Alkylation of catechol with cyclohexene. Novel sterically hindered *o*-quinones and catechols

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A synthetic procedure for the preparation of sterically hindered catechols and *o*-quinones by the reaction of catechol with cyclohexene was developed. Novel cyclohexyl substituted catechols displayed remarkable stability during redox transformations and could be used as redox-active ligands.

Key words: *o*-quinones, catechols, redox-active ligands, alkylation, cyclohexene.

The development of new approaches for the synthesis of substituted catechols remains relevant, despite the fact that these compounds have been objects of study for many decades. Catechols are used as biologically active compounds,[1] food components,[2] and pharmaceuticals.[3—8]

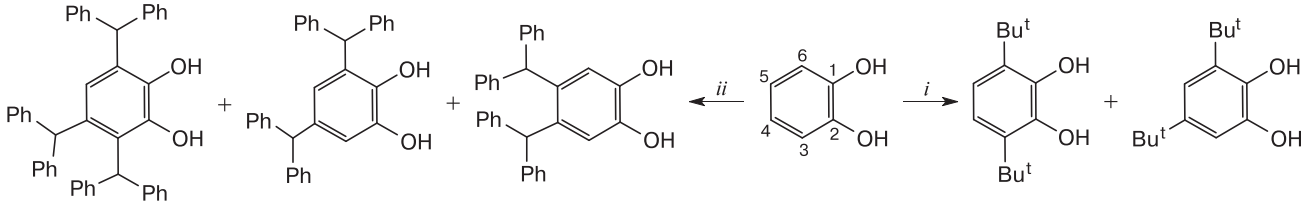
A characteristic feature of catechols is their redox activity. Catechols are capable of reversibly changing their oxidation state, successively transforming into semiquinones and *o*-quinones both in the non-coordinated form and as a dioxolene ligand in the coordination sphere of the metal.[9,10] The redox activity of dioxolene ligands underlies the most interesting phenomena discovered during the study of their metal complexes, in particular, the temperature-dependent reversible bending of crystals of rhodium semiquinone complexes,[11] as well as spin crossover on cobalt semiquinone complexes.[12]

In contrast to catechols, their oxidized forms are usually very reactive. An example is the Diels—Alder cycloaddition of *o*-quinones.[13] The stability of the oxidized forms of dioxolene ligands is increased by steric blockage of the chelating site, usually with bulky *tert*-butyl substituents which provide protection for both the dioxolene fragment and the peripheral positions 4 and 5 of the *o*-quinone ring.[14] The peripheral positions 4 and 5 are used for additional functionalization. In such substituted derivatives, *tert*-butyl groups experience steric repulsion from carbonyl quinone groups, as well as from substituents at positions 4 and 5 of the ring, which results in significant distortions of the *o*-quinone skeleton.[15—18] The distortion can be reduced by decreasing the bulkiness of protecting substituents, for example, by replacing tertiary carbon substituents with secondary ones.

Results and Discussion

There are many approaches for introduction of alkyl substituents into the aromatic ring. Some of them, such as free radical reactions and reactions with organometallic compounds,[19,20] have rather limited application. The most universal is the Friedel—Crafts alkylation. This method is used for the preparation of *tert*-butyl-substituted *o*-quinones (Scheme 1).[14] The composition of the alkylation products depends significantly on the nature of the electrophilic agent (alcohol, halogenated hydrocarbon, or alkene), catalyst, solvent, and reaction temperature. The alkylation of catechol with tertiary alcohols at an alco-

Scheme 1



Reagents and conditions: *i*. Bu^tOH or $H_2C{=}CMe_2$, *ii*. Ph_2CHOH.

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hol : catechol molar ratio ≥2 : 1 gives a mixture of 3,5- and 3,6-disubstituted derivatives. An excess amount of alkylating agent does not lead to the formation of any additional products.

The available data on the regioselectivity and quantitative composition of the alkylation products of catechol with secondary alcohols and alkenes are rather contradictory. In the case of benzhydrol, a 4,5-disubstituted product is formed in >50% yield, 3,5-di- and 3,4,6-trisubstituted derivatives are formed in smaller amounts,[21] while a symmetric 3,6-disubstituted product is not formed at all (see Scheme 1). It is noted that alkylation of catechol with cyclohexene in the presence of aluminum phenoxide leads to 3,5- and 3,6-disubstituted derivatives, with their ratio varying depending on the concentration of the catalyst and the process temperature.[22] The formation of 3,4,6-triisopropyl-substituted catechol upon alkylation with propan-2-ol is mentioned.[23]

In the present work, we studied the possibility of controlling the acid-catalyzed alkylation of catechol with cyclohexene. The reactions were carried out by heating a neat mixture of the starting compounds at a molar ratio of catechol : cyclohexene = 1 : 2.5. Sulfuric, polyphosphoric, and perchloric acids were used as the catalyst. Preference was given to perchloric acid, since sulfuric and polyphosphoric acids caused polymerization of the alkylating agent, which resulted in significant resinification. The conditions for the process were selected taking into account the data[24] on the alkylation of phenols with cyclohexene. According to these data, the alkylation proceeds most efficiently at 120 °C without solvent using 57% perchloric acid as a catalyst.

We found that the reaction of catechol with cyclohexene gives 3,6-di-, 3,5-di-, and 3,4,6-trialkylated products **1—3**, respectively (Scheme 2). The products were separated as follows. The major part of 3,5-dicyclohexylcatechol (**2**) was isolated by recrystallization from hexane. The mixture of catechols remaining in the mother liquor was oxidized with potassium ferricyanide in an alkaline medium to the corresponding quinones. Most of 3,6-dicyclohexyl-*o*-benzoquinone (**4**) precipitated during recrystallization of the mixture of quinones from hexane. 3,4,6-Tricyclohexyl-*o*-benzoquinone (**6**) was isolated from the mother liquor by column chromatography. Products **1** and **3** were obtained in pure form by reduction of *o*-quinones **4** and **6** with hydrazine hydrate (see Scheme 2). Catechols **1—3** are colorless and air-stable solids. The corresponding quinones **4—6** are also stable on storage in air at room temperature.

The quantitative composition of alkylation products **1—3** was monitored by reverse phase chromatography. Preliminary experiments showed that the mixture of catechols **1—3** is rather difficult to separate chromatographically; therefore, the reaction mixture prior to analysis was oxidized with an excess of potassium ferricyanide in an alkaline medium to quinones. Table 1 shows the results of the analysis of the composition of the mixture of alkylation products of catechol with cyclohexene based on the data of reverse phase chromatography and ^{1}H NMR spectroscopy.

Using ^{1}H NMR spectroscopy, it was possible to compare the quantitative composition of the primary mixture of catechols and the corresponding mixture of *o*-quinones (see Table 1). For this purpose, we compared the integral intensities of the signals for protons bonded directly to the catechol (quinone) ring of the molecule. Both the catechol and the quinone signals are well resolved in this spectral region. The chemical shifts for the catechol protons of compounds **1** and **3** are δ 6.72 and 6.61, respectively. Two nonequivalent catechol ring protons of 3,5-dicyclohexylcatechol (**2**) are observed at δ 6.58 and 6.62, with the second signal overlapping with signals of compound **3**. For this reason, the amount of product **3** in the reaction mixture was determined as the difference between the integral

Scheme 2

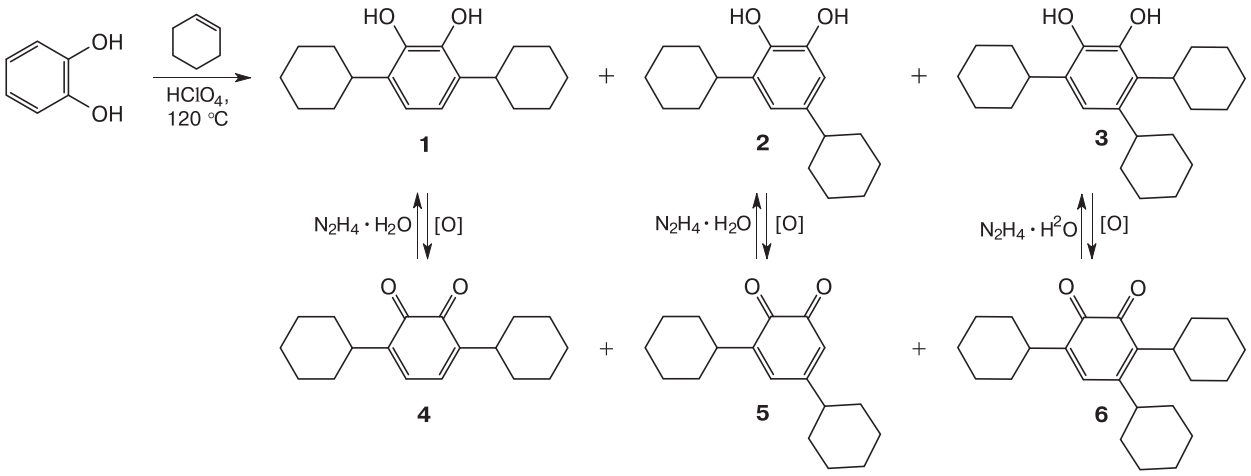

Table 1. Composition of the mixture of alkylation products of catechol with cyclohexene

Method	Object of study	Product (mol.%)		
		1 or **4**	**2** or **5**	**3** or **6**
HPLC	After oxidation (quinones)	18	68	14
^{1}H NMR	Primary mixture (catechols)	19	64	17
^{1}H NMR	After oxidation (quinones)	17	65	18

intensities of the signal in the region δ 6.61—6.62 and the signal of the proton of catechol **2** at δ 6.58. Analysis of the ^{1}H NMR spectra of the mixture of quinones **4—6** was somewhat simpler, since the proton signals of the quinone ring of different products do not overlap. Thus, the signals at δ 6.66 and 6.64 belong to the protons of quinones **4** and **6**, respectively, while the protons of quinone **5** appear as singlets at δ 6.07 and 6.59.

The used procedures for determining the quantitative composition of the mixture of alkylation products give similar results (see Table 1). The predominant reaction product was 3,5-dialkylated derivative **2**. 3,6-Dicyclohexylcatechol **1** and 3,4,6-tricyclohexylcatechol **3** are formed in approximately equal proportions.

It was indicated above that a 25% excess of cyclohexene was used in the alkylation of catechol. It is obvious that this excess amount is a reason of the formation of the trialkylated product. At the same time, with a stoichiometric ratio of catechol and cyclohexene (1 : 2) the number of products would increase, namely, isomeric monoalkylated 3- and 4-cyclohexylcatechols were added to dicyclohexyl derivatives **1—3**. The question about the mechanism of formation and the precursor of 3,4,6-tricyclohexylcatechol **3** requires a separate study. The available data allow suggestion that the rate of formation of this compound is comparable with the rate of introduction of the second cyclohexyl group in the catechol ring.

Quinones **4—6** and catechols **1—3** were characterized by physicochemical methods. The IR spectra of quinones exhibit strong bands in the region of 1640—1700 cm^{-1} characteristic of the stretching vibrations of carbonyl groups in sterically hindered *o*-quinones.

3,4,6-Tricyclohexyl-*o*-quinone (**6**) was characterized by X-ray diffraction analysis. The unit cell contains two independent molecules of *o*-quinone **6** slightly differing in geometrical characteristics. The structural parameters of compound **6** are typical of sterically hindered *o*-quinones (Fig. 1, Tables 2 and 3). In particular, an alternation of bond lengths characteristic of *o*-quinones is observed in the central six-membered ring. Deviation from the planar structure is observed in the geometry of the quinone ring because of the close spatial arrangement of two bulky

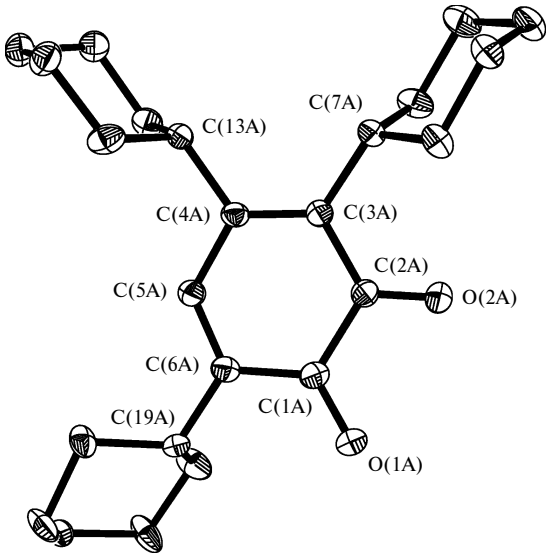

Fig. 1. The structure of the independent molecule **A** of *o*-quinone **6**. Thermal ellipsoids are shown with a 30% probability. Hydrogen atoms are omitted.

Table 2. Principal bond lengths (*d*) in two independent molecules **A** and **B** in the unit cell of *o*-quinone **6**

Bond	*d*/Å	
	A	**B**
O(1)—C(1)	1.222(4)	1.215(4)
O(2)—C(2)	1.212(4)	1.212(4)
C(1)—C(2)	1.540(4)	1.540(4)
C(2)—C(3)	1.481(4)	1.485(4)
C(3)—C(4)	1.357(4)	1.356(4)
C(4)—C(5)	1.475(4)	1.471(4)
C(5)—C(6)	1.346(4)	1.343(4)
C(1)—C(6)	1.460(4)	1.465(4)
C(3)—C(7)	1.525(4)	1.517(4)
C(4)—C(13)	1.523(4)	1.516(4)
C(6)—C(19)	1.519(4)	1.509(5)

cyclohexyl substituents at positions 3 and 4. In addition, in order to minimize steric interactions the substituents at positions 3 and 4 in the crystal structure are forced to be turned perpendicular to the plane of the *o*-quinone ring.

The study of the electrochemical characteristics of new *o*-quinones (Table 4) showed that the substituted derivatives **4** and **5** are stronger acceptors than their *tert*-butyl counterparts.* The first reduction potential of compounds **4** and **5** is shifted towards positive values by ~0.1 V com-

* S. V. Norkov, A. V. Cherkasov, A. S. Shavyrin, M. V. Arsenyev, V. A. Kuropatov, V. K. Cherkasov, *Beilstein J. Org. Chem.*, 2020; in press.

Table 3. Basic crystallographic data and structure refinement statistics for compound **6**

Parameter	Value
Molecular formula	$C_{24}H_{34}O_2$
Molecular weight	354.51
T/K	100(2)
Crystal system	Orthorhombic
Space group	*Pbca*
a/Å	11.1571(9)
b/Å	20.4996(16)
c/Å	35.525(3)
α/deg	90
β/deg	90
γ/deg	90
V/Å^3	8125.0(11)
Z	16
d/g cm^{-3}	1.159
μ/mm^{-1}	0.071
F(000)	3104
Crystal size/mm	0.22×0.14×0.06
θ-Range for data collection/deg	2.07—25.35
Indices of h, k, l regions	$-13 \leqslant h \leqslant 13$ $-24 \leqslant k \leqslant 24$ $-42 \leqslant l \leqslant 42$
Number of collected reflections	103067
Number of unique reflections (R_{int})	7447 (0.1167)
GOOF (F^2)	1.055
R_1/wR_2 ($I > 2\sigma$ (I))	0.0816/0.1509
R_1/wR_2 (for all parameters)	0.1308/0.1732
Residual electron density /e Å^{-3}, ρ_{max}/ρ_{min}	0.271/−0.228

Table 4. Reduction potentials of quinones **4**—**6** according to cyclic voltammetry*

Quinone	$-E_{1/2}(1)$	$-E_{1/2}(2)$
	V	
4	0.43	0.76
5	0.47	0.91
6	0.53	0.77

* Ag/AgCl/KCl (sat.), MeCN, $C = 5 \cdot 10^{-3}$ mol L^{-1}.

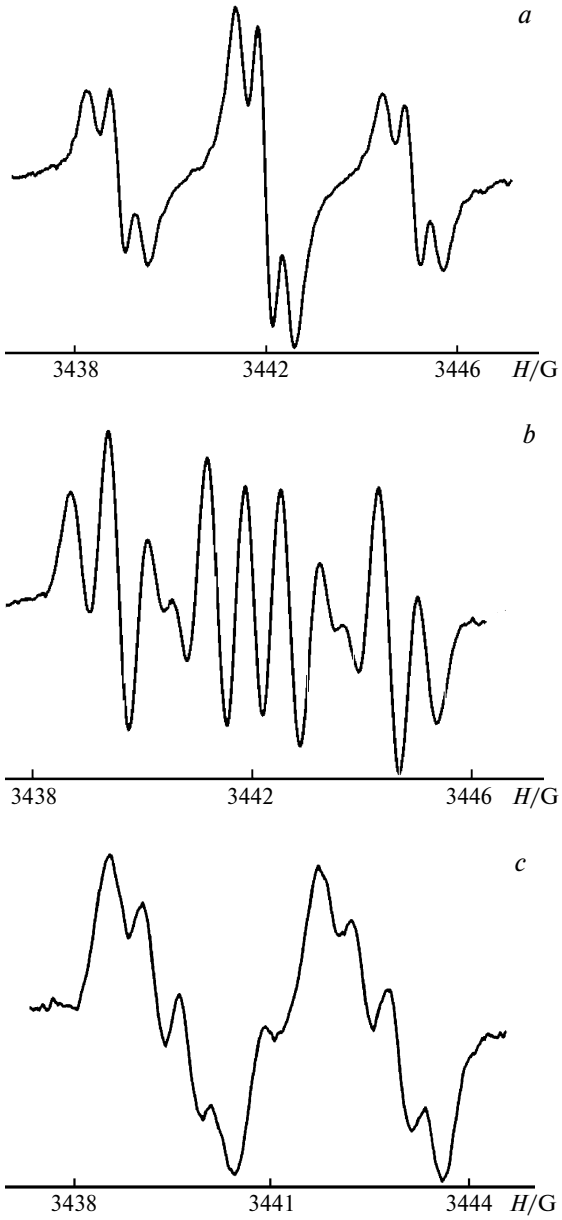

Fig. 2. EPR spectra of mono-reduced potassium derivatives of *o*-quinones **4** (*a*), **5** (*b*), and **6** (*c*) recorded in a THF solution at 293 K.

pared to *tert*-butyl derivatives. In addition, a decrease in the interval between the first and second reduction potentials by ~0.15 V is observed for cyclohexyl *o*-quinones. The first and second reduction waves for all investigated quinones can be characterized as quasi-reversible and one-electron ones.

The ability of quinones **4**—**6** to one-electron stepwise reduction in solution is also confirmed by reactions with alkali metals. The EPR spectroscopy data show that the reduction of *o*-quinones **4**—**6** with potassium metal at the first stage gives paramagnetic semiquinone adducts (Fig. 2). With further reduction, the intensity of the EPR signal gradually decreases to almost zero, which is explained by the formation of diamagnetic catecholate species. The reduced forms of quinones are relatively stable in solution in the absence of oxygen. Thus, the intensity of the EPR signal of semiquinone complexes in a sealed tube in the absence of metallic potassium remains unchanged for several hours.

The spin density distribution in the semiquinone ligand is generally similar to the distribution observed for their counterparts with *tert*-butyl substituents.[25] At the same time, the presence of a proton at the tertiary carbon atom of cyclohexyl substituents in quinones **4**—**6** allows evalu-

Table 5. Parameters of EPR spectra of mono-reduced potassium derivatives of quinones **4—6** in solution in THF*

Quinone	*g*-Factor	HFS constants for aromatic ring protons (methine protons of cyclohexyl substituent)/G**			
		3	4	5	6
4	2.0047	— (0.50)	(3.13) —	(3.13) —	— (0.50)
5	2.0047	— (0.65)	(3.13) —	— (1.80)	(0.715) —
6	2.0046	— (0.10)	— (1.06)	(3.13) —	— (0.47)

* The spectra were recorded at 293 K.

** The positions of aromatic protons for which the interaction with an unpaired electron is observed are given in accordance with the notation in Scheme 1. The experimentally measured HFS constant values on protons were refined using the simulated spectra.

ation of the spin density at positions of the quinone ring bound to the alkyl groups.

The hyperfine splitting constant values for hydrogen atoms observed for mono-reduced potassium derivatives of *o*-quinones **4—6** are given in Table 5. The correlation of the constant values with specific atoms in the semiquinone ligand was carried out by analogy with the previously described derivatives of bis(diphenylmethyl)-substituted *o*-quinones.[21] It should be noted that the character of the spin density distribution in cyclohexyl semiquinonate species are very similar to that in corresponding bis-(diphenylmethyl)-substituted derivatives.

In conclusion, we have developed a convenient procedure for the preparative synthesis of cyclohexyl-substituted *o*-quinones, the degree of steric protection of the dioxolene fragment in which is lower than in the *tert*-butyl analogs. Despite the reduced hindering, the new *o*-quinones and their reduced derivatives are stable and can be used as redox-active dioxolene ligands for the preparation of metal complexes. It is important that the reaction of catechol with cyclohexene gives a symmetric 3,6-disubstituted derivative, which is absent in the products of the alkylation of catechol with benzhydrol.

Experimental

NMR spectra were recorded on a Bruker Avance III 400 spectrometer (400 (^{1}H) and 100 MHz (^{13}C and DEPT)). EPR spectra were obtained on a Bruker EMX 8/2.7 spectrometer. The WinEPR SimFonia v1.25 program (Bruker) was used for spectra simulation. IR spectra were recorded on a Bruker Vertex 70 FT-IR spectrometer with a RAM II diffuse reflectance sampling accessory. The elemental analysis was performed on an Elementar vario EL cube automatic elemental analyzer (Germany).

The reduction potentials were measured by cyclic voltammetry (CV) in a three-electrode cell using an Elins P-45X potentiostat in acetonitrile in an argon atmosphere. The working electrode was a stationary glassy carbon (GC) electrode with a diameter of 2 mm, the auxiliary electrode was a platinum grid. The reference electrode was Ag/AgCl/KCl (sat.) with a waterproof diaphragm. The potential sweep rate was 100 mV s^{-1}. Supporting electrolyte was 0.1 *M* Bu_4NClO_4 recrystallized twice from aqueous EtOH and vacuum dried (48 h) at 50 °C. The concentration of *o*-benzoquinones **4—6** in acetonitrile was $5 \cdot 10^{-3}$ mol L^{-1}.

HPLC was carried out on a Knauer liquid chromatograph equipped with a UV detector (λ = 254 nm) and a steel column 100×6 mm in size filled with a Silasorb 600 SPH sorbent; eluent hexane—THF, 150 : 1, the eluent flow rate was 1.5 mL min^{-1}.

Solvents were purified and dehydrated using standard procedures.[26] Commercially available catechol and cyclohexene were used without prior purification.

Samples of potassium semiquinolates for recording EPR spectra were prepared according to the procedure described earlier.[27]

Alkylation of catechol. Cyclohexene (25 mL, 0.25 mol) was slowly added dropwise to a melt of catechol (11 g, 0.1 mol) with perchloric acid (2 mL, 0.02 mol) in a flat-bottom flask equipped with a condenser at 120 °C with continuous stirring. After cooling, the solidified reaction mixture was dissolved in diethyl ether, washed from acid with water until neutral pH, and the solvent was evaporated under reduced pressure on a rotary evaporator. The solid residue was dissolved in hexane (200 mL) with heating; 3,5-dicyclohexylcatechol (**2**) (10.5 g, 38%) was crystallized upon cooling the solution to −18 °C. The solvent was evaporated from the mother liquor under reduced pressure, the residue was dissolved in diethyl ether and the solution was oxidized with a solution of $K_3Fe(CN)_6$ (100 g), KOH (5 g), and Na_2CO_3 (10 g) in water (250 mL) with magnetic stirring. Then, the organic layer was washed with water until the washings were neutral and dried with anhydrous Na_2SO_4, the solvent was evaporated under reduced pressure. The solid residue was dissolved in hexane (100 mL) upon heating, quinone **4** (2.5 g) was precipitated from the solution at −18 °C. The remaining mixture of *o*-quinones was separated by column chromatography (eluent hexane—ethyl acetate (25 : 1), silica gel (0.063—0.2 mm, Macherey-Nagel)) and crystallized from hexane to isolate quinone **6** (4.9 g, 14%), quinone **4** (3.3 g, 12%) (total from the reaction mixture and after column chromatography), and quinone **5** (5.4 g, 20%). Crystals of 3,4,6-tricyclohexyl-*o*-quinone (**6**) suitable for X-ray diffraction analysis were obtained after recrystallization upon cooling to −18 °C from hexane—diethyl ether (10 : 1).

3,6-Dicyclohexylbenzene-1,2-diol (1). Hydrazine hydrate was added dropwise from a capillary to a solution of 3,6-dicyclohexyl-*o*-quinone (**4**) (0.25 g, 1 mmol) in anhydrous methanol (10 mL) with magnetic stirring until the solution was completely discol-

ored. Product **1** was precipitated from the solution by the gradual addition of water with constant vigorous stirring. The precipitate was collected by filtration, washed with water, and dried under reduced pressure. A colorless powder. The yield was 0.14 g (56%), m.p. 128—129 °C. Found (%): C, 78.34; H, 9.48. $C_{18}H_{26}O_2$. Calculated (%): C, 78.79; H, 9.55. IR, ν/cm^{-1}: 3580—3100 (v.br), 1630 (w), 1611 (w), 1577 (w), 1550 (w), 1504 (m), 1350 (s), 1295 (s), 1260 (s), 1235 (s), 1209 (s), 1175 (s), 1131 (s), 1087 (m), 1075 (m), 1050 (m), 1030 (m), 1017 (m), 975 (s), 937 (s), 920 (m), 890 (m), 850 (w), 815 (m), 800 (s), 766 (w), 754 (m), 732 (m), 630 (m), 590 (w), 571 (w), 532 (m), 493 (m), 466 (m). ^{1}H NMR ($CDCl_3$), δ: 1.14—1.98 (m, 20 H, CH_2 in *cyclo*-C_6H_{11}); 2.58—2.80 (m, 2 H, CH in *cyclo*-C_6H_{11}); 5.12 (s, 2 H, OH); 6.72 (s, 2 H, C(4) and C(5)). ^{13}C NMR ($CDCl_3$), δ: 26.2 (CH_2); 27.0 (CH_2); 33.1 (CH_2); 37.5 (CH); 117.9 (CH); 131.0 (C); 140.6 (C).

3,5-Dicyclohexylbenzene-1,2-diol (2). A colorless powder. The yield was 10.5 g (38%), m.p. 118—119 °C. Found (%): C, 78.16; H, 9.34. $C_{18}H_{26}O_2$. Calculated (%): C, 78.79; H, 9.55. IR, ν/cm^{-1}: 3585—3076 (v.br), 1714 (w), 1620 (m), 1600 (m), 1506 (s), 1485 (m), 1460 (s), 1446 (s), 1378 (s), 1366 (s), 1346 (m), 1338 (m), 1296 (s), 1264 (s), 1244 (s), 1229 (s), 1184 (s), 1145 (m), 1134 (m), 1122 (m), 1078 (w), 1043 (w), 1030 (w), 1010 (w), 972 (s), 955 (s), 920 (w), 890 (w), 870 (w), 848 (s), 813 (w), 795 (w), 778 (m), 745 (m), 722 (m), 640 (m), 610 (w), 597 (w), 522 (w), 498 (w), 484 (w). ^{1}H NMR ($CDCl_3$), δ: 1.13—1.52 and 1.67—1.97 (both m, 10 H each, CH_2 in *cyclo*-C_6H_{11}); 2.31—2.46 and 2.70—2.87 (both m, 1 H each, CH in *cyclo*-C_6H_{11}); 5.04 and 5.06 (both s, 1 H each, OH); 6.58 and 6.62 (both s, 1 H each, C(4)H and C(6)H). ^{13}C NMR ($CDCl_3$), δ: 26.2 (CH_2); 26.3 (CH_2); 26.9 (CH_2); 27.0 (CH_2); 33.1 (CH_2); 34.7 (CH_2); 37.7 (CH); 44.2 (CH); 110.9 (CH); 117.2 (CH); 133.9 (C); 138.9 (C); 140.6 (C); 142.7 (C).

3,4,6-Tricyclohexylbenzene-1,2-diol (3) was obtained from 3,4,6-tricyclohexyl-*o*-quinone (**6**) similar to catechol **1**. A colorless powder. The yield was 0.22 g (61%), m.p. 158—159 °C. Found (%): C, 81.06; H, 9.92. $C_{24}H_{36}O_2$. Calculated (%): C, 80.85; H, 10.18. IR, ν/cm^{-1}: 3630—3090 (v.br), 1701 (w), 1678 (w), 1670 (w), 1654 (w), 1612 (m), 1576 (m), 1489 (s), 1348 (s), 1325 (m), 1297 (s), 1282 (s), 1262 (s), 1232 (s), 1226 (s), 1216 (s), 1193 (s), 1180 (s), 1136 (s), 1126 (m), 1080 (m), 1055 (m), 1026 (m), 1010 (m), 977 (m), 919 (m), 891 (m), 849 (m), 840 (w), 808 (w), 803 (w), 787 (w), 770 (w), 735 (w), 720 (w), 710 (w), 680 (w), 658 (w), 607 (w), 594 (w), 555 (w), 503 (w). ^{1}H NMR ($CDCl_3$), δ: 1.14—2.22 (m, 30 H, CH_2 in *cyclo*-C_6H_{11}); 2.54—2.76 (m, 2 H, CH in *cyclo*-C_6H_{11}); 2.77—2.91 (m, 1 H, CH in *cyclo*-C_6H_{11}); 4.77 and 5.41 (both s, 1 H each, OH); 6.61 (s, 1 H, H(5)). ^{13}C NMR ($CDCl_3$), δ: 26.2 (CH_2); 26.4 (CH_2); 27.0 (CH_2); 27.3 (CH_2); 27.6 (CH_2); 30.47 (CH_2); 30.48 (CH_2); 33.1 (CH_2); 34.9 (CH_2); 38.0 (CH); 38.4 (CH); 40.3 (CH); 114.7 (CH); 128.1; 130.3 (C); 137.9 (C); 138.6 (C); 143.1 (C).

3,6-Dicyclohexylcyclohexa-3,5-diene-1,2-dione (4). Brown green crystals, m.p. 129—131 °C. Found (%): C, 79.61; H, 9.43. $C_{18}H_{24}O_2$. Calculated (%): C, 79.37; H, 8.88. IR, ν/cm^{-1}: 1674 (s), 1668 (s), 1652 (s), 1464 (s), 1451 (s), 1396 (s), 1378 (s), 1357 (m), 1345 (m), 1325 (m), 1300 (m), 1268 (m), 1233 (m), 1180 (m), 1154 (w), 1134 (w), 1108 (w), 1076 (w), 1052 (w), 1027 (w), 1003 (w), 953 (m), 920 (w), 905 (w), 885 (m), 864 (m), 855 (w), 845 (w), 833 (w), 786 (w), 721 (m), 669 (w), 621 (m), 570 (w), 527 (w), 490 (w), 468 (w). ^{1}H NMR ($CDCl_3$), δ: 1.06—1.45 and 1.66—1.84 (both m, 5 H each, CH_2 in *cyclo*-C_6H_{11}); 2.48—2.65 (m, 1 H, CH in *cyclo*-C_6H_{11}); 6.66 (s, 1 H). ^{13}C NMR ($CDCl_3$), δ: 26.1; 26.4; 32.2; 36.6; 133.6; 146.4; 181.0.

3,5-Dicyclohexylcyclohexa-3,5-diene-1,2-dione (5). Cherry-red crystals, m.p. 47—48 °C. Found (%): C, 79.25; H, 9.10. $C_{18}H_{24}O_2$. Calculated (%): C, 79.37; H, 8.88; O, 11.75. IR, ν/cm^{-1}: 1682 (s), 1660 (s), 1634 (s), 1597 (w), 1576 (m), 1464 (m), 1450 (s), 1400 (m), 1377 (m), 1357 (m), 1333 (m), 1315 (m), 1306 (m), 1290 (m), 1254 (s), 1240 (m), 1200 (m), 1180 (w), 1134 (w), 1118 (w), 1078 (w), 1030 (w), 1001 (w), 992 (w), 964 (w), 946 (m), 920 (w), 891 (m), 858 (m), 798 (m), 780 (w), 763 (w), 720 (w), 648 (w), 618 (w), 603 (w), 580 (w), 555 (w), 507 (w), 499 (w), 475 (w). ^{1}H NMR ($CDCl_3$), δ: 1.11—1.45 and 1.68—1.95 (both m, 10 H each, CH_2 in *cyclo*-C_6H_{11}); 2.10—2.21 and 2.58—2.68 (both m, 1 H each, CH in *cyclo*-C_6H_{11}); 6.07 and 6.59 (both s, 1 H each, C(4)H and C(6)H). ^{13}C NMR ($CDCl_3$), δ: 25.7 (CH_2); 26.0 (CH_2); 26.1 (CH_2); 26.4 (CH_2); 30.8 (CH_2); 32.3 (CH_2); 36.8 (CH); 44.9 (CH); 122.2 (CH); 135.5 (CH); 148.1 (C); 160.9 (C); 180.3 (C); 180.8 (C).

3,4,6-Tricyclohexylcyclohexa-3,5-diene-1,2-dione (6). Dark cherry crystals, m.p. 136—137 °C. Found (%): C, 81.37; H, 9.90. $C_{24}H_{34}O_2$. Calculated (%):C, 81.31; H, 9.67. IR, ν/cm^{-1}: 1675 (s), 1653 (s), 1626 (m), 1562 (w), 1450 (s), 1400 (m), 1377 (m), 1360 (m), 1347 (m), 1325 (m), 1313 (m), 1289 (m), 1267 (m), 1253 (m), 1232 (m), 1208 (w), 1187 (w), 1177 (w), 1140 (w), 1127 (w), 1060 (w), 1047 (w), 1027 (w), 1000 (w), 985 (m), 964 (w), 928 (m), 892 (m), 878 (m), 850 (w), 842 (w), 833 (w), 800 (w), 788 (w), 734 (w), 714 (w), 669 (w), 656 (w), 588 (m), 532 (w), 505 (w), 488 (w), 459 (w). ^{1}H NMR ($CDCl_3$), δ: 1.11—1.96 (m, 30 H, CH_2 in *cyclo*-C_6H_{11}); 2.50—2.61, 2.63—2.75 and 2.78—2.88 (all m, 1 H each, CH in *cyclo*-C_6H_{11}); 6.72 (s, 1 H, H(5)). ^{13}C NMR ($CDCl_3$), δ: 25.7 (CH_2); 25.8 (CH_2); 25.9 (CH_2); 26.1 (CH_2); 26.4 (CH_2); 27.1 (CH_2); 30.2 (CH_2); 30.7 (CH_2); 32.2 (CH_2); 36.8 (CH); 38.0 (CH); 40.6 (CH); 135.1 (CH); 140.0 (C); 145.7 (C); 153.1 (C); 180.7 (C); 181.9 (C).

X-ray diffraction study of compound 6 was carried out on a Bruker D8 Quest diffractometer (ω- and ϕ-scan technique, MoKα radiation, λ = 0.71073 Å, T = 100 K). The experimental sets of intensities were integrated using the SAINT program.[28] The structure was solved by the direct method and refined by the full-matrix least squares method with anisotropic displacement parameters based on F^2_{hkl} for non-hydrogen atoms. Hydrogen atoms were positioned geometrically and refined isotropically. The structure calculations were performed using the SHELXTL software package.[29] Absorption was taken into account using the SADABS program.[30] In the crystal of compound **6**, the cyclohexyl substituents are disordered, in molecule **A** all three cyclohexyl substituents (only two in molecule **B**) were refined over two positions. The crystallographic data and parameters of the X-ray diffraction experiment for compound **6** are given in Tables 2 and 3. Structure **6** is registered at the Cambridge Crystallographic Data Center (CCDC 2014585) and is available at ccdc.cam.ac.uk/getstructures.

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