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Polyfunctional Tetrazolic Thioethers through Electrooxidative/Michael-Type Sequential Reactions of 1,2- and 1,4-Dihydroxybenzenes with 1-Phenyl-5-mercaptotetrazole

Mohammad M. Khodaei,* Abdolhamid Alizadeh,* and Narges Pakravan

Chemistry Department & Nanoscience and Nanotechnology Research Center (NNRC), Razi University, Kermanshah, 67149 Iran

ahalizadeh2@hotmail.com

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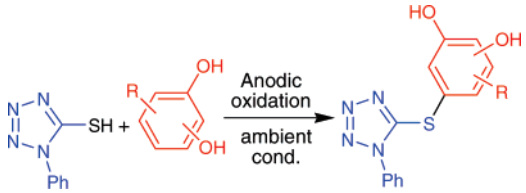

In the presence of 1-phenyl-5-mercaptotetrazole as a nucleophile, electrochemical oxidations of 1,2- and 1,4-dihydroxybenzenes have been investigated in aqueous solution using cyclic voltammetry and controlled-potential coulometry. The voltammetric results indicate that an electrooxidative/Michael-type sequential reaction occurs between the mercaptide anion and the electrochemically generated benzoquinones leading to the corresponding polyfunctional tetrazolic thioethers. The mechanism of electrochemical reaction is proved as an EC pathway using controlled-potential coulometry. In addition, the electrosyntheses of tetrazolic thioethers have been successfully performed in ambient conditions in an undivided cell using an environmentally friendly method with high atom economy.

Tetrazolic thioethres have found widespread use in the modern approach to the synthesis of biologically active compounds and various drugs. Despite their scarcity in natural systems, tetrazoles are important aromatic heterocyclic compounds because of their diverse applications in medicine, biochemistry, agriculture, photography, information recording systems, and others.[1,2] For instance, it was determined that 1-aryl-5-alkylthiotetrazoles (**I**) have well-known antiviral and anti-inflammatory properties,[3] 1-aryl-thiotetrazolyl acetanilides (**II, III**) have demonstrated activities as HIV-1 non-nucleoside reverse transcriptase inhibitors,[4] and 1-phenyl-5-arylthiotetrazole (**IV**) is used as activating reagent in RNA synthesis[5] (Figure 1). Bearing a 5-arylthio moiety, compound **IV** is a significantly better activator than the corresponding 5-aryl- or 5-alkyltetrazoles. Interestingly, in the context of peptidomimetic chemistry, it has long been recognized that the tetrazole moiety can serve as a metabolically stable surrogate for the carboxylic acid moiety

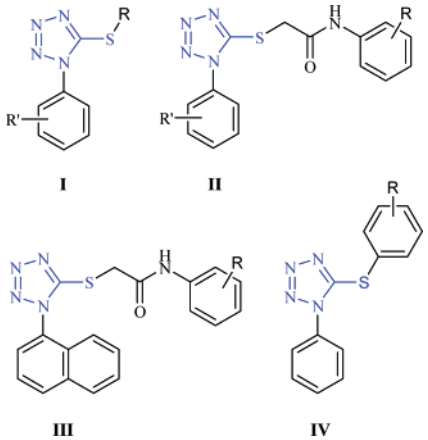

FIGURE 1. Structures of biologically active molecules with thiotetrazolyl moieties.

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and this ability of tetrazole compounds has motivated the incorporation of tetrazole derivatives into biologically active molecules.[6]

o- and *p*-dihydroxybenzenes are ubiquitous in nature. Their functionalized derivatives are extensively used in the chemical and pharmaceutical industries as well as synthetic intermediates in the manufacturing of food antioxidants and antioxidants.[7−9] A literature survey revealed that despite their promising biological features, the synthesis of polyfunctional adducts bearing dihydroxybenzene and thiotetrazolyl moieties have not been subjected to detailed investigations and only a ~ 40-year-old study of Porter and co-workers has reported the 1,4-addition of 1-phenyl-5-mercaptotetrazole to *p*-benzoquinone resulting in tetrazolic thioether-substituted hydroquinones via a chemical oxidative route.[10] Similar to most conventional chemical transformations, the oxidative routes to produce active intermediates like benzoquinones involve toxic oxidizing agents and/or metal additives. Here we demonstrate an alternative procedure for synthesizing novel tetrazolic thioether-substituted dihydroxybenzenes using electrochemically initiated oxidative coupling reactions of dihydroxybenzenes with 1-phenyl-5-mercaptotetrazole that avoids organic solvents, metal-based reagents, catalysts, and stoichiometric oxidants. Electrochemical reactions work based on the electron transfer in the Helmholtz layer at the electrode−solution interface,[11] and through these reactions conditions, highly reactive intermediates (i.e., benzoquinones) can be generated under very mild conditions, such as ambient temperatures, normal pressure, and often in non-halogenated solvents.[12] Direct electrochemical oxidations/reductions of substrates utilize practically mass-free electrons as the only reagents. In this sense, electrochemistry is frequently referred to as one of the prototypical green procedures for synthesizing various organic molecules and structures.[13]

In continuation of our efforts to develop more versatile and convenient chemical and electrochemical synthesis of highly functionalized dihyroxybenzenes,[14] we envisaged that the incorporation of thiotetrazolyl moiety into the biologically active dihydroxybenzene structures might lead to a series of tetrazolic thioethers with even better biological activities. This idea prompted us to investigate the anodic oxidation of dihydroxybenzenes (**1a**−**f**) (Schemes 1 and 3) to their corresponding benzoquinones in the presence of 1-phenyl-5-mercaptotetrazole (**3**) as a very acidic nucleophile (a desirable property in ionic addition reactions to unsaturated compounds).[15]

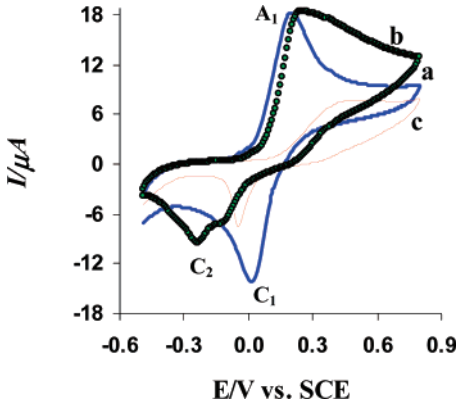

FIGURE 2. Cyclic voltammograms of 1.0 mM catechol (**1a**) in the absence (a) and presence (b) of 1.0 mM of 1-phenyl-5-mercaptotetrazole (**3**) and 1.0 mM of **3** in the absence of **1a** at glassy carbon electrode versus SCE in water/acetonitrile (90/10) solution containing 0.2 M sodium acetate. Scan rate: 50 mV s^{-1}; $t = 25 \pm 1$ °C.

The present study describes a straightforward, environmentally friendly, and reagentless protocol with high atom economy and safe waste, for the synthesis of a series of new polyfunctional tetrazolic thioethrs (**5a**−**f**) via an EC electrochemical mechanism pathway in a sequential fashion. The electrosyntheses of **5a**−**f**, in high yields and purity, have been successfully performed in ambient conditions in an undivided cell using graphite electrode. To the best of our knowledge, this is the first report aimed at the synthesizing of polyfunctional tetrazolic thioethers.

Although *o*-benzoquinones are extremely reactive and often difficult to isolate, they can be easily generated in situ by oxidation of the corresponding catechols and then trapped by sulfur nucleophiles. Cyclic voltammogram of a 1 mM solution of catechol (**1a**) in water/acetonitrile (90/10) solution containing 0.2 M sodium acetate shows one anodic peak (A_1) and a corresponding cathodic peak (C_1), which correspond to the transformation of **1a** to *o*-benzoquinone (**2a**) and vice versa through a quasi-reversible two-electron process (Figure 2, curve a). A peak current ratio (I_p^{C1}/I_p^{A1}) of nearly unity, particularly during the repetitive recycling of potential, can be considered as a criterion for the stability of *o*-benzoquinone produced at the surface of 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.[16−19] To get further support on the electrochemical oxidation of **1a**, it was studied in the presence of 1-phenyl-5-mercaptotetrazole (**3**) as a nucleophile. The proton of thiol **3** is acidic enough so it seems that its ionic 1,4-addition to various quinones can proceed in a quick and simple way. Figure 2, curve b, shows the cyclic voltammogram obtained

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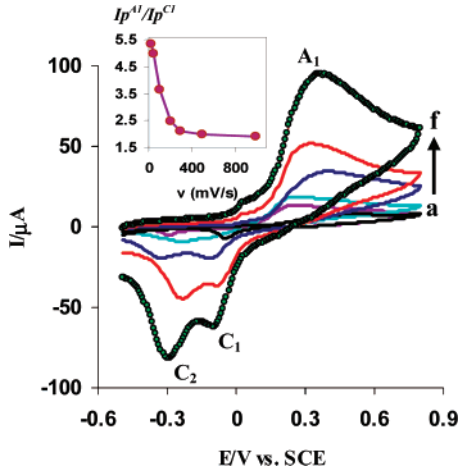

FIGURE 3. Typical cyclic voltammograms of 1.0 mM catechol (**1a**) in the presence of 1.0 mM 1-phenyl-5-mercaptotetrazole (**3**) at a glassy carbon electrode versus SCE in water/acetonitrile (90/10) solution containing 0.2 M sodium acetate. Scan rates for a−f are: 20, 50, 100, 200, 500, 1000 mV s^{-1}, respectively. (g) Variation of peak current ratio (I_p^{A1}/I_p^{C1}) versus scan rate, $t = 25 \pm 1$ °C.

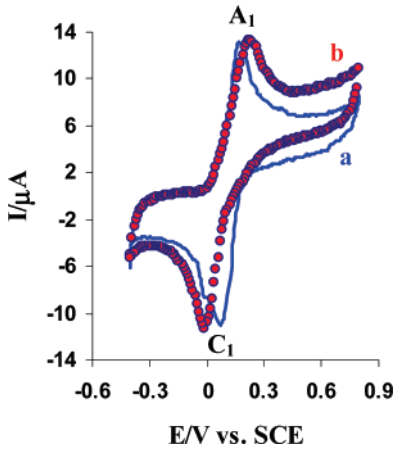

FIGURE 4. Cyclic voltammogram of (a) 1 mM catechol (**1a**), (b) saturated solution of obtained product (**5a**) at glassy carbon electrode versus SCE in water/acetonitrile (50/50) solution containing 0.2 M sodium acetate. Scan rate: 50 mV s^{-1}; $t = 25 \pm 1$ °C.

for a 1 mM solution of **1a** in the presence of 1 mM of **3**. The voltammogram exhibits one anodic peak (A_1) and two cathodic peaks (C_1 and C_2). The comparison of C_1 peaks in the absence and presence of **3** shows a considerable decrease of the current density for the latter and this obviously indicates the reactivity of electrochemically derived highly active *o*-benzoquinone (**2a**) toward mercaptide anion **3a**. The observed negative 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.[20] The cyclic voltammogram of a 1 mM solution of **3** is shown in Figure 2, curve c, for comparison. The cathodic peak (C_2) that can be seen in both curves b and c is probably corresponding to the reduction of product of dimerization of **3**.

Furthermore, we examined the effects of potential scan rate and concentration of **3** on the peak current ratio (I_p^{A1}/I_p^{C1}) in cyclic voltammograms of **1a** in the presence of **3**. It is seen that, proportional to the increasing of the potential scan rate (Figure 3, curves a−f) or decreasing of **3** to **1a** concentration ratio, the peak current ratio (I_p^{A1}/I_p^{C1}) decreases. A plot of the peak current ratio (I_p^{A1}/I_p^{C1}) versus the scan rate for a mixture of **1a** and **3** confirms the reactivity of *o*-benzoquinone (**2a**) toward **3** (Figure 3, curve g). Meanwhile, the peak current function for A_1 peak (I_p^{A1}/I_p^{C1}) decreases with increasing scan rate, which is adapted as indication of an EC mechanism.[21]

Similar to the oxidation of 2-mercaptobenzoxazole, which leads to the formation of bis(benzoxazolyl) disulfide,[22] 1-phenyl-5-mercaptotetrazole (**3**) can be oxidized to the corresponding disulfide. Considering the closeness of oxidation potential peaks of **1a** and **3** (Figure 2, curves a and c), to minimize the oxidation of **3** and hence, achieving higher selectivity, we applied 0.20 V potential versus SCE in both coulometry and preparative synthesis processes. To determine electrochemical efficiency, controlled potential coulometry of catechol (**1a**) in the presence of **3** was performed at 0.20 V versus SCE. On the basis of obtained results, the electrochemical efficiency is >80%. The preparative synthesis was performed in potentiostatic condition by oxidation of **1a** in the presence of **3** at 0.20 V versus SCE potential on a graphite rode anode electrode in an undivided cell. More detail is described in the Experimental Section.

The aforementioned coulometry and voltammetry results allow us to propose the pathways shown in Scheme 1 for the electro-oxidation of catechol (**1a**) in the presence of **3**. According to our results, it seems that upon anodic oxidation of **1a** to *o*-benzoquinone **2a** (Scheme 1, eq 1), an intermolecular Michael-type reaction of mercaptide anion (**3a**) (Scheme 1, eq 2) with **2a** occurs in a sequential fashion and this reaction seems to occur much faster than other side reactions, leading to the formation of N-arylthiotetrazolyl catechol (**5a**) (Scheme 1, eq 3). The overoxidation of **5a** was circumvented during the preparative reaction because of the presence of a thiotetrazolyl moiety with electron-withdrawing character on the catechol ring (Figure 4) as well as the insolubility of **5a** in reaction medium. As can be seen, there is an electrooxidative/Michael-type addition sequence in this one-pot coupling reaction of **1a** with **3** leading to the formation of novel arylthiotetrazolyl catechol **5a** as a final product in excellent yield (Scheme 1).

In examining the scope and generality of the developed protocol as well as the influence of structural variation of catechol ring on the reactivity of electrochemically derived *o*-benzoquinones toward **3**, we studied the electrochemically induced reaction of 1-phenyl-5-mercaptotetrazole (**3**) with some other catechols bearing methyl, methoxy, or 4-*tert*-butyl groups at the C-3 or C-4 positions (**1b**−**e**) in the conditions similar to that of **1a**. The electro-oxidation of 3-methylcatechol (**1b**) and 3-methoxycatechol (**1c**) in the presence of **3** proceed in a way similar to that of **1a**. The existence of a methyl or methoxy group at the C-3 position of **1b** or **1c** may has subtle electronic and steric effects on the reactivity of their relevant *o*-bezoquinones (**2b**,**c**) and would probably cause these Michael acceptors (**2b**,**c**) to be attacked by **3a** at the C-4 or C-5 positions to yield two types of product in each case (**5b**,**c** or **6b**,**c**, Scheme 2). Because the methyl and methoxy groups are both electron-donating substituents, we suggest that *o*-benzoquinones **2b** and **2c** are more electropositive at C-5 position and therefore, can be selectively attacked from C-5 position by the mercaptide anion **3a** leading to the formation of **5b**,**c**, respectively, and not

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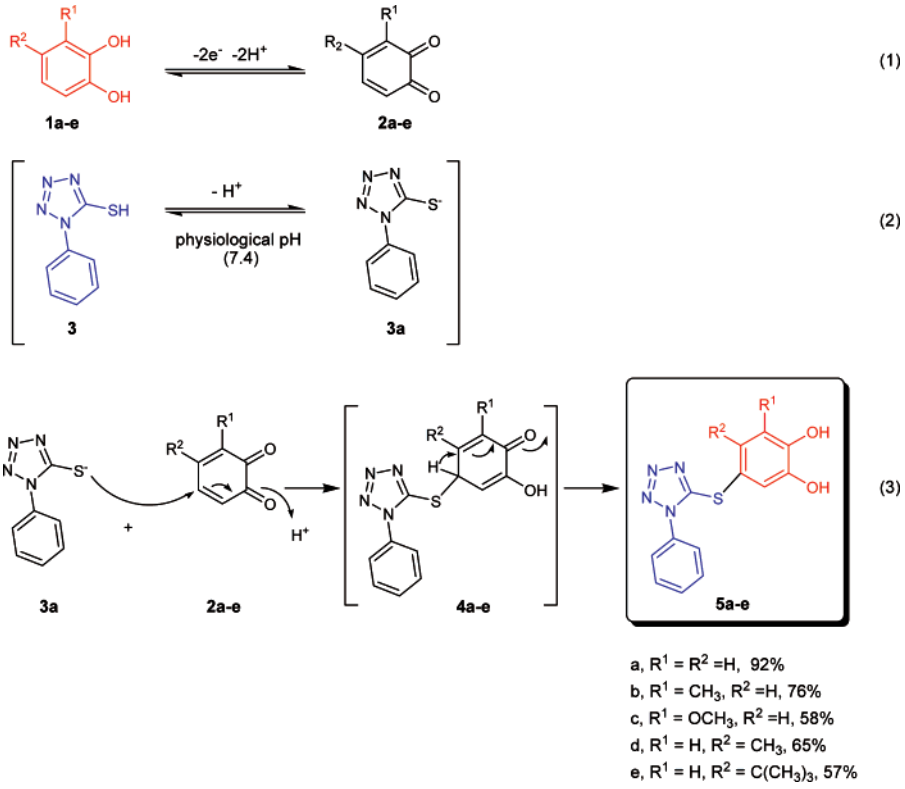
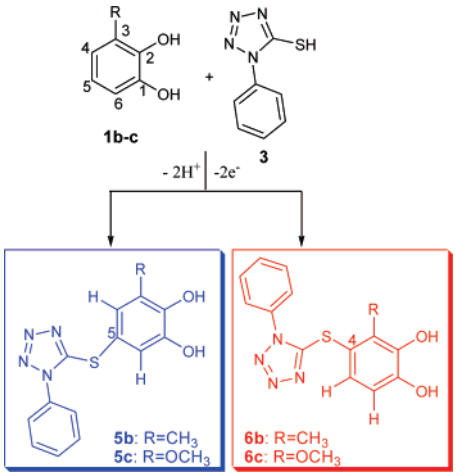
SCHEME 1



SCHEME 2. Schematic Possible Structures of 5b,c and 6b,c



6b,**c**. The accuracy of theses suggestions was proved by comparing the calculated[23] and experimentally obtained ^{1}H and ^{13}CNMR data of the possible structures **5b**,**c** and **6b**,**c**. Spectroscopic characterization of the product obtained from (**1b**) by ^{1}H NMR indicated the presence of two doublets at 6.70 and 6.94 ppm with small coupling constant value (^{4}J or ^{w}J) which is in a good agreement with two aromatic protons in the meta position[24] and supports the addition of **3a** to the C-5 position. The addition to C-4 in the generation of more complex feature, once ortho hydrogens, would couple, which would result in a doublet with a coupling constant, *J*, of about 10 Hz. Also, comparison of the calculated and experimental ^{13}CNMR data

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TABLE 1. Experimental and Calculated ^{13}CNMR Data for Methyl and Methoxy Carbons in Catechol Ring

compd	exptl δ (ppm)	calcd δ (ppm)
product obtained from **1b**	14.05	
5b		14.00
6b		7.01
product obtained from **1c**	56.08	
5c		56.20
6c		50.80

of the methyl and methoxy carbons in the catechol rings for the suggested possible structures (Table 1) can support the formation of **5b**,**c** instead of **6b**,**c**. According to these results, it is obvious that *o*-benzoquinones **2b**,**c** are selectively attacked from C-5 position by **3a**. Therefore, these sequential electrooxidative/Michael-type one-pot coupling reactions of **1b** and **1c** with **3** lead to the formation of novel tetrazolic thioether-substituted catechols **5b** and **5c** as final products in high yields (Scheme 1).

Furthermore, the effect of a group located at the reactive site of *o*-quinones (C-4 or β-position to carbonyl group) on their reactivity toward mercaptide anion **3a** was investigated in some details. The electrochemical oxidations of 4-methylcatechol (**1d)** and 4-*tert*-butylcatechol (**1e)** bearing methyl and *tert*-butyl groups at the C-4 position were studied in the presence of **3** in water/acetonitrile (90/10) solution containing 0.20 M sodium acetate. As mentioned earlier, any decrease observed in the current density for the cathodic peak in cyclic voltammograms of catechols obviously relates to the reactivity of electrochemically derived *o*-benzoquinones toward mercaptide anion **3a**. Comparison of the cyclic voltammograms of **1d** and **1a** in the presence of **3**, shows less decrease in the current density for the cathodic part of **1d** which means *o*-benzoquinone **2d** has less reactivity in the Michael-addition reaction toward mercap-

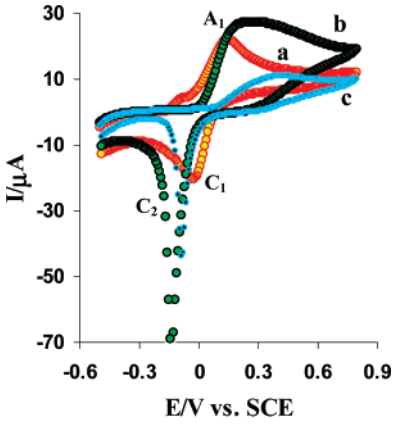


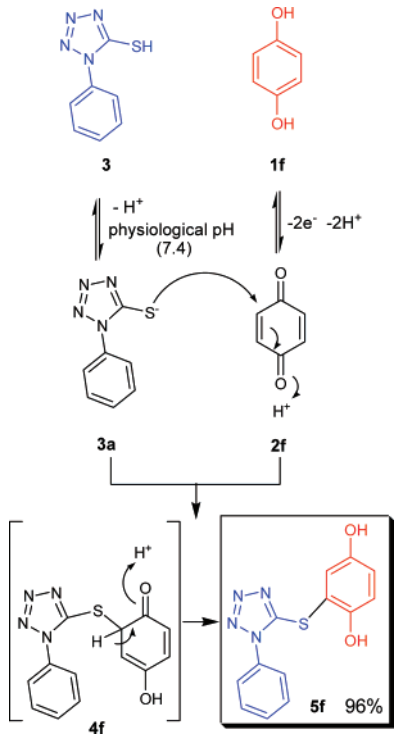
FIGURE 5. Cyclic voltammograms of 1.0 mM hydroquinone (**1f**). (a) In the absence and (b) in the presence of 1.0 mM of 1-phenyl-5-mercaptotetrazole (**3**), (c) 1.0 mM 1-phenyl-5-mercaptotetrazole in the absence of **1f** at glassy carbon electrode versus SCE in water/acetonitrile (90/10) solution containing 0.2 M sodium acetate. Scan rate: 100 mV s^{-1}; $t = 25 \pm 1$ °C.

tide anion **3a**, appearing as an increase in peak current ratio (I_p^{C1}/I_p^{A1}). In addition, comparing the cathodic peaks of cyclic voltammograms of **1e** and **1a** in the presence of **3**, suggests that the presence of *tert*-butyl group, a bulky substituent, at the C-4 position of **2e** would probably cause a streic inhibition of the accessibility of C-5 position to the mercaptide anion **3a** and therefore, this Michael acceptor (**2e**) will be attacked by **3a** at the C-5 position in a difficult and slower process. The considerable increase in peak current ratio (I_p^{C1}/I_p^{A1}) for **1e** clearly supports this suggestion. Except longer reaction time and lower yield, other electrochemical investigations for **1d** and **1e**, including cyclic voltammetry and controlled potential coulometry showed a behavior similar to that of **1a**. These one-pot oxidative coupling reactions of **1d** and **1e** with **3** lead to the formation of tetrazolic thioether-substituted catechols **5d**−**e** in high yields (Scheme 1).

Finally, the electrochemical oxidation of *p*-dihydroxybenzene (**1f**) (hydroquinone) in the presence of **3** was studied in some detail. Cyclic voltammogram of a 1 mM solution of hydroquinone (**1f**) in water/acetonitrile (90/10) solution containing 0.2 M sodium acetate shows one anodic peak (A_1) and a corresponding cathodic peak (C_1), which correspond to the transformation of hydroquinone (**1f**) to *p*-benzoquinone (**2f**) and vice versa through a quasi-reversible two-electron process (Figure 5, curve a). The cyclic voltammogram obtained for a 1 mM solution of **1f** in the presence of 1 mM of **3** is shown in Figure 5, curve b. This voltammogram exhibits one anodic peak (A_1) and compared to the curve a, shows a nearly complete decrease of the current density for cathodic peak (C_1). This observation is in a good agreement with the reactivity of the electrochemically derived highly active *o*-benzoquinone (**2a**) toward mercaptide anion **3a**. The cyclic voltammogram of a 1 mM solution of **3** is shown in Figure 5, curve c, for comparison and the cathodic peak (C_2) that can be seen in both curves b and c is probably corresponding to the reduction of product of dimerization of 1-phenyl-5-mercaptotetrazole (**3**).

The obtained coulometry and voltammetry results allow us to propose the pathways shown in Scheme 3 for the electrooxidation of hydroquinone (**1f**) in the presence of 1-phenyl-5-mercaptotetrazole (**3**). According to our results, it seems that similar to the case of **1a**, upon anodic oxidation of **1f** to *p*-benzoquinone **2f** (Scheme 3, eq 1), an intermolecular Michael-

SCHEME 3



type reaction of mercaptide anion (**3a**) (Scheme 3, eq 2) with **2f** occurs in a domino fashion and this sequential reaction seems to occur much faster than other side reactions, leading to the formation of tetrazolic thioether-substituted hydroquinone (**5f**) (Scheme 3, eq 3).

Conclusion

The results of this work show that 1,2- and 1,4-dihydroxybenzenes are electrochemically oxidized to their corresponding benzoquinones and these benzoquinones can be attacked by 1-phenyl-5-mercaptotetrazole leading to the novel polyfunctional tetrazolic thioethers. In addition, our results suggest that the electronic and steric nature of the substituents attached to benzoquinones rings have important effects on their reactivity toward nucleophile and also control the structures of final products. In conclusion, we have described a general, convenient, environmentally friendly and reagent-less protocol for the preparation of a series of polyfunctional tetrazolic thioethers through a sequential oxidation/Michael addition reaction of commercially available starting materials.

We believe that this easy and selective electrooxidative coupling reaction with its advantages of complementary reactivity and mild reaction conditions and using electrons as reagent instead of oxidative ones (only 2F charge consumption per each mol of dihydroxybenzene is needed), working in ambient conditions, technical feasibility, and especially dramatically high atom economy (>99%) may find potential applications in synthetic organic chemistry and more importantly, can compliment the existing chemical strategies.

In addition, we hope that because of the diversity of this method, it can be adopted in organic heterocyclic chemistry to synthesize and screen libraries of related biologically important polycyclic thiotetrazoles.

Experimental Section

Apparatus and Reagents. Electrolysis equipment is described in the Supporting Information. All chemicals were of reagent-grade and used without further purification. Throughout all experiments distilled water was used and all the experiments were done at room temperature.

Electroorganic Synthesis of 5a−f. In a typical procedure, a solution (ca. 100 mL) of water/acetonitrile (90/10), containing 0.2 M acetate sodium, 1.0 mmol of dihydroxybenzene (**1a−f**) and 1.0 mmol of 1-phenyl-5-mercaptotetrazole (**3**), was electrolyzed in an undivided cell equipped with a carbon anode (an assembly of four rods, 6-mm diameter, and ∼10-cm length), and a large platinum gauze cathode at 0.20 V vs SCE, at 25 °C. The electrolysis was terminated when the decay of the current became more than 95%. 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, a few drops of acetic acid were added to the solution and the cell was placed in a refrigerator overnight. The precipitated solid was collected by filtration, washed copiously with distilled water and characterized by: FT-IR, ^{1}H NMR, ^{13}C NMR and HR-MS. The final products (**5a−f**) were obtained purely and no extra purification was needed.

4-(1-Phenyl-1*H*-tetrazol-5-ylthio)benzene-1,2-diol (5a): mp 135−136 °C; yield 92%; ^{1}H NMR δ ppm (200 MHz DMSO-d_6) 4.51 (broad, 2H), 6.79−7.01 (m, 3H), 7.58−7.69 (m, 5H); ^{13}C NMR δ ppm (50 MHz DMSO-d_6) 114.3, 116.4, 121.4, 125.1, 126.1, 129.9, 130.7, 133.1, 146.2, 147.8, 154.5; MS (EI, 70 eV) 286 (M^+, 23), 141 (48), 118 (100), 91 (10), 77 (10), 65 (6); HRMS (EI) calcd for $C_{13}H_{10}O_2N_4S$ 286.0524, found 286.0512.

3-Methyl-5-(1-phenyl-1*H*-tetrazol-5-ylthio)benzene-1,2-diol (5b): mp 160−161 °C; yield 76%; IR (dropcast on NaCl) 653, 695, 710, 810, 847, 910, 1083, 1302, 1428, 1490, 1520, 1610, 2993, 3050, 3450 cm^{-1}; ^{1}H NMR, δ ppm (200 MHz DMSO-d_6): 2.16 (s, 3H), 6.70 (d, J = 8.34, 1H), 6.94 (d, J = 8.34, 1H), 7.66−7.74 (m, 5H), 8.67 (broad, 1H), 9.86 (broad, 1H); ^{13}C NMR δ ppm (50 MHz DMSO-d_6) 14.0, 113.2, 114.6, 124.9, 127.3, 129.2, 130.0, 130.7, 133.2, 144.4, 147.7, 154.5; MS (EI, 70 eV) 300 (M^+, 45), 230 (9), 213 (6), 155 (80), 118 (100), 93 (17), 77 (17), 65 (21); HRMS (EI) calcd for $C_{14}H_{12}O_2N_4S$ 300.0681, found 300.0675.

3-Methoxy-5-(1-phenyl-1*H*-tetrazol-5-ylthio)benzene-1,2-diol (5c): mp 82−83 °C; yield 58%; ^{1}H NMR δ ppm (200 MHz DMSO-d_6) 3.69 (s, 3H), 6.61−670 (m, 2H), 7.62−7.69 (m, 5H), 8.75−9.40 (broad); ^{13}C NMR δ ppm (50 MHz DMSO-d_6) 56.0, 109.7, 113.8, 115.4, 124.9, 125.1, 129.9, 130.7, 133.2, 136.5, 146.4, 148.6, 149.7, 154.3; MS (EI, 70 eV) 316 (M^+, 32), 256 (4), 230 (5), 171 (100), 156 (10), 118 (65), 84 (38), 77 (8), 65 (6); HRMS (EI) calcd for $C_{14}H_{12}O_3N_4S$ 316.0630, found 316.0625.

4-Methyl-5-(1-phenyl-1*H*-tetrazol-5-ylthio)benzene-1,2-diol (5d): mp 169−171 °C; yield 65%; IR (dropcast on NaCl) 690, 715, 723, 821, 874, 1050, 1098, 1130, 1198, 1250, 1450, 1490, 1529, 1601, 2902, 3075, 3480 cm^{-1}; ^{1}H NMR δ ppm (200 MHz DMSO-d_6) 2.16 (s, 3H), 6.76 (s, 1H), 6.95 (s, 1H), 7.66−7.70 (m, 5H), 9.22−9.48 (broad, 2H); ^{13}C NMR δ ppm (50 MHz DMSO-d_6) 19.5, 113.1, 117.9, 122.6, 124.9, 129.9, 130.7, 133.2, 133.3, 144.0, 148.0, 154.3; MS (EI, 70 eV) 300 (M^+, 46), 267 (21), 155 (64), 118 (100), 93 (17), 91 (18), 77 (12), 65 (16); HRMS (EI) calcd for $C_{14}H_{12}O_2N_4S$ 300.0681, found 300.0686.

4-*tert*-Butyl-5-(1-phenyl-1*H*-tetrazol-5-ylthio)benzene-1,2-diol (5e): mp 181−183 °C; yield 57%; IR (dropcast on NaCl) 560, 610, 691, 700, 725, 880, 943, 1055, 1090, 1155, 1287, 1340, 1355, 1401, 1490, 1539, 1599, 2902, 3088, 3510 cm^{-1}; ^{1}H NMR δ ppm (200 MHz DMSO-d_6) 1.12 (s, 9H), 6.80 (s, 1H), 6.91 (s, 1H), 7.63−7.80 (m, 5H), 9.08 (broad, 1H), 9.56 (broad, 1H); ^{13}C NMR δ ppm (50 MHz DMSO-d_6) 31.1, 33.8, 112.1, 114.8, 120.8, 124.8, 129.7, 130.5, 133.3, 142.0, 143.8, 145.4, 153.2; MS (EI, 70 eV) 342 (M^+, 100), 298 (9), 283 (10), 255 (7), 197 (22), 180 (35), 164 (24), 135 (14), 118 (46), 91 (15), 77 (14), 65 (9); HRMS (EI) calcd for $C_{17}H_{18}O_2N_4S$ 342.1150, found 342.1152.

2-(1-Phenyl-1*H*-tetrazol-5-ylthio)benzene-1,4-diol (5f): mp 217−218 °C (lit.[10] mp 216−217 °C); yield 96%; ^{1}H NMR δ ppm (200 MHz DMSO-d_6): 6.87−6.97 (m, 3H), 7.76−7.92 (m, 5H), 9.25 (s, 1H), 9.72 (s, 1H); ^{13}C NMR δ ppm (50 MHz DMSO-d_6) 113.3, 116.7, 118.0, 119.3, 124.6, 124.9, 129.8, 130.6, 133.2, 149.3, 150.1; MS (EI, 70 eV) 286 (M^+, 45), 243 (8), 141 (29), 118 (100), 112 (28), 91 (16), 77 (21), 65 (11); HRMS (EI) calcd for $C_{13}H_{10}O_2N_4S$ 286.0524, found 286.0512.

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Supporting Information Available: Copies of ^{1}H, ^{13}C NMR, FT-IR, and HR-MS of all compounds (**5a−f**) as well as general information for cyclic voltammetry, controlled-potential coulometry, and preparative electrolysis procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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