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PII: S0040-4020(14)00611-5

DOI: [10.1016/j.tet.2014.04.077](https://doi.org/10.1016/j.tet.2014.04.077)

Reference: TET 25527

To appear in: *Tetrahedron*

Received Date: 27 January 2014

Revised Date: 9 April 2014

Accepted Date: 25 April 2014

Please cite this article as: Habibi D, Nematollahi D, Meshkinghalam S, Varmaghani F, An unexpected oxidative decarboxylation reaction of 2,3-dihydroxybenzoic acid in the synthesis of new dibenzyltetrahydroquinoxalinediones, *Tetrahedron* (2014), doi: 10.1016/j.tet.2014.04.077.

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# An unexpected oxidative decarboxylation reaction of 2,3-dihydroxybenzoic acid in the synthesis of new dibenzyltetrahydroquinoxalinediones

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**Abstract:** Chemical and electrochemical oxidation of different catechols were carried out in the presence of *N,N'*-dibenzylethylenediamine (DBEDA) in a phosphate buffer/acetonitrile solution for the synthesis of different new dibenzyltetrahydroquinoxalinedione derivatives. The oxidation of catechol (**1a**), 2,3-dihydroxybenzoic acid (**1e**) and 3,4-dihydroxybenzoic acid (**1d**) led to the same product, probably due to the decarboxylation reaction of intermediates. An oxidative decarboxylation reaction of 3,4-dihydroxybenzoic acid (**1d**) has been reported before, while an unexpected oxidative decarboxylation reaction of 2,3-dihydroxybenzoic acid (**1e**) in the presence of DBEDA is reported for the first time.

**Keywords:** Catechols; *N,N'*-Dibenzylethylenediamine; Dibenzyltetrahydroquinoxalinediones; Chemical and electrochemical synthesis;  $K_3Fe(CN)_6$

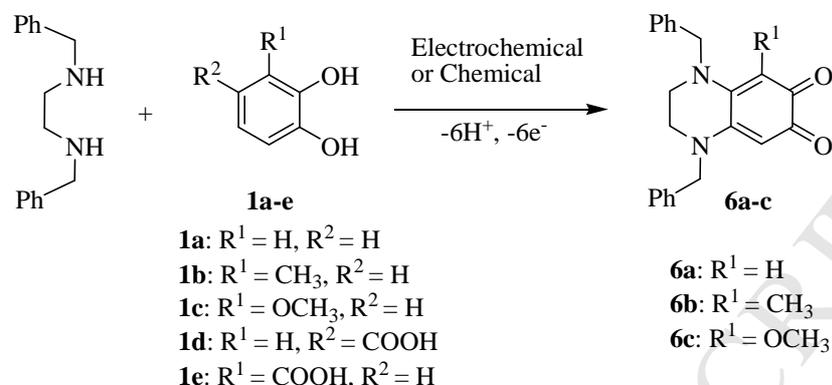
## 1. Introduction

A vast number of quinones with great structural divergence are provided by nature which some of them play a major role in the redox electron-transport chains of living systems.<sup>1-4</sup> Large libraries of quinones, substituted quinones, bisquinones and polyquinones were synthesized during the last century and their properties studied.<sup>5</sup> The aminoquinone derivatives are obtained from the reactions between quinones and the ordinary amines (primary and secondary). When the steric hindrance is absent, two molecules of the amine add to the quinone, while only one molecule will usually be added to non-hindered quinones.<sup>6</sup>

Quinoxalinediones have been used extensively as pharmaceutical agents for treatment of different diseases.<sup>7-10</sup> Also, they have affinities to the quisqualate receptors and are suitable as pharmaceutical agents for treatment of diseases of the central nervous system.<sup>11</sup> In addition, they can be used for treatment of neurological and psychiatric disorders that are triggered by the over stimulation of the AMPA receptors.<sup>12</sup>

In continuation of our studies on the synthesis of nitrogen- and oxygen-containing heterocycles and application of different catalysts in the organic syntheses,<sup>13-16</sup> we would like to report the synthesis of the new

dibenzylquinoxalinedione derivatives from the reaction of various catechols with DBEDA as a nucleophile by both chemical and electrochemical methods (Scheme 1).



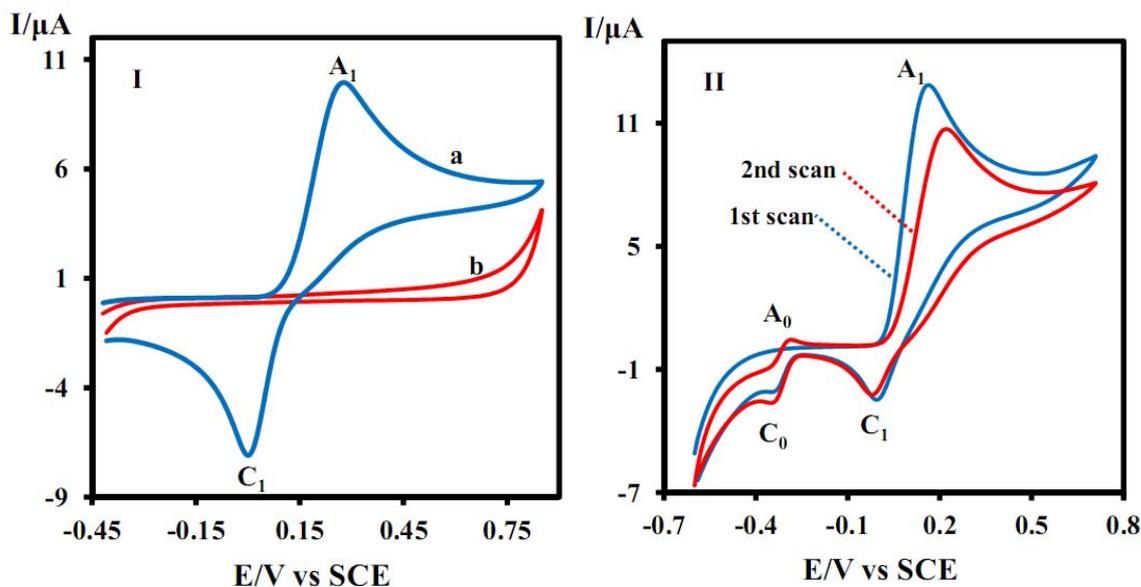
**Scheme 1.** Synthesis of different dibenzyltetrahydroquinoxalinedione derivatives

Also, we have shown three pathways for the synthesis of 1,4-dibenzyl-1,2,3,4-tetrahydroquinoxaline-6,7-dione (**6a**). The results of these studies as well as the full characterization of the obtained products are presented and discussed.

## 2. Results and Discussion

2.1. Electrochemical oxidation of catechol (**1a**), 3-methylcatechol (**1b**) and 3-methoxycatechol (**1c**) in the presence of DBEDA:

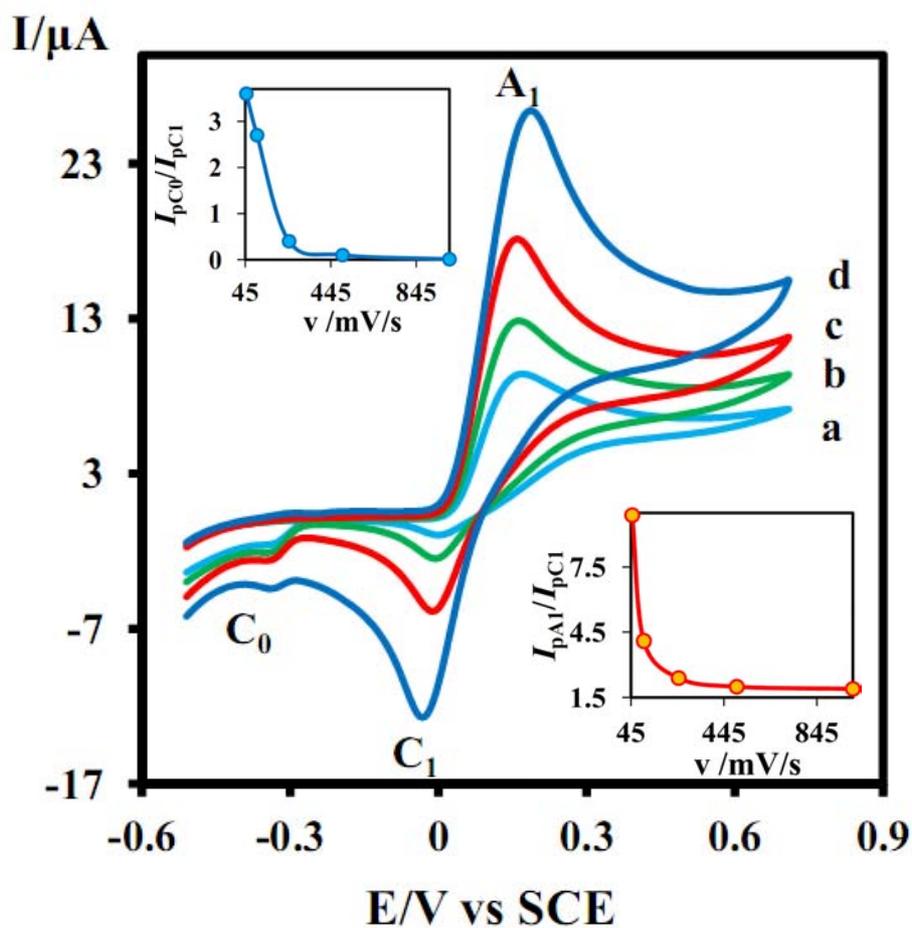
A cyclic voltammetry (CV) of **1a** (1.0 mM) in a mixture of phosphate buffer solution (PBS) (pH = 7.0,  $c = 0.15$  M) and  $\text{CH}_3\text{CN}$  (70:30 v/v) shows one anodic peak ( $A_1$ ) at 0.27 V and the corresponding cathodic peak ( $C_1$ ) at 0.01 V versus SCE which correspond to the transformation of **1a** to *o*-benzoquinone (**2a**) and vice versa within a quasi-reversible two-electron process (Figure 1, curve a).<sup>13</sup> The peak-current ratio ( $I_{pC1}/I_{pA1}$ ) is near unity, which can be considered as a criterion for the stability of **2a** produced at the surface of the electrode under the experimental conditions. This indicates that any hydroxylation<sup>17</sup> or dimerization<sup>18</sup> reactions are too slow to be observed on the time scale of CV.<sup>13</sup> The oxidation of **1a** in the presence of DBEDA (1.0 mM) was studied in some details. Figure 1, II shows the first CV obtained for **1a** (1.0 mM) in the presence of DBEDA. The CV exhibits a new cathodic peak  $C_0$  with  $E_p = -0.34$  V versus SCE. In the second cycle, a new peak ( $A_0$ ) appears with an  $E_p$  value of  $-0.31$  V versus SCE. These new redox peaks ( $A_0$  and  $C_0$ ) are related to the electrooxidation of intermediate **5a** to *p*-benzoquinone **6a** and vice-versa. In this Figure, curve b is the voltammogram of DBEDA which shows the nucleophile is not electroactive in the studied potential range.



**Figure 1.** (I): CVs of 1.0 mM (a) **1a** and (b): DBEDA, (II) first and second cycle CVs of **1a** (1.0 mM) in the presence of DBEDA (1.0 mM) at a glassy carbon electrode in a mixture of PBS (pH = 7,  $c = 0.15$  M) and CH<sub>3</sub>CN (70:30 v/v). Scan rate:  $50 \text{ mVs}^{-1}$ ,  $T = 25 \pm 1$  °C.

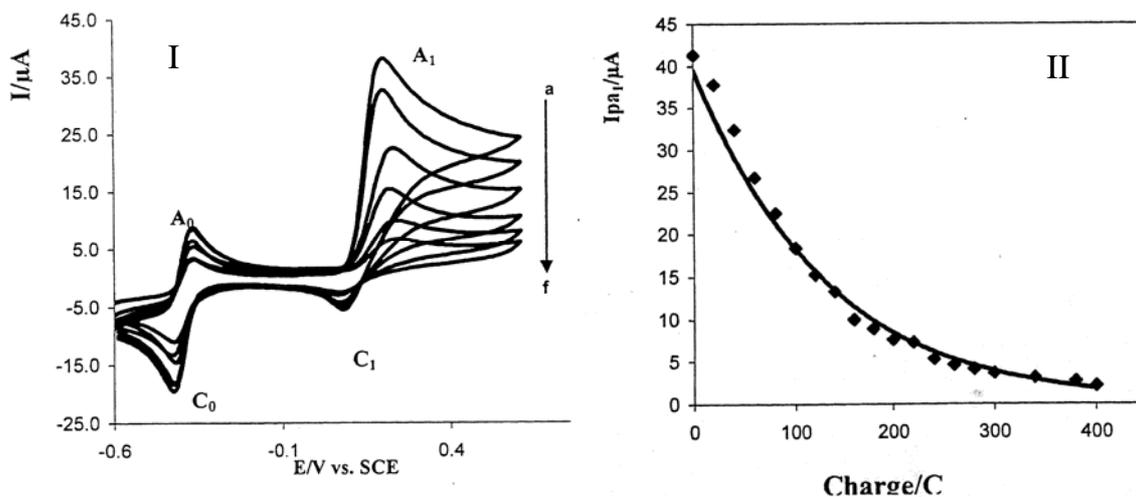
Furthermore, it is seen that proportional to the augmentation of the potential sweep rate and in parallel with decreasing in the height of C<sub>0</sub>, the height of C<sub>1</sub> increases (Figure 2). The subsequent chemical reactions between *o*-benzoquinone (**2a**) and DBEDA is supported by the following evidence:

- Appearance of an anodic peak A<sub>0</sub> and its cathodic counterpart (C<sub>0</sub>) in less positive potentials that show the formation of an electroactive species;
- Decreasing of  $I_{pC1}$  during the reverse scan. This could be indicative of the fact that electrochemically generated *o*-benzoquinone (**2a**) is partially removed by the chemical reaction with DBEDA;
- Variation of peak current ratios ( $I_{pA1}/I_{pC1}$ ) and ( $I_{pC0}/I_{pC1}$ ) versus scan rate for a mixture of **1a** and DBEDA which appear as a decrease in the  $I_{pA1}/I_{pC1}$  and  $I_{pC0}/I_{pC1}$  ratios at higher scan rates.



**Figure 2.** Typical CVs of **1a** (1.0 mM) in the presence of DBEDA (1.0 mM) at various scan rates. Scan rates from a to d are: 25, 50, 100 and 250  $\text{mVs}^{-1}$ , respectively at a glassy carbon electrode in a mixture of PBS (pH = 7,  $c = 0.15$  M) and  $\text{CH}_3\text{CN}$  (70:30 v/v). Inset: Variation of peak current ratios ( $I_{\text{pA}1}/I_{\text{pC}1}$ ) and ( $I_{\text{pC}0}/I_{\text{pC}1}$ ) versus scan rate.

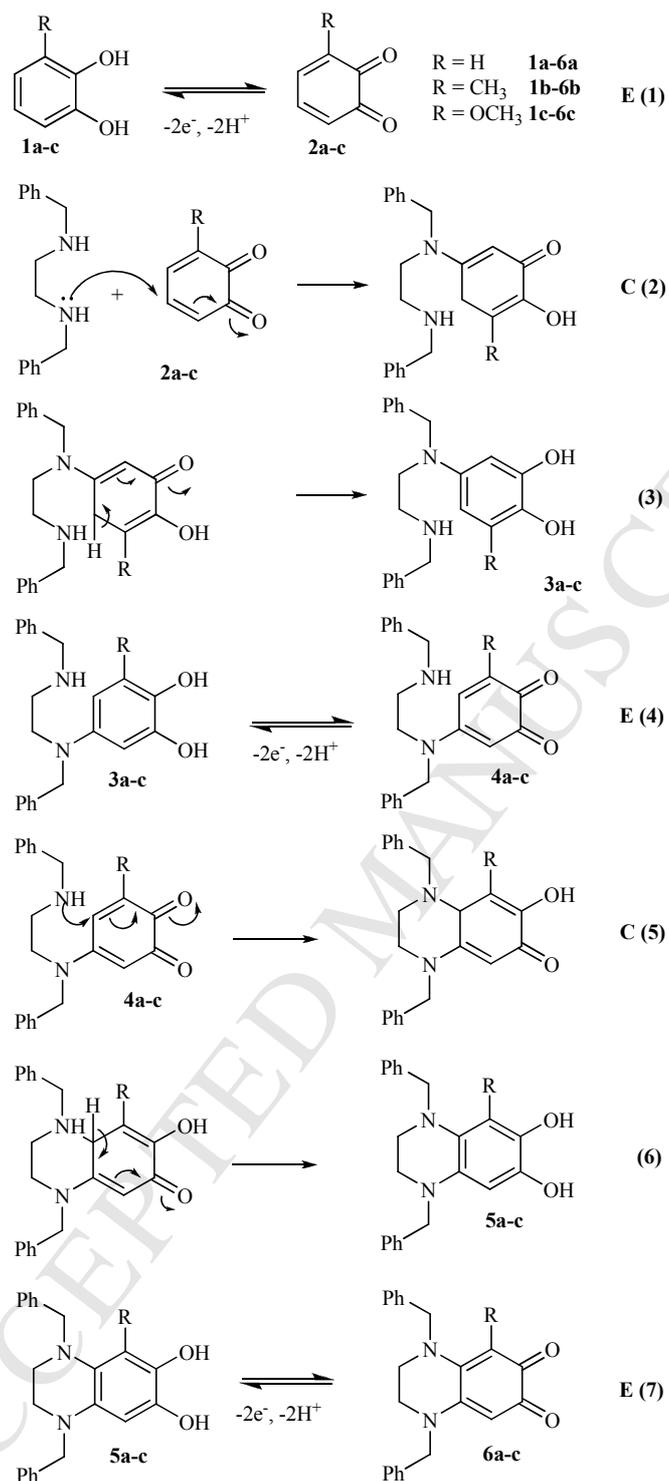
Constant-current coulometry was performed in a mixture of PBS (pH = 7,  $c = 0.15$  M) and  $\text{CH}_3\text{CN}$  (70/30 v/v) containing **1a** (0.25 mmol) and DBEDA (0.25 mmol) in an undivided cell under a low constant current density ( $1 \text{ mA/cm}^2$ ). Monitoring of the electrolysis progress was carried out by CV (Figure 3). It is shown that proportional to the advancement of coulometry and in parallels with decreasing the height of the anodic peak  $A_1$ , the heights of  $A_0$  and  $C_0$  increase. A characteristic feature of electrolysis is that a low-current density is required.



**Figure 3.** (I) CVs of **1a** (0.25 mmol) in the presence of DBEDA (0.25 mmol) in a mixture of PBS (pH = 7,  $c = 0.15$  M) and  $\text{CH}_3\text{CN}$  (70:30 v/v) at a glassy carbon electrode during constant-current coulometry. Scan rate  $50 \text{ mVs}^{-1}$ . (II) Variation of peak current  $I_{\text{PA1}}$  vs. charge consumed during constant-current coulometry.

Controlled-potential coulometry also performed in an undivided cell in the above mentioned condition. It is shown that proportional to the advancement of coulometry, anodic peak  $A_1$  and its counterpart ( $C_1$ ) decrease and disappear when the charge consumption was about  $6e^-$  per molecule of **1a**. These observations allow us to propose the *ECECE* pathway for the electrooxidation of **1a** in the presence of DBEDA (Scheme 2).

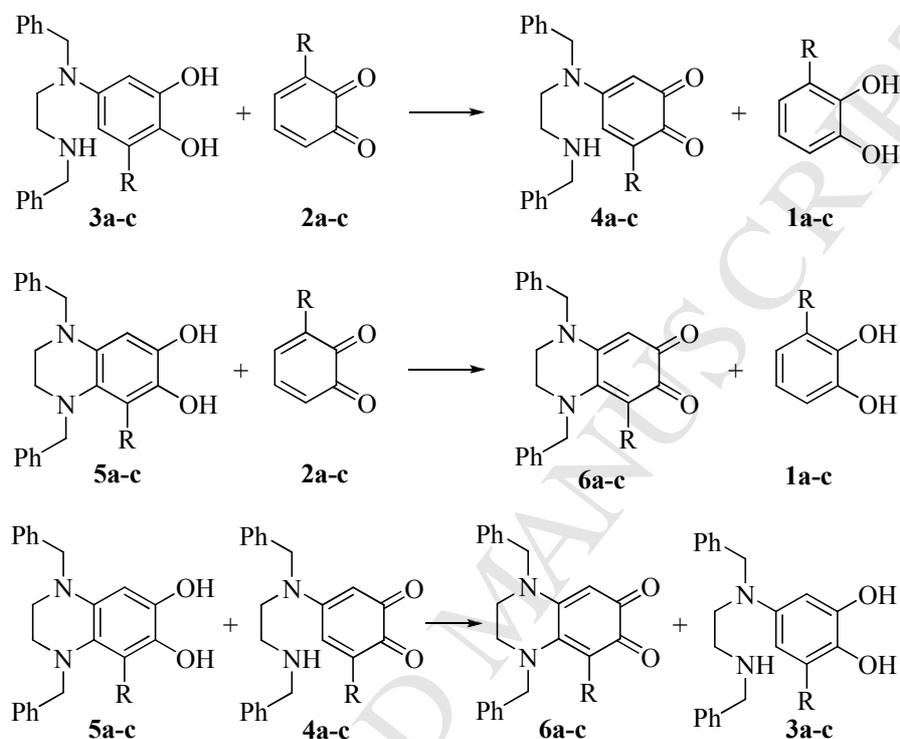
It should be noted that the electrooxidation of **1b** or **1c** in the presence of DBEDA occurs in a similar manner to that of **1a**.



**Scheme 2.** Proposed mechanism for the electrochemical oxidation of **1a-c** in the presence of DBEDA.

Formation of **2a-c** was followed by a 1,4-Michael addition of DBEDA to the quinone to produce the adducts **3a-c**. These adducts then undergo the abstraction of a second pair of electrons leading to *o*-benzoquinone **4a-c**. Intramolecular addition produces catechol derivatives **5a-c** and further oxidation of these compounds led to

formation of the final product **6a-c**. Oxidation of intermediates **3a-c** and **5a-c** is easier than oxidation of the parent starting molecules **1a-c** by virtue of the presence of the electron rich amino groups on the quinone ring. Besides, it is possible that the oxidation of **3a-c** and **5a-c** take place through a solution electron transfer reaction (Scheme 3).<sup>13</sup>



**Scheme 3.** Solution electron transfer reaction.

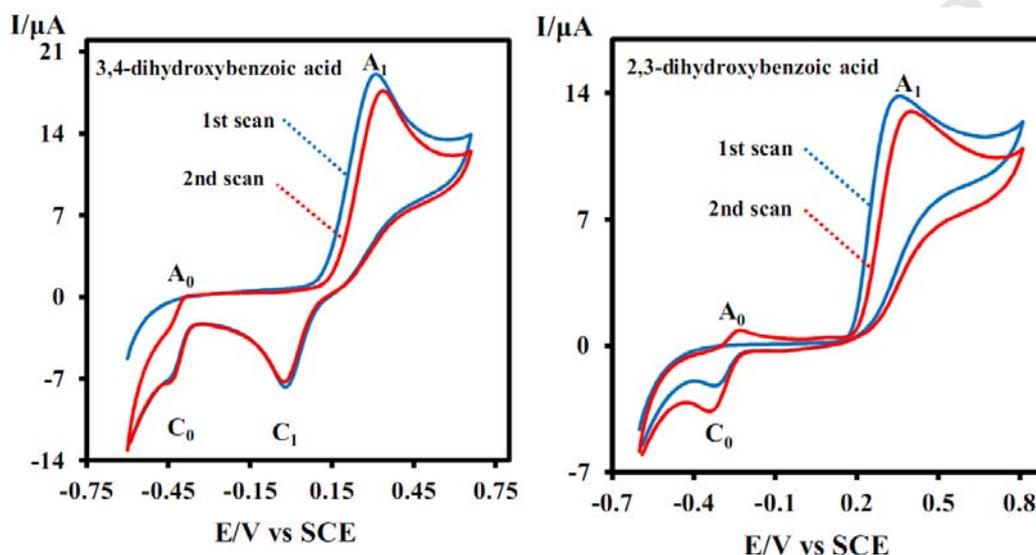
According to our results, the anodic peaks of the voltammograms presented in Figure 1 ( $A_1$  and  $A_0$ ) are related to the oxidation of **1a** and 1,4-dibenzyl-1,2,3,4-tetrahydroquinoline-6,7-diol (**5a**) to *o*-benzoquinone (**2a**) and 1,4-dibenzyl-1,2,3,4-tetrahydroquinoline-6,7-dione (**6a**), respectively. Obviously, the cathodic peaks  $C_1$  and  $C_0$  shown in Figure 1 can also correspond to the reduction of **2a** and **6a**, respectively. Due to the fast intramolecular Michael addition reaction (Scheme 2, Eq. 4), the anodic and cathodic counterpart peak for the oxidation of **3a-c** were not observed.

## 2.2. Electrochemical oxidation of 3,4-dihydroxybenzoic acid (**1d**) in the presence of DBEDA

In order to study the effect of the presence of a group in a reactive site of catechol ring, the electrochemical oxidation of **1d** has been studied in the presence of DBEDA. A first and second cycle CVs of **1d** (1.0 mM) in the presence of DBEDA (1.0 mM) in a mixture of PBS (pH = 7,  $c = 0.15$  M) and  $\text{CH}_3\text{CN}$  (70:30 v/v) is shown

in Figure 4. The CVs exhibit two cathodic peaks  $C_1$  and  $C_0$  with two anodic counterparts  $A_1$  and  $A_0$ , respectively. Also, other voltammetry and coulometry data are as same as the previous cases.

According to the obtained electrochemical data in accompany with the spectroscopic data of final product, an *ECECE* mechanism is proposed with a decarboxylation reaction for the electrooxidation of **1d** in the presence of DBEDA.

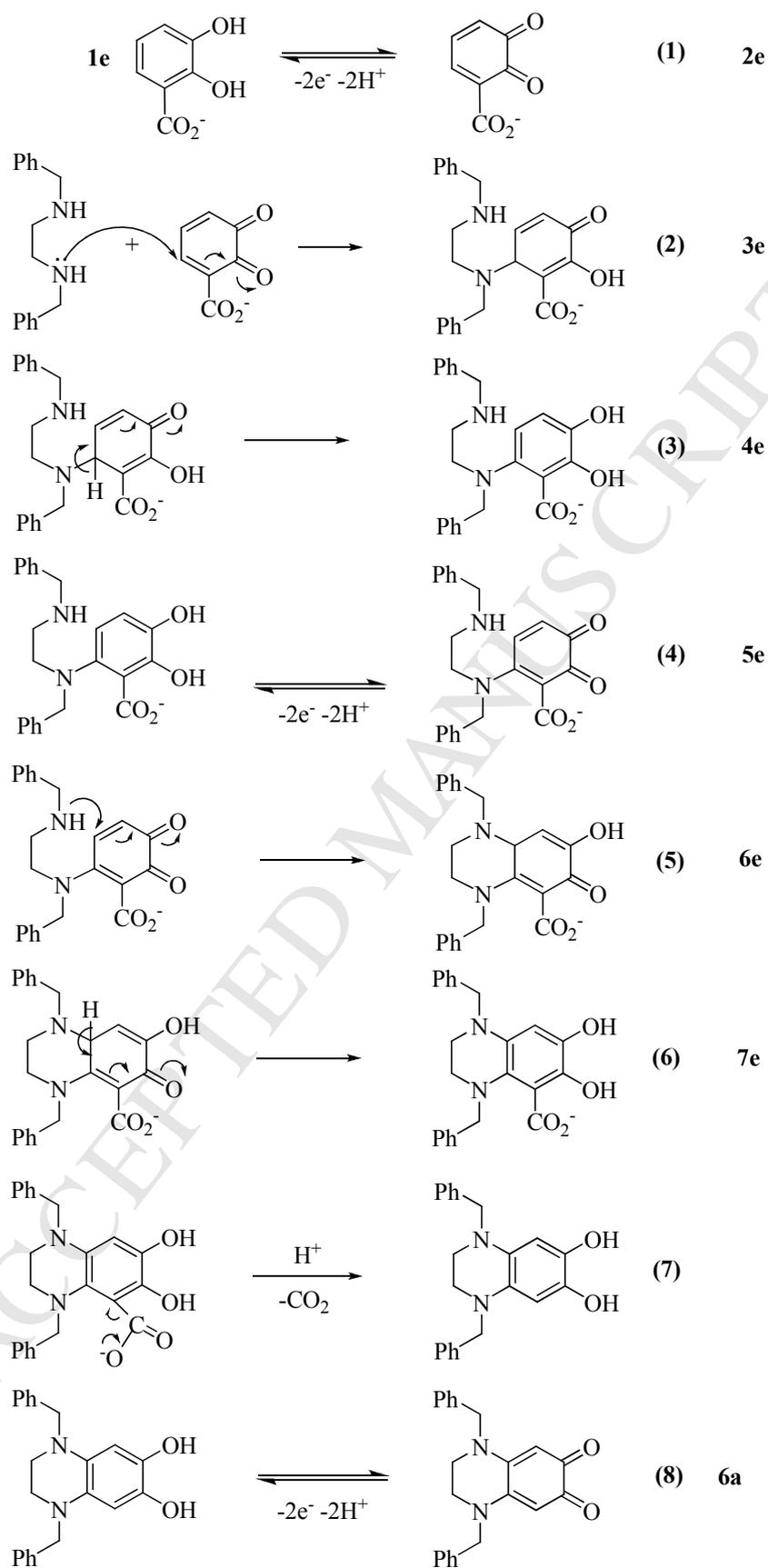


**Figure 4.** First and second cycle CVs of **1d** (left, 1.0 mM) and **1e** (right, 1.0 mM) in the presence of DBEDA (1.0 mM) at a glassy carbon electrode in a mixture of PBS (pH = 7,  $c = 0.15$  M) and  $\text{CH}_3\text{CN}$  (70:30 v/v). Scan rate:  $50 \text{ mVs}^{-1}$ ;  $T = 25 \pm 1$  °C.

### 2.3. Electrochemical oxidation of 2,3-dihydroxybenzoic acid (**1e**) in the presence of DBEDA

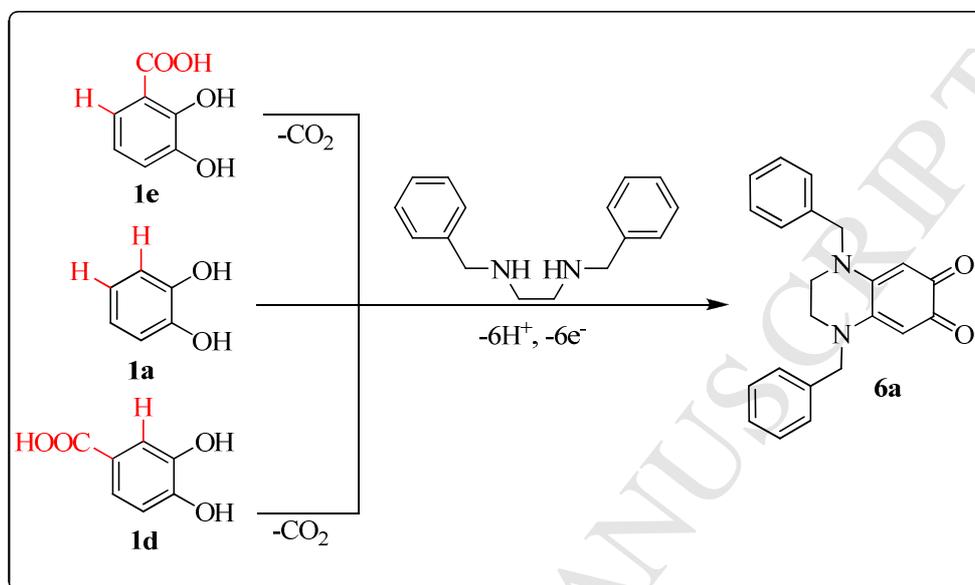
The CVs of **1e** in the presence of DBEDA was shown in Figure 4. Comparison of the first and second cycle CVs with that of other studied catechol derivatives represent that the electrochemical oxidation of **1e** in the presence of DBEDA behaves in the same manner by appearing the new redox peaks ( $A_0$  and  $C_0$ ).

Also, the spectroscopic data indicates that the electrochemically generated *o*-quinones **2a**, **2d** and **2e** participate in the Michael addition reaction with DBEDA via the *ECECE* mechanism to produce **6a**; the decarboxylation reaction occurs during the oxidation of 2,3-dihydroxybenzoic acid (**1e**) in the presence of DBEDA (Scheme 4.).



**Scheme 4.** Proposed mechanism for the oxidation of **1e** in the presence of DBEDA.

As shown in Scheme 5, three pathways can be presented for the synthesis of **6a**. Unlike 3,4-dihydroxybenzoic acid (**1d**), the decarboxylation reaction of 2,3-dihydroxybenzoic acid (**1e**) in the presence of nucleophile has not been reported so far.



**Scheme 5.** Three pathways for the synthesis of 1,4-dibenzyl-1,2,3,4-tetrahydroquinoxaline-6,7-dione (**6a**).

#### 2.4. Chemical oxidation of catechol derivatives (**1a-e**) in the presence of DBEDA

In chemical oxidation, a suitable oxidizing agent is one that only oxidizes catechols and intermediates without any side effects on DBEDA. Potassium ferricyanide is a stable, easily handled and commercially available oxidizing agent. The oxidation potential of potassium ferricyanide is close to catechols. When potassium ferricyanide was treated with catechols (**1a-e**) in the presence of DBEDA, dibenzyltetrahydroquinoxalinediones (**6a-c**) were obtained in good yields.

#### Conclusion

Different catechols (**1a-e**) were oxidized in the mixture of PBS and  $\text{CH}_3\text{CN}$  solution to their *o*-benzoquinones by chemical or electrochemical methods and attacked by DBEDA to form the corresponding dibenzyl- tetrahydroquinoxalinedione derivatives (**6a-c**). The overall reaction mechanisms for anodic oxidation of these derivatives in the presence of DBEDA as a nucleophile are presented in Schemes 2 and 4. An unexpected oxidative decarboxylation reaction of 2,3-dihydroxybenzoic acid (**1e**) in the presence of DBEDA was shown in Scheme 4. The paper introduced three pathways for the synthesis of 1,2,3,4-tetrahydro-

quinoxaline-6,7-dione (**6a**). In addition, from the green chemistry point of view, application of the electro-synthetic method has some important advantages. Clean synthesis, use of electricity as an alternative source of energy instead of oxidative reagents, one-step reaction, working in room temperature, technical feasibility and high atom economy are of prominent green advantages. Both chemical and electrochemical methods give the same products. While the chemical synthesis is faster, the electrochemical synthesis provides higher yields.

Also, the  $M^+$  peaks of nitrogen- or oxygen-containing compounds usually show some extra mass units which are more than the exact molecular masses. It usually depends on the number of the nitrogen or oxygen in the molecule and is related to protonation of the quinonic moiety or/and amino group.<sup>6</sup>

### 3. EXPERIMENTAL

#### 3.1. Apparatus and reagents

CV and controlled-potential coulometry were performed using an Auto lab model PGSTAT 20 potentiostat/galvanostat. A glassy carbon electrode, 1.8 mm<sup>2</sup> areas was used as working electrode and platinum wire was used as the counter electrode. The potential of working electrode was measured versus SCE (all electrodes from Azar Electrode). Macroscale electrolyses were carried out in an undivided cell using the assembly of four graphite rods (0.6 × 6 cm, total area 31 cm<sup>2</sup> and a large platinum gauze cylinder (25 cm<sup>2</sup> area) constituted the counter electrode.

The peak current ratios ( $I_{pc1}/I_{pa1}$ ) were determined using the following equation:<sup>19</sup>

$$I_{pc}/I_{pa} = (I_{pc})_0/I_{pa} + 0.485(I_{sp})_0/I_{pa} + 0.086$$

$(I_{pc})_0$  and  $(I_{sp})_0$  are cathodic peak current and switching potential current respect to the zero current, respectively.  $I_{pc}$  and  $I_{pa}$  have their usual meanings.

#### 3.2. Chemical synthesis of **6a-c**

##### 3.2.1. Chemical synthesis of 1,4-dibenzyl-1,2,3,4-tetrahydroquinoxaline-6,7-dione (**6a**)

To a stirred PBS (80 mL, pH = 7,  $c = 0.15$ ) and CH<sub>3</sub>CN (70:30 v/v), were added K<sub>3</sub>Fe(CN)<sub>6</sub> (6.0 mM) and DBEDA (1.0 mM). A solution of **1a** (1.0 mM) dissolved in PBS/CH<sub>3</sub>CN (70:30, 10 mL) was dropwise added during the period of 15 min which the solution became dark and precipitated. At the end of reaction, the product was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 25 mL) and the solvent evaporated. The product was purified by recrystallization from n-hexane/acetone mixture (20:80) and characterized by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and MS.

The residue was not dissolved in any solvent, which could be attributed to the oligomers or polymers of catechols. The same method as above was applied for the synthesis of **6b-c**.

### 3.3. Electrochemical synthesis of dibenzyltetrahydroquinoxalinediones (6a–c)

A mixture of PBS (80 mL, pH = 7.0,  $c = 0.15$  M) and CH<sub>3</sub>CN (70/30 v/v) containing 1.0 mmol of catechols (**1a–e**) and DBEDA (1.0 mmol) was electrolyzed at 25 °C under constant-current density of 1 mA/cm<sup>2</sup>. Progress the reaction was followed by TLC. The process was interrupted during the electrolysis and the graphite anode was washed in acetone in order to reactivate it. At the end of electrolysis (~ 20 h), the product was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 25 mL) and the solvent evaporated. The product was purified by recrystallization from n-hexane/acetone mixture (20:80) and characterized by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and MS.

### 3.4. Characterisation of products (6a–c)

#### 3.4.1 1,4-Dibenzyl-1,2,3,4-tetrahydroquinoxaline-6,7-dione (6a)

Isolated yields 98 % (electrochemical) and 36 % (chemical synthesis); IR<sub>(KBr)</sub>  $\nu_{\max} = 3050$  (=C-H), 3025 (-C-H), 1597 (C=O), 1494, 1451 (CH<sub>2</sub> bending), 1415, 1391, 1361, 1299, 1244 (C=O bending), 1191, 1130, 1090, 1076, 1027, 960, 916 (C-N), 886, 841, 786, 747, 736, 702 and 597 cm<sup>-1</sup>; <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>):  $\delta = 3.48$  (s, 4H), 4.42 (s, 4H methylene), 5.44 (s, 2H quinone) and 7.24 (s, 10H benzyl); <sup>13</sup>C NMR (22.5 MHz, CDCl<sub>3</sub>):  $\delta = 46.0$  (2 C of CH<sub>2</sub> in piperazine ring), 55.2 (2 C of benzyl CH<sub>2</sub>), 98.6 (2 C of CH of quinone ring), 126.1, 127.2 and 128.2 (10 C of CH of phenyl aromatic rings), 133.2 (2 C of phenyl aromatic rings), 148.7 (2 C of fused rings) and 178.0 (2 C of carbonyl groups); MS:  $m/z$  (relative intensity): 346 [M+2H] (100), 329 (64), 251 (100), 163 (95), 91 (97), 65 (96).<sup>6</sup>

It should be noted that the chemical and electrochemical oxidation of **1a**, **1d** and **1e** in the presence of DBEDA led to the same product (**6a**).

#### 3.4.2 1,4-Dibenzyl-5-methyl-1,2,3,4-tetrahydroquinoxaline-6,7-dione (6b)

Isolated yields 98 % (electrochemical) and 42 % (chemical synthesis); IR<sub>(KBr)</sub>:  $\nu_{\max} = 3026$  (=C-H), 2879 (-C-H), 1600 (C=O), 1543, 1494, 1476, 1449 (CH<sub>2</sub> bending), 1349, 1320, 1234 (C=O bending), 1155, 1095, 1074, 1026, 950, 916 (C-N), 823, 759, 729 and 696 cm<sup>-1</sup>; <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>):  $\delta = 1.90$  (s, 3H methyl), 3.33 (s, 4H methylene), 4.52 (s, 4H, benzylic CH<sub>2</sub>), 5.37 (s, 1H quinone) and 7.26 (s, 10H benzene ring); <sup>13</sup>C NMR (22.5 MHz, CDCl<sub>3</sub>):  $\delta = 13.2$  (C of methyl), 46.1 (2 C of CH<sub>2</sub> in piperazine ring), 55.7 (C of benzyl CH<sub>2</sub>, near to methyl), 58.0 (C of benzyl CH<sub>2</sub>, far to methyl), 95.5 (ipso carbon in quinone ring), 111.6 (C of CH in quinone ring), 126.6, 127.7 and 128.8 (10 C of CHs of phenyl aromatic rings), 134.2 (C of phenyl aromatic ring, near to methyl), 136.0 (C of phenyl aromatic ring, far to methyl), 149.5 (C of fused ring, near to methyl), 154.5 (C of fused ring, far to methyl), 177.5 (C of carbonyl group, near to methyl) and 180.8 (C of carbonyl group, far to methyl); MS:  $m/z$  (relative intensity): 343 [M+2H] (50), 269 (100), 177 (98), 91 (97).<sup>6</sup>

**3.4.3 1,4-Dibenzyl-5-methoxy-1,2,3,4-tetrahydroquinoxaline-6,7-dione (6c)**

Isolated yields 66 % (electrochemical) and 28 % (chemical synthesis); IR<sub>(KBr)</sub>:  $\nu_{\max}$  = 3062 (=C-H), 3027, 2982 (-C-H), 2973, 1711 (C=O), 1601, 1528, 1495, 1476, 1450 (CH<sub>2</sub> bending), 1422, 1361, 1234 (C=O bending), 1156, 1088, 1027 (C-O-C), 952 (C-N), 848, 727, 693 and 590 cm<sup>-1</sup>; <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.52 (s, 3H methoxy), 4.45 (s, 2H methylene), 4.82 (s, 2H methylene), 5.32 (s, 1H quinone) and 7.23 (s, 10H benzyl); <sup>13</sup>C NMR (22.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 46.8 (C of methoxy), 55.9 (2 C of CH<sub>2</sub> in piperazine ring), 57.2 (C of benzyl CH<sub>2</sub>, far to methoxy), 59.6 (C of benzyl CH<sub>2</sub>, near to methoxy), 95.1 (C of CH in quinone ring), 126.1, 126.4, 126.8, 127.2, 128.1 and 128.3 (10 C of CHs of phenyl aromatic rings), 133.7 (ipso carbon in quinone ring), 136.2 (2 C of phenyl aromatic rings), 139.5 (C of fused ring, near to methoxy), 152.0 (C of fused ring, far to methoxy), 174.8 (C of carbonyl group, near to methoxy) and 176.4 (C of carbonyl group, far to methoxy); MS: *m/z* (relative intensity): 376 [M+2H] (100), 359 (100), 285 (100), 267 (66), 251 (50), 221 (33), 191 (100), 91 (100), 65 (100).<sup>6</sup>

**Acknowledgments**

The authors gratefully acknowledge the financial supports from the Bu-Ali Sina University, Hamedan 6517838683, Iran.

**References**

1. Thompson, R. H. *Naturally Occurring Quinones*; 4<sup>th</sup> ed.; Academic: London, **1997**.
2. Rich, P. R. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 349.
3. Sutherland, H. S.; Higgs, K. C.; Taylor, N. J.; Rodrigo, R. *Tetrahedron* **2001**, *57*, 309.
4. Bringmann, G.; Tasler, S. *Tetrahedron* **2001**, *57*, 331.
5. Patai, S.; Rappoport, Z. *The Chemistry of Quinonoid Compounds*; Wiley: New York, **1988**.
6. Nematollahi, D.; Hesari, M. *J. Electroanal. Chem.* **2005**, *577*, 197.
7. Cheon, H. G.; Lee, C. M.; Kim, B. T.; Hwang, K. J. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 2661.
8. Sarhan, S.; Wettstein, J. G.; Maynard, K. I. *Neurosci. Lett.* **2003**, *347*, 147.
9. Katayama, S.; Ae, N.; Nagata, R. *Tetrahedron: Asym.* **1998**, *9*, 4295.
10. Nagata, R.; Ae, N.; Tanno, N. *Bioorg. Med. Chem. Lett.* **1995**, *5*, 1527.
11. Ottow, E.; Kruger, M.; Schneider, H.; Turski, L.; Seidelmann, D.; Huth, A.; Neuhaus, R. *US Patent* **2000**, 6136805.
12. Ottow, E.; Kruger, M.; Schneider, H.; Turski, L.; Seidelmann, D.; Huth, A.; Jones, G. H. *US Patent* **2000**, 6143733.
13. Habibi, D.; Nematollahi, D.; Seyyed Al-Hoseini, Z. *Electrochim. Acta* **2006**, *52*, 1234.
14. Habibi, D.; Marvi, O. *Catal. Commun.* **2007**, *8*, 127.
15. Habibi, D.; Nematollahi, D.; Azimi, S. *Tetrahedron Lett.* **2008**, *49*, 5043.

16. Habibi, D.; Nasrollahzadeh, M.; Kamali, T. A. *Green Chem.* **2011**, *13*, 3499.
17. Papouchado, L.; Petrie, G.; Adams, R. N. *J. Electroanal. Chem.* **1972**, *38*, 389.
18. Ryan, M. D.; Yueh, A.; Chen, W.-Y. *J. Electrochem. Soc.* **1980**, *127*, 1489.
19. Bard A. J.; Faulkner, L. R. *Electrochemical Methods*, Wiley, New York, 2<sup>nd</sup> ed, 2001.

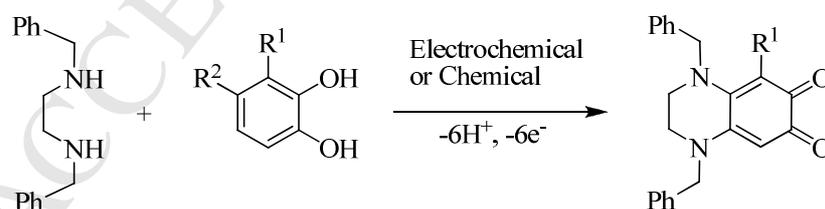
### Graphical Abstract

## An unexpected oxidative decarboxylation reaction of 2,3-dihydroxybenzoic acid in the synthesis of new dibenzyltetrahydroquinoxalinediones

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Synthesis of different dibenzyltetrahydroquinoxalinedione derivatives