Alkoxylation of 3,6-Di-*tert*-butyl-1,2-benzoquinone. New Bis-1,2-benzoquinones

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> > Received July 13, 2010

Abstract—Alkoxylation of 3,6-di-*tert*-butyl-1,2-benzoquinone with a number of diols, including propane-1,3diol, butane-1,4-diol, di-, and triethylene glycols, and cyclohexane-1,4-diyldimethanol, was studied. Nine new 4-alkoxy-3,6-di-*tert*-butyl-1,2-benzoquinones were synthesized, four of which were bis-1,2-benzoquinones with different tethers (6–13 atoms) between the quinone fragments. Depending on the length of the chain between the hydroxy groups in glycols, bicyclic 4,5-disubstituted 3,6-di-*tert*-butyl-1,2-benzoquinones were formed or their stepwise alkoxylation occurred. The newly synthesized *o*-benzoquinone derivatives can be reduced with alkali metals to give radical anions and converted into semiquinone chelates with manganese carbonyl.

DOI: 10.1134/S1070428011040038

Interest in sterically hindered *o*-benzoquinones is determined by their wide application as precursors in the synthesis of organometallic compounds [1]. 3,6-Ditert-butyl-1,2-benzoquinone (I) and its derivatives are capable of undergoing one- and two-electron reduction with formation of o-semiguinone radical anion and pyrocatechol dianion [2]. These species are observed in coordination compounds with metals, depending on the ratio of the redox parameters of o-quinone and metal. Functionalization of o-benzoquinone with a view to vary their redox properties can be performed in several ways. Like most conjugated unsaturated ketones, the most typical reaction of 3,6-di-tert-butyl-1,2-benzoquinone is nucleophilic 1,4-addition [3]. Various reagents may be used as nucleophiles: organometallic compounds [4], alcohols [5], primary and secondary amines [6, 7], CH acids [8, 9]. New sterically hindered *o*-benzoquinones can be synthesized via nucleophilic replacement from 4-substituted 3,6-di*tert*-butyl-1,2-benzoquinones. For example, fluoro [10], sulfur-containing [11], and alkoxy derivatives [5] of 3,6-di-*tert*-butyl-1,2-benzoquinone were obtained in such a way. In the recent time, polyfunctional *o*-benzoquinones, including bis-*o*-benzoquinones, attract specific interest. Up to now, only a few examples of sterically hindered bis-*o*-benzoquinones have been reported; the quinone fragments therein were linked either directly [12] or through an ethylene [4], ethene [13], piperidine [7], and *m*-phenylene bridges [14]. The goal of the present work was to synthesize new alkoxy-substituted bis-*o*-benzoquinones with different lengths of the bridge between the quinone fragments.

3,6-Di-*tert*-butyl-1,2-benzoquinone reacted with primary alcohols according to the nucleophilic 1,4-ad-





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dition pattern with participation of the carbonyl group (Scheme 1) [5]. As in reactions of 3,6-di-tert-butyl-1,2benzoquinone with other nucleophiles described previously [7], in all cases 3,6-di-tert-butylbenzene-1,2-diol (II) was formed in \sim 50% yield calculated on the initial compound I. Presumably, the primary addition product, the corresponding 4-alkoxy-3,6-di-tert-butylbenzene-1,2-diol, is oxidized with the initial quinone. Alkoxylation of o-benzoquinones can also follow nucleophilic replacement mechanism, as in the reaction with 3,6-di-tert-butyl-4-methoxy-1,2-benzoquinone (III). This reaction seems to be more advantageous than nucleophilic 1,4-addition due to high rate, economic consumption of o-benzoquinone, and the absence of additional pyrocatechol oxidation step (correspondingly, no pyrocatechol II is formed as byproduct).

In this work we used as nucleophiles a number of glycols: propane-1,3-diol, butane-1,4-diol, diethylene and triethylene glycols, and cyclohexane-1,4-diyldimethanol. Taking into account that these diols possess two independent reaction centers, their reaction with 3,6-di-*tert*-butyl-1,2-benzoquinone was expected to produce mono- and bis-*o*-benzoquinones **IVa–VIIIa** and **Vb–VIIIb**, depending on the reactant ratio (Scheme 2). In the first step the reaction of *o*-benzoquinone with glycols gives 4-alkoxy-3,6-di-*tert*-butyl-1,2-benzoquinone (**IVa**), 3,6-di-*tert*-butyl-4-(3-hydroxypropoxy)-1,2-benzoquinone (**IVa**), 3,6-di-*tert*-

butyl-4-(4-hydroxybutoxy)-1,2-benzoquinone (Va), 3,6-di-*tert*-butyl-4-hydroxy-5-[2-(2-hydroxyethoxy)ethoxy]-1,2-benzoquinone (VIa), 3,6-di-*tert*-butyl-4hydroxy-5-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}-1,2-benzoquinone (VIIa), and 3,6-di-*tert*-butyl-4-{[4-(hydroxymethyl)cyclohexyl]methoxy}-1,2-benzoqui-



Fig. 1. Structure of the molecule of 6,9-di-*tert*-butyl-3,4-dihydro-2*H*-1,5-benzodioxepine-7,8-dione (**IX**) according to the X-ray diffraction data.

Table 1. Selected bond lengths in the molecules of 4,4'-[2,2'-oxybis(ethane-2,1-diyl)bis(oxy)]bis(3,6-di-*tert*-butylcyclohexa-3,5-diene-1,2-dione) (**VIb**), <math>4,4'- $\{2,2'-$ [ethane-1,2-diylbis(oxy)]bis(ethane-2,1-diyl)bis(oxy)}bis(3,6-di-*tert*-butylcyclohexa-3,5-diene-1,2-dione) (**VIb**), and 6,9-di-*tert*-butyl-3,4-dihydro-2*H*-1,5-benzodioxepine-7,8-dione (**IX**)

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å				
Compound VIb							
$O^{1A} - C^{1A}$	1.214(2)	$C^{1A} - C^{2A}$	1.548(2)				
$O^{2A} - C^{2A}$	1.220(2)	$C^{2A} - C^{3A}$	1.457(2)				
$O^1 - C^1$	1.450(2)	$C^{3A} - C^{4A}$	1.353(2)				
$O^1 - C^{4A}$	1.355(2)	$C^{4A} - C^{5A}$	1.510(3)				
O^{1B} – C^{1B}	1.211(2)	$C^{5A} - C^{6A}$	1.342(3)				
O^{2B} – C^{2B}	1.224(2)	$C^{1A} - C^{6A}$	1.459(3)				
$O^2 - C^2$	1.423(2)	$C^{1B} - C^{2B}$	1.548(3)				
$O^2 - C^3$	1.417(3)	C^{2B} – C^{3B}	1.457(3)				
$O^3 - C^4$	1.494(3)	C^{3B} – C^{4B}	1.360(3)				
$O^3 - C^{4B}$	1.351(2)	$C^{4B} - C^{5B}$	1.476(3)				
$C^{1B} - C^{6B}$	1.478(3)	$C^{5B} - C^{6B}$	1.342(3)				
Compound VIIb ^a							
$O^{1A} - C^{1A}$	1.213(2)	$C^{1A} - C^{2A}$	1.552(3)				
$O^{2A} - C^{2A}$	1.224(2)	$C^{2A} - C^{3A}$	1.454(3)				
$O^1 - C^1$	1.444(2)	$C^{3A} - C^{4A}$	1.360(3)				
$O^1 - C^{4A}$	1.352(2)	$C^{4A} - C^{5A}$	1.473(3)				
$O^2 - C^2$	1.417(2)	$C^{5A} - C^{6A}$	1.338(3)				
$O^2 - C^3$	1.416(2)	$C^{1A} - C^{6A}$	1.475(3)				
Compound IX							
$O^1 - C^1$	1.207(2)	C^1-C^2	1.548(2)				
$O^2 - C^2$	1.216(2)	C^2-C^3	1.457(2)				
$O^3 - C^4$	1.397(2)	C^3-C^4	1.353(2)				
$O^{3}-C^{15}$	1.433(3)	C^4-C^5	1.510(3)				
$O^4 - C^5$	1.382(3)	$C^{5}-C^{6}$	1.342(3)				
$O^4 - C^{17}$	1.407(3)	C^1-C^6	1.459(3)				

^a Molecule occupies the inversion center.

none (VIIIa). 4-Alkoxy-o-benzoquinones IVa–VIIIa were formed in high yield (~80%) when the reaction was carried out in excess diol. Compounds Va–VIIIa were isolated as individual substances and characterized by spectral methods (see Experimental). In the reaction of o-benzoquinone I with propan-1,3-diol compound IVa was detected only by TLC. Presumably, it rapidly underwent intramolecular cyclization to 6,9-di-*tert*-butyl-3,4-dihydro-2*H*-1,5-benzodioxepine-7,8-dione (IX) which was isolated as the only product (Scheme 3). The structure of quinone **IX** was proved by X-ray analysis (Fig. 1, Table 1). According to the X-ray diffraction data, the $O(CH_2)_3O$ fragment in molecules **IX** in crystal is disordered. The principal geometric parameters of molecule **IX** are typical of such compounds, but the C=O bond lengths differ from each other [1.207(2) and 1.216(2) Å]. The $O^1C^1C^2O^2$ fragment is not planar, and the corresponding torsion angle is equal to 30.6°.

Prokof'eva at al. [15] previously studied the reaction of 3,6-di-*tert*-butyl-1,2-benzoquinone with ethylene glycol and observed formation of only bicyclic 4,5-disubstituted product, 5,8-di-*tert*-butyl-2,3-dihydro-1,4-benzodioxine-6,7-dione. Increase of the length of the hydrocarbon chain in glycol to four carbon atoms and more hampers intramolecular ring closure.

4-Substituted 3,6-di-tert-butyl-1,2-benzoquinones Va-VIIIa possess a side-chain hydroxy group which can be involved in further transformations. Therefore, quinones Va-VIIIa were used as substrates in the second functionalization step to obtain bis-o-benzoquinones (Scheme 2). By carrying out alkoxylation with two- (nucleophilic substitution in III) or fourfold (nucleophilic 1,4-addition to compound I) excess of initial o-quinone I or III with respect to glycol we isolated four new bis-o-benzoquinones: 4.4'-[butane-1,4-diylbis(oxy)]bis(3,6-di-tert-butyl-1,2-benzoquinone) (Vb), 4,4'-[2,2'-oxybis(ethane-2,1-diyl)bis(oxy)]bis(3,6-di-*tert*-butyl-1,2-benzoquinone) (VIb), 4,4'-{2,2'-[ethane-1,2-diylbis(oxy)]bis(ethane-2,1-diyl)bis(oxy)}bis(3,6-di-tert-butyl-1,2-benzoquinone) (VIIb), and 4-{[4-(2,5-di-tert-butyl-3,4-dioxocyclohexa-1,5-dien-1-yloxy)cyclohexyl]methoxy}-3,6-ditert-butyl-1,2-benzoquinone (VIIIb). All new o-quinones were characterized by elemental analyses and IR and ¹H and ¹³C NMR spectra. The IR spectra of all compounds contained a number of characteristic absorption bands [16], in particular a strong narrow band typical of carbonyl group (1680 cm⁻¹) and a band belonging to ether C-O-C bond (1250 cm⁻¹). Compounds Va-VIIIa displayed a broadened band at 3300 cm⁻¹ due to stretching vibrations of the hydroxy group. The ¹H NMR spectra of the isolated compounds were very similar: protons in the tert-butyl groups resonated as two singlets at δ 1.2–1.4 ppm, the OCH₂ groups gave multiplet signals in the region δ 3.80– 4.20 ppm, and the 5-H signal appeared as a singlet at δ 6.82–6.85 ppm. The structure of compounds **VIb** and **VIIb** was proved by X-ray analysis (Figs. 2, 3; Table 1). The OCCO fragments in molecules VIb and VIIb are nonplanar with the torsion angles equal to



m = 2, 3.

 30.8° (34.0°) and 6.7° (6.7°), respectively. The tethers connecting the quinone fragments are packed differently. The OCH₂CH₂OCH₂CH₂O fragment in molecule **VIb** is bent in such a way that the quinone fragments are arranged one above the other with a distance of 5.864 Å between them. The triethylene glycol fragment OCH₂CH₂OCH₂CH₂OCH₂CH₂OCH₂CH₂O in compound **VIIb** is almost linear. Obviously, different conformations of the polyether fragments **VIb** and **VIIb** are related to specificity of their crystal packing.

The yields of bis-o-benzoquinones did not exceed 30%. It was found previously [17] that 3,6-di-tertbutyl-4-methoxy-1,2-benzoquinone undergoes hydrolvsis with formation of 3,6-di-tert-butyl-2-hydroxy-1,4benzoquinone. Probably, 4-alkoxy-1,2-benzoquinones are also hydrolyzed during the process. We have revealed several side reactions which impair the yield of the target products (Scheme 4). Alkoxylation in alkaline medium is accompanied by hydrolysis of o-benzoquinones Va-VIIIa to hydroxy-p-benzoquinone in up to 50% yield [Scheme 4, reaction (1)]. 3,6-Di-tertbutyl-2-hydroxy-1,4-benzoquinone reacts with 3,6-ditert-butylbenzene-1,2-diol to give 2',4,5',7-tetra-tertbutyl-3'-hydroxyspiro[1,3-benzodioxole-2,1'-cyclohexa[2,5]dien]-4'-one (X); we specially synthesized the latter by reaction (2) (Scheme 4). Compound X was isolated as individual substance, and its structure was confirmed by NMR and IR spectra and elemental

analysis. *o*-Benzoquinones **VIa** and **VIIa** underwent one more transformation [Scheme 4, reaction (3)]. Their alkaline hydrolysis leads to the formation of not



Fig. 2. Structure of the molecule of 4,4'-[2,2'-oxybis(ethane-2,1-diyl)bis(oxy)]bis(3,6-di-*tert*-butylcyclohexa-3,5-diene-1,2-dione) (**VIb**) according to the X-ray diffraction data.



Fig. 3. Structure of the molecule of 4,4'-{2,2'-[ethane-1,2-diylbis(oxy)]bis(ethane-2,1-diyl)bis(oxy)}bis(3,6-di-*tert*-butylcyclohexa-3,5-diene-1,2-dione) (**VIIb**) according to the X-ray diffraction data.

only monohydroxy-*p*-benzoquinone but also bicyclic product described previously [15] in up to 30% yield. The contribution of reactions (1)–(3) becomes appreciable due to considerably increased reaction time (equimolar amounts of the reactants) as compared to the first functionalization step.

o-Quinones can be reduced to radical anions via addition of one electron. With a view to determine spin density distribution in radical anions derived from the newly synthesized *o*-quinones, the corresponding potassium and tetracarbonylmanganese complexes were obtained and their ESR spectra were recorded. These metals were selected taking into account specificity of their coordination properties. It is known that potassium usually gives rise to solvent-separated ion pair [18] and that manganese typically forms chelate structures [19]. In the reaction of compound **VIIIa** with potassium evolution of hydrogen was observed



Fig. 4. (1) Experimental and (2) simulated ESR spectra of radical anion derived from bis-*o*-benzoquinone **Vb**.

initially, and then blue color due to *o*-semiquinone appeared. The ESR spectra of potassium complexes with radical anions derived from **Vb–VIIb**, **VIIIa**, and **VIIIb** were similar; they displayed doublets of triplets due to hyperfine coupling of the unpaired electron with proton in position 5 of the pseudoaromatic *o*-semiquinone ring (hyperfine coupling constant 0.35–0.37 mT) and two protons in the α -CH₂ group (HCC 0.02–0.03 mT (Scheme 5, Fig. 4). Both HCC values are typical of such compounds [5]. The ESR spectral parameters are given in Table 2.



Irradiation of toluene solutions of *o*-quinones Vb, VIb, VIIIa, and VIIIb with visible light in the presence of Mn₂(CO)₁₀ resulted in the formation of paramagnetic manganese chelate complexes (Scheme 6, Fig. 5). The ESR spectra of *o*-semiquinone tetracarbonyl manganese chelates are sextets of doublets of triplets due to hyperfine coupling of the unpaired electron with magnetically active manganese isotope (⁵⁵Mn, I = 5/2, 100%), proton in position 5 of the semiquinone ring, and two protons in the side-chain α -methylene group. As follows from the data in Tables 2 and 3, the *g*-factors and HCCs for the examined radical anion adducts of *o*-quinones are similar to each other and are comparable to those reported for structurally related compounds [5].

The ESR spectra of complexes formed by radical anion of IX showed a different pattern. The spectrum of the potassium complex at room temperature is satisfactorily simulated as a triplet of triplets with HCCs of 0.046 and 0.022 mT (due to interactions with pairwise equivalent protons in the α -CH₂ groups). However, both reduction and rise in temperature changed the spectral pattern, depending on the solvent (Fig. 6). This may be the result of two independent processes: association on cooling which is related to transformation of solvent-separated ion pairs into contact and "defrosting" of hindered molecular motions on heating. The formation of contact ion pairs follows from the appearance of additional hyperfine structure on cooling to 230-250 K in diethyl ether. Furthermore, in this solvent we observed monotonic increase of the g-factor from 2.0051 at 290 K to 2.0054 at 230 K,





which corresponds to increase of the contribution of heteroatom (oxygen) orbitals to the unpaired electron orbital due to approach of positively charged species (K^+) . No analogous pattern was observed in tetrahydrofuran which is characterized by stronger solvating power.

The presence of a seven-membered ring in molecule IX implies the existence of different conformers and their interconversions. Figure 7 shows three possible conformers of IX together with the corresponding enantiomers. The most energetically favorable conformer is A, next follows conformer B, and structure C is the least stable. Molecular modeling (HyperChem 7.01) gave the following energies (arbitrary units): 26.59 (A), 29.77 (B), and 31.21 (C). Variation of temperature should change the relative contributions of these conformers. In addition, variation of temperature is accompanied by change of the rate of their interconversions; therefore, it is difficult to unambiguously interpret the observed variations in the ESR spectra.

To conclude, we have synthesized nine new 4-alkoxy-3,6-di-*tert*-butyl-1,2-benzoquinone derivatives. Among these, four compounds are bis-o-benzoquinones with different lengths of the tether (6–13 atoms) connecting the quinone fragments. Depending on the length of the chain between the hydroxy groups in glycols, their reactions with 3,6-di-*tert*-butyl-1,2-benzoquinones lead to the formation of bicyclic 4,5-disubstituted 3,6-di-*tert*-butyl-1,2-benzoquinones or involve stepwise alkoxylation. The newly synthesized o-benzoquinone derivatives are capable of being converted into radical anions via reduction with alkali metals and forming o-semiquinone chelates with transition metals.

EXPERIMENTAL

The ¹H and ¹³C NMR spectra were recorded on a Bruker Avance DPX-200 spectrometer at 200 and 50 MHz, respectively, using CDCl₃ as solvent and tetramethylsilane as internal reference. The ESR spectra were measured on a Bruker ER 200D-SRC spectrometer equipped with an ER 4105 DR double resonator (operating frequency 9.5 GHz). The IR spectra were recorded on FSM-1201 (Russia) and Specord M-40 spectrometers. The solvents used were purified and dehydrated by standard methods [20]. 3,6-Di-*tert*-butyl-1,2-benzoquinone and 3,6-di-*tert*-butyl-4-me-thoxy-1,2-benzoquinone were synthesized according to the procedures described in [5, 21]. Propane-1,3-diol, butane-1,4-diol, diethylene and triethylene glycols, and cyclohexane-1,4-diyldimethanol were commercial products (Fluka).



Fig. 5. (1) Experimental and (2) simulated ESR spectra of tetracarbonylmanganese chelate with radical anion derived from *o*-benzoquinone **VIIIa**.



Fig. 6. ESR spectra of potassium complex with radical anion IX at (1) 290 K (THF), (2) 210 K (Et_2O), and (3) 350 K (2-methyltetrahydrofuran).

Table 2. Parameters of the ESR spectra of radical anions derived from quinones **Vb–VIIb**, **VIIIa**, and **VIIIb** (THF, 290 K)

Parameter	Vb	VIb	VIIb	VIIIb	VIIIa
g_i	2.0056	2.0052	2.0055	2.0055	2.0057
<i>a_i</i> (1H), mT	0.362	0.359	0.367	0.367	0.366
<i>a_i</i> (2H), mT	0.024	0.025	0.026	0.026	0.029

Table 3. Parameters of the ESR spectra of the complexes formed by quinones **Vb**, **VIb**, **VIIIa**, and **VIIIb** with do-decacarbonyldimanganese in toluene at 290 K

Parameter	Vb	VIb	VIIIa	VIIIb
g_i	2.0034	2.0033	2.0034	2.0035
<i>a_i</i> (1H), mT	0.363	0.363	0.362	0.361
<i>a_i</i> (2H), mT	0.054	0.051	0.058	0.058
<i>a_i</i> (Mn), mT	0.644	0.646	0.622	0.623

o-Quinones Va–VIIIa and IX (general procedure). A mixture of 50 ml of acetonitrile, 2.2 g (10 mmol) of compound I or 1 g (4 mmol) of III, 5 ml (50 mmol) of the corresponding diol, and solid potassium hydroxide was slightly heated for 5–15 h under stirring using a magnetic stirrer. The progress of the reaction was monitored by TLC. As compound I was consumed, PbO₂ was added to the mixture. When the reaction was complete, the mixture was filtered, washed with an aqueous solution of sodium carbonate and water, and extracted with diethyl ether. The extract was evaporated, and the products were isolated by chromatography on silica gel (0.2–0.5 mm) using benzene–ethyl



Fig. 7. Enantiomer pairs of radical anion **IX** (*tert*-butyl groups are not shown for the sake of simplicity).

acetate (20:1 to 1:1) as eluent; a dark red fraction was collected.

3,6-Di-*tert*-butyl-4-(4-hydroxybutoxy)cyclohexa-**3,5-diene-1,2-dione (Va).** Yield 2.50 g (81%), dark red oily substance. IR spectrum (mineral oil), v, cm⁻¹: 3450, 1685, 1640, 1625, 1550, 1485, 1460, 1395, 1380, 1360, 1300, 1240, 1200, 1080, 945, 890, 830, 735, 682, 640, 600. ¹H NMR spectrum, δ , ppm: 1.24 s and 1.32 s (9H each, *t*-Bu), 1.71–1.81 m (2H, CH₂), 1.85–1.96 m (2H, CH₂), 3.71–3.79 m (2H, CH₂O), 4.13 t (2H, CH₂O, *J* = 6.2 Hz), 6.85 s (1H, 5-H). ¹³C NMR spectrum, δ_C , ppm: 28.96 and 30.54 (CH₃), 35.09 and 35.16 (CMe₃), 62.32 and 69.46 (CH₂O), 129.74 (C³), 130.05 (C⁵), 149.53 (C⁶), 162.71 (C⁴), 181.62 and 182.23 (C=O). Found, %: C 70.02; H 9.07. C₁₈H₂₈O₄. Calculated, %: C 70.13; H 9.09.

3,6-Di-*tert*-**butyl**-4-hydroxy-5-[2-(2-hydroxyethoxy)ethoxy]cyclohexa-3,5-diene-1,2-dione (VIa). Yield 2.49 g (77%), dark red oily substance. IR spectrum (mineral oil), v, cm⁻¹: 3450, 1750, 1690, 1650, 1635, 1560, 1490, 1465, 1400, 1390, 1360, 1300, 1250, 1200, 1160, 1140, 1075, 1030, 1000, 970, 920, 890, 855, 740. ¹H NMR spectrum, δ , ppm: 1.24 s and 1.32 s (9H each, *t*-Bu), 1.71–1.81 m (2H, CH₂), 1.85– 1.96 m (2H, CH₂), 3.71–3.79 m (2H, CH₂O), 4.09– 4.16 m (2H, CH₂O), 6.91 s (1H, 5-H). ¹³C NMR spectrum, δ_{C} , ppm: 28.95 and 30.48 (CH₃), 35.17 (CMe₃); 61.81, 68.64, 69.59, and 72.62 (CH₂O); 129.74, 130.05, 149.53, and 162.71 (C³, C⁵, C⁶, C⁴); 181.62 and 182.23 (C=O). Found, %: C 66.60; H 8.62. C₁₈H₂₈O₅. Calculated, %: C 66.67; H 8.64.

3,6-Di-*tert*-butyl-4-hydroxy-5-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}cyclohexa-3,5-diene-1,2-dione (VIIa). Yield 2.58 g (70%), dark red oily substance. IR spectrum (mineral oil), v, cm⁻¹: 3450, 1690, 1650, 1635, 1555, 1490, 1470, 1405, 1390, 1365, 1310, 1250, 1205, 1135, 1085, 1040, 1005, 940, 925, 895, 860, 840, 740. ¹H NMR spectrum, δ , ppm: 1.24 s and 1.32 s (9H each, *t*-Bu), 1.71–1.81 m (2H, CH₂), 1.85–1.96 m (2H, CH₂), 3.71–3.79 m (2H, CH₂O), 4.09–4.16 m (2H, CH₂O), 6.92 s (1H, 5-H). ¹³C NMR spectrum, δ_{C} , ppm: 28.95 and 30.48 (CH₃), 35.16 (CMe₃); 61.81, 68.64, 69.46, and 72.62 (CH₂O); 130.50, 130.93, 149.54, and 162.55 (C³, C⁵, C⁶, C⁴); 181.48 and 182.38 (C=O). Found, %: C 65.23; H 8.70. C₂₀H₃₂O₆. Calculated, %: C 65.21; H 8.69.

3,6-Di-*tert*-butyl-4-{[4-(hydroxymethyl)cyclohexyl]methoxy}cyclohexa-3,5-diene-1,2-dione (VIIIa). Yield 2.49 g (68%), dark red powder, mp 141–143°C. IR spectrum (mineral oil), v, cm⁻¹: 3315, 1682, 1640, 1638, 1550, 1460, 1400, 1390, 1370, 1302, 1240, 1200, 1084, 1037, 954, 897, 884, 826. ¹H NMR spectrum, δ , ppm: 0.98–1.16 m (4H, CH₂), 1.24 s and 1.31 s (9H each, *t*-Bu), 1.50–1.80 m (2H, CH), 1.84–2.00 m (4H, CH₂), 3.50 d (2H, CH₂OH, *J* = 6.1 Hz), 3.88 d (2H, CH₂O, *J* = 6.2 Hz), 6.83 s (1H, 5-H). ¹³C NMR spectrum, δ_{C} , ppm: 29.1 and 30.7 (CH₃), 28.8 and 29.3 (CH₂), 35.2 and 35.3 (CMe₃), 38.4 and 40.4 (CH), 68.5 and 75.1 (CH₂O); 129.7, 130.4, and 149.5 (C³, C⁵, C⁶); 163.1 (C⁴), 181.7 and 182.3 (C=O). Found, %: C 72.90; H 9.38. C₂₂H₃₄O₄. Calculated, %: C 72.93; H 9.39.

6,9-Di-*tert***-butyl-3,4-dihydro-2***H***-1,5-benzodiox-epine-7,8-dione (IX).** Yield 2 g (68%), red crystals, mp 148–150°C. IR spectrum (mineral oil), v, cm⁻¹: 1660, 1645, 1585, 1540, 1460, 1395, 1375, 1365, 1320, 1295, 1255, 1240, 1200, 1165, 1115, 1070, 1020, 995, 950, 930, 883, 870, 855, 825, 815, 781, 720, 660, 650, 630. ¹H NMR spectrum, δ , ppm: 1.30 s (18H, *t*-Bu), 2.22 quint (2H, CH₂, J = 5.77 Hz), 4.25 t (4H, CH₂O, J = 5.77 Hz). ¹³C NMR spectrum, $\delta_{\rm C}$, ppm: 29.52 (CH₃), 30.52 (CH₂), 35.55 (CMe₃), 70.07 (CH₂O), 132.47 (C³, C⁶), 161.07 (C⁵, C⁴), 186.40 (C=O). Found, %: C 69.84; H 8.21. C₁₇H₂₄O₄. Calculated, %: C 69.86; H 8.22.

Bis-o-quinones Vb–VIIIb (general procedure). The reactions were carried out as described above, the reactant ratio quinone I–glycol being 4:1 (III–glycol 2:1); reaction time 100 h. When 4-alkoxy-3,6-di-*tert*butyl-1,2-benzoquinones Va–VIIIa were used as starting compounds, the ratio quinone–glycol was 1:1.

4,4'-[Butane-1,4-diylbis(oxy)]bis(3,6-di-*tert***-butyl-cyclohexa-3,5-diene-1,2-dione)** (Vb). Yield 0.8 g (31%), dark red crystals, mp 182–185°C. IR spectrum (mineral oil), v, cm⁻¹: 1690, 1650, 1625, 1585, 1490, 1470, 1410, 1400, 1390, 1370, 1335, 1310, 1255, 1240, 1230, 1200, 1175, 1080, 1040, 950, 930, 905, 890, 830, 740. ¹H NMR spectrum, δ , ppm: 1.25 s and 1.32 s (18H each, *t*-Bu), 1.97–2.06 m (4H, CH₂), 4.12–4.20 m (4H, CH₂O), 6.84 s (2H, 5-H). ¹³C NMR spectrum, δ_{C} , ppm: 26.54 (CH₂), 28.96 and 30.57 (CH₃), 35.14 (CMe₃), 69.05 (CH₂O), 129.79 and 149.75 (C⁵, C⁶), 162.32 (C⁴), 181.48 and 182.27 (C=O). Found, %: C 73.12; H 8.76. C₃₂H₄₆O₆. Calculated, %: C 73.00; H 8.74.

4,4'-[2,2'-Oxybis(ethane-2,1-diyl)bis(oxy)]bis-(**3,6-di-***tert*-**butylcyclohexa-3,5-diene-1,2-dione)** (**VIb).** Yield 0.65 g (24%), dark red crystals, mp 73– 75°C. IR spectrum (mineral oil), v, cm⁻¹: 1690, 1650, 1625, 1550, 1490, 1470, 1400, 1385, 1360, 1305, 1250, 1235, 1200, 1160, 1140, 1130, 1090, 1075, 1040, 1010, 940, 920, 905, 860, 835, 740. ¹H NMR spectrum, δ , ppm: 1.21 s and 1.32 s (18H each, *t*-Bu), 3.83–3.90 m (4H, CH₂), 4.18–4.25 m (4H, CH₂O), 6.87 s (2H, 5-H). ¹³C NMR spectrum, δ_{C} , ppm: 28.97 and 30.53 (CH₃), 35.19 (CMe₃), 68.53 and 69.88 (CH₂O); 130.59, 130.72, 149.66, and 162.29 (C³, C⁵, C⁶, C⁴); 181.41 and 182.37 (C=O). Found, %: C 70.79; H 8.48. C₃₂H₄₆O₇. Calculated, %: C 70.84; H 8.49.

4,4'-{2,2'-[Ethane-1,2-diylbis(oxy)]bis(ethane-2,1-diyl)bis(oxy)}bis(3,6-di-*tert*-butylcyclohexa-3,5diene-1,2-dione (VIIb). Yield 0.59 g (20%), dark red crystals, mp 113–115°C. IR spectrum (mineral oil), v, cm⁻¹: 1690, 1645, 1630, 1550, 1490, 1460, 1425, 1405, 1385, 1360, 1330, 1310, 1255, 1245, 1200, 1150, 1115, 1090, 1050, 1040, 1010, 925, 905, 875, 860, 740, 725. ¹H NMR spectrum, δ , ppm: 1.21 s and 1.32 s (18H each, *t*-Bu), 3.67 s (4H, CH₂), 3.76–3.82 m (4H, CH₂O), 4.17–4.24 m (4H, CH₂O), 6.87 s (2H, 5-H). ¹³C NMR spectrum, δ_{C} , ppm: 28.98 and 30.53 (CH₃), 35.16 (CMe₃); 68.62, 69.81, and 70.86 (CH₂O); 130.32, 131.06, 149.40, and 162.62 (C³, C⁵, C⁶, C⁴); 181.53 and 182.38 (C=O). Found, %: C 69.60; H 8.50. C₃₄H₅₀O₈. Calculated, %: C 69.62; H 8.53.

3,6-Di-tert-butyl-4-{[4-(2,5-di-tert-butyl-3,4-dioxocyclohexa-1,5-dien-1-yloxy)cyclohexyl]methoxy}cyclohexa-3,5-diene-1,2-dione (VIIIb). Yield 0.67 g (23%), dark red powder, mp 263-265°C. IR spectrum (mineral oil), v, cm⁻¹: 1680, 1660, 1635, 1540, 1460, 1405, 1395, 1380, 1295, 1250, 1230, 1195, 1095, 1075, 1020, 945, 895, 736, 722, 680, 595. ¹H NMR spectrum, δ, ppm: 1.12–1.20 m (4H, CH₂), 1.25 s and 1.32 s (18H each, t-Bu), 1.75–1.90 m (2H, CH), 1.95– 2.05 m (4H, CH₂), 3.89 d (4H, CH₂O, J = 6.2 Hz), 6.82 s (2H, 5-H). ¹³C NMR spectrum, δ_{C} , ppm: 29.09 and 30.7 (CH₃), 29.11 (CH₂), 35.2 (CMe₃), 38.2 (CH), 74.9 (CH₂O); 130.0, 130.4, and 149.6 (C³, C⁵, C⁶); 162.9 (C⁴O), 181.7 and 182.3 (C=O). Found, %: C 74.40; H 8.95. C₃₆H₅₂O₆. Calculated, %: C 74.48; H 8.97.

2',4,5',7-Tetra-*tert*-butyl-3'-hydroxy-4'*H*-spiro-[1,3-benzodioxole-2,1'-cyclohexa[2,5]dien]-4'-one (X). A solution of 0.094 g (0.4 mmol) of 2-hydroxy-3,6-di-*tert*-butyl-1,4-benzoquinone (II) and 0.089 g (0.4 mmol) of compound II in acetonitrile in the presence of potassium hydroxide was heated for 1 h under reflux. The mixture was extracted with toluene, and the extract was evaporated. Light yellow powder separated from hexane. Yield 0.093 g (53%), mp 236–238°C. IR spectrum (mineral oil), v, cm⁻¹: 3790, 1655, 1635, 1625, 1490, 1470, 1410, 1400, 1390, 1370, 1350, 1340, 1290, 1260, 1240, 1205, 1140, 1090, 1045, 1035, 995, 980, 950, 935, 875, 810, 795, 670, 645, 615. ¹H NMR spectrum, δ , ppm: 1.18 s (9H, *t*-Bu), 1.33 s (18H, *t*-Bu), 1.34 s (9H, *t*-Bu), 6.50 s (1H, 12-H), 6.78 s (2H, 4-H, 5-H). ¹³C NMR spectrum, $\delta_{\rm C}$, ppm: 28.85, 29.05, and 29.32 (CH₃); 33.75, 34.02, and 35.53 (CMe₃); 118.63 and 138.54 (C⁴, C⁵, C¹²); 109.86, 125.30, 132.29, 140.76, 144.70, and 146.28 (C¹, C², C³, C⁶, C⁸, C⁹, C¹¹); 181.66 (C=O). Found, %: C 76.30; H 9.05. C₂₈H₄₀O₄. Calculated, %: C 76.36; H 9.09.

Potassium and manganese *o*-semiquinone complexes were obtained according to standard procedures [22, 23]. An ESR ampule was charged with the corresponding *o*-quinone and metallic potassium, degassed tetrahydrofuran was recondensed thereto, the ampule was shaken until the mixture changed its color, and its ESR spectrum was recorded. A degassed toluene solution containing dodecacarbonyldimanganese and *o*-quinone was irradiated in an ESR ampule with a KGM-24-150 lamp until change of color.

X-Ray analysis of single crystals of VIb, VIIb, and IX was performed on a Smart Apex diffractometer (Mo K_{α} irradiation, graphite monochromator, $\lambda =$ 0.71073 Å). Compound VIb: crystal dimensions 1.02× 0.22×0.20 mm at 100(2) K; C₃₅H₅₃O₇; monoclinic crystal system; unit cell parameters: a = 24.942(2), b =18.318(2), c = 15.006(1) Å; $\beta = 93.004(2)^{\circ}$; V =6846.8(10) Å³; Z = 8; space group C2/c; $d_{calc} =$ 1.137 g/cm³; $\mu = 0.077$ mm⁻¹; 1.91 $\leq \theta \leq 26^{\circ}$; total of 20121 reflections were measured, 6706 of which were independent ($R_{int} = 0.0453$); $R_1 = 0.0583$ [$I > 2\sigma(I)$], $wR_2 = 1.022$ (all reflections).

Compound **VIIb**: crystal dimensions $0.72 \times 0.20 \times 0.14 \text{ mm}$ at 100(2) K; $C_{34}H_{50}O_8$; rhombic crystal system; unit cell parameters: a = 14.3063(6), b = 18.6475(5), c = 19.7693(8) Å; V = 3294.2(2) Å³; Z = 4; space group *Pbca*; $d_{calc} = 1.183 \text{ g/cm}^3$; $\mu = 0.083 \text{ mm}^{-1}$; $2.06 \le \theta \le 25^{\circ}$; total of 24297 reflections were measured, 2886 of which were independent ($R_{int} = 0.0430$); $R_1 = 0.0530 [I > 2\sigma(I)]$, $wR_2 = 0.1581$ (all reflections).

Compound IX: crystal dimensions $0.40 \times 0.10 \times 0.08$ mm at 100(2) K; $C_{17}H_{24}O_4$; monoclinic crystal system; unit cell parameters: a = 5.7990(8), b = 15.460(2), c = 17.879(2) Å; $\beta = 96.856(2)^\circ$; V = 1591.4(4) Å³; Z = 4; space group $P2_1/n$; $d_{calc} = 1.220$ g/cm³; $\mu = 0.086$ mm⁻¹; $2.29 \le \theta \le 26^\circ$; total of 13462 reflections were measured, 3123 of which were independent ($R_{int} = 0.0525$); $R_1 = 0.0655$ [$I > 2\sigma(I)$], $wR_2 = 0.1810$ (all reflections).

The structures were solved by the direct method and were refined by the least-squares procedure with respect to F_{hkl}^2 in anisotropic approximation for all nonhydrogen atoms. Hydrogen atoms were placed into ideal positions (from the viewpoint of geometry considerations) and were refined in isotropic approximation according to the riding model. All calculations were performed using SHELXTL software package [24]. Corrections for absorption by crystals of **VIb**, VIIb, and IX were introduced using SADABS^{2x} program. The complete sets of crystallographic data for compounds VIb, VIIb, and IX were deposited to the Cambridge Crystallographic Data Centre [entry nos. CCDC 728527 (VIb), CCDC 728528 (VIIb), and CCDC 728526 (IX)]. The principal bond lengths in molecules VIb, VIIb, and IX are collected in Table 1.

This study was performed under financial support by the Russian Foundation for Basic Research (project nos. 09-03-00668-a, 09-02-01118-a, 10-03-00788-a, 11-03-97040-r_povolzh'e_a) and by the President of the Russian Federation (project no. NSh-7065.2010.3).

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