

A Green Electrochemical Method for the Synthesis of 2-(phenylthio)-1*H*-benzo[d]imidazole Derivatives

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The electrochemical oxidation of 4,4'-biphenol (**4BP**) was studied by cyclic voltammetry in the absence and presence of 2mercaptobenzimidazole (**2MB**) in aqueous/ethanol (50/50 v/v) mixture, to evaluate whether the electrogenerated 4,4'-diphenoquinone (**4BP**_{ox}) reacts with **2MB** and determine the electrochemical oxidation pathway of **4BP** in the presence of **2MB**. The data show that the reaction of **4BP**_{ox} with **2MB** can be accomplished in an undivided cell equipped with carbon anode and stainless steel cathode leads to the formation of 3-((1*H*-benzo[d]imidazol-2-yl)thio)-[1,1'-biphenyl]-4,4'-diol. This method has led to the development of a green, reagentless and facile galvanostatic method for the synthesis of 2-(phenylthio)-1*H*-benzo[d]imidazole derivatives. © 2018 The Electrochemical Society. [DOI: 10.1149/2.0241811jes]

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Thioethers are important materials that are used in organic, bioorganic and medicinal chemistry.¹ These compounds also can serve as building blocks for the synthesis of different biologically important sulfur compounds.² The oxidation of thioethers leads to chiral sulfoxides, which can be used in asymmetric syntheses.^{3–6} Aromatic thioethers are also known to exhibit different biological activities such as antioxidant and antibacterial.⁷ Various synthetic methods used for the synthesis of aromatic thioethers.^{8–24} Most common approaches involve the use of transition metals such as Rh,^{8,9} Pd,^{10,11} Co,¹² Cu,^{13–15} Fe,¹⁶ etc.^{17–19} These methods have significant drawbacks including the use of expensive reagents and toxic metal catalysts, solvents and reagents. Other methods including iodinemediated synthesis,^{20–22} 1,8-diazabicyclo[5,4,0]undec-7-enium acetate ionic liquid.²³ Although these methods do not have any heavy metal pollution, however, still have the disadvantages such as tedious work-up, safety problems, expensive reagents and toxic solvents.

A group of aromatic thioethers is catechol thioethers which are known to exhibit some biological activities such as antioxidant and antibacterial activities.⁷ Most of these compounds were synthesized by the reaction of in situ generated *o*-benzoquinones with the corresponding thiols. The generation of *o*-benzoquinones was performed mostly by using laccase-catalyzed²⁴ or electrochemical methods.^{25–32} Although both methods are suitable for the synthesis of catechol thioethers, however, the laccase-catalyzed method faces the problem of expensive enzyme. These findings prompted us to synthesize new aromatic thioethers by the galvanostatic oxidation of 4,4'-biphenol, 4-*tert*-butylcatechol and catechol in the presence of 2-mercaptobenzimidazole. In this research, we have developed a facile and green method for the synthesis of some new aromatic thioethers in a water/ethanol solution using an ordinary carbon electrode and a simple power supply.

Experimental

Apparatus and reagents.—Cyclic voltammetry was performed using a Sama-500 potentiostat/galvanostat. The working electrode used in the voltammetry experiments was a glassy carbon disc (1.8 mm² area) and platinum wire was used as counter electrode. The working electrode potentials were measured versus Ag/AgCl (3M KCl) (all electrodes from AZAR electrode). Macro-scale electrolysis and controlled-potential coulometry were carried out with a threeelectrode system, using a Behpajooh C 2056 potentiostat equipped with a digital coulometer. The working electrode used in macro-scale electrolysis was an assembly of three ordinary soft carbon plates (20 mm length, 10 mm width and 44 mm height), and a stainless steel cylinder (25 cm² area) constituted the counter electrode (Fig. 1).

The electrosynthesis were performed under constant-current condition in an undivided cell. 4,4'-Biphenol (4BP), catechol (Cat), 4-*tert*-Butylcatechol (4TC) and 2-mercaptobenzimidazole (2MB), phosphate salts, perchloric acid and ethanol were obtained from Sigma-Aldrich. These chemicals were used without further purification. The glassy carbon electrode was polished using alumina slurry (3.0 μ m–0.1 μ m). Melting points were measured with an Electrothermal 9100 apparatus (Rochford, UK). IR spectra (KBr) were recorded on Perkin–Elmer GX FT-IR spectrometer. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance DPX-300 spectrometer at 300 MHz and a Bruker Avance DRX-400 spectrometer at 400 MHz. The mass spectra were recorded on MS Model: 5975C VL MSD with Tripe-Axis Detector.

Synthesis of P1 ($C_{19}H_{14}N_2O_2S$).—A mixture of aqueous perchloric acid solution (40 ml, c = 0.1 M)/ethanol (40 ml) (50/50 v/v) containing **4BP** (1.6 mmol) and **2MB** (1.6 mmol) was subjected to electrolysis under constant current conditions (J = 0.35 mA/cm²) in an undivided cell. Progress of the electrolysis was checked by TLC using *n*-hexane/ethyl acetate (50:50) as eluent. The process was interrupted during the electrolysis and the carbon anode was washed in acetone in order to reactivate it. At the end of electrolysis, the solution neutralized with a saturated sodium bicarbonate solution. The crude product was separated by filtration and was purified by thin-layer chromatography with *n*-hexane/ethyl acetate (50:50). The product was characterized by its physical and spectroscopic data.



3-((1H-benzo[d]imidazol-2-yl)thio[1,1'-biphenyl]-4,4'-diol

Isolated yield: 51%. M.p = $209-211^{\circ}$ C (Dec). ¹H NMR (400 MHz, DMSO- d_6) δ (ppm): 6.79 (d, J = 8.8 Hz, 2H, aromatic), 6.99 (d, J = 8.4 Hz, 1H, aromatic), 7.11 (dd, J = 3.2 and 6.0 Hz, 2H, aromatic), 7.35 (d, J = 8.8 Hz, 2H, aromatic), 7.44 (dd, J = 3.2 and 6 Hz, 2H, aromatic), 7.47 (d, J = 2.4 Hz, 1H, aromatic), 7.53 (d, J = 2.4 Hz, 1H, aromatic), 1.47 (d, J = 2.4 Hz, 1H, aromatic), 7.53 (d, J = 2.4 Hz, 1H, aromatic).

¹³C NMR (100 MHz, DMSO-*d*₆) δ (ppm): 114.2, 115.6, 116.5, 116.9, 121.4, 127.0, 128.0, 130.2, 131.0, 131.7, 139.8, 148.9, 156.5, 156.6. IR (KBr) ν (cm⁻¹): 3386 (medium, N-H), 3239 (medium, O-H), 1612 (medium, C=C), 1490 (medium, C=C), 1404, 1175, 817, 737, 430. MS (EI, 70 eV) *m*/*z* (relative intensity): 334 (M, 72), 317 (100), 301 (16), 218 (15), 150 (23), 77 (15).

Synthesis of P2 ($C_{13}H_{10}N_2O_2S$) and P3 ($C_{17}H_{18}N_2O_2S$).—A mixture of aqueous phosphate buffer solution (55 ml, c = 0.2 M, pH = 2.0)/ethanol (25 ml) (70/30 v/v) .containing Cat (or 4TC) (1.6 mmol) and 2MB (1.6 mmol) was subjected to electrolysis under constant current conditions (J = 0.35 mA/cm²) in an undivided cell. Progress



Figure 1. The position of the electrodes in the cell.

of the electrolysis was checked by TLC using *n*-hexane/ethyl acetate (50:50) as eluent. The process was interrupted during the electrolysis and the carbon anode was washed in acetone in order to reactivate it. At the end of electrolysis, the solution neutralized with a saturated sodium bicarbonate solution. The crude product was separated by filtration and was washed several times with cold water and dried. The products were characterized by their physical and spectroscopic data.



Characteristics of P2.—Isolated yield: 51%. M.p = 208–210°C (Dec). ¹H NMR (300 MHz, DMSO-d₆) δ (ppm): 6.83 (d, J = 8.2 Hz, 1H, aromatic), 6.93 (dd, J = 2.1 and 8.1 Hz, 1H, aromatic), 6.99 (d, J = 2.1 Hz, 1H, aromatic), 7.13 (dd, J = 3 and 6 Hz, 2H, aromatic), 7.45 (dd, J = 3 and 6 Hz, 2H, aromatic), 9.42 (2H, OH), 12.3 (broad, 1H, NH). ¹³C NMR (75 MHz, DMSO-d₆) δ (ppm): 114.8, 117.1, 117.9, 121.4, 122.2, 125.9, 140.0, 146.6, 147.5, 150.1. IR (KBr) ν (cm⁻¹): 3265 (medium, O-H), 1596 (medium, C=C), 1511 (medium, C=C), 1404, 1271, 1121, 989, 809,588. MS (EI, 70 eV) *m/z* (relative intensity): 258 (M, 100), 257 (100), 197 (9), 150 (21), 106 (15), 63 (9).

Characteristics of P3.—Isolated yield: 71%. M.p = 187–189°C (Dec). ¹H NMR (300 MHz, DMSO-d₆) δ (ppm): 1.19 (s, 9H, aliphatic), 6.79 (d, J = 2.1 Hz, 1H, aromatic), 6.90 (d, J = 2.1 Hz, 1H, aromatic), 7.15 (dd, J = 3 and 5.8 Hz, 2H, aromatic), 7.45 (s, 2H, aromatic), 9.44 (2H, OH), 12.49 (broad band, 1H, NH). ¹³C NMR (75 MHz, DMSO-d₆) δ (ppm): 31.7, 34.2, 114.5, 115.9, 120.5, 122.2, 142.5, 143.9, 146.2, 149. IR (KBr) ν (cm⁻¹): 3437 (medium, N-H), 3301(medium, O-H), 2962 (medium, C-H), 1570 (medium, C=C), 1483 (medium, C=C), 1412, 1285, 1233, 960, 743, 615. MS (EI, 70 eV) *m/z* (relative intensity): 314 (M, 48), 299 (84), 150 (100), 91 (64), 41 (67).

Results and Discussion

Electrochemical study of 4BP.—The cyclic voltammogram of **4BP** in aqueous perchloric acid (c = 0.1 M)/ethanol mixture (50/50 v/v) is shown in Fig. 2a. It shows an anodic peak A₁ in the positivegoing scan and a corresponding cathodic peak C₁ in the negativegoing scan. These peaks are assigned to the oxidation of **4BP** to 4,4'-diphenoquinone (**4BP**_{ox}) and reduction of **4BP**_{ox} to **4BP**, respectively.³³ Comparison of Fig. 2a with that of **4BP** in the presence of **2MB** (Fig. 2b) shows that the cathodic peak C₁ decreases significantly and a new anodic peak A₂ and its cathodic counterpart (C₂)



Figure 2. Cyclic voltammograms of **4BP** (1.0 mM): (a) in the absence and (b) in the presence of **2MB** (1.0 mM) and, (c) cyclic voltammogram of **2MB** (1.0 mM) in the absence of **4BP**, at a glassy carbon electrode, in aqueous perchloric acid (c = 0.1 M)/ethanol mixture (50/50 v/v). Scan rate: 100 mV s⁻¹. $t = 25 \pm 1^{\circ}$ C.

appears at more positive potentials. In addition under these conditions a new anodic peak A_N appears at less positive potentials. From these data it can be concluded that a chemical reaction follows the electron transfer process.

The effects of the **2MB** on the cyclic voltammogram **4BP** disappear when the potential scan rate significantly increases. Under these conditions, anodic and cathodic peaks A_2 and C_2 disappear and the peak current ratio (I_{pC1}/I_{pA1}) becomes about one. The data confirm that peaks A_2 and C_2 belong to the product of the reaction of **2MB** with **4BP**_{ox}. Another result that can be obtained from this figure is that, the product is more difficult to oxidize than the starting material (**4BP**) which shows that the **2MB** added to the **4BP** plays the role of an electron withdrawing group. A literature survey shows that, the oxidation potential of catechol thioethers are lower than those of parent catechols, would cause greater oxidative damage than their parent catechols.³⁴ Accordingly, the adduct formed from the reaction of **2MB** with **4BP**_{ox} mediated less oxidative damage than **4BP**.

In Fig. 2, curve c is the cyclic voltammogram of **2MB** in the absence of **4BP**. It exhibited anodic (A_N) and cathodic (C_N) peaks at 0.51 and 0.31 V vs. Ag/AgCl, respectively. The anodic peak, A_N , can be attributed to the oxidative dimerization of **2MB** via the formation of sulfur-sulfur bond.³⁵ Comparison of voltammogram **2MB** (curve c) with voltammogram **4BP** in the presence of **2MB** (curve b) confirms that the anodic peak observed at about 0.51 V is due to the anodic oxidation of **2MB**.

The constant current electrolysis and voltammetry of the electrolyzed solution can give us more information. The constant current electrolysis of **4BP** (0.25 mmol) in the presence of **2MB** (0.25 mmol) was performed in aqueous perchloric acid solution (40 ml, c = 0.1 M)/ethanol (40 ml) (50/50 v/v) at J = 0.35 mA/cm². The electrolysis progress was monitored using linear sweep voltammetry (Fig. 3). As shown, during the electrolysis progress, the current of the anodic peaks A_N and A₁ decrease and finally disappear after consumption of about 2e⁻ per molecule of **4BP**. It should be noted that the number of transferred electrons (n = 2) has also been confirmed using controlled potential coulometry.

The electrochemical results and spectroscopic data of the isolated electrolysis product (for example, the molecular mass of 334) all point out to product **P1** which might have been formed according to the pathway shown in Scheme 1. Accordingly, the first step would be the electrochemical generation of $4BP_{ox}$. The second step, would be the reaction of $4BP_{ox}$ with 2MB and the formation of intermediate, BPMB and the third step, is the aromatization of **P1** along with its insolubility



Figure 3. Linear sweep voltammograms of **4BP** (0.25 mmol) in the presence of **2MB** (0.25 mmol), at a glassy carbon electrode in aqueous perchloric acid (c = 0.1 M)/ethanol mixture (50/50 v/v) during constant current electrolysis at 0.35 mA/cm². (a) At the beginning of electrolysis, (b and c) during electrolysis and (d) at the end of electrolysis. Scan rate: 100 mV s⁻¹. $t = 25 \pm 1^{\circ}$ C.

in the electrolysis medium, has prevented its further oxidation during preparative electrolysis. The yield of **P1** in less acidic, neutral and basic solutions becomes less due to the participation of **4BP**_{ox} in the pH dependent dimerization^{36,37} and/or hydroxylation^{38,39} reactions. The rate of these reactions increases with increasing pH.^{36–39}

Based on Scheme 1, the peak A_2 observed in cyclic voltammetry of **4BP** in the presence of **2MB** (Fig. 2, curve b) is related to the oxidation of **P1** to **P1**_{ox}. Clearly, peak C_2 belongs to the reduction of **P1**_{ox} to **P1**. Figure 4 compares the cyclic voltammograms of **4BP** and **P1**. This figure clearly shows that the half wave potential ($E_{1/2}$) of **P1** is about 40 mV more positive than that of **4BP**.

4BP_{ox} can react with 2MB to form two types of products, *ortho*-Is and *meta*-Is (Fig. 5). The calculated steric energy for *ortho*-Is and *meta*-Is using MM2 program show that *ortho*-Is is significantly more stable than *meta*-Is. Fig. 5 shows the structure of *ortho*-Is and *meta*-Is after minimization of energy. The calculated steric energy for *ortho*-Is and *meta*-Is and *meta*-Is are 6.88 and 15.34, respectively. In conclusion, we think that *ortho*-Is (P1) is more probable structure in electrooxidation of 4BP in the presence of 2MB.

Constant current synthesis.—Here, galvanostatic synthesis of **P2** was studied and parameters including current density and charge passed were optimized to obtain the maximum yield of product. In this way, the current density changed from 0.12 to 1.18 mA/cm², whereas the other parameters such as charge passed (100 C), catechol amount (0.25 mmol), **2MB** amount (0.25 mmol), electrode surface (85 cm²), solvent (aqueous phosphate buffer solution, 55 ml, c = 0.2 M, pH = 2.0/ethanol, 25 ml mixture) and temperature (298 K), are kept constant. The data show that the best yield was obtained at J = 0.35 mA/cm² (Fig. 6). The oxidation of solvent and/or further oxidation of product at higher current densities would decrease the



Scheme 1. The oxidation pathway of **4BP** in the presence of **2MB**.



Figure 4. (a) Cyclic voltammogram of **4BP** and (b) cyclic voltammogram of **P1** (saturated solution) at a glassy carbon electrode, in aqueous perchloric acid (c = 0.1 M)/ethanol mixture (50/50 v/v). Scan rate: 100 mV s⁻¹. $t = 25 \pm 1^{\circ}$ C. For better comparison with curve a, the currents of curve b, are multiplied by 1.7.

product yield. On the other hand, the decrease of the yield at lower current densities can be due to the oxidation **2MB**.

The effect of the amount of electricity passed in the range of 1.0 F/mol to 4.0 F/mol on the product yield was studied at $J = 0.35 \text{ mA/cm}^2$, while other parameters were kept constant (Fig. 7). This figure shows that, the product yield decreases with increasing charge passed from theoretical amount (2.0 F/mol). It seems that, the further oxidation of the product can be significant factor in reducing the product yield.



Figure 6. The effect of current density on the yield of P2. Charge passed, 100 C.

Synthesis using catechol and 4-tert-butylcatechol.—In this study we obtained the same results in the oxidation pathway of catechol and 4-tert-butylcatechol in the presence of **2MB**, so their related data is not included in this paper. The only issue that needs to be addressed is the structures of **P2** and **P3**. The product **P2** is obtained from the oxidation of catechol (**Cat**) in the presence of **2MB**. The *ortho*benzoquinone (**Cat**_{ox}) formed from oxidation of **Cat** can be reacted by **2MB** to form two types of products, **1,2,3-Is** and **1,2,4-Is** (**P2**) (Scheme 2). The ¹H NMR of the isolated product shows a doublet peak at 6.99 ppm with coupling constant, 2.1 Hz and integration of one proton, which indicates that this proton is at the *meta* position of



Figure 5. The possible structures in electrooxidation of 4BP in the presence of 2MB and the results of MM2 calculation for *ortho* and *meta* isomers.



Figure 7. The effect of charge passed on the yield of P2. Current density, 0.35 mA/cm².

other aromatic protons.⁴⁰ Accordingly, this result rejects the formation of the compound **1,2,3-Is**.

The product **P3** is obtained from the oxidation of 4-*tert*butylcatechol (**4TC**) in the presence of **2MB**. The electrochemically generated 4-*tert*-butyl-*o*-benzoquinone ($4TC_{ox}$) is an asymmetric Michael acceptor that can be reacted by **2MB** to form three types of products, **4,6-Is** (**P3**), **4,5-Is** and **3,4-Is** (Fig. 8). The ¹H NMR of the isolated product shows two doublet peaks at 6.79 and 6.90 ppm with coupling constants, 2.1 Hz and integration of one proton, which displays that two protons are *meta*-coupled to each other.⁴⁰ Accordingly, these data rejects the formation of the compounds **4,5-Is** and **3,4-Is**. On the other hand, the calculated steric energy using MM2 program, was found to vary in the order **3,4-Is** > **4,5-Is** > **4,6-Is** (Fig. 8), which shows that the formation of **4,6-Is** (**P3**) is presumably energetically favorable compared to other isomers (**4,5-Is** and **3,4-Is**).

Conclusions

Our voltammetric and coulometric data along with the spectroscopic results of the products (**P1-P3**) show that the pathway of electrochemical oxidation of the studied diols in the presence of **2MB** is an *EC* mechanism (*E* represents an electron transfer and "*C*" represents a homogeneous chemical reaction) (Scheme 1). Here, we have synthesized some new diol derivatives containing 2-mercaptobenzimidazole group under galvanostatic conditions, in a simple cell, using a green strategy. In addition, in this work, we optimize the affecting factors such as, current density and charge passed for the synthesis of products, **P1-P3** and discuses on the structure of products. In conclusion, this environment friendly strategy have many advantages such as one-pot synthesis of product, catalyst free condition and safe solvent.



Figure 8. The possible structures in electrooxidation of 4TC in the presence of 2MB and the results of MM2 calculation for 4,6-Is, 4,5-Is and 3,4-Is isomers.

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Scheme 2. The possible structures in electrooxidation of Cat in the presence of 2MB.

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