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Electrochemical Synthesis and Mechanestic Study of Quinone Imines Exploiting the Dual Character of *N,N*-Dialkyl-*p*-phenylenediamines

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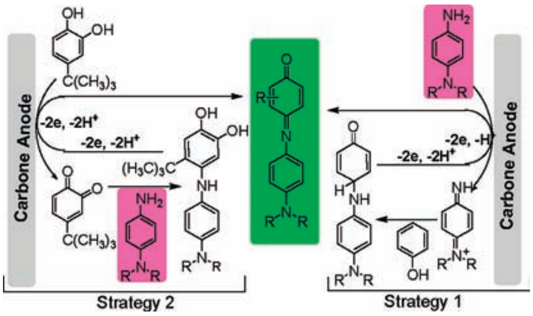
ABSTRACT



Two one-pot electrochemical approaches for the synthesis of similar quinone imines via either the nucleophilic character of *N,N*-dialkyl-*p*-phenylenediamines or electrophilic reactivity of their oxidized forms through Michael-type addition reactions are reported.

Synthesis of molecules with desirable functional groups in the absence of catalysts and drastic conditions continues to be of great interest. In organic synthesis, electrochemical electron-transfer-driven reactions have been widely used for various transformations.[1] However, their potential has not yet been fully utilized. Quinone imines and diimines have been of long-standing interest in chemistry.[2] Quinone imine dyes are commonly used as redox indicators[3,4] as well as solvent polarity indicators.[5] The preparation of simple quinone imines by chemical oxidation of aniline derivatives is often complicated by the reactivity of the quinone imine under the reaction conditions. Thus, the electrochemical synthesis of stable quinone imines is desirable. In previous studies, we have shown that *N,N*-dialkyl-*p*-phenylenediamines and catechols can be oxidized electrochemically to corresponding quinone diimines[6] and quinones,[7] respectively, that can, further, be attacked as Michael acceptors by a variety of nucleophiles. To the best of our knowledge, designing two synthesis platforms in order to synthesize a common pruduct with a specific functional group via two

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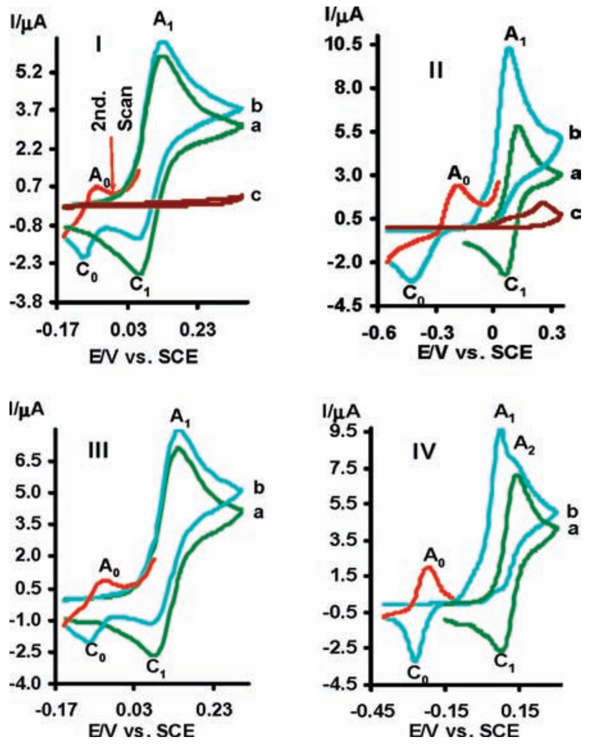

Figure 1. Cyclic voltammograms of (I,a and II,a) 1 mM **1a**; (III,a and IV,a) 1 mM **1b**; (I,b) 1 mM **1a** in the presence of 1 mM **3**; (II,b) 1 mM **1a** in the presence of 1 mM **4**; (III,b) 1 mM **1b** in the presence of 1 mM **3**; (IV,b) 1 mM **1b** in the presence of 1 mM **4**; (I,c) 1 mM **3**; and (II,c) 1 mM **4**, at glassy carbon electrode, in aqueous solution containing 0.2 M phosphate buffer (pH = 8.0). Scan rate: 20 mV s^{-1}.

different pathways where a reagent with either nucleophilic or electrophilic character is used has not yet been reported.

In the current study, we present two one-pot easy electrochemical approaches by which *N,N*-dialkyl-*p*-phenylenediamines having nucleophilic or electrophilic reactivities can be successfully applied to the synthesis of similar quinone imines. Either the nucleophilic characteristics of *N,N*-dialkyl-*p*-phenylene diamines or electrophilic reactivity of their oxidized forms which subsequently engage in the Michael addition reaction were utilized for the synthesis of similar quinone imines. The following two electrochemical strategies based on the dual character of *N,N*-dialkyl-*p*-phenylenediamines, electrochemical oxidation of *N,N*-diethyl-*p*-phenylenediamine (**1a**) and *N,N*-dimethyl-*p*-phenylenediamine (**1b**) in the presence of phenol (**3**) and 1-naphthol (**4**) as nucleophiles, were studied. In addition, the electrochemical oxidation of 4-*tert*-butylcatechol (**1c**) in the presence of **1a** and **1b** as nucleophiles was investigated.

In the first strategy, the electrochemical oxidation of **1a** was studied in the presence of **3**. Cyclic voltammetry of 1 mM of **1a** shows one anodic peak (A_1) and its cathodic peak (C_1), which correspond to the transformation of **1a** to quinone-diimine **2a** and vice versa, through a quasi-reversible two-electron process (Figure 1I,a).[6,8] Under these experimental conditions, a peak current ratio (I_{pC1}/I_{pA1}) that is close to 1 can be considered as a criterion for the stability of **2a**. In the presence of **3**, the first cycle of the voltammogram of **1a** shows a decrease in the cathodic peak C_1 and the appearance of a new cathodic peak (C_0) in the more negative potentials (Figure 1I,b). In the second cycle, a new anodic peak (A_0), which is the counterpart of C_0, appears with an E_p value of -0.05 V versus SCE. This new peak is related to the electro-oxidation of intermediate **6a**. Furthermore, with increasing the potential sweep rate and the decrease in the peak height of C_0, the peak current ratio (I_{pC1}/I_{pA1}) increases. An increase in the ratio of (I_{pC1}/I_{pA1}) and (I_{pC1}/I_{pC0}) with increasing the scan rate for a mixture of **1a** and **3** confirms the reactivity of **2a** toward **3** (see Supporting Information, Figure S1).

On the other hand, the current function for peak A_1 ($I_{pA1}/v^{1/2}$) decreases with increasing the scan rate and such a behavior is an indication of an *ECE* mechanism.[9] Monitoring the electrolysis progress by cyclic voltammetry synchronously during controlled-potential coulometry in an aqueous solution containing **1a** and **3** at 0.15 V versus SCE shows that as the coulometry progresses, the I_{pA1} and I_{pC1} decrease (See Supporting Information, Figure S2). These peaks (A_1 and C_1) disappear when the charge consumption becomes about $4e^-$ per molecule of **1a**.

Furthermore, time-dependent absorption spectra of the mixture of **1a** and **3** were measured during a controlled-potential coulometry experiment (see Supporting Information, Figure S3). As the coulometry experiment progresses, absorption peaks with λ_{max} at 275 and 670 nm that belong to the blue color of the product **7a** appear and their heights gradually increase.

The diagnostic criteria of cyclic voltammetry, the consumption of four electrons per molecule of **1a**, and the spectroscopic data of the final product support the quinone-imine structure of **7a**.

According to our results, the Michael addition reaction of the anion phenolate **3** to quinone-diimine **2a** is faster than other secondary reactions, leading to the intermediate **6a**. Because the oxidation of intermediate **6a** is easier than the oxidation of **1a**, following the chemical reaction the apparent number of electrons transferred increases from 2 to 4 electrons and quinone-imine **7a** is synthesized. The electrochemical oxidation of **1a** in the presence of 1-naphthol (**4**) proceeds in a similar way to that of **3** (see Supporting Information, Scheme S1) and produces quinone-imine **9a** as the final product (see Scheme 1, inset). However, its cyclic voltammogram shows an intense increase in the current for peak A_1 as well as a complete disappearance of peak C_1 even with high scan rates (Figure 1II,b). This might be related to the adsorption of **4** on the surface of the electrode. Under these conditions, the surface concentration of **4** is high and remains

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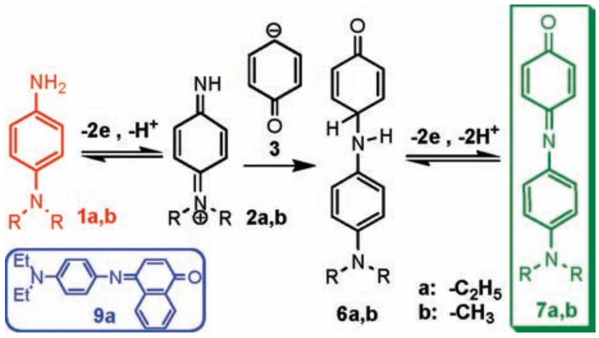
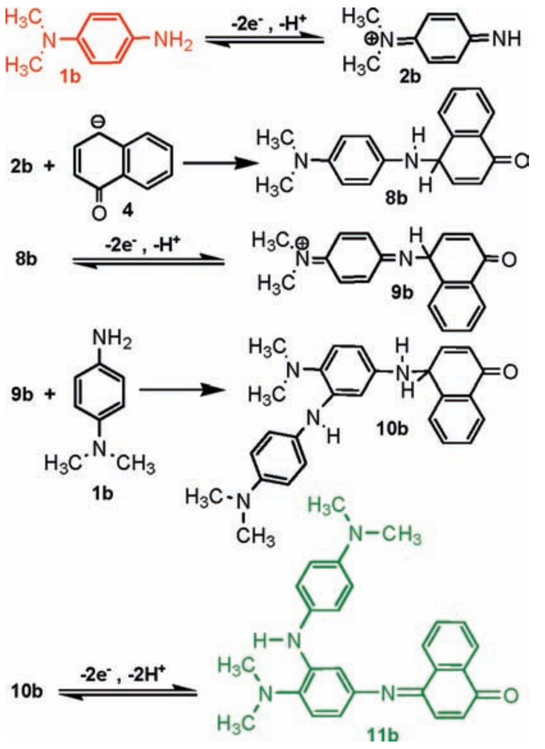
Scheme 1. Strategy 1 for the Synthesis of Quinone Imine



Scheme 2. Electrochemical Synthesis of **11b** by Strategy 1



essentially unchanged during the voltammetric experiment. However, **2a** is gradually generated at the electrode surface and reacts with the large amount of **4**. In this case, the rate of reaction of **4** with **2a** increases and subsequent oxidation leads to a fast growth in the current of peak A_1. The rapid reaction of generated **2a** with **4** causes the surface concentration of **2a** to become effectively zero. Such behavior is a general treatment of the *ECE* system with pure kinetic conditions.[9]

To follow this strategy for the electrochemical synthesis of quinone imines, electrochemical oxidation of **1b** in the presence of **3** and **4** was studied under the same conditions. The electrochemical oxidation of **1b** in the presence of **3** proceeds similarly to that of **1a** (Scheme 1); however, the electrochemical oxidation of **1b** in the presence of **4** proceeds differently.

Cyclic voltammograms of **1b** in the presence of **4** have been shown in Figure 1IV,b. Controlled-potential coulometry of **1b** in an aqueous solution containing 0.2 M phosphate buffer (pH = 8.0) at 0.15 V versus the SCE yields an n_{app} value of about 3.

The diagnostic criteria of cyclic voltammetry, the consumption of three electrons per molecule of **1b**, and the spectroscopic data of the isolated product indicate that the reaction mechanism of the electrooxidation of **1b** in the presence of **4** is *ECECE* (Scheme 2). According to our results, it seems that the Michael-type addition reaction of **4** to quinone-diimine **2b** leads to the intermediate **8b**. Another oxidation process converts **8b** to quinone-diimine **9b**, and next Michael addition of **1b** to **9b** transforms **9b** to intermediate **10b**. Because of the presence of an electron-donating group, the oxidation of this compound (**10b**) is easier than the oxidation of **1b**. Further oxidation converts intermediate **10b** to the final product **11b**.

Based on Scheme 2, in Figure 1IV,b, the anodic peaks of A_1 and A_2 pertain to the oxidation of **1b** and **8b** to quinone-diimines **2b** and **9b**, respectively. Also the anodic peak A_0 and its counterpart (C_0) correspond to the oxidation of **10b** to **11b** and vice versa. Another less probable pathway for the formation of **11b** is proposed in Supporting Information, Scheme S2.

In the second strategy for the electrochemical synthesis of quinone imines, **1a** and **1b** act as nucleophiles. Using cyclic voltammetry, the electrochemical oxidation of 4-*tert*-butylcatechol (**1c**) was studied in the presence of **1a** and **1b** as nucleophiles in an aqueous solution containing 0.2 M phosphate buffer (pH = 7.5). Cyclic voltammetry of **1c** shows one anodic (A_1) and the corresponding cathodic peak (C_1), which correspond, through a quasi-reversible two-electron process, to the transformation of **1c** to related *o*-benzoquinone **2c** and vice versa (Figure 2, curve a).[7] Also one anodic (A_2) and the corresponding cathodic peak (C_2) were observed in the cyclic voltammograms of **1b** alone (Figure 2, curve b). Figure 2 (curve c) shows the cycle voltammogram of **1c** in the presence of **1b**. Under these conditions, I_{pA1} increases and its cathodic counterpart (C_1) decreases. Also the voltammogram exhibits a new cathodic peak C_0 at more negative potentials. In the second cycle (curve d), a new peak (A_0) appears with an E_{p} value of −0.14 V versus SCE. This new peak is related to the oxidation of intermediate **13b**. Furthermore, the height of the peak C_1 increases with increasing potential sweep rate (see Supporting Information, Figure S4). This indicates the reactivity of electrochemically generated *o*-benzoquinone **2c** toward **1b**.

These observations are indicative of an *ECE* mechanism[9] and allow us to propose a mechanism for the electrooxidation of **1c** in the presence of **1a,b** (Scheme 3). Accordingly, the 1,4-addition (Michael) reaction of **1a,b** to the *o*-benzoquinone **2c** leads to the intermediate **13a,b**. The oxidation of **13a,b** is easier than the oxidation of **1c** due to the presence of an amine group as an electron-donating group. Therefore, **1c** in the presence of **1a,b** after consumption of four electrons converts to quinone-imine **14a,b**.

In the case where two substrates are susceptible to oxidation and their oxidation potentials are close to each other, the

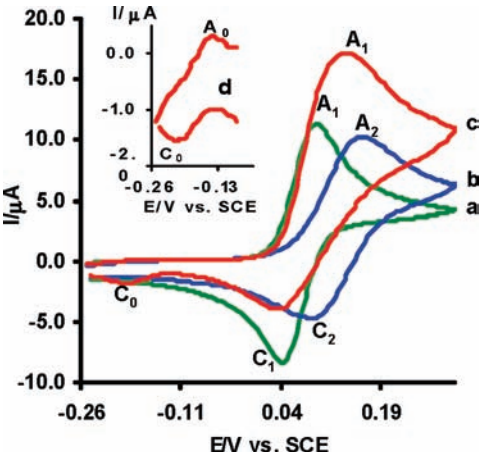
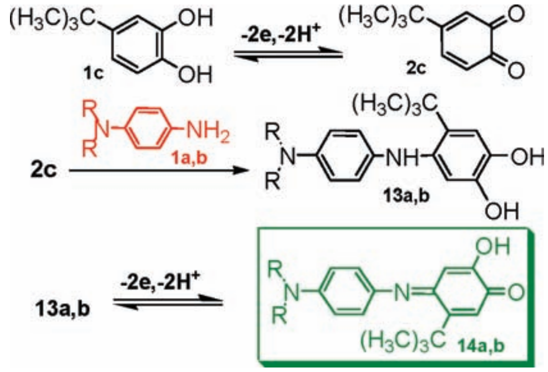


Figure 2. Cyclic voltammogram of 1 mM (a) **1c**, (b) **1b**, (c) **1c** in the presence of **1b**, and (d) initial part of second cycle of cyclic voltammogram of **1c** in the presence of **1b**, at glassy carbon electrode, in aqueous solution containing 0.2 M phosphate buffer (pH = 7.5). Scan rate: 50 mV s^{-1}; t = 25 ± 1 °C.

choice of an appropriate potential is often crucial for the success of an electrode reaction. In this case, for the selective oxidation of **1c**, a controlled-potential method was used. In contrast to one-pot chemical synthesis where there is no control on the oxidation of a single component, controlled-potential electrolysis serves as a powerful method for the synthesis of a desirable product via selective oxidation of a target reagent. As expected, at the small applied potential of 0.05 V, the selective electrochemical oxidation of **1c** proceeds preferentially, thereby providing the desired quinone imine **14a,b**.

From the point of view of green chemistry, the use of an electrosynthesis method has some important advantages. Clean synthesis, the use of electricity instead of chemical reagents, and the achievement of high atom economy via a one-step process conducted under ambient conditions are attractive features with respect to green chemistry ideas.

Scheme 3. Strategy 2 for the Synthesis of Quinone Imine



Although one-pot reactions are performed potentiostatically on a mmol scale in divided cells, there is little difficulty in producing larger quantities by using larger cells.

Information for the preparative electrolysis including the potential, electricity, temperature, and yields is described in the Supporting Information.

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Supporting Information Available. Experimental procedures, some electrochemical investigations, and full spectroscopic data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.