and 131.4 d (*E*-$C^{4'}$, $C^{5'}$), 134.1 s (*E*-$C^{1'}$), 134.6 s (*Z*-$C^{1'}$), 135.8 d (*E*-C^4), 136.2 d (*Z*-C^4), 157.5 s (*E*-$C^{2'}$), 157.8 s (*Z*-$C^{2'}$), 164.0 s (*E*-CO_2), 167.0 s (*Z*-CO_2), 193.0 s (*Z*-C^2), 200.0 s (*E*-C^2)
III[a]	1.19 t (*Z*-Me), 1.32 t (*E*-Me), 2.33 s (*Z*-MeCO), 2.18 s (*E*-MeCO), 3.79 s, 3.81 s, 3.82 s (2OMe), 4.16 q (*Z*-CH_2), 4.24 q (*E*-CH_2), 7.71 s (*Z*-CH=), 7.73 s (*E*-CH=), 6.88 m (3H, H_{arom})	13.8 q (*Z*-Me), 14.1 q (*E*-Me), 26.5 q (*Z*-C^1), 30.8 q (*E*-C^1), 55.7 q and 60.9 q (2OMe), 61.1 t (CH_2), 114.1 s (*Z*-$C^{4'}$), 114.6 s (*E*-$C^{4'}$), 120.7 d and 123.8 d (*Z*-$C^{5'}$,$C^{6'}$), 121.4 d and 123.9 d (*E*-$C^{5'}$, $C^{6'}$), 127.5 s (*Z*-C^3), 127.8 s (*E*-C^3), 135.0 s (*E*-$C^{1'}$), 135.6 s (*Z*-$C^{1'}$), 136.1 d (*Z*-C^4), 136.7 d (*E*-C^4), 148.5 s and 152.6 s ($C^{2'}$, $C^{3'}$), 164.2 s (*Z*-CO_2), 167.2 s (*E*-CO_2), 194.1 s (*Z*-C^2), 200.1 s (*E*-C^2)
IV	0.27 s (9H, Me_3SiO), 3.85 s (3H, OMe), 4.35 s and 4.40 s (2H, CH_2=), 6.57 d (1H, CH=, 15.5), 6.84 m (2H, H_{arom}), 7.08 d (1H, CH=, 15.5), 7.17 m (1H, H_{arom}), 7.41 m (1H, H_{arom})	0.2 s (Me_3SiO), 53.3 q (OMe), 96.4 t (C^4), 110.8 d ($C^{3'}$), 120.8 d ($C^{6'}$), 124.8 s (C^2), 126.0 s ($C^{1'}$), 126.8 d and 127.1 d ($C^{4'}$, $C^{5'}$), 128.5 d (C^1), 155.6 s (C^3), 157.1 s ($C^{2'}$)
V	0.26 s (9H, Me_3SiO), 1.08 t (3H, Me), 3.77 s (3H, OMe), 4.10 q (2H, CH_2), 4.41 s and 4.50 s (2H, CH_2=), 6.81 m (2H, H_{arom}), 7.19 s (1H, CH=), 7.19 m (2H, H_{arom})	–0.1 s (Me_3SiO), 13.7 q (Me), 55.1 q (OMe), 60.5 t (CH_2), 94.9 t (C^4), 110.2 d ($C^{3'}$), 120.1 d ($C^{6'}$), 124.6 s (C^2), 125.5 d (C^1), 128.4 d and 129.3 d ($C^{4'}$, $C^{5'}$), 132.6 s ($C^{1'}$), 152.6 s (C^3), 157.1 s ($C^{2'}$), 168.3 s (CO_2)
VI	0.24 s (9H, Me_3SiO), 1.08 t (3H, Me), 3.65 s and 3.85 s (6H, 2OMe), 4.07 q (2H, CH_2), 4.41 s and 4.49 s (2H, CH_2=), 6.84 m (3H, H_{arom}), 7.14 s (1H, CH=)	

[a] *Z*/*E* ratio 1.6 : 1.

(crotonization); ketones **II** and **III** were obtained from ethyl acetoacetate and 2-methoxy- or 2,3-dimethoxybenzaldehyde, respectively, according to Knoevenagel (Cope modification) [7]. The products, *E* isomer of **I** and *Z*/*E* isomeric mixtures of **II** and **III**, were isolated in 74, 76, and 78% yield, respectively; bp 107–112 (1 mm), 145–146 (2 mm), and 161–163°C (3 mm).

1-Substituted 3-trimethylsiloxy-1,3-butadienes IV–VI. To a suspension of 5 mmol of anhydrous $ZnCl_2$ and 19 ml of triethylamine, heated to 80°C, we added with stirring under argon a solution of 50 mmol of ketone **I**–**III** in 30 ml of anhydrous acetonitrile and then 18.9 ml of chlorotrimethylsilane. The mixture was stirred for 5 h at 50°C and cooled, 250 ml of dry diethyl ether was added, and the precipitate was filtered off. The filtrate was evaporated under reduced pressure (water-jet pump), and the residue was treated with 100 ml of dry diethyl ether (as above). The solvent was removed, and the residue was distilled under reduced pressure. Compound **IV**: yield 55%, bp 96–

Table 2. Yields, melting points, IR and UV spectra, and elemental analyses of naphthoquinones **VII** and **VIII** and anthraquinones **X**–**XIV** and **XVII**–**XX**

Comp. no.	Yield, %	mp, °C	IR spectrum, ν, cm^{-1}	UV spectrum, λ_{max}, nm (log ε)	Found, %		Formula	Calculated, %	
					C	H		C	H
VII	40	134–136 (decomp.)	3400, 1650, 1595, 1560, 1345, 1250	267 (4.34), 374 (3.41)	73.0	4.5	$C_{18}H_{14}O_4$	73.4	4.8
VIII	35	155–157	3425, 1650, 1560, 1350, 1240, 1220	269 (4.44), 381 (3.32)	68.1	5.0	$C_{21}H_{18}O_6$	68.8	4.9
X	47	213–215	3450, 1715, 1640, 1615, 1485, 1450, 1275, 1240	275 (4.11), 420 (3.57), 517 (3.16), 719 (2.71)	72.0	4.8	$C_{21}H_{16}O_5$	72.4	4.6
XI	36	264–266	3365, 1669, 1591, 1558, 1361, 1293	245 (4.50), 372 (3.51)	76.5	4.2	$C_{21}H_{14}O_4$	76.4	4.3
XII	66	155–159	3400, 1680, 1645, 1450, 1365, 1245, 840	233 (4.32), 352 (3.61)	65.4	6.1	$C_{27}H_{30}O_7Si$	65.6	6.1
XIII	10	198–200	3425, 1650, 1610, 1450, 1310, 1275, 1245, 1210	251 (4.30), 422 (3.64), 661 (2.30)	68.5	4.7	$C_{24}H_{20}O_7$	68.6	4.8
XIV	7	230–235	3400, 1640, 1560, 1455, 1455, 1225	272 (4.30), 409 (3.69)	68.6	4.7	$C_{24}H_{18}O_7$	68.9	4.3
XVII	18	168–172	3430, 1660, 1610, 1325, 1290, 1275, 1245, 1210	250 (4.30), 340 (3.48), 530 (2.70)	71.0	4.9	$C_{24}H_{20}O_6$	71.3	5.0
XVIII	25	205–208	3425, 1660, 1590, 1460, 1340, 1250	270 (4.30), 390 (3.65)	71.3	4.2	$C_{24}H_{18}O_6$	71.6	4.5
XIX	34	152–155	3440, 1675, 1660, 1300, 1280, 1250, 1225	250 (4.48), 334 (3.52), 523 (2.72)	69.0	5.0	$C_{25}H_{22}O_7$	69.1	5.1
XX	17	184–188	3425, 1670, 1660, 1590, 1460, 1340, 1250	272 (4.04), 370 (3.38)	69.1	4.8	$C_{25}H_{20}O_7$	69.4	4.6

100°C (1 mm); **V**: yield 50%, bp 133–134°C (3 mm); **VI**: yield 28%, bp 158–164°C (2 mm). According to the ^{1}H NMR data, diene **VI** contained 20% of ketone **III**.

Reactions of siloxydienes IV–VI with 2-bromo-5-methyl-1,4-benzoquinone, 2-bromo-1,4-naphthoquinone, juglone (IX), and 1,4-naphthoquinone (XVI). *a*. A solution of 2–3.5 mmol of 2-bromo-5-methyl-1,4-benzoquinone, 2-bromo-1,4-naphthoquinone, juglone (**IX**), or 1,4-naphthoquinone (**XVI**) and 1.1–1.5 equiv of diene **IV**–**VI** in 20 ml of benzene was refluxed for 14–26 h under argon. The solvent was distilled off on a rotary evaporator, and the residue was ground with diethyl ether to isolate primary adduct **XII** or unchanged quinone **XVI**. The products were isolated from the filtrate by column chromatography. Compounds **VII**–**XI** and **XVII**–**XIX** were recrystallized from diethyl ether, and **XII**–**XIV**, from diethyl ether–hexane (1 : 2).

b. A suspension of 2 mmol of 2-bromo-1,4-naphthoquinone, 3 mmol of diene **IV**, and 1 mmol of zinc(II) trifluoromethanesulfonate in 15 ml of CH_2Cl_2 was stirred for 3 days at room temperature. The mixture was treated with 10 ml of 1 N HCl in THF and with chloroform (3 × 10 ml), washed with a saturated aqueous solution of NaCl (3 × 10 ml), and evaporated under reduced pressure. Column chromatography of the residue gave anthraquinone **XI** in 44% yield.

Table 3. ^{1}H NMR spectra of naphthoquinones **VII** and **VIII** and anthraquinones **X**–**XV** and **XVII**–**XX** in $CDCl_3$

Comp. no.	Chemical shifts δ, ppm (*J*, Hz)
VII	2.03 s (3H, Me), 3.67 s (3H, OMe), 6.73 s (1H, 3-H), 6.90 d (1H, 6-H), 6.91 d (1H, 3′-H), 7.00 t (1H, 4′-H), 7.08 d.d (1H, 6′-H), 7.34 t (1H, 5′-H), 7.54 d (1H, 8-H), 11.04 s (1H, OH)
VIII	0.75 t (3H, **Me**CH_2), 2.00 s (3H, Me), 3.68 s (3H, OMe), 3.93 q (3H, MeC**H**$_2$), 6.75 s (1H, 3-H), 6.90 m (3H, 3′-H, 4′-H, 6′-H), 7.35 m (1H, 5′-H), 7.67 s (1H, 8-H), 11.04 s (1H, OH)
X[a]	2.65 d.t (1H, 2α-H, $J_{2\alpha,1}$ = 1.5, $J_{2\alpha,2\beta}$ = 14.5, $J_{2\alpha,4\alpha}$ = 1.5), 3.05 d.d (1H, 2β-H, $J_{2\beta,2\alpha}$ = 14.5, $J_{2\beta,1}$ = 7), 3.35 d.t (1H, 4α-H, $J_{4\alpha,2\alpha}$ = 1.5, $J_{4\alpha,1}$ = 1.5, $J_{4\alpha,4\beta}$ = 23), 3.60 d (1H, 4β-H, $J_{4\beta,4\alpha}$ = 23), 3.85 s (3H, OMe), 5.18 d.t (1H, 1-H, $J_{1,2\alpha}$ = 1.5, $J_{1,2\beta}$ = 7, $J_{1,4\alpha}$ = 1.5), 6.82 m (1H, H_{arom}), 7.01 m (1H, H_{arom}), 7.23 m (2H, H_{arom}), 7.23 (2H), 7.28 (1H), 11.96 s (1H, OH)
XI[a]	3.66 s (3H, OMe), 7.01 m (2H, H_{arom}), 7.01 m (1H, 2-H), 7.14 m (1H, H_{arom}), 7.38 m (1H, H_{arom}), 7.68 m (2H, 6-H, 7-H), 7.79 m (1H, 4-H), 8.10m and 8.22 m (2H, 5-H, 8-H), 11.96 s (1H, OH)
XII	0.36 s (9H, Me_3SiO), 0.99 t (3H, **Me**CH_2), 2.40 d.d (1H, 4β-H, 18, 8), 3.21 d.d (1H, 4β-H, 18, 8), 3.56 m (2H, 9a-H, 4a-H), 3.78 s (3H, OMe), 3.96 q (3H, MeC**H**$_2$), 5.00 d (1H, 1-H, 5), 6.12 m (1H, 3′-H), 6.52 m (1H, 4′-H), 6.80 m (2H, 5′-H, 6′-H), 7.00 m (2H), 7.28 m (1H), 11.88 s (1H, 8-OH)
XIII	1.22 t (3H, **Me**CH_2), 3.60 d.d (2H, 4-H, 9, 4), 3.71 s (3H, OMe), 4.12 k (3H, MeC**H**$_2$), 5.30 d.d (1H, 4a-H, 4, 5), 6.80 m (2H, H_{arom}), 7.17 m (1H, H_{arom}), 7.17 m (1H), 7.53 m (1H, H_{arom}), 7.53 m (2H), 11.96 s (1H, 3-OH), 12.48 s (1H, 8-OH)
XIV	0.90 t (3H, **Me**CH_2), 3.65 s (3H, OMe), 3.91 q (3H, **Me**CH_2), 6.96 m (2H, H_{arom}), 7.25 m (2H, H_{arom}), 7.34 m (1H), 7.73 m (1H), 7.83 m (1H), 7.94 s (1H, 4-H), 12.54 s (1H, 3-OH), 13.67 s (1H, 8-OH)
XV	1.09 t (3H, **Me**CH_2), 2.68 d.d (1H, 4α-H, 18, 8), 2.71 d.d (1H, 4β-H, 18, 8), 3.49 s (3H, OMe), 3.60 m (2H, 9a-H, 4a-H), 3.99 q (3H, MeC**H**$_2$), 4.81 d (1H, 1-H, 5), 6.25 m (1H, H_{arom}), 6.50 m (1H, H_{arom}), 6.86 m (2H, H_{arom}), 7.02 m (2H), 7.49 m (1H), 11.95 s (1H, 3-OH), 12.52 s (1H, 8-OH)
XVII	1.21 t (3H, **Me**CH_2), 3.61 d.d (2H, 4-H, 10, 4), 3.70 s (3H, OMe), 4.11 q (3H, MeC**H**$_2$), 5.32 d.d (1H, 4a-H, 5, 3.5), 6.74 m and 6.90 m (2H, H_{arom}), 7.13 m (1H, H_{arom}), 7.46 m (1H, H_{arom}), 7.65 m (2H), 8.00 m (2H), 12.47 s (1H, 3-OH)
XVIII	0.90 t (3H, **Me**CH_2), 3.64 s (3H, OMe), 3.90 q (3H, MeC**H**$_2$), 6.64 m (2H, H_{arom}), 7.05 m (2H, H_{arom}), 7.10 m (1H), 7.83 m (1H), 8.00 s (1H, 4-H), 8.10 m (1H), 11.40 s (1H, 3-OH)
XIX	1.22 t (3H, **Me**CH_2), 3.60 d.d (2H, 4-H, 7, 4), 3.66 s and 3.75 s (6H, 2OMe), 4.13 q (3H, MeC**H**$_2$), 5.24 d.d (1H, 4a-H, 4, 5.5), 6.76 m (1H, 4′-H), 6.96 m (1H, 5′-H), 7.13 m (1H, 6′-H), 7.60 m (2H, 6-H, 7-H), 7.95 m (2H, 5-H, 8-H), 12.48 s (1H, 3-OH)
XX[a]	0.94 t (3H, **Me**CH_2), 3.60 s and 3.91 s (6H, 2OMe), 4.00 q (3H, MeC**H**$_2$), 7.09 m (3H, H_{arom}), 7.83 m (2H), 8.00 s (1H, 4-H), 8.18 m (2H), 11.38 s (1H, 3-OH)

[a] In acetone-d_6.

Table 4. ^{13}C NMR spectra of naphthoquinones **VII** and **VIII** and anthraquinones **X**–**XIV** and **XVII**–**XX** in $CDCl_3$[a]

Atom no.	Chemical shifts δ_C, ppm										
	VII	**VIII**	**X**	**XI**	**XII**	**XIII**	**XVII**	**XIX**	**XIV**	**XVIII**	**XX**
C^1	184.3	183.5	36.3	143.3	43.9	142.6	142.8	143.0	148.8	143.5	143.5
C^{9a}	130.4	129.7	127.8	125.9	51.8	128.5	128.8	133.9	123.7[b]	123.5[b]	123.5[b]
C^2	150.3	151	44.5	125.4	117.7	97.9	98.1	98.4	120.2[b]	122.0[b]	122.0[b]

Table 4. (Contd.)

Atom no.	Chemical shifts δ_C, ppm										
	VII	**VIII**	**X**	**XI**	**XII**	**XIII**	**XVII**	**XIX**	**XIV**	**XVIII**	**XX**
C^3	133.6	133.5	204.8	162.1	158.9	168.6	168.7	168.7	164.2[c]	157.3	157.3
C^4	185.7	183.9	38.0	113.0	28.2	29.5	29.3	29.3	116.3	118.5	118.5
C^{4a}	123.8	123	145.5	132.3[b]	54.3	38.1	38.4	38.9	130.1	133.4	133.4[c]
C^5	142.7	143.6	124.8	129.3	122.1	124.2	128.0[b]	126.0[b]	124.7	126.9[c]	126.9[d]
C^{10a}			134.3	133.8[b]	133.3	131.7	131.7[c]	131.7[c]	132.7	134.9[d]	134.9[e]
C^6	124	120.4	137.4	134.0[c]	135.7	135.8	133.2[d]	133.4[d]	135.6	135.5[e]	135.5[f]
C^7	159.6	163.7	119.5	135.0[c]	116.6	118.7	133.2[d]	133.3[d]	118.8	134.8[e]	134.8[f]
C^8	112.3	115.1	162.3	129.6	160.3	161.3	128.1[b]	126.4[b]	162.2[c]	127.4[c]	127.4[d]
C^{8a}			116.9	135.8[b]	111.4	114.9	132.1[c]	132.0[c]	117.1	135.3[d]	135.3[e]
C^9			190.1	182.2	204.4	188.4	182.8	182.9	187.5	182.4	182.4
C^{10}			184.0	183.8	194.0	183.3	184.0	184.0	182.1	185.2	185.2
CO_2Et		169.8			165.5	171.2	171.2	171.2	169.8	167.2	167.2
Me**C**H_2		62.0			59.7	60.4	60.5	60.6	62.0	62.1	62.1
MeCH_2		12.9			13.9	13.6	13.8	13.9	12.9	13.9	13.9
OMe	55.3	55.4	55.6	55.7	54.3	55.5	55.5	55.4 56.0	55.5	55.5	56.1 60.0
$C^{1'}$	135.2	138.6	146.7	137.52	126.0	140.8	139.4	139.4	138.6	139.4	133.9[c]
$C^{2'}$	156	156.8	157.7	157.4	156.8	157.8	157.8	148.1[d]	156.8	157.8	153.3[g]
$C^{3'}$	110.4	109.9	112.1	111.5	108.2	111.1	111.1	152.4[d]	109.9	111.1	149.1[g]
$C^{4'}$	128.7[b]	127.9[b]	129.0[b]	127.0[d]	128.5[b]	128.3[b]	129.5[e]	111.2	127.9[d]	129.5[e]	113.5
$C^{5'}$	128.9[b]	128.6[b]	129.5[b]	127.4[d]	130.6[b]	133.3[b]	126.5[e]	125.5	128.6[d]	126.5[e]	126.6[h]
$C^{6'}$	120.7	120.4	121.4	121.29	119.3	120.1	120.1	122.7	120.4	120.1	124.1[h]

[a] The spectra of compounds **X**, **XI**, and **XX** were recorded in acetone-d_6; δ_C(2-Me), ppm: 16.8 (**VII**), 17.0 (**VIII**); $\delta_C(Me_3SiO)$ 0 ppm.

[b–h] Alternative assignment is possible (within a single column).

c. By reaction of 2.21 mmol of juglone (**IX**) and 2.44 mmol of diene **V** in 20 ml of benzene containing 0.12 mmol of $Eu(fod)_3$ as catalyst (reaction time 26 h) we obtained compounds **XIII** (yield 19%) and **XIV** (yield 51%).

2-Ethoxycarbonyl-3,8-dihydroxy-1-(2-methoxyphenyl)-1,4,4a,9a-tetrahydro-9,10-anthraquinone (XV). A 50-mg portion of compound **XII** was dissolved in 5 ml of methanol, and the solution was evaporated. According to the ^{1}H NMR data, the residue was a mixture of compounds **XV** and **XII** at a ratio of 9:1.

Alkaline treatment of compound XII. To 102 mg of compound **XII** we added 10 ml of methanol and 5 mg of K_2CO_3, and the mixture (which turned green) was stirred for 2 h. The finely crystalline precipitate was filtered off. Yield of compound **XIII** 73 mg (84%). According to the ^{1}H NMR data, the filtrate contained a mixture of compounds **XIII** and **XV** at a ratio of 3:2.

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