Electrosynthesis of Symmetric and Highly Conjugated Benzofuran via a Unique ECECCC Electrochemical Mechanism: Evidence for Predominance of Electrochemical Oxidation versus Intramolecular Cyclization

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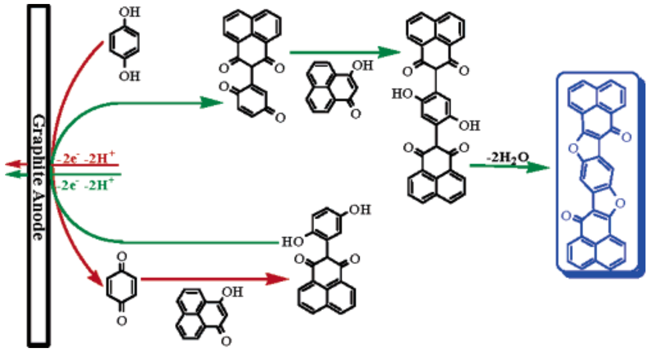
Received December 2, 2006



Electrochemical oxidation of hydroquinone, catechol, and some of their monosubstituted derivatives has been studied in the presence of 3-hydroxy-1*H*-phenalen-1-one (**2**) as a nucleophile in water/acetonitrile (80/20) solutions using cyclic voltammetry and controlled-potential coulometry methods. The results revealed that quinones derived from oxidation of hydroquinones and catechols participate in Michael addition reactions with **2**. The formed adducts convert to the corresponding benzofuran derivatives via different mechanisms. In this work, we derived a variety of products with good yields using controlled potential electrochemical oxidation at a graphite electrode in an undivided cell.

In nature's collection of biologically active heterocycles, benzofuran derivatives constitute a major group. They are usually important constituents of plant extracts used in traditional medicine[1] and were shown to be effective as antitumor agents,[2] antidepressants,[3] and antihypertensives and even to be cytotoxic.[4] On the other hand, catechol derivatives play an important role in mammalian metabolism. In addition, many compounds of this type are known to be secondary metabolites of higher plants.[5] Several methodologies are available for the synthesis of simple benzofurans; however, less attention has been given to the synthesis of hydroxylated benzofurans. The reported methodologies for the synthesis of natural hydroxylated benzofurans usually involve formation of C−C bond between benzofuran and a substituted aryl halide,[6a] arylation of a benzofuranone,[6b] Sonogashira coupling of terminal acetylenes with aryl halides,[6c] coupling of a diphenyl ketone with the

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10.1021/jo062468b CCC: $37.00

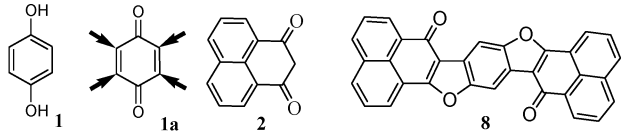


FIGURE 1. Structure of initial (**1**, **2**), intermediate (**1a**), and final product (**8**).

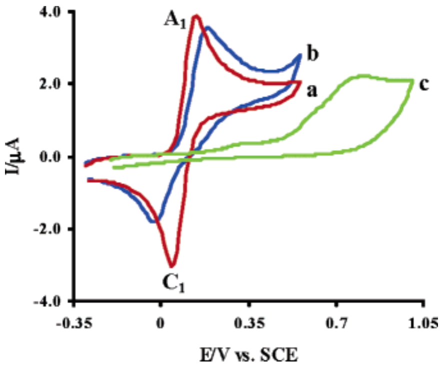


FIGURE 2. Cyclic voltammograms of (a) 0.50 mM hydroquinone (**1**), (b) 0.50 mM hydroquinone in presence of 0.5 mM **2**, and (c) 0.5 mM 3-hydroxy-1*H*-phenalen-1-one (**2**), at a glassy carbon electrode in water/acetonitrile (80/20) solution containing 0.1 M acetate buffer (pH = 5.5). Scan rate: 25 mV s^{-1}; $t = 25 \pm 1$ °C.

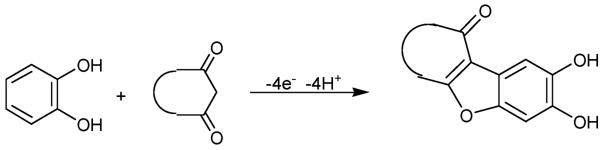
lithium salt of trimethylsilyldiazomethane,[6d] and use of an intramolecular Wittig reaction.[6e]

To synthesize new benzofuran derivatives we studied the electrochemical oxidation of benzenediols in aqueous solutions and in the presence of a variety of nucleophiles derived from CH acids.[7] In this direction, we investigated the electrochemical oxidation of catechols in the presence of β-diketone such as acetylacetone[8a] and dimedone.[7a] The results showed that benzofuran derivatives are formed (Scheme 1). In addition, the preparation of new benzofuran derivatives via the electrooxidation of 2,3-dimethylhydroquinone in the presence of 3-hydroxy-1*H*-phenalen-1-one (**2**) has been recently reported by us[9] (Scheme 2).

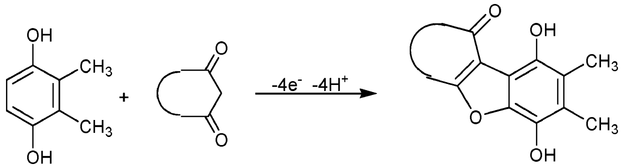
In the present paper, we describe the preparation of a new, symmetric, and highly conjugated benzofuran derivative (**8**) using electrooxidation of hydroquinone (**1**) in the presence of 3-hydroxy-1*H*-phenalen-1-one (**2**) as a nucleophile via a unique ECECCC electrochemical mechanism. Contrary to previous cases, electrochemically generated *p*-benzoquinone (**1a**) has four electrophilic reactive sites (Figure 1).

In addition, in order to extend the above-mentioned strategy, we describe the preparation of other some new benzofuran derivatives using the electrooxidation of hydroquinone and catechol derivatives in the presence of **2**. The presented work has led to the development of a facile, environmentally friendly and reagentless method with high atom economy and safe wastes, for synthesis of some new benzofuran derivatives in ambient conditions in an undivided cell using a graphite electrode.

SCHEME 1



SCHEME 2



The cyclic voltammogram of a 0.5 mM solution of hydroquinone (**1**) in water/acetonitrile (80/20) solution containing 0.10 M acetate buffer (pH 5.5) is shown in Figure 2. As can be seen, one anodic (A_1) and its corresponding cathodic (C_1) peak was obtained, which correspond to the transformation of hydroquinone to *p*-benzoquinone and vice versa, within a quasi-reversible two-electron process (Figure 2, curve a).

A peak current ratio (I_p^{C1}/I_p^{A1}) of nearly unity in the cyclic voltammogram can be considered as a criterion for the stability of *p*-benzoquinone produced at the surface of the electrode under the experimental conditions. In other words, any side reactions such as hydroxylation and/or dimerization reactions are too slow to be observed at the time scale of cyclic voltammetry.[10,11] The oxidation of hydroquinone (**1**) in the presence of **2** as a nucleophile was studied in some detail. Figure 2, curve b shows the cyclic voltammogram obtained for a 0.5 mM solution of hydroquinone (**1**) in the presence of 0.5 mM of **2**. The voltammogram exhibits one anodic peak (A_1) at 0.19 V versus SCE, and its cathodic counterpart at −0.03 V versus SCE. The comparison of C_1 peaks in the absence and presence of **2** shows a decrease of the current density for the latter. This indicates the reactivity of electrochemically generated *p*-benzoquinone toward **2**. The observed shift of the C_1 peak in curve b, relative to curve a, is probably due to the formation of a thin film of product at the surface of the electrode, inhibiting to a certain extent the performance of the electrode process.[12] In this figure, curve c is the voltammogram of **2**.

Controlled-potential coulometry was performed in water/acetonitrile (80/20) solution containing 0.25 mmol of **1** and 0.25 mmol of **2** at 0.25 V versus SCE. The electrolysis progress was monitored using cyclic voltammetry (Figure 3). It is shown that, proportional to the advancement of coulometry, the A_1 anodic peak decreases. All anodic and cathodic peaks disappear when the charge consumption becomes about $4e^-$ per molecule of **1**.

The spectroscopic data (^1H, ^{13}C NMR spectra and molecular mass of 462) support the symmetrical structure and aromaticity of **8**, which has an orange color. These observations allow us to propose the pathway in Scheme 3 for the electrochemical oxidation of **1** in the presence of **2**. According to our results, it seems that the Michael addition reaction of **2** to *p*-benzoquinone **1a** (eq 2) is faster than other secondary reactions, leading to the intermediate **4**. The oxidation of this compound (**4**) is easier than the oxidation of the parent-starting molecule (**1**) by virtue

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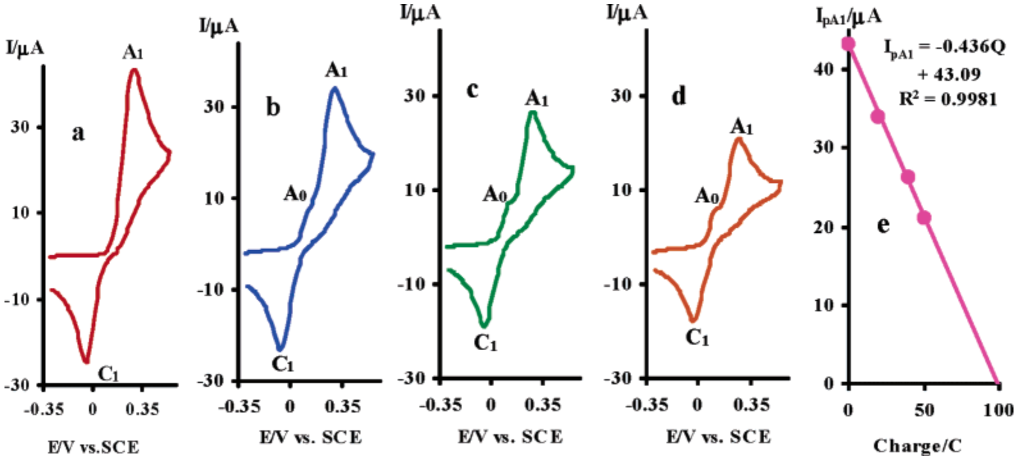
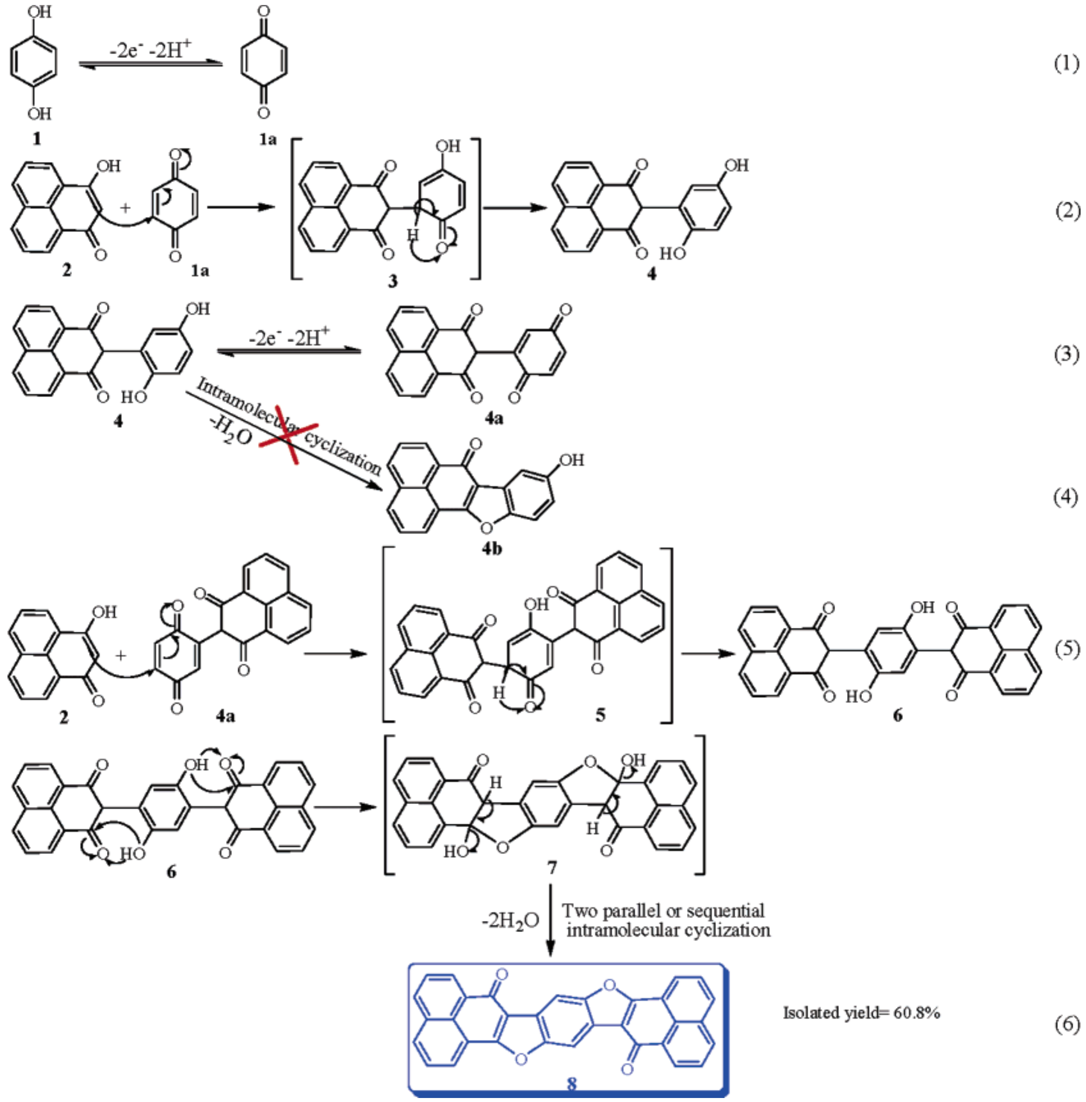


FIGURE 3. Cyclic voltammograms of 0.25 mM of hydroquinone (**1**) in the presence of 0.25 mM **2**, at a glassy carbon electrode in water/acetonitrile (80/20) solution containing 0.2 M acetate buffer (pH = 5.5) during controlled potential coulometry at 0.25 V versus SCE after consumption of (a) 0, (b) 20, (c) 40, and (d) 50 C. (e) Variation of peak current (I_p^{A1}) versus charge consumed. Scan rate 100 mV s^{-1}; $t = 25 \pm 1$ °C.

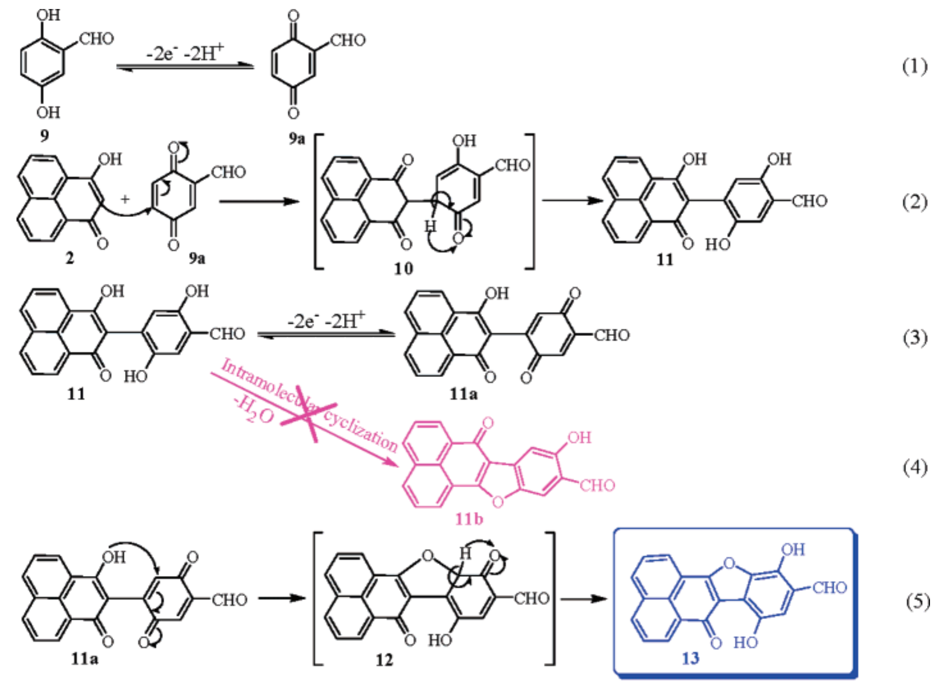
SCHEME 3



of the presence of an electron-donating group.[8] Thus, as the chemical reaction takes place, the apparent number of electrons transferred increases from the limits of $n = 2$ to 4 electrons per molecule. Further Michael addition reaction of **2** to *p*-benzoquinone **4a** (eq 4) followed by elimination of two molecules of H_2O leads to the final product **8**.

According to Scheme 3, in Figure 3 the anodic peak (A_1) is due to the oxidation of hydroquinone (**1**) to *p*-benzoquinone **1a**

SCHEME 4



Isolated Yield= 57.2%

and the anodic peak (A_0) is due to the oxidation of intermediate **4**. A rigorous look at presented mechanism helps us to evaluate the relative kinetic rates of the two intramolecular cyclizations (eq 4) and the second Micheal addition (eq 5). Scheme 3 clearly shows that for the formation of **8**, the electrooxidation of **4** is necessary before its intramolecular cyclization (eq 4). It means that in a competition between electrochemical oxidation and intramolecular cyclization reactions (eqs 3 and 4), the first is faster. In fact, compound **4b** is a two-electron (not four electrons) product, and oxidation of it does not occur at the applied potential for synthesis of **8** (0.25 V vs SCE).[8a]

The electrochemical oxidation of 2,5-dihydroxybenzaldehyde (**9**) in the presence of **2** in water/acetonitrile (80/20) solution containing 0.10 M acetate buffer (pH 5.5) proceeds in a way similar to that of **1** (Scheme 4). Under these conditions, the cathodic counterpart of anodic peak decreases. In comparison with cyclic voltammograms of **1**, *p*-benzoquinone **9a** derived from the oxidation of **9** has more reactivity toward the intermolecular Michael addition reactions, appearing as a decrease in peak current ratio (I_p^{C1}/I_p^{A1}). Other electrochemical investigations including cyclic voltammetry and controlled potential coulometry showed a behavior similar to that of **1**. According to both electrochemical data and spectroscopic data of the final product, we propose a pathway in Scheme 4 for the electrooxidation of **9** in the presence of **2**.

According to our results, it seems that the inter- and intramolecular Michael addition reaction of **2** to *p*-benzoquinone **9a** and a subsequent intramolecular addition of **11a** leads to the product **13**. Also, as shown by Scheme 4, electrochemical oxidation of **11** (eq 3) is faster than the intramolecular cyclization reactions (eq 4), leading to the product **13**. Since the oxidation of the formed dihydroxybenzofuran occurs at more positive potentials, the overoxidation of **13** was circumvented during the controlled potential preparative reaction.[8a] The electroorganic synthesis of **13** has been performed using oxidation of **9** in the presence of **2** as described in the Experimental Section.

The electrochemical oxidation of catechol and some of its derivatives (**14a**−**d**) in the presence of **2**, in water/acetonitrile (80/20) solution containing 0.10 M acetate buffer (pH 5.5) proceeds in a similar way to that of **1**. Figure 4 shows the voltammograms of catechol (**14a**) in the presence and absence of **2**. In this figure, curve a shows the well-defined redox peaks for catechols.[7−9] The oxidation of **14a** in the presence of **2** was studied in some detail (Figure 4, curve b). Under these conditions, the cathodic counterpart of A_1 peak decreases. The multicyclic voltammetry of **14a** in the presence of **2** shows that parallel to the shift of the A_1 peak in a positive direction a new peak (A_0) appears as shoulder at less positive potential in the second cycle (Figure 4, curve c). Since the existence of a β-diketone type group, as an electron-donating group, on the catechol ring makes its oxidation easier, this new peak (A_0) is related to electro-oxidation of intermediate **17a**. Other conditions are similar to those for the electro-oxidation of **1** in the presence of **2**. In this case, and other similar cases (**14b**−**d**), each

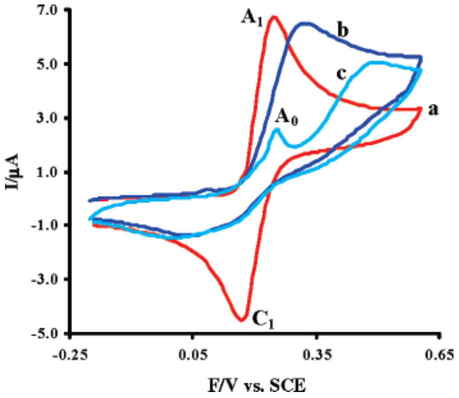
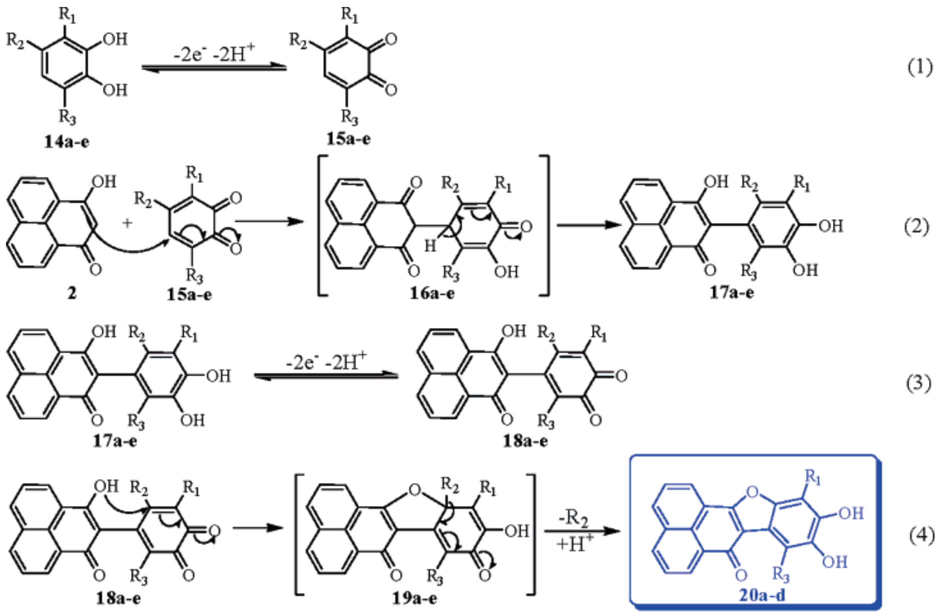


FIGURE 4. Cyclic voltammograms of 0.50 mM catechol: (a) in the absence of **2**, (b and c) first and second scan in presence of 0.5 mM of **2**, at a glassy carbon electrode in water/acetonitrile (80/20) solution containing 0.1 M acetate buffer (pH = 5.5). Scan rate: 50 mV s^{-1}; t = 25 ± 1 °C.

SCHEME 5



$R_1 = R_2 = R_3 = H$,	14a-20a	Isolated Yield	76.8%
$R_1 = CH_3$, $R_2 = R_3 = H$,	14b-20b	Isolated Yield	53.2%
$R_1 = OCH_3$, $R_2 = R_3 = H$,	14c-20c	Isolated Yield	69.3%
$R_1 = R_2 = H$, $R_3 = COOH$,	14d-20d	Isolated Yield	54.2%
$R_1 = R_3 = H$, $R_2 = COOH$,	14e-20a		

molecule of **14a** in the presence of **2** converts to **20a**, via inter- and intramolecular Michael addition reactions with consumption of 4e$^-$. In comparison with *p*-benzoquinone **1a**, *o*-benzoquinone (**15a**) derived from the oxidation of **14a** has more reactivity toward the intermolecular Michael addition reactions, appearing as a decrease in peak current ratio (I_p^{C1}/I_p^{A1}). The reaction mechanism for electro-oxidation of **14a**−**d** in the presence of **2** is presented in Scheme 5.

In order to study of the effect of the presence of a electron-withdrawing group at a reactive site on the catechol ring, the electrochemical oxidation of 3,4-dihydroxybenzoic acid **14e** was studied in the presence of **2**. From the electrochemical and spectroscopic data, we propose a comparable mechanism involving an electro-decarboxylation (Scheme 5).

In conclusion, the results of this work show that hydroquinone (**1**) is oxidized to its respective *p*-benzoquinone (**1a**). The formed *p*-benzoquinone is attacked by **2** and via an ECECCC electrochemical mechanism, including two intermolecular Michael addition reactions of **2** and two parallel or sequential intramolecular cyclizations followed by elimination of H_2O, converts to symmetric and highly conjugated benzofuran **8** as the final product. We observed an interesting diversity in the mechanisms and products of reaction of other electrochemically generated quinones with **2**. Contrary to the hydroquinone, in the case of 2,5-dihydroxybenzaldehyde (**9**), the final product (**13**) is a dihydroxybenzofuran derivative that was obtained after consumption of 4e$^-$ per molecule **9** via inter- and intramolecular Michael addition reactions. In this case, because of low nucleophilicity of the hydroxide group due to the electron-withdrawing character of the CHO group, the intramolecular cyclization and elimination of H_2O from **11** does not take place. In the case of **14a**−**e**, the final products **20a**−**d**, which are also dihydroxybenzofuran derivatives, were obtained after consumption of 4e$^-$ per molecule via inter- and intramolecular Michael addition reactions. Finally because there is no hydroxyl group at R^3, intermediates **17a**−**d** cannot undergo an intramolecular cyclization and elimination of H_2O.

Experimental Section

Apparatus and Reagents. Reaction equipment is described in the Supporting Information. All chemicals (hydroquinone, catechols and 3-hydroxy-1*H*-phenalen-1-one) were reagent-grade materials. Sodium acetate, solvents, and reagents were of pro-analysis. These chemicals were used without further purification.

Electroorganic Synthesis of 8, 13, and 20a−**d.** In a typical procedure, 60 mL of sodium acetate solution (0.2 M, pH = 5.5) in water/acetonitrile (80/20) was pre-electrolyzed at 0.5 V versus SCE, in an undivided cell, and then 0.25 mmol of **1**, **9**, and **14a**−**e** and 0.25 mmol of **2** were added to the cell. The electrolysis was terminated when the current decayed to 5% of its original value. The process was interrupted several times during the electrolysis and the carbon anode was washed in tetrahydrofuran (THF) in order to reactivate it. At the end of electrolysis, to achieve a better precipitation, a few drops of acetic acid were added to the solution and the cell was placed in refrigerator overnight. The precipitated solid was collected by filtration and was washed several times with water. After recrystallization, products were characterized by IR, ^{1}H NMR, ^{13}C NMR, and MS. The isolated yields of **8**, **13**, and **20a**−**d** after recrystallization are reported in Schemes 3, 4, and 5 respectively.

Characteristic of Products (8, 13, and 20a−**d). 8** ($C_{32}H_{14}O_4$): mp >273 °C (dec) ^{1}H NMR, δ ppm (300 MHz, DMSO-d_6): 7.05 (s, 2H, aromatic), 7.64 (t, $J = 7.3$ Hz, 4H, aromatic), 8.17, 8.22 (dd, $J = 8$ Hz, $J' = 7.1$ Hz, 8H, aromatic). ^{13}C NMR, δ ppm (500 MHz, DMSO-d_6): 112, 116, 121.7, 125.7, 125.8, 126, 126.5, 127.4, 127.9, 131.2, 132.6, 133.1, 136.8, 142.4, 148.6, 185.3. IR$_{(KBr)}$: 1708, 1659, 1631, 1605, 1512, 1433, 1382, 1331, 1292, 1223, 1099, 1026, 966, 876, 846, 784, 591 cm^{-1}. MS: *m*/*e* (relative intensity); 462 (M$^{+\cdot}$, 100), 348 (29), 174 (19.5), 56 (47.5), 33 (96.3).

13 ($C_{20}H_{10}O_5$): mp >232 °C (dec) ^{1}H NMR, δ ppm (300 MHz, DMSO-d_6): 7.25 (s, 1H, aromatic), 7.81 (t, J = 7.4 Hz, 1H, aromatic), 7.91 (t, J = 7.3 Hz, 1H, aromatic), 8.28, 8.35 (dd, J = 8.2 Hz, J' = 6.4 Hz, 2H, aromatic), 8.44 (d, J = 7.6 Hz, 1H, aromatic), 8.57 (d, J = 7.1 Hz, 1H, aromatic), 9.07 (s, 1H, OH), 10.40 (s, 1H, OH), 13 (broad, 1H, aldehyde).^{13}C NMR, δ ppm (300 MHz, DMSO-d_6): 99.1, 111.9, 116.7, 120.3, 125.2, 125.3, 127.5, 127.8, 129.6, 130.6, 132.5, 132.6, 135.8, 141.8, 146.5, 149.1, 159.8, 168.2. IR$_{(KBr)}$: 3331, 2880, 1631, 1581, 1529, 1383, 1271, 1226, 1148, 1000, 964, 907, 779, 720, 569 cm^{-1}. MS: *m*/*e* (relative intensity); 330 ($M^{+\cdot}$, 100), 286 (32), 189 (19.5), 163 (25.6), 126 (14.6), 95 (18.3), 69 (19.5), 44 (45).

20a ($C_{19}H_{10}O_4$): mp >307 °C (dec). ^{1}H NMR, δ ppm (300 MHz, DMSO-d_6): 7.18 (s, 1H, aromatic), 7.52 (s, 1H, aromatic), 7.80 (t, J = 7.4 Hz, 1H, aromatic), 7.90 (t, J = 7 Hz, 1H, aromatic), 8.26, 8.32 (dd, J = 8 Hz, J' = 6.6 Hz, 2H, aromatic), 8.40 (d, J = 7.8 Hz, 1H, aromatic), 8.60 (d, J = 7.1 Hz, 1H, aromatic), 9.43 (s, 1H, OH), 9.53 (s, 1H, OH). ^{13}C NMR, δ ppm (300 MHz, DMSO-d_6):99, 106.5, 115.5, 117, 120.5, 125, 125.5, 127.5, 127.75, 129.5, 130.5, 132.5, 132.6, 136, 145, 146.6, 149.75, 159.5, 180.5. IR$_{(KBr)}$: 3335, 1709, 1634, 1617, 1574, 1100, 1001, 904, 782, 750, 720,-568 cm^{-1}. MS: *m*/*e* (relative intensity); 302 ($M^{+\cdot}$, 100), 189 (16).

20b ($C_{20}H_{12}O_4$): mp >276 °C (dec) ^{1}H NMR, δ ppm (90 MHz, DMSO-d_6): 2.40 (s, 3H, methyl), 7.40 (s, 1H, aromatic), 7.84−8.79 (broad, 6H, aromatic), 9.68 (s, 2H, OH). ^{13}C NMR, δ ppm (300 MHz, DMSO-d_6):9.5, 103.3, 108.6, 114.6, 120.6, 124.9, 125.4, 127.4, 127.6, 129.7, 130.3, 132.3, 132.6, 135.9, 144.3, 144.4, 149.4, 149.75, 155.6, 180.4. IR$_{(KBr)}$: 3361, 2961, 2919, 2850, 1727, 1634, 1617, 1575, 1550, 1518, 1442, 1380, 1316, 1287, 1167, 1100, 1026, 840, 799, 782, 750, 568 cm^{-1}. MS: *m*/*e* (relative intensity); 316 ($M^{+\cdot}$, 100), 213 (17).

20c ($C_{20}H_{12}O_5$): mp >236 °C (dec) ^{1}H NMR, δ ppm (300 MHz, DMSO-d_6): 4.12 (s, 3H, methoxy), 7.23 (s, 1H, aromatic), 7.75 (t, J = 7.7 Hz, 1H, aromatic), 7.85 (t, J = 7.7 Hz, 1H, aromatic), 8.30, 8.41 (dd, J = 7 Hz, J' = 6.6 Hz, 2H, aromatic), 8.44 (d, J = 8 Hz, 1H, aromatic), 8.55 (d, J = 7.2 Hz, 1H, aromatic), 9.05 (s, 1H, OH), 9.55 (s, 1H, OH). ^{13}C NMR, δ ppm (300 MHz, DMSO-d_6): 60.7, 100.5, 115.6, 116.2, 119.9, 124.7, 125, 126.9, 127.2, 129.3, 130, 132.1, 133.6, 135.6, 137.8, 141.6, 145.6, 159.4, 180.0. IR$_{(KBr)}$: 3196, 2841, 1621, 1576, 1527, 1449, 1338, 1103, 1005, 905, 784,734, 561 cm^{-1}. MS: *m*/*e* (relative intensity); 332 ($M^{+\cdot}$, 100), 317 (152), 205 (37), 176 (32), 88 (26).

20d ($C_{20}H_{10}O_6$). mp >268 °C (dec) ^{1}H NMR, δ ppm (90 MHz, DMSO-d_6): 7.25 (s, 1H, aromatic), 7.88−8.60 (broad, 6H, aromatic), 9.07 (broad, 1H, OH), 10.39 (broad, 1H, OH), 12.92 (broad, 1H, acid). ^{13}C NMR, δ ppm (300 MHz, DMSO-d_6): 99.1, 111.9, 116.6, 116.8, 120.3, 125.1, 125.4, 127.5, 127.8, 129.6, 130.6, 132.5, 132.6, 135.8, 141.8, 146.5, 149.1, 159.9, 168.2, 179.1. IR$_{(KBr)}$: 3296, 3082, 1701, 1631, 1604, 1551, 1440, 1381, 1209, 999, 944,843, 779, 747, 682 cm^{-1} MS: *m*/*e* (relative intensity); 302 ($M^{+\cdot} - CO_2$, 100), 228 (14.6), 189 (12), 46 (17).

Supporting Information Available: Copies of ^{1}H, ^{13}C NMR, FTIR, and MS of all compounds (**8**, **13**, and **20a−d**) as well as general information for cyclic voltammetry, controlled-potential coulometry, and bulk electrolysis procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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