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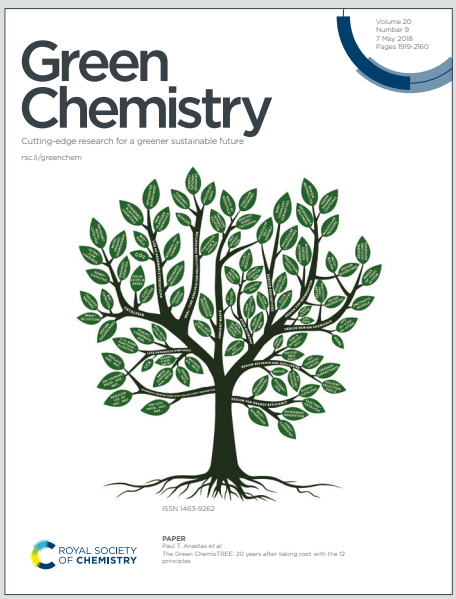




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# Electrochemical Synthesis of Sulfonamides in Graphite Powder Macro Electrode

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**The electrochemical generation of sulfinyl radicals from commercially available and non-expensive sodium salts of sulfinic acids is described. Electrooxidation reactions were carried out in graphite powder macroelectrode using aqueous electrolyte and cavity cell. Further reaction with primary or secondary amines gave the corresponding sulfonamides, a unit present in several biologically active compounds and pharmaceuticals, in good yields.**

The synthesis of sulfonamides is a subject of great interest, not only due to their application in pharmaceuticals,[1-4] but also as protecting group.[5] These class of compounds have a wide range of applications as chemotherapeutical agents against several diseases and, due to date several drugs containing the sulfonamide functionality, they are available for clinical use. Perhaps, the most famous example of commercial drug containing the sulfonamide function is the sildenafil, better known under its commercial name, Viagra.[6]

The classical method for the synthesis of sulfonamides is based on the reactions of sulfonyl chlorides[7] or thiols[8] with amines. In both cases, there is a need for manipulate thiols (known for their unpleasant odor) or sulfonyl halides (sensitive to moisture and difficult to store or handle).

Salts of sulfinic acids appeared as an alternative to the use of sulfonyl chlorides and thiols. These chemicals are stable, inexpensive and a wide range of them is now commercially available.[9] These characteristics made these reagents attractive for the synthesis of sulfonamides. To date methodologies based on the use of copper (II) bromide,[10-11] iodine,[12-15] and TBAI[16] were already described.

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Despite the wide variety of methods described for the preparation of sulfonamides, the need to use transition metals, toxic solvents and excess oxidants make them difficult to apply in the manufacture of pharmaceutical products, since its preparation suffers a limitation of residual tolerance level limit on active pharmaceutical ingredients (API).[17]

The use of electrochemical techniques is no longer just a curiosity from research laboratories Electrolysis is a centuries-old synthesis methodology[18] that can be applied to the preparation of both organic[19,20] and inorganic[21] compounds. More specifically, it also has been increasingly used in the synthesis of pharmaceutical compounds.[22]

Within this context, electrochemistry provides a green[23] and efficient method of synthesis, particularly due to the high yield of the products, current efficiency and control of the process.[24] There are some reports for the electrochemical synthesis of sulfonamides based on the use of the $I^-/I_2$ redox pair as catalyst.[25,26]

In an attempt to improve electrosynthesis processes, keeping in mind the environmental requirements,[23] our research group has developed a new way of performing electrochemical reactions in a cavity cell (Fig. 1) and absence of solvent.[27,28] The procedure involves an easy to handle cell where redox reactions are performed inside a graphite powder macroelectrode. Essentially, the graphite powder (a renewable material)[29] works as reaction medium and the reagents are directly reduced/oxidized, avoiding redox mediators or catalysts. After electrolysis, the aqueous supporting electrolyte can be recycled, and the products are extracted from graphite powder with small amounts of solvent, avoiding waste production.[27]

In this work, an alternative strategy for the synthesis of sulfonamides based on the electrochemical oxidation of sodium aryl sulfinates, using the newly developed electrochemical cavity cell (Fig. 1).[27-29] Electrolyses were carried out with different amines, without the need of any catalyst. The macroelectrode (anode) is prepared by mixing reagents and

graphite powder (particle size < 20μm), and added into the cavity of the cell. Experimental details are described in Supporting Information (Figs. S1 to S5).

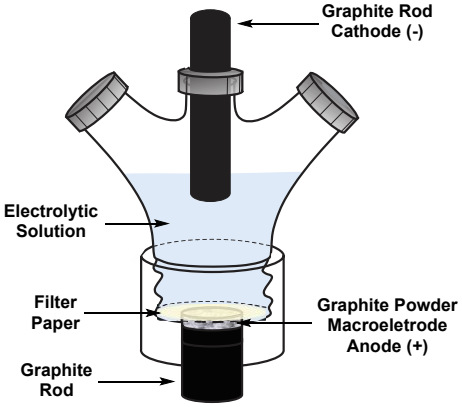


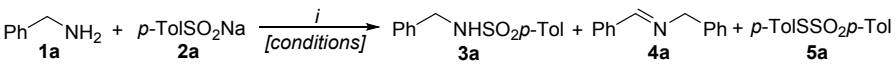

**Figure 1.** Representative illustration of electrochemical cavity cell.

In the course of developing the best reaction conditions, **1a** (0.5 mmol) and **2a** (1.0 mmol) were used as model-substrates and different reaction parameters were evaluated. The results are depicted on Table 1. When the reaction was carried out by using 100 mg of graphite powder, the heterocoupling product **3a** was not obtained, being traces of **5a** observed as a by-product (Table 1, entry 1). This result can be explained by the low homogenization of **2a** in the graphite powder, which probably did not fully adsorb the reagent used. In addition, the starting material **1a** was not fully consumed during the reaction. When the amount of graphite powder was increased to 200 mg, **3a** was obtained in 57% yield together with a similar amount of **4a** (Table 1, entry 2). Better results were observed when 300 mg of graphite powder was used in the reaction, where **3a** was obtained in 95% yield together with a small amount of by-product **4a** (Table 1, entry 3).

The increase in current from 20 mA to 30 mA or 40 mA led to mixtures of **3a**, **4a** and **5a** (Table 2, entries 4 and 5). The current is proportional to the potential applied in the cell, elevated potentials led to an increase in concentration of radical species involved in the reaction medium, decreasing the selectivity.

The time required for electrolysis has also been evaluated. It was observed that the increase in reaction time led to a decrease in the yield and in the selectivity of the reaction (Table 1, entries 6-8). Finally, a study of the best supporting electrolyte to promote the reaction was carried out. The preference was given to water-soluble electrolytes, and also to verify if the use of $LiClO_4$, would indeed be the best choice. When a solution of $KNO_3$ was used, lower yields and selectivities were observed (Table 1, entry 9). The use of NaI as electrolyte was chosen in an attempt to improve the selectivity of the reaction based on a literature procedure.[25] However, no improvement in yield or selectivity of the reaction was observed (Table 1, entry 10). When the reaction was carried out at constant potential, **3a** was obtained in 77% yield (Table 1, entry 11).

**Table 1.** Optimization of reaction conditions for the synthesis of sulfonamide **3a**.[a]



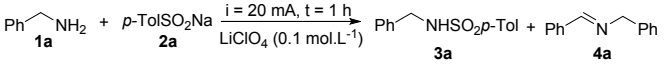

| Entry | Graphite powder (mg) (anode) | i (mA) | Time (h) | Supporting electrolyte (0.1 mol.L$^{-1}$) | (%)[b] | |
|---|---|---|---|---|---|---|
| | | | | | **3a** | **4a** |
| 1 | 100 | 20 | 1.0 | $LiClO_4$ | - | - |
| 2 | 200 | 20 | 1.0 | $LiClO_4$ | 57 | 40 |
| 3 | 300 | 20 | 1.0 | $LiClO_4$ | 95 | 5 |
| 4 | 300 | 30 | 1.0 | $LiClO_4$ | 65 | 30 |
| 5 | 300 | 40 | 1.0 | $LiClO_4$ | 57 | 25 |
| 6 | 300 | 20 | 2.0 | $LiClO_4$ | 81 | 5 |
| 7 | 300 | 20 | 3.0 | $LiClO_4$ | 75 | 10 |
| 8 | 300 | 20 | 4.0 | $LiClO_4$ | 65 | 25 |
| 9 | 300 | 20 | 1.0 | $KNO_3$ | 32 | 34 |
| 10 | 300 | 20 | 1.0 | NaI[c] | 71 | 15 |
| 11 | 300 | -[d] | 2.5[d] | $LiClO_4$ | 77 | 8 |

[a] *Reaction conditions:* **2a** (1.0 mmol) and the appropriate amount of graphite powder were mixed and then transferred to the macroelectrode cavity (anode). **1a** (0.5 mmol) was added to the macroelectrode cavity containing the graphite powder and **2a**, and submitted to electrolysis using the indicated parameters. A graphite rod was used as cathode. 0.1 mol.L$^{-1}$ salt solution was used as supporting electrolyte (Fig.1). [b] Determined by GC with respect to **1a.** [c] Adapted from Ref. 25. [d] Electrolysis was carried out at constant potential E = 0.8 V *vs*. Ag/AgCl, KCl (sat.), passing Q = 53 C (1F.mol$^{-1}$ + 10%).

An additional study was performed in order to determine the best ratio between starting materials **1a** and **2a**. The previously established parameters were fixed and the model-substrates were submitted to a constant current (*i*) electrolysis at 20 mA for 1 h. 0.1 mol.L$^{-1}$ $LiClO_4$ solution was used as supporting electrolyte, and the macroelectrode (anode) was composed of 300 mg of graphite powder. Table 2 shows that the use of an excess **2a** gave better results, while **3a** was obtained as the major product in all cases (Table 2, entries 1-3), being the best result observed when 0.5 mmol of **1a** and 1.0 mmol of **2a** were

used (Table 2, entry 3). Equimolar amounts of **1a** and **2a** led to to the desired product **3a** in a good yield together with a small amount of **4a** (Table 2, entry 4). When an excess of **1a** was used, lower yields of the desired product were observed along with an increase in the formation of **4a** (Table 2, entries 5-7).

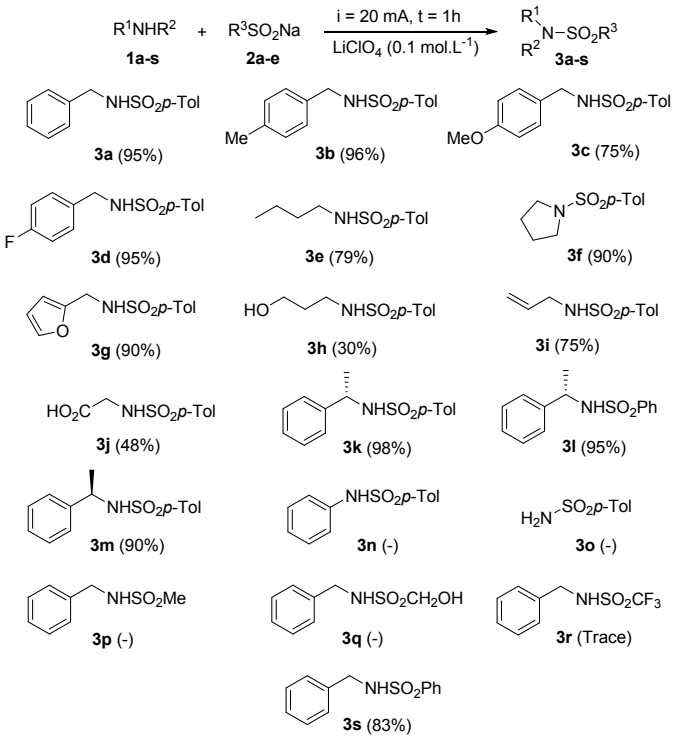
**Table 2.** Molar ratio optimization for sulfonamide **3a**.[a]




| Entry | 1a (mmol) | 2a (mmol) | (%)[b] | |
|---|---|---|---|---|
| | | | 3a | 4a |
| 1 | 0.5 | 2.0 | 46 | 20 |
| 2 | 0.5 | 1.5 | 78 | 13 |
| 3 | 0.5 | 1.0 | 95 | 5 |
| 4 | 0.5 | 0.5 | 91 | 7 |
| 5 | 1.0 | 0.5 | 48 | 10 |
| 6 | 1.5 | 0.5 | 49 | 40 |
| 7 | 2.0 | 0.5 | 26 | 64 |
| 8 | 0.5 | - | - | 54 |
| 9[c] | - | 1.0 | - | - |

[a]*Reaction conditions:* The appropriate amount of **2a** and graphite powder (300 mg) were mixed and then transferred to the macroelectrode cavity (anode). The appropriate amount of **1a** was added to the macroelectrode cavity containing the graphite powder and **2a**, and submitted to a constant current ($i$ = 20 mA) for 1 h. 0.1 mol.L$^{-1}$ $LiClO_4$ solution was used as supporting electrolyte (Fig. 1). A graphite rod was used as cathode. [b] Determined by GC with respect to **1a**. [c] Only traces of **5a** were observed.

Once the best conditions for the electrosynthesis of sulfonamides were determined, they were applied to different substrates in order to verify the versatility of the new method (Scheme 1).




**Scheme 1.** Electrosynthesis of different sulfonamides in cavity cell.

From Scheme 1 it can be seen that the method proved to be versatile since different amines can be used, and the corresponding sulfonamides were obtained in good yields, in most cases. In addition, the reaction did not appear to be sensitive to electronic or steric effects. Since primary or secondary amines, as well as benzylamines containing electron-donating or electron-withdrawing groups in the aromatic ring, gave the corresponding products in high yield. For example, benzylamines containing electron-donating groups in the aromatic ring gave the corresponding products **3b** and **3c** in good yield. Likewise, the presence of the fluorine, a strong electron-withdrawing group, in the aromatic ring gave the corresponding product **3d** in excellent yield. When an aliphatic primary amine was used, the corresponding product **3e** was also obtained in good yield after 1h. When pyrrolidine was used, **3f** was obtained in 90% yield indicating that the reaction was not sensitive to sterics. The electrochemical reaction was also efficient for heteroaromatic compounds where **3g** was obtained in good yield.

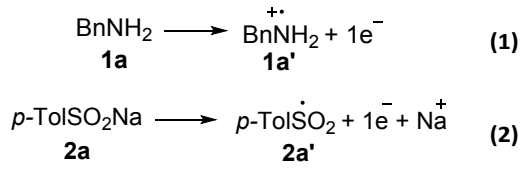
The chemoselectivity of the method was evaluated using an amino alcohol. The corresponding sulfonamide **3h** was obtained exclusively, however, in low yield. When an amine containing an unsaturated chain was used, the corresponding product **3i** was obtained in 75% yield.

As previously mentioned, sulfonamides can be used as protecting groups for amino acids. In this context, glycine was used as substrate and the corresponding sulfonamide **3j** was obtained in 48% yield. It is noteworthy that the reaction can be carried out without the need to convert the amino acid into the corresponding ester. When (*S*)-(-)-α-methylbenzylamine was submitted to the reaction conditions using two different sulfinate salts, the corresponding sulfonamides, **3k** and **3l** were obtained with 98% and 95% yields, respectively, without any observable racemization. A similar result was observed when the (*R*)-isomer was used, where **3m** was also obtained without racemization.

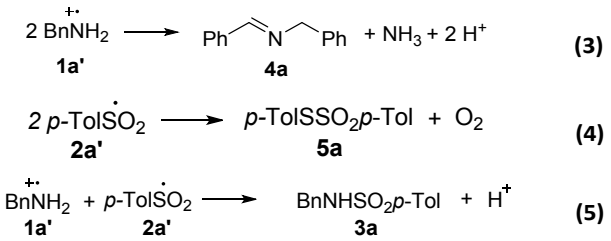
When aniline was used as the starting material, the corresponding sulfonamide **3n** was not observed. Only nitrobenzene, the corresponding oxidation product, was observed. The use of aqueous ammonium hydroxide solution did not give the corresponding product **3o** being only the by-product **5a** observed in the reaction.

The use of non-aromatic sodium sulfinates did not lead to the desired products. When sodium methanesulfinate was used, the corresponding product **3p** was not obtained. The same behavior was observed when rongalite and sodium triflinate were used, where the corresponding products **3q** and **3r** were not obtained. These results indicated that the species electrochemically generated from the sodium salts of sulfinic acids must be sufficiently stable for the subsequent reaction with amines. This effect was confirmed by the reaction of benzylamine **1a** and benzenesulfinic acid sodium salt, where the corresponding product **3s** was obtained in 83% yield. Some reports in the literature describe the formation of aryl sulfinyl radicals by a one-electron oxidation of the respective sodium sulfinate salts.[30] However, this reaction strategy requires the use of metals as catalytic oxidizing agents. Thus, for a better

understanding about the reactions occurring in the electrochemical cavity cell, linear sweep voltammetries were carried out to determine the oxidation peak potentials for **1a** and **2a**, separately. A linear sweep voltammetry (Fig. 2) of **1a** (50 mmol.L$^{-1}$) was carried out in $LiClO_4$ (0.1 mol.L$^{-1}$) in a MeCN/water (7:3) solution, using a glassy carbon anode, Ag/AgCl, KCl (sat.) as reference and stainless steel grid as cathode. Scan rate was 100 mV.s$^{-1}$ and the potential ranged from zero to 1.8 V in a standard cell of three electrodes (Fig. S5). Thus, it was observed a one-electron oxidation peak at 1.45 V, which is in accordance with previously described data,[31] leading to the formation of the benzylamine cation radical $[BnNH]^{+\bullet}$ (**1a'**) (Eq. 1). The same procedure was applied to the linear sweep voltammetry of **2a** (50 mmol.L$^{-1}$) solution (Fig 2). It was observed a peak at 1.04 V, due to the one-electron oxidation of *p*-$TolSO_2Na$ to give the corresponding $[p\text{-}TolSO_2]^{\bullet}$ radical (**2a'**) (Eq. 2).[25,32]




Thus, during electrolysis carried out in the electrochemical cavity cell, homo and heterocoupling reactions would be expected (Eqs. 3 to 5).




The homocoupling product **4a** (Eq. 3) was identified in most reaction conditions described in Table 1, reaching 40% yield when 200 mg of graphite powder was used as reaction medium (Table 1, entry 2). On the other hand, only traces of the **5a**, the homocoupling product, were observed (Eq. 4). The formation of the homocoupling product **4a** was evidenced by an electrolysis carried out using only **1a**, under the standard reaction conditions: *i* = 20 mA and t = 1 h (Table 2, entry 8), giving **4a** in 54% yield. When the same electrolysis was carried out using only **2a** as reagent, under the experimental conditions, only traces of **5a**, the homocoupling product was observed (Table 2, entry 9). The heterocoupling product **3a** was also observed in most reactions described in Table 1, reaching 95% by using 300 mg of graphite powder as reaction medium (Table 1, entry 3).

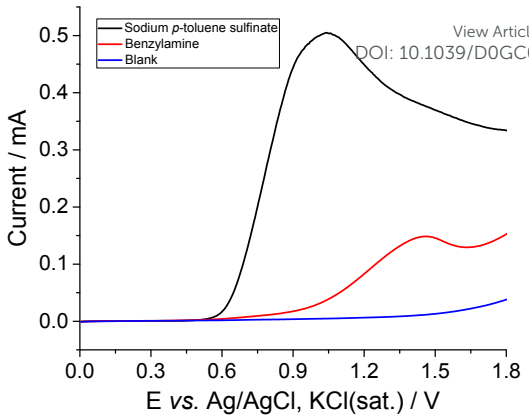
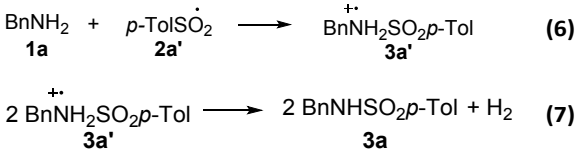



**Figure 2.** Linear sweep voltammetry of 50 mmol.L$^{-1}$ **1a**, and 50 mmol.L$^{-1}$ **2a** in 0.1 mol.L$^{-1}$ $LiClO_4$ MeCN/water (7:3) solution, using a glassy carbon anode, Ag/AgCl, KCl(sat.) as reference, stainless steel grid as cathode, and scan rate = 100 mV.s$^{-1}$.

Electrochemical reactions allow the electron transfer control by following the experimental charge ($Q_{exp}$) passed during the electrolysis [$Q_{exp}$ = i x t, where *i* = current (A) and t = reaction time (s)]. The $Q_{exp}$ can be associated to theoretical charge $Q_t$ = n x z x F, where n = number of mols (mol), z = number of electrons, and F = 96,485 C.mol$^{-1}$ (Faraday constant). In the heterocoupling reaction (Eq. 5), 1 e-/equivalent is necessary for the oxidation of **1a** (limiting reagent, 0.5 mmol), and 1 e-/equivalent for the oxidation of **2a**. Thus, the charge necessary for oxidation of **1a** and **2a** should be $Q_t$ = 96.5 C, which is higher than the $Q_{exp}$ passed during the electrolysis carried out for 1 h ($Q_{exp}$ = 0,02 A x 3600 s = 72.0 C). Therefore, only 75% of the total charge was necessary for the consumption of reagents (**1a** + **2a**), giving 95% of **3a** and 5% of **4a** (Table 1, entry 3).

As observed in linear voltammograms (Fig. 1), the oxidation peak potentials of **1a** and **2a** are not close ($\Delta E$ = 410 mV), thus, the oxidation of **1a** is more difficult than **2a**. In addition, the current peak intensity for the oxidation of **2a** (*i* = 0.504 mA) is 3.7 times higher than **1a** (*i* = 0.137 mA), thus, showing a higher electron transfer rate for **2a**. As described in Table 1, the ideal reaction conditions require 2 equivalents of **2a** *vs.* 1 equivalent of **1a**, which also favours the formation of **2a'** radical. Therefore, in agreement to linear voltammetry experiments, **1a** and **2a** homocoupling products obtained (Table 2, entries 8 and 9), and the lower charge (75%) necessary for total consumption of reagents **1a** and **2a** (Table 1, entry 3), it can be proposed another mechanism for the N-S heterocoupling occurring on the graphite powder macroelectrode surface, according to Eqs. 6 and 7.




The electrochemical and reaction conditions favor the oxidation of **2a**: lower oxidation potential (1.04 V), higher electron transfer rate, higher concentration of **2a** (2 eq.) and low yield of

the by-product **5a** (S-S homocoupling). Thus, **2a'** radical should be formed in high concentrations and reacts with the amino group of **1a** to give the intermediate specie $[BzNH_2SO_2p\text{-Tol}]^{+\bullet}$ (**3a'**) (Eq. 6), which is not stable and loses $H^{\bullet}$ which combines to give $H_2$ (Eq. 7). This mechanism was confirmed by an electrolysis carried out under the standard reaction conditions at constant potential E = 0.8 V vs. Ag/AgCl, KCl (sat.). At this potential, **2a** was selectively oxidized to give **2a'** radical as the major product. The electrolysis gave 77% yield of **3a**, 8% of **4a**, and 15% of unreacted **1a** (Table 1, entry 11). Thus, the electrochemical heterocoupling reaction between sodium sulfinates and amines can occur through the coupling of the respective radicals generated from the 1F.mol$^{-1}$ oxidation (Eq. 5), at the same time that the heterocoupling reaction can occur from the single sulfinate oxidation (0.5 F.mol$^{-1}$).

## Conclusions

The electrochemical generation of sulfinyl radicals from commercially available and non-expensive sodium salts of aryl sulfinic acids was carried out in graphite powder macroelectrode, using an electrochemical cavity cell. The formation of the arylsulfinyl radical was evidenced by the oxidation potential determined by voltammetry experiments. The lower theoretical charge consumption can be explained by simultaneous 2e$^-$/1e$^-$ equivalent mechanisms. Further reactions with different amines gave the corresponding sulphonamides in good to moderate yields, depending on the structure of the amine used. The methodology is simple, fast, efficient, and it could be applied for the synthesis of more complex sulfonamides.

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