



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.

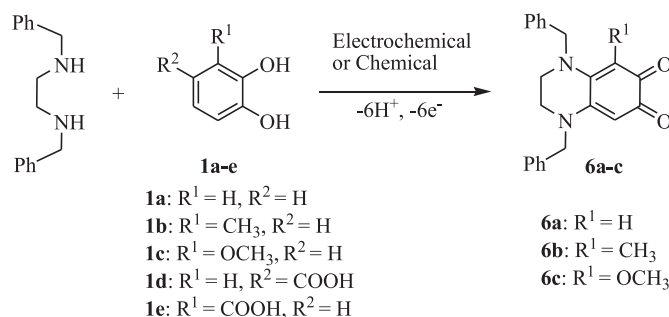
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1. Introduction

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.^{1–4} Large libraries of quinones, substituted quinones, bisquinones, and polyquinones were synthesized during the last century and their properties studied.⁵ 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.⁶

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

In continuation of our studies on the synthesis of nitrogen- and oxygen-containing heterocycles and application of different catalysts in the organic syntheses,^{13–16} 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.

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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 CH_3CN (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 (Fig. 1, curve a).¹³ 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 hydroxylation¹⁷ or dimerization¹⁸ reactions are too slow to be observed on the time scale of CV.¹³ The oxidation of **1a** in the presence of DBEDA (1.0 mM) was studied in some details. Fig. 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.

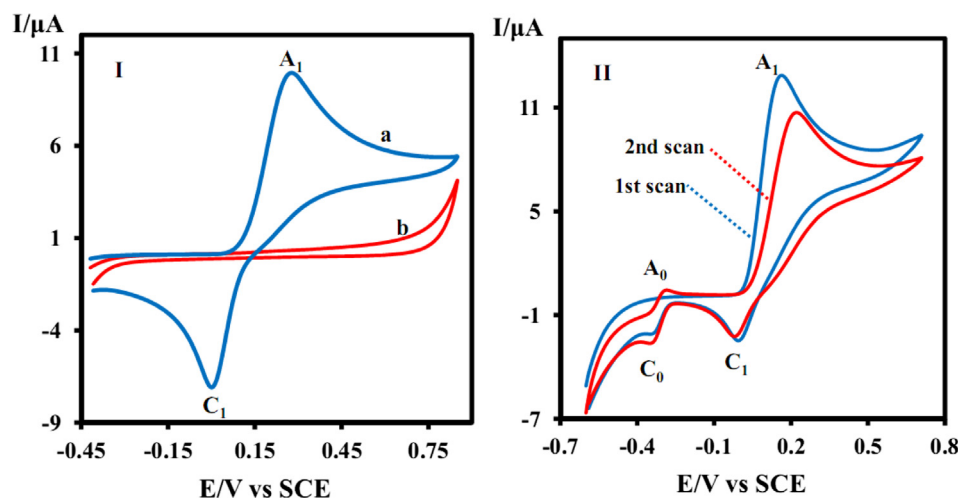


Fig. 1. (I): CVs of 1.0 mM (a): **1a** and (b): DBEDA, (II) first and second cycle CVs of **1a** (1.0 mM) in the presence of DBEDA (1.0 mM) at a glassy carbon electrode in a mixture of PBS (pH=7, $c=0.15$ M) and CH_3CN (70:30 v/v). Scan rate: 50 mV s^{-1} , $T=25\pm 1$ °C.

Furthermore, it is seen that proportional to the augmentation of the potential sweep rate and in parallel with decreasing in the height of C_0 , the height of C_1 increases (Fig. 2). The subsequent chemical reactions between *o*-benzoquinone (**2a**) and DBEDA is supported by the following evidence:

- appearance of an anodic peak A_0 and its cathodic counterpart (C_0) in less positive potentials that show the formation of an electroactive species;

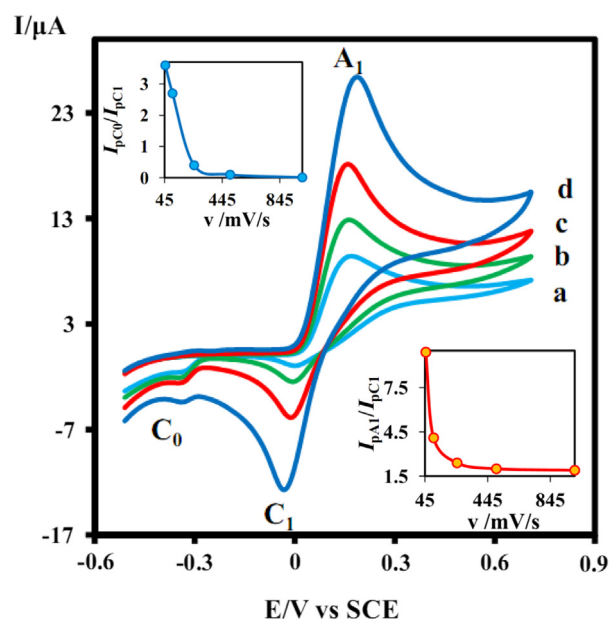


Fig. 2. Typical CVs of **1a** (1.0 mM) in the presence of DBEDA (1.0 mM) at various scan rates. Scan rates from a to d are: 25, 50, 100, and 250 mV s^{-1} , respectively, at a glassy carbon electrode in a mixture of PBS (pH=7, $c=0.15$ M) and CH_3CN (70:30 v/v). Inset: variation of peak current ratios (I_{pA1}/I_{pC1}) and (I_{pC0}/I_{pC1}) versus scan rate.

- 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.

Constant-current coulometry was performed in a mixture of PBS (pH=7, $c=0.15$ M) and CH_3CN (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 mA/cm^2). Monitoring of the electrolysis progress was carried out by CV (Fig. 3). It is shown that

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