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PAPER

Paired electrochemical conversion of nitroarenes to sulfonamides, diarylsulfones and bis(arylsulfonyl)aminophenols.†

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Banafsheh Mokhtari,[a] Davood Nematollahi,*[a] and Hamid Salehzadeh[b]

A paired electrochemical method using nitrobenzene derivatives (NBs) and arylsulfinic acids (ASAs) as starting materials was developed for the synthesis of some new sulfonamides, diarylsulfones and bis(arylsulfonyl)aminophenols. The synthetic strategy was designed using the data provided by electrochemical studies involving cyclic voltammetry on NBs oxidation in the absence and presence of ASAs. The reactions have been successfully performed in an undivided cell, at carbon rod electrodes, in aqueous solutions, by constant current electrolysis at room temperature. This strategy does not need to use catalysts, toxic solvents and challenging workups. It is also applicable to a wide range of nitroarenes.

Introduction

Sulfonamides are a class of antibacterial compounds which have no interference with the mechanism of host defense.[1] They are widely used for the treatment of various diseases such as gut infections, mucous membrane and urinary tract infections. In veterinary medicine, sulfonamides are classified as highly soluble, standard, topical and potentiated compounds.[2,3] These bioactivities have motivated researchers to the development of efficient methods for the synthesis of sulfonamide derivatives. The most general method to prepare of *N*-arylsulfonamides is direct N–S bond formation.[4] This method is effective, but employs aromatic amines as nitrogen sources which are genotoxic and lead to undesired impurities in the synthesis of pharmaceutical ingredients.[4] Also, functional groups such as hydroxyl, thiols and amines may need to be protected to avoid undesired reactions.

To overcome these problems, the use of metal-catalysts for the formation of C–N bond has been widely proposed.[5-19] In these methods, desired products were produced by the reaction of sulfonamides as nitrogen-based source with aryl activated esters,[5,6] halides,[7-10] arylboronicacids[11-13] and alcohols.[14-19] This is a straightforward strategy for the synthesis of *N*-arylsulfonamides and doesn't require the use of anilines, but various catalysts, harsh conditions, bases and/or ligands should be used and also starting materials must first be synthesized. In another strategy, we have used electrochemical methods for the synthesis of some sulfonamide derivatives.[20-22] However, these methods need to use aromatic amines as a starting reagents

In this context, we have developed a mild electrochemical procedure for the synthesis of new *N*-hydroxyaryl sulfonamides, diarylsulfones and bis(arylsulfonyl) aminophenols without using organic solvents, catalysts and ligands in room temperature using nitrobenzene (**NB**) and arylsulfinic acid derivatives (**ASAs**) as starting materials.

Results and discussion

Cyclic voltammograms of **NB** were recorded in two potential ranges (Fig. 1 part I). When the potential was scanned from -0.40 V to +0.34 V vs. Ag/AgCl, **NB** does not show any oxidation or reduction peak (curve a). But, upon scanning the electrode potential from +0.34 V to a sufficiently negative voltage (−1.20 V) (curve b), the cyclic voltammogram exhibits a large irreversible cathodic peak (C_0) corresponding to the reduction of **NB** to phenylhydroxylamine (**PHA**) and a reversible redox system (A_1/C_1) ascribed to the redox couple phenylhydroxylamine/nitrosobenzene (**PHA/NSB**) (Scheme 1, Eq. 1).[23]

In the same manner, electrochemical behavior of *p*-nitroaniline (**NA**), *p*-nitrophenol (**NP**) and 1-chloro-2-nitrobenzene (**CNA**) were studied (Fig. 1, Parts II-IV). A similar behavior was observed for **CNA**, **NA** and **NP** (Scheme 1, Eq. 1). However, in the case of **NP**, a new redox couple (A_2/C_2) appears at less positive potentials than the A_1/C_1 peaks potential. The pathway leading to the oxidation/reduction peaks A_1/C_1 and A_2/C_2 is given in Scheme 1. An important feature of the peak current ratio, I_{pA2}/I_{pA1} (and I_{pC2}/I_{pC1}) is that the current ratio is depends on the potential scan rate, as, with increasing potential scan rate, I_{pA2}/I_{pA1} (and I_{pC2}/I_{pC1}) increases

[a]Faculty of Chemistry, Bu-Ali-Sina University, Hamedan 65174, Iran. nemat@basu.ac.ir.
[b]Faculty of Chemistry, Kharazmi University, Tehran, Zip Code 15719-14911. Iran.
†Electronic Supplementary Information (ESI) available: Cyclic voltammograms of all starting materials and FT-IR and MS of all compounds.. See DOI: 10.1039/x0xx00000x

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(ESI, Fig. S10). From this data it can be concluded that with increasing potential scan rate, the required time to convert 4-(hydroxyamino)phenol to 4-aminophenol (six-electron reduction process) is not sufficient, which results is a decrease in the I_{pA1} and I_{pC1}.

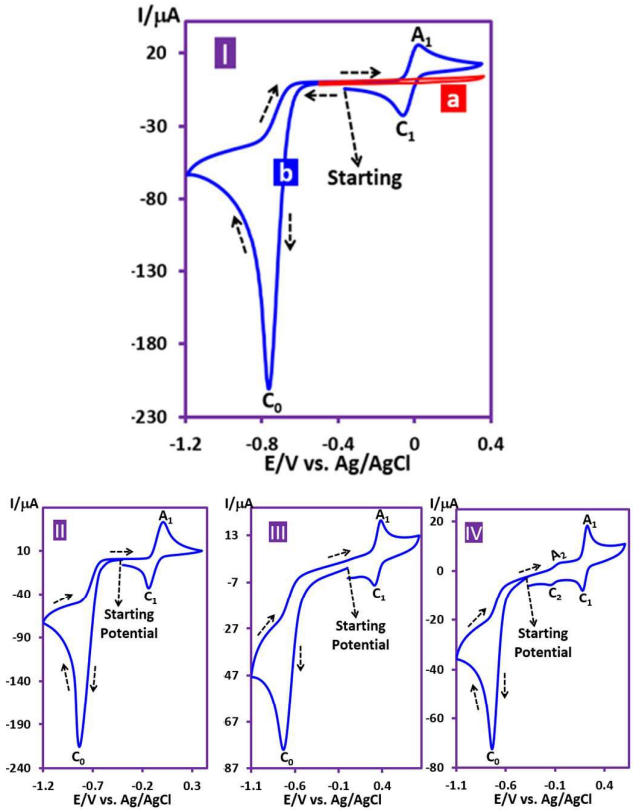
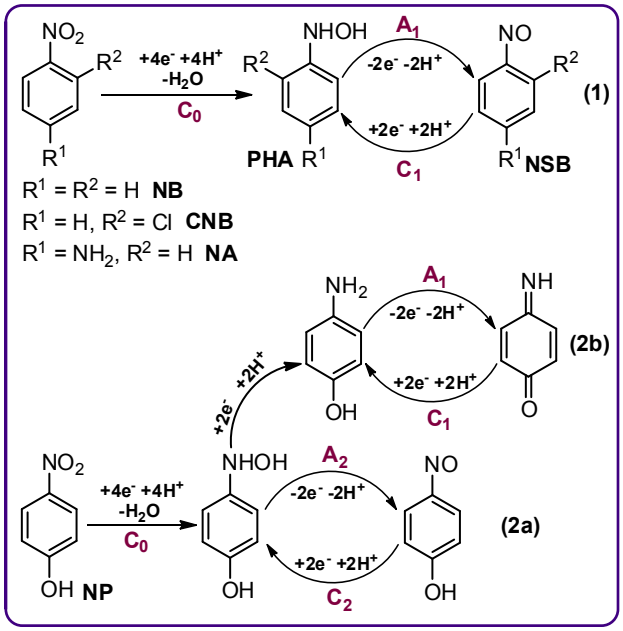


Figure 1. Cyclic voltammograms of 1.0 mM of I) **NB**, II) **CNA**, III) **NA** and IV) **NP** at glassy carbon electrode, in aqueous solution containing phosphate buffer (c = 0.2 M, pH = 3.5). Scan rate: 100 mV s^{-1}; t = 25 ± 1 °C.

The difference observed between the cyclic voltammogram of **NP** and those of other nitroarenes (**NB**, **CNA**, **NA**) can be related to the effect of solution pH on the substituent appended to the aromatic ring. The protonation of the amine group changes it from an electron-donating group to an electron-withdrawing substituent. Under our experimental conditions (pH, 3.5), if a six-electron reduction process takes place, an amine substituted adduct could result which is converted into the corresponding protonated form (Fig. 2).

Under these conditions, the oxidation of protonated aniline synthesized from **NB**, **CNA** and **NA**, does not take place within the potential window examined. In contrast, in the case of **NP**, the hydroxyl group is not in the protonated form, acting as an electron-donating group and facilitate oxidation of protonated aminophenol. This can be the reason for the presence of two anodic peaks (A_1 and A_2) in the cyclic voltammogram of NP (Fig. 1, Part IV).



Scheme 1 Electrochemical behaviour of **NB**, **CNB**, **NA** and **NP**.

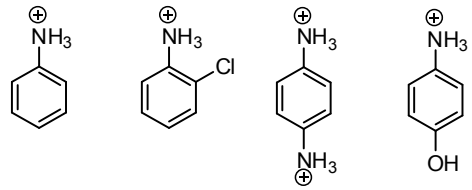


Figure 2. The structure of protonated aniline derivatives.

The effect of pH on the cyclic voltammetric response of **NB** has been examined (Fig. 3).The data show that the potential of all three peaks (A_1, C_1 and C_0) are pH-dependent. In addition, the potential-pH diagram for phenylhydroxylamine/nitroso benzene (**PHA**/**NSB**) redox system (redox couple A_1/C_1) confirms a two-electron/two-proton process.

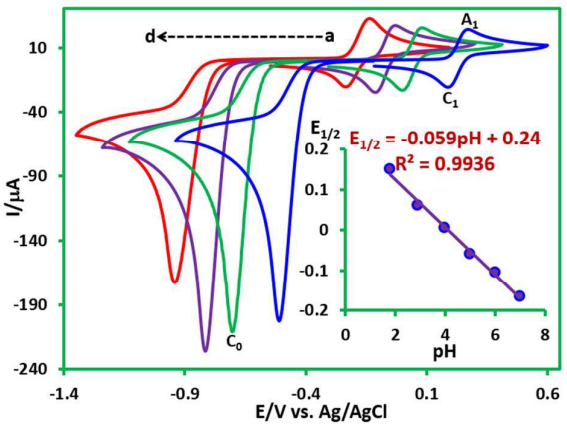


Figure 3. Cyclic voltammograms of 1.0 mM nitrobenzene at glassy carbon electrode, in water/ethanol (80/20) mixture with various pH values and same ionic strength. pHs from (a) to (d) are: 1.0, 4.0, 5.0 and 7.0. Working electrode: glassy carbon. Scan rate:

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100 mV/s. Inset: The potential-pH diagram of phenylhydroxylamine/nitrosobenzene (redox couple A_1/C_1). Temperature = 25 °C.

The influence of pH on the cyclic voltammograms of **NA**, **NP** and **CNA** was also studied (ESI Figs. S1-S3). Our data show that, the influence of pH on the half wave potential of the redox couple A_1/C_1 (and also A_2/C_2, in the case of **NP**) of these nitroarenes are similar to that of **NB**.

The effect of benzenesulfinic acid (**BSA**) on the cyclic voltammetric response of **NB** was also examined (Fig. 4, part I). As can be seen, the important change in the cyclic voltammogram of **NB** in the presence of **BSA** is the decrease of I_p^{C1} which is a sign of the reaction between electro-generated **NSB** and **BSA**.[24-27] The increasing of peak current ratio (I_p^{C1}/I_p^{A1}) with increasing potential sweep rate (ESI Fig. S6) is another sign of the occurrence of a chemical reaction between electrogenerated **NSB** and **BSA**.[24-27]

The influence of **BSA** on the cyclic voltammograms of **NA**, and **NP** was also shown in Fig. 4, parts II and III. In these cases, a new anodic peak (A_p) also appears in more positive potentials which is related to the oxidation of product (**1**-**4**). It also should be noted that, in the case of **NP** in the presence of **BSA** all cathodic peaks were removed (Fig. 4, part III).

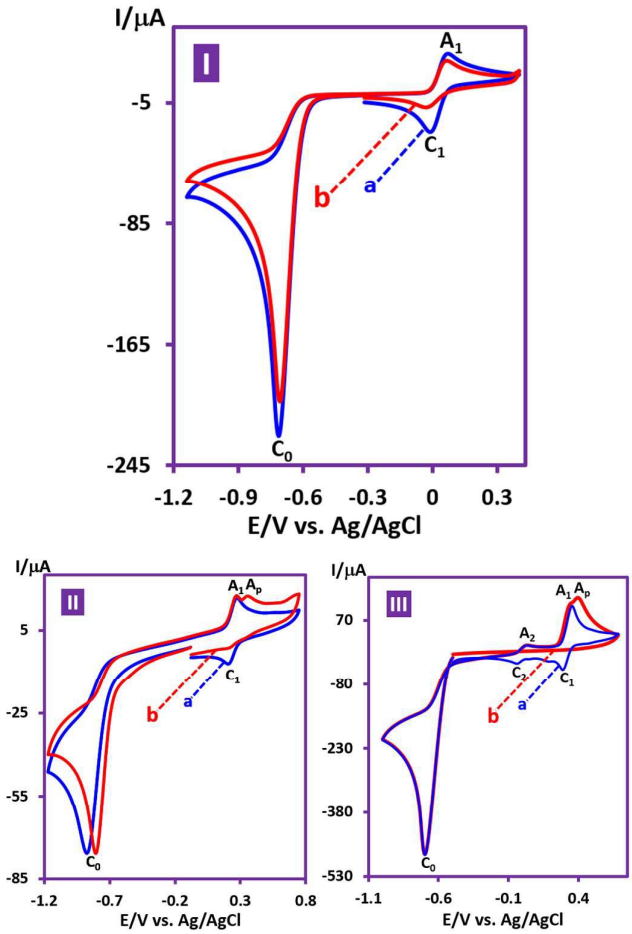

Figure 4. Cyclic voltammograms of 1.0 mM I) **NB**, II) **NA** and III) **NP**: a) in the absence (blue line) and b) in the presence of 1 mM **BSA** (red line) at glassy carbon electrode, in aqueous solution containing phosphate buffer (c = 0.2 M, pH = 3.5). Scan rate: 100 mV s^{-1}; t = 25 ± 1 °C.

These studies were followed by controlled potential coulometry of a solution containing **NB** (1.0 mM) and **BSA** (1.0 mM) at -1.0 V vs. Ag/AgCl. In addition, cyclic voltammetry was employed for electrolysis monitoring to obtain more information on the reaction process and the number of transferred electrons. The voltammograms of peak C_0 show a gradual decrease with the progress of electrolysis (Fig. 5). The current of peak C_0 (I_{pC0}) becomes about zero after the transfer of about 4e$^-$ per molecule of **NB** (Fig. 5, inset).

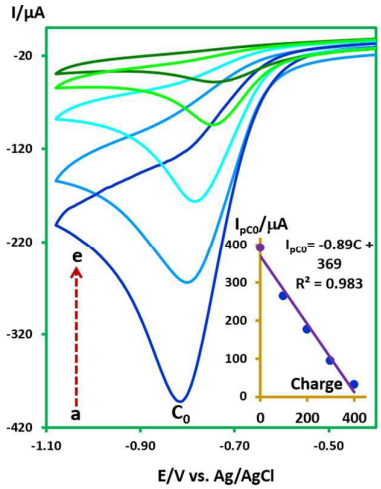

Figure 5. Cyclic voltammograms of **NB** (1.0 mmol) in the presence of **BSA** (1.0 mmol), in phosphate buffer solution (c = 0.2 M, pH 3.0), at glassy carbon electrode during controlled-current coulometry at -1.0 V, after consumption of: (a) 0, (b) 100, (c) 200, (d) 300 and (e) 400 C. Inset: variation of I_{pC0} versus charge consumed. Scan rate 100 mV/s; t = 25±1 °C.

The synthesis of desired products was carried out by constant-current electrolysis of **NB**, **NP**, **NA** and **CNB** in the presence of **ASAs**. The suggested mechanism for the synthesis of *N*-hydroxy-*N*-phenylbenzenesulfonamide (**1**) is shown in Scheme 2. As can be seen, the cathodically generated **PHA** is oxidized at the anode (direct oxidation) to produce **NSB**. The reaction of **NSB** with **ASAs** produces sulfonamide **1**.[28] In order to get higher yields of **1**, an indirect method, mediated by ferrocyanide ions (indirect oxidation) was also developed. A similar pathway was found for the electrochemical conversin of **CNB** in the presence of **ASAs**.

The Schemes for the electrochemical oxidation of **NA** and **NP** in the presence of **ASAs** are shown below. The synthesis mechanism of diarylsulfones **3** is shown in Scheme 3. As can be seen, the cathodically generated phenylhydroxylamine is oxidized at the anode to related nitroso benzene. The reaction of this compound with **ASAs** as a nucleophile give the corresponding sulfonamide (**Int$_R$**). At the applied current density, **Int$_R$** oxidized and converted into **Int$_{ox}$**. The reaction of **ASAs** with this electrochemically generated Michael acceptor (**Int$_{ox}$**) produces diarylsulfones **3** as a final product.[20-22,28,29]

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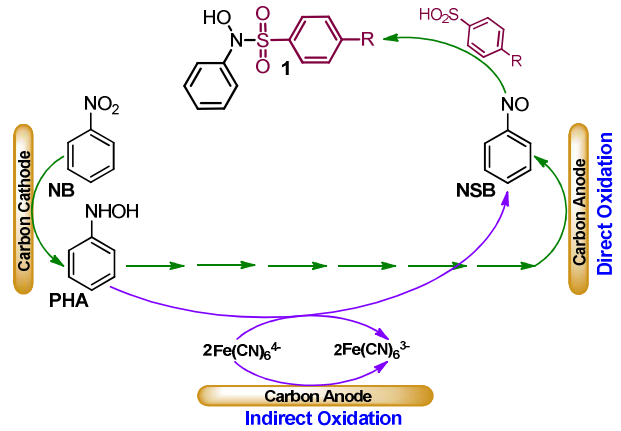
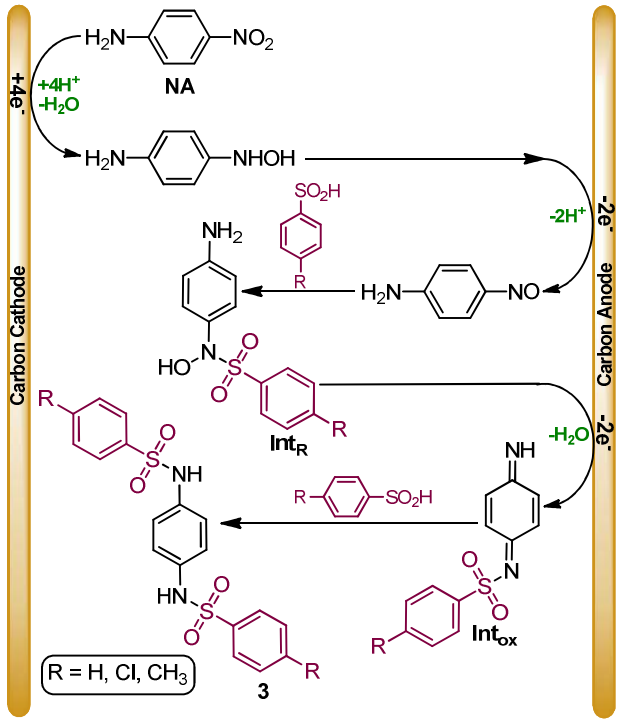


Scheme 2. Electrochemical oxidation of **NB** in the presence of **ASAs**.

According to this mechanism, the anodic peak A_p is related to the oxidation of $\mathbf{Int_R}$ (intermediate in reduced form) to $\mathbf{Int_{ox}}$ (intermediate in oxidized form) (Fig. 1, part II).



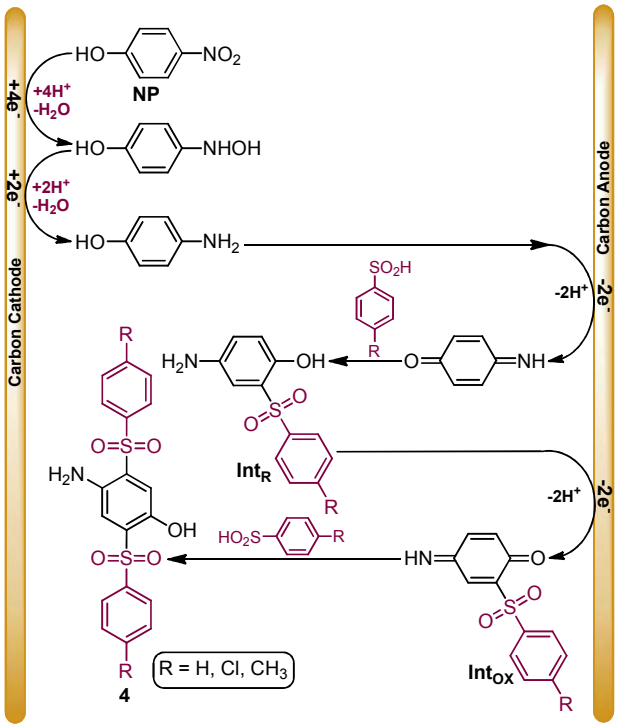
Scheme 3. Electrochemical oxidation of **NA** in the presence of **ASAs**.

I.

A mechanism accounting for the synthesis of 4-amino-2,5-bis(phenyl sulfonyl)phenols **4**, using **NP**, as starting material is shown in Scheme 4. Recently, Beppu and coworkers[31] reported that slufonylaniline-based dyes such as 2,5-bis(methylsulfonyl)-1,4-diaminobenzene are green strong fluorophores. They have stated that: the fluorescence activity of these compounds is established based on an effective push–pull system supported by intramolecular hydrogen bonding. Comparison of 2,5-bis(methylsulfonyl)-1,4-diaminobenzene structure with that of **4**, reveals that the phenol group in compounds **4**, also can be act as push moiety in push-pull system. So, here, we have reported a facile, green and one-pot method for the synthesis of some sulfonylaniline derivatives.

The Scheme for the synthesis of **4**, is different from the previous ones in that the electrochemical reduction is a six-electron transfer process which converts **NP** to *p*-aminophenol. This compound after oxidation to *p*-quinoneimine, was attacked by **ASAs** to form $\mathbf{Int_R}$**.** From a molecular point of view, $\mathbf{Int_R}$ is a substituted *p*-aminophenol which oxidizes at the applied current density to the corresponding *p*-quinoneimine ($\mathbf{Int_{ox}}$). The reaction of another nucleophile (**ASA**) with $\mathbf{Int_{ox}}$, in the next step, gives disubstituted *p*-aminophenol as a final product (**4**).[30]

According to Scheme 4, the anodic peak A_p (Fig. 1, part III) belongs to the oxidation of 4-amino-2-(phenylsulfonyl)phenol ($\mathbf{Int_R}$) to related phenylsulfonyl-quinoneimine ($\mathbf{Int_{ox}}$). The reaction of electro-generated *p*-quinoneimine with **ASAs**, in addition to removing the cathodic peak C_1, removed peaks A_2 and C_2 because of the predominance of six-electron reduction of nitro group over the four-electron reduction (Scheme 1, Eq. 2b).



Scheme 4. Electrochemical synthesis 4-amino-2,5-bis(phenylsulfonyl)phenols **4** using **NP** as starting materia

Current density, charge passed and solution pH are important parameters affecting the yield of products. The experiments performed showed that the optimal charge needed to synthesize products **1-4**, is its theoretical value. For

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example, in the case of **NB**, the maximum yield of 75% was obtained for the synthesis of **1a** after consumption of 4.1 F/mol (Fig. 6, inset). The over-reduction of **PHA** and/or **1a** (or over-oxidation of **NSB** and/or **1a**) are the main factors in decreasing product yield when more electricity is consumed. The data also suggest that the optimum current density for the synthesis of products **1-4** is 0.7 mA/cm^2 (Fig. 6). The insufficient amount of over-voltage at lower current densities and over-reduction of **PHA** and/or **1a** (or over-oxidation of **NSB** and/or **1a**) at higher current densities are responsible for decreasing the yield. In addition, the optimum pH value for the synthesis of products **1-5** is 3.0. The products and their yields are summarized in Table 1.

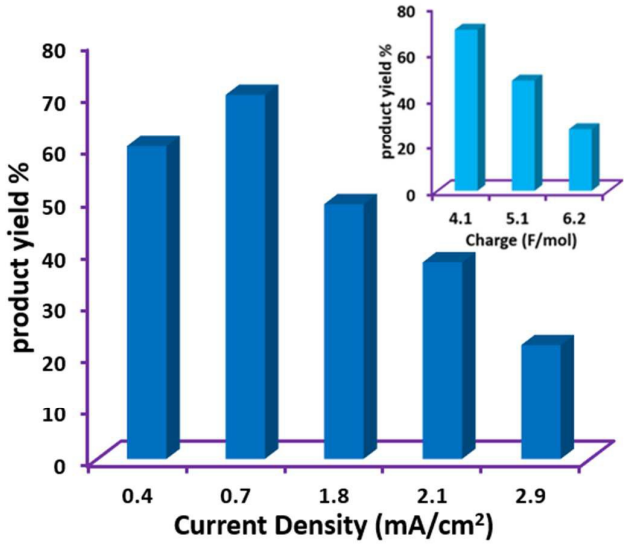


Figure 6. The effect of charge passed (inset) and current density on electrochemical synthesis of **1a**.

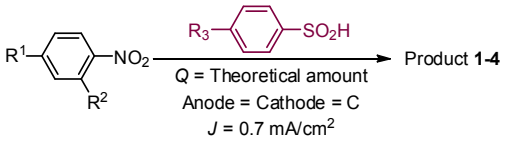
Conclusions

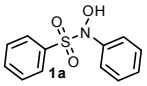
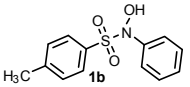
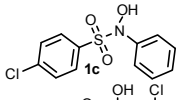
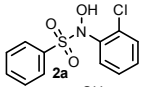
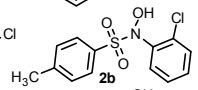
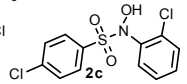
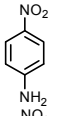
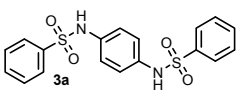
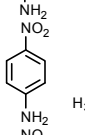
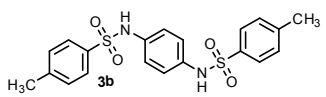
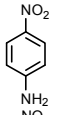
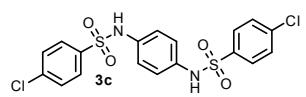
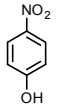
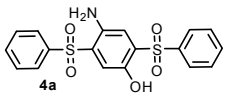
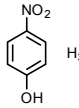
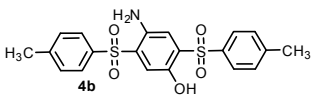
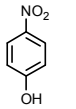
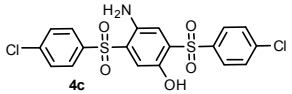
Synthesis of the title compounds (**1-4**) via a paired electrolysis, using a simple cell, and under constant current conditions, in safe water/ethanol solvent mixture, without any catalysis, easy work up (filtration and washing with distilled water), at room-temperature, using the common electrodes (carbons electrodes) with high atom economy and good yields are the prominent features of this work. In addition, another important feature of this method is its adaptability to a wide range of nitroarenes. The results of this study also indicate that the product selectivity was greatly affected by the nature of the functional group.

Experimental section

Apparatus and reagents

Cyclic voltammetry, controlled-potential coulometry, constant current electrolysis and preparative electrolysis were performed using an Autolab model PGSTAT 20 potentiostat/galvanostat. The working electrode used in the voltammetry experiments was a glassy carbon disc and a platinum wire was used as the counter electrode. Before each experiment, the GC electrode was polished using alumina slurry (from Iran Alumina Co). The anode used in controlled-potential coulometry, constant current electrolysis and preparative electrolysis was an assembly of two carbon plates (each one, 10 cm diameter and 7 cm length). The similar configuration carbon constitutes the cathode electrode.



Entry	Substrate	Product	Yield %	mp °C
1			70	133-134
2			75	139-141
3			78	128-129
4			73	153-155
5			75	139-140
6			72	143-145
7			60	170-1172
8			72	158-159
9			77	156-158
10			70	158-160
11			70	158-159
12			72	157-159

The working electrode potentials were measured vs. Ag/AgCl (saturated KCl) electrode (all electrodes from AZAR

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Electrodes). More details are described in our previous paper.[32]

Nitrobenzene (NB), *p*-nitroaniline (NA), *p*-nitrophenol (NP), arylsulfinic acids (ASAs), phosphate salts and ethanol were obtained from commercial sources.

Table 1. Galvanostatic paired electrochemical synthesis of compounds **1-4**.

General electrochemical procedure

Electroorganic synthesis of compounds **1-4** were performed under constant current conditions In a typical procedure, a solution (80 mL) of water (phosphate buffer, pH = 3.0, *c* = 0.2 M)/ethanol mixture (20/80, v/v) containing nitrobenzene derivatives (**NB**, **CNB**, **NA** or **NP**) (1 mmol) and arylsulfinic acids sodium salt (1 mmol for the synthesis of compounds **1** and **2**, and 2 mmol for the synthesis of compounds **3** and **4**) was electrolyzed in an undivided cell at 25 ^{o}C under a constant-current density of 0.7 mA/cm^{2}. The electrolysis was terminated after consumption of the theoretical amount of the charge consumed. Since, the products are insoluble in water (phosphate buffer, pH = 3.0, *c* = 0.2 M)/ethanol mixture (80/20, v/v), separation is carried out only by filtration. The collected solids were washed several times with distilled water.

Conflicts of Interest

There are no conflicts of interest to declare.

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Paired electrochemical conversion of nitroarenes to sulfonamides, diarylsulfones and bis(arylsulfonyl)aminophenols. A green strategy

Banafsheh Mokhtari, Davood Nematollahi,* and Hamid Salehzadeh

Graphical Abstract

A paired electrochemical synthesis of sulfonamides, diarylsulfones and bis(arylsulfonyl)aminophenols using nitrobenzene derivatives and arylsulfinic acids as starting materials under green conditions.