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ARTICLE

An Approach to C-N Activation: Coupling of Arenesulfonyl Hydrazides and Arenesulfonyl Chlorides with *tert*-Amines via a Metal-, Oxidant- and Halogen-free Anodic Oxidation

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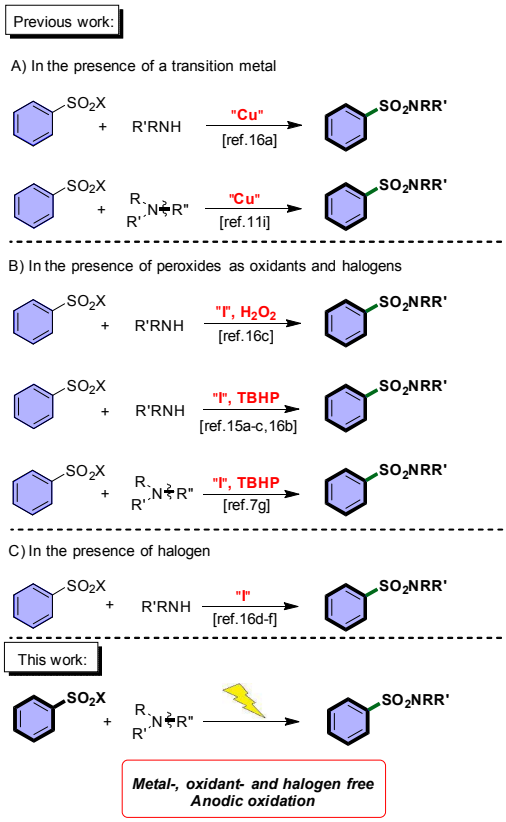
tert-Amines were harnessed to meet arenesulfonyl hydrazides and arenesulfonyl chlorides via a *metal-*, *oxidant-* and *halogen free* electrochemical oxidative coupling in an *undivided cell* at rt. This environmentally benign approach afforded a wide spectrum of sulfonamides in satisfactory yields using cheap and renewable Pencil Graphite Electrodes (PGEs).

Introduction

The past few years have witnessed revolutionary changes in the way various motifs can be forged. One of these changes is the utility of *tert*-amines in place of their secondary or primary counterparts. This replacement is mainly due to high reactivity of primary or secondary amines which can be destructive for some amine-sensitive functional groups. *tert*-Amines, in contrast, are less nucleophilic thus if used under specific conditions can be easily directed to a target functional group without any unwanted side-reaction. They are also easily available and widespread in nature. Hence, lately *tert*-amines have been vastly used as a surrogate for primary or secondary amines to donate an amino group via a C-N cleavage. To highlight the value of C-N bond activation, it suffices to say that oxidative dealkylation of *tert*-amines are common in chemistry,[1] biochemistry [2] and above all in our body for DNA repairs which is catalyzed by enzymes.[3] Regarding the importance of such reactions, growing interest has been drawn in this realm, either via precious metals such as Pd,[4a-f] Ni [4g] and Ag[4h] or through cost-effective copper [5] and iron metals.[6] Moreover, most recently some metal-free reactions [7] have emerged which can promote these reactions with the aid of peroxides as oxidants.[7c-g] Having said that, so far no report on C-N activation of *tert*-amines under electrolysis has been disclosed. Instead, only Cα-H activation has taken place and C-N activation always failed to win this competition.[8]

It is noteworthy that lately utilization of electrochemistry in promotion of synthetic reactions has been an attractive area of research in the direction of sustainable and green chemistry guidelines.[9]



Scheme 1. Methods for the synthesis of sulfonamides

Regarding the substantial features of sulfonamides,[10] to date significant efforts have been devoted for the synthesis of these compounds (Scheme 1).[11] Conventional synthesis of sulfonamides includes the reaction between arenesulfonyl chlorides and primary or secondary amines.[12] However, as mentioned earlier, since primary or secondary amines are

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among reactive bases/nucleophiles, they can get involved in side reactions by attacking other vulnerable parts of the molecule thus lowering the yield of the favourable products. Therefore, to control their tendency a multi-step superfluous protection/deprotection seems to be essential giving rise to a drop of overall efficiency. Another way to synthesize these entities is transition metal-catalyzed *N*-substitution of sulfonamides[13] or sulfonyl azides[11f] in which both a toxic metal as a promoter and a pre-functionalized reagent such as arylboronic acids or aryl halides are needed. Furthermore, in these approaches mostly bases and/or ligands are requisite to drive the reaction. A distinctive method to prepare sulfonamide was executed in a Cu-catalyzed reaction of sulfur dioxide and aryl triazenes.[11g] Despite its novelty, it imposed some safety problems resulted from the use of toxic, corrosive SO_2 and explosive parent diazonium salts together with the handling issues of working with a gaseous regent. In other attempts, DABSO was supplanted SO_2 in preparation of sulfonamides. Although, these strategies circumvented the use of SO_2, they usually offered a multi-step synthesis to the target molecule. The first examples in this field was released by Willis [14a] and Waldmann [14b] who utilized organolithium, organozinc or Grignard reagents which are highly sensitive to even traces of moisture and might ignite. Therefore, their reactions must be conducted under extremely anhydrous conditions and with necessary precautions for keeping the reaction at a very low temperature. Additionally, these reagents are destroyed upon exposure to any protic sources thus posing restrictions on extension of substrate scope and the variety of functional groups used. Afterwards, another two-step reaction using DABSO was emerged in which O-benzoyl hydroxylamines as pre-prepared starting materials were needed.[11a] Besides, in this report both steps required transition metals to proceed. The last method in this line was disclosed by Han *et al.* who succeeded in realization of sulfonamides in a single-step with the aid of aryl hydrazines, amines and DABSO,[11b] yet it still needed copper and a free NH containing amine to yield the desired products. Lately, due to the simplicity and eco-compatibility, direct S-N bond formations between a latent sulfonyl donor and an amine group for the synthesis of these privileged motifs have prevailed. In this respect, numerous reports have been disclosed in which arenesulfonyl hydrazides,[15] sodium arenesulfinates,[16] and thiophenols[17] have been frequently used as sulfonyl sources. Of the impediments to the prevalence of these methods as well as the utility of primary and secondary amines is the necessity to exploit a halogen source and a stoichiometric amount of an oxidant (mostly highly explosive TBHP) neither of which is favoured from environmental standpoint due to the toxicity and corrosion. Song *et al.* and Yuan *et al.* in separate reports released an oxidant-free sulfonamidation in water by coupling primary/secondary amines with sodium arenesulfinates albeit using a halogen source.[16e,f] In this context, Zeng *et al.* disclosed the only report in this area via an electrochemical approach.[16g] Despite all virtues associated with this work, it suffers from the same drawbacks which can limit its usage and disfavour it from green point of view. As opposed to their peers, *tert*-amines are stable enough to survive under many reaction conditions, easily available as well as widely found in natural products. Thus, the synthesis of sulfonamides via *tert*-amines could provide desired late-stage synthetic strategy. Sun and Yuan developed new approaches patterned on this idea and utilized *tert*-amines in place of their counterparts in reaction with arenesulfonyl chlorides [11i] and sodium arenesulfinates.[7g] Although these reactions were major breakthroughs in this field, use of either Cu_2O as a metal source or I_2/TBHP seems to be inevitable. As mentioned earlier, utility of peroxides as oxidants which are categorized as hazardous substances are not consistent with the principles of Green Chemistry and causes difficulties such as over-oxidation of sensitive functional groups together with the dangerous or difficult scale-up. In spite of all endeavours in this area, there is still a great demand for a green manner.

Given the fact that thus far no report has been published concerning the reaction of *tert*-amines with arenesulfonyl hydrazides, we contrived to innovate a protocol to realize sulfonamidation through the reaction of arenesulfonyl hydrazides with *tert*-amines. Generally speaking, arenesulfonyl hydrazides are used in preference to other sources of sulfonyl group, since they liberate N_2 as the mere waste of the reaction, thereby the need for tedious purifications is obviated. It is notable that even the chemical reaction of arenesulfonyl hydrazides with *tert*-amines had not been reported previously.

Here, we introduce a cutting-edge electrochemical strategy through which activation of both arenesulfonyl hydrazides and *tert*-amines takes place under anodic oxidation. To the best of our knowledge, thus far neither arenesulfonyl hydrazides nor *tert*-amines have been activated in a *halogen-free* reaction and this is the first report in this area which enables one to harmonize two differently reactive components under benign reaction conditions. Obviously, discarding halogens as the waste of the reaction is a great challenge faced by chemists today. Here for the first time, we managed to conduct a novel reaction which is doable in the absence of any halogens, metals and oxidants hence the major concern for purification process would be eradicated. Formation of a non-toxic by-product is the other privilege which is quite satisfactory. The reaction then was extended to arenesulfonyl chlorides. The current procedure benefited from an added advantage over and above the aforementioned which makes it more appealing and this is the use of water as solvent. This results in a reaction which is totally in accordance with instructions issued by green chemistry.

Results and Discussion

To evaluate the formation of S-N bond in electrochemical conditions we chose the reaction of benzenesulfonyl hydrazide **1** and triethylamine **2** (Table 1). The reaction was performed in an undivided cell equipped with a graphite anode and a platinum cathode and 0.5 M NaI as the electrolyte in ACN at rt. (applied current: 10 mA, current density: 6 mA/cm^2, charge consumed after 9 h: 6.7 F/mol) (Table 1). Pleasingly, the

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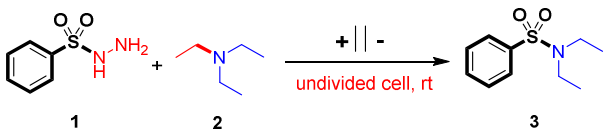
reaction led to the desired product in 33% yield (entry 1). It was found that changing current density into 9 mA/cm^2 or 12 mA/cm^2 instead of 6 mA/cm^2 marginally reduced the yield (entries 2-3).

Various solvents were also tested and a 1:1 mixture of water/ACN was found to be superior to other alternatives (entries 4-7).

Table 1. Screening the reaction conditions [a]



1 2 3

entry	electrolyte (mmol)	anode-cathode	solvent (2.5 mL)	current density (mA/cm^2)	yield (%)
1	NaI (0.25)	C-Pt	ACN	6	33
2[b]	NaI (0.25)	C-Pt	ACN	9	32
3[c]	NaI (0.25)	C-Pt	ACN	12	30
4	NaI (0.25)	C-Pt	DMSO	6	0
5	NaI (0.25)	C-Pt	MeOH	6	0
6	NaI (0.25)	C-Pt	THF	6	17
7	NaI (0.25)	C-Pt	H_2O/ACN (1:1)	6	38
8	NH_4Br (0.25)	C-Pt	H_2O/ACN (1:1)	6	47
9	NH_4Cl (0.25)	C-Pt	H_2O/ACN (1:1)	6	40
10	Na_2SO_4 (0.25)	C-Pt	H_2O/ACN (1:1)	6	54
11	Na_2SO_3 (0.25)	C-Pt	H_2O/ACN (1:1)	6	52
12	Na_2SO_4 (0.5)	C-Pt	H_2O/ACN (1:1)	6	33
13	Na_2SO_4 (0.05)	C-Pt	H_2O/ACN (1:1)	6	46
14[d]	Na_2SO_4 (0.25)	C-Pt	H_2O/ACN (1:1)	6	30
15[e]	Na_2SO_4 (0.25)	C-Pt	H_2O/ACN (1:1)	6	50
16	**Na_2SO_4 (0.25)**	**C-C**	**H_2O/ACN (1:1)**	**6**	**60**
17	Na_2SO_4 (0.25)	Pt-Pt	H_2O/ACN (1:1)	6	0
18[f]	Na_2SO_4 (0.25)	C-Pt	H_2O/ACN (1:1)	6	0
19[g]	Na_2SO_4 (0.25)	C-Pt	H_2O/ACN (1:1)	6	30

[a] Reaction conditions: Benzenesulfonyl hydrazide **1** (0.5 mmol), triethylamine **2** (2 equiv.), rt, in an undivided cell, 9 h. Unless otherwise noted. In cases of entries 1-6, 2 equiv. of water was added. [b] 6 h. [c] 4.5 h. [d] Performed at 60 °C. [e] Reaction in an ice bath. [f] In the presence of 0.5 mL AcOH. [g] In the presence of 0.5 mmol K_2CO_3 as a base.

To our delight, among various electrolytes tested, non-halogenated, cheap and nonhazardous Na_2SO_4 gave the best results (entries 8-11).

Then, we tried to find the optimal concentration of electrolyte under which the reaction is carried out. After some trials we found out that any deviation from the optimal concentration, either an increase to 1 M or a decrease to 0.1 M, had a detrimental effect on the yield (entries 12-13). Changing the temperature did not improve the yield (entries 14-15). By use of pencil graphite both in cathode and anode, a good 60% yield was attained (entry 16). It is also worth mentioning that in a Pt-Pt cell the reaction was completely suppressed (entry 17). No satisfactory results were found when acids or bases were added to the reaction medium (entries 18-19).

With the optimized conditions in hand, the diversity of electrochemical reaction was investigated by using a variety of arenesulfonyl hydrazides and *tert*-amines (Table 2). Reaction of simple or alkyl substituted arenesulfonyl hydrazides with triethylamine resulted in the related sulfonamides in moderate yields (**3a-d**). The reaction proceeded well in the presence of a halo group at the *ortho*-position (**3e**). The yield increased by the electron-donating methoxy group (**3f**). Then, the reaction of various arenesulfonyl hydrazides was evaluated with *N,N*-dimethylbenzylamine and the same results were obtained (**3g-l**). In all cases using this substrate no demethylation was observed but rather debenzylation of amine took place. Formation of debenzylated products instead of demethylated ones is due to more stability of the radical formed in benzylic position which makes it more preferential to the other positions. Therefore, the methylene of benzyl group is cleaved more selectively in the presence of a methyl group. Electron-withdrawing (Br, Cl) groups had little effect on the yield (**3i-k**). Bear in mind that the presence of a halo-substituent within the framework of a molecule renders it highly valued and prepares the ground for installation of other motifs on the structure. The reaction of linear trimethylamine with naphthyl- and *ortho*-bromobenzenesulfonyl hydrazide was also proceeded to the corresponding sulfonamides in good yields (**3m-n**). Also when *N,N*-dimethylcyclohexyl amine was used, the reaction led to the corresponding sulfonamides in satisfactory yields (**3o-p**). For aromatic *tert*-amines, the reaction didn't proceed to the desired product (**3q**). The reason may be related to the results reported by Compton *et al.* and Seo *et al*. that observed different types of electrochemical dimerization in the case of aromatic *tert*-amines.[18]

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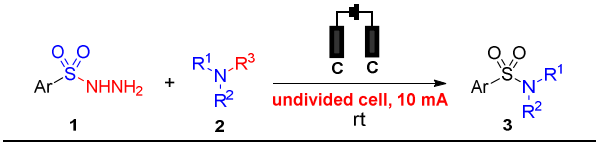
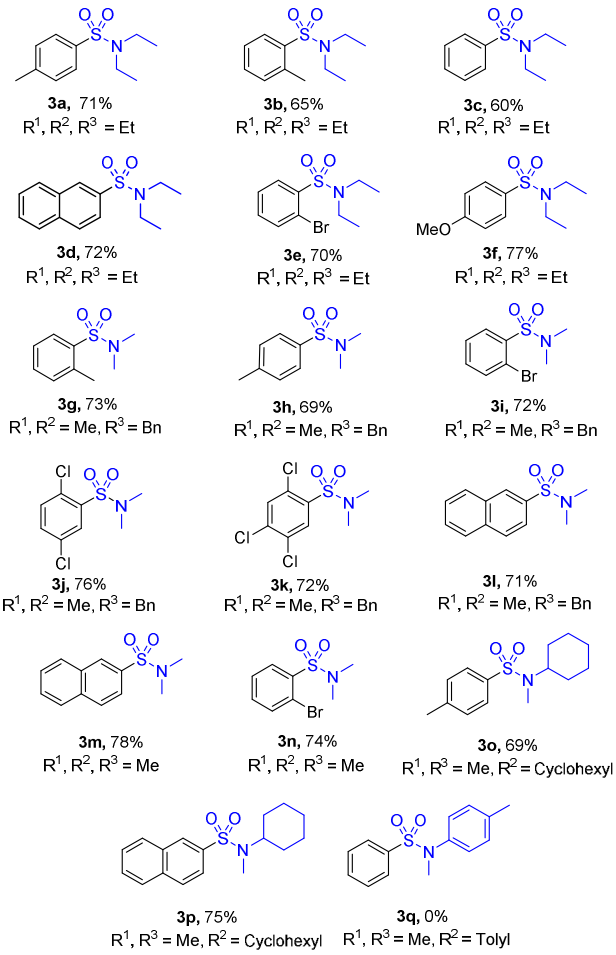
Table 2. Scope of the reaction[a]

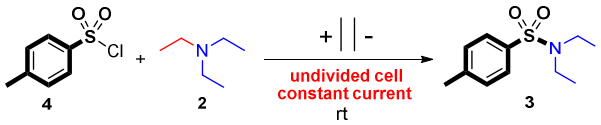




[a] Reaction conditions: Arenesulfonyl hydrazide (0.5 mmol), *tert*-amine (2 equiv), Na_2SO_4 (0.5 M), H_2O/ACN (1:1, 2.5 mL), rt, current density of 6 mA/cm^2 in an undivided cell, 9 h (6.7 F/mol).

These results prompted us to extend this reaction to arenesulfonyl chlorides as another source of sulfonyl group. With this aim, the reaction of *p*-toluenesulfonyl chloride and triethylamine was conducted under the optimized conditions obtained for arenesulfonyl hydrazides (Table 3). Pleasingly, the reaction resulted in **3a** in 69% yield (entry 1). To optimization of the reaction conditions, we screened different solvents and electrodes in the mentioned reaction. In the presence of ACN and MeOH no good results found (entries 2-3). Screening showed that using water as solvent slightly enhanced the yield (entry 4). Then the reaction was repeated in the presence of Pt cathode and the yield dropped sharply (entry 5). Due to the encumbrance of organic solvent wastes removal which are produced during various synthetic procedures, and given the fact that disposal of toxic solvents is a thorny issue in terms of Green Chemistry, search for organic reactions in water lately prevailed. In view of the demands in this realm, our achievement in electrochemical sulfonamidation of *tert*-amines without oxidant, metal, halogen and in water could be an important advance in organic synthesis.

Table 3. Effect of reaction parameters in direct sulfonamidation of *tert*-amines by arenesulfonyl chlorides[a]



entry	conditions	yield %
1	H_2O/ACN (1:1), Na_2SO_4 (0.5M), 10 mA	69
2	entry 1 but in ACN as solvent	58
3	entry 1 but in THF as solvent	25
4	entry 1 but in H_2O as solvent	78
5	entry 1 but Pt as cathode	54
6	entry 1 but 15 mA, 2.1 h	75
7	entry 1 but 20 mA, 1.6 h	73

Reaction conditions: Graphite anode (diameter: 2 mm), graphite cathode (diameter: 2 mm), **4** (0.5 mmol), **2** (2 equiv.), solvent (2.5 mL), 3.2 h (2.4 F/mol). In cases of entries 2-3, 2 equiv. of water was added.

To explore the scope of this reaction, a variety of arenesulfonyl chlorides were tested under optimal condition (Table 4). First, we reacted miscellaneous arenesulfonyl chlorides with triethylamine as a symmetrical amine. *p*-Toluenesulfonyl chloride readily gave sulfonamidation product virtually in 78% yield (3a). When *o*-toluenesulfonyl chloride and benzenesulfonyl chloride were used the yield dropped slightly (3b-c). In contrast, 2-naphthalenesulfonyl chloride smoothly underwent the reaction furnishing the corresponding product in 79% isolated yield (3d). Bromo substituent at C2, despite imposing a considerable steric hindrance did not exert any deleterious effect and led to the desirable product (3e). Also, when the electron-donating methoxy substituent was incorporated on the ring, a surge in the yield was observed (3f). To broaden the generality of this reaction, the ongoing protocol was extended to several amines as well. For this purpose, amines bearing benzyl (3g-l), methyl (m-n), cyclohexyl (3o-p) and *p*-tolyl group (3q) were examined. Except for *p*-tolyl, which didn't give the product, all of them resulted in comparable to better yields to those gained from arenesulfonyl hydrazides.

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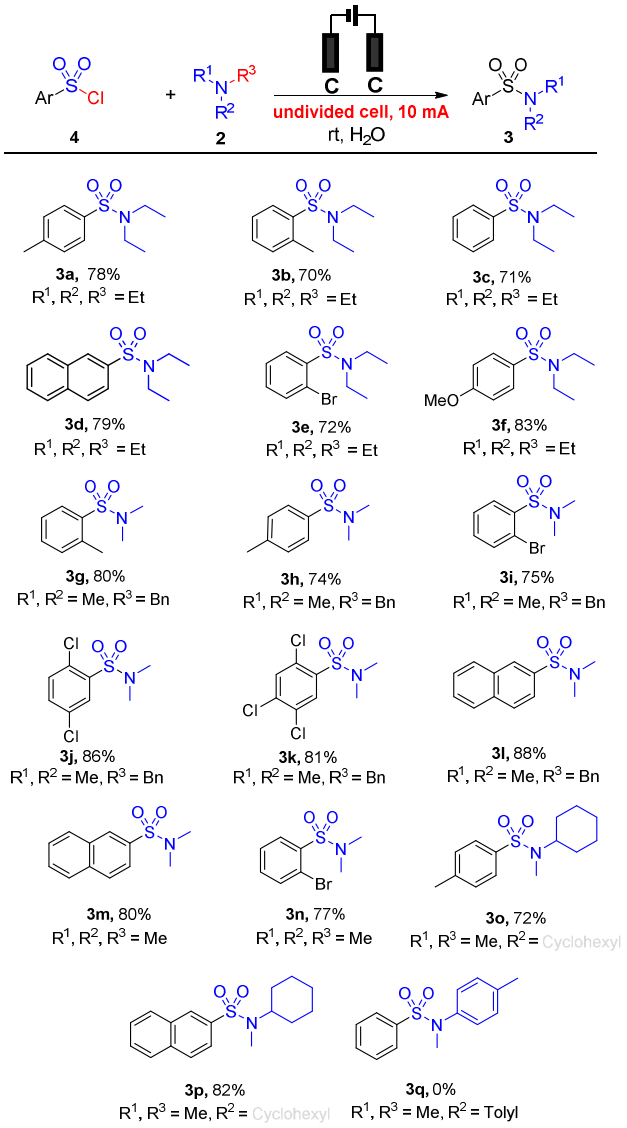
Table 4. Scope of the reaction of *tert*-amines and arenesulfonyl chlorides in water[a]



[a] Reaction conditions: Arenesulfonyl chloride (0.5 mmol), *tert*-amine (2 equiv.), Na_2SO_4 (0.5 M), H_2O (2.5 mL), rt, current density of ~ 6 mA/cm^2 in an undivided cell, 3.2 h (2.4 F/mol).

In continuation, cyclic voltammetry (CV) experiments were performed to analyse the redox potential of the reaction partners and their electroactivity to cast light on mechanistic views.

Triethylamine was electrolysed in 0.5 M Na_2SO_4 in (1:1) H_2O/ACN. As shown in Figure 1 the wave at about +1.0 V (*vs* Ag/AgCl) is related to the oxidation potential of triethylamine under standard conditions.[19] Also, the CV of benzenesulfonyl hydrazide was recorded in 0.5 M Na_2SO_4 in H_2O/ACN (1:1) (Figure 2) to study its redox potential. Analysis within -2 to 2 V potential range (*vs* Ag/AgCl) showed one oxidation wave at 1.5 V. Because the applied voltage of 2.5 V was used in the reaction, the analyses proved that the oxidation of both partners was possible under the reaction conditions.

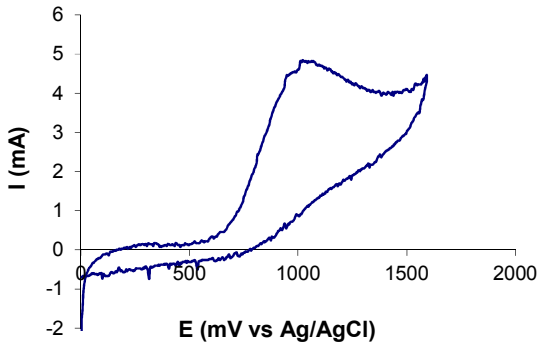


Figure 1. Cyclic voltammogram of 1 mmol triethylamine in the presence of Na_2SO_4 (0.5 M) in H_2O/ACN (1:1, 2.5 mL) recorded at a glassy carbon electrode, Sweep rate: 0.1 V/s, at room temperature.

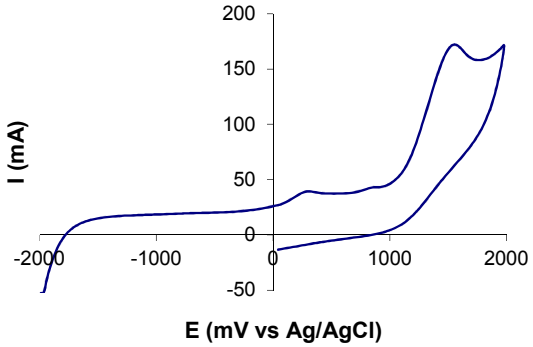


Figure 2. Cyclic voltammogram of 0.5 mmol benzenesulfonyl hydarazide in the presence of Na_2SO_4 (0.5 M) in H_2O/ACN (1:1, 2.5 mL) recorded at a glassy carbon electrode, Sweep rate: 1 V/s, at room temperature.

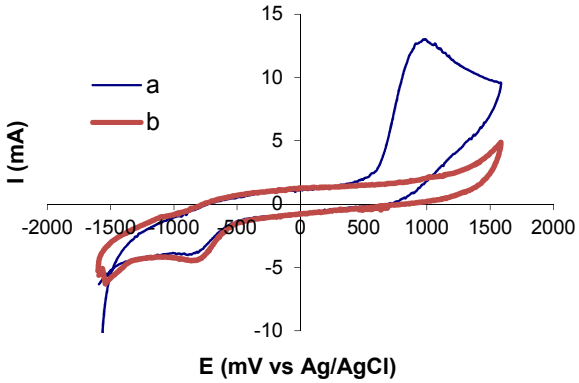


Figure 3. Cyclic voltammogram of (a) reaction mixture of benzenesulfonyl hydrazide and triethylamine at the end of reaction monitored by TLC and (b) 0.5 mmol of purified sulfonamide **3c** in H_2O/ACN (1:1, 2.5 mL) in the presence of Na_2SO_4 (0.5 M) recorded at a glassy carbon electrode, Sweep rate: 0.1 V/s, at room temperature.

Cyclic voltammogram of reaction mixture under the optimized reaction conditions (benzenesulfonyl hydrazide and

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triethylamine in the presence of Na_2SO_4 (0.5 M) in H_2O/ACN (1:1) at the end of reaction monitored by TLC at a glassy carbon electrode was recorded (Figure 3 trace a). In addition, the CV of purified sulfonamide **3c** (0.5 mmol) in H_2O/ACN (1:1, 2.5 mL) was recorded at the same potential window for comparison (Figure 3 trace b). The reduction wave observed in both CVs of **3c** and the reaction mixture at below -0.7 V (*vs* Ag/AgCl) is related to water electrolysis into H_2 and OH^- ion.[20] Since an excess of triethylamine was used in the reaction, the residue remained intact in the mixture at the end of reaction which was proved by the presence of its irreversible oxidation wave at around 1.0 V in the CV. As expected from the literature [21] and clear from the CV, sulfonamide **3c** is stable in the potential window used.

According to the literature and experiments performed, a graph is presented in Figure 4 to better clarify the issue which summarized the half-peak potentials of some reagents involved in this work.

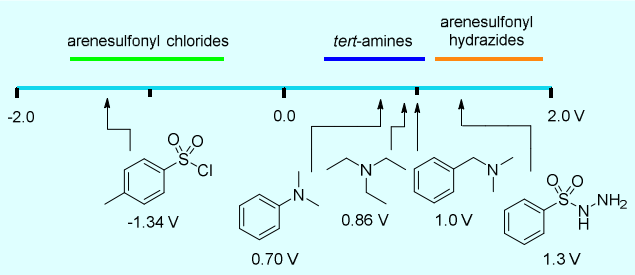

Figure 4. Electrochemical series of some of reaction partners; half-peak potentials ($E_{p/2}$) are reported *vs* Ag/AgCl

Mechanistic study:

To determine the mechanism of the reaction, benzenesulfonyl hydrazide and triethylamine were electrolysed, separately. After electrolysis of benzenesulfonyl hydrazide alone for 9 h, triethylamine was added and stirred for further 2 h. Afterwards, no product was detected.

In another experiment, triethylamine was electrolysed for 9 h then benzenesulfonyl hydrazide was added to the resulted solution and the mixture allowed to stir for further 2 h. Analysis showed the benzenesulfonyl hydrazide remain intact and no product was detected. These two experiments showed both benzenesulfonyl hydrazide and triethylamine should be electroactivated to drive the reaction.

Also, the electrolysis of *p*-toluenesulfonyl chloride and triethylamine was carried out. After electrolysis of *p*-toluenesulfonyl chloride alone for 3.2 h, triethylamine was added and stirred for 2 h. Finally, the mixture was analysed in which proved *p*-toluenesulfonyl chloride remain intact.

In another experiment, when triethylamine was electrolysed for 3.2 h, *p*-toluenesulfonyl chloride was added to the solution and the mixture was stirred for further 2 h, the corresponding sulfonamide **3a** was obtained with a yield of 72%. These results showed that only triethylamine was electroactive substrate in this reaction.

On the basis of experiments, finally, a plausible mechanism for the aforementioned transformation is proposed in Figure 5. It is assumed that in the anode, the electrochemical C-N activation proceeds via the same mechanism as does the chemical transition metal-mediated approach.[4d,5c,5g-h,6b] After oxidation of C-H bond adjacent to N, the produced α-amino radical converts to iminium ion intermediate. In the cathode, water reduced to hydrogen and hydroxide ion. The generated hydroxide ion hydrolysed the iminium ion into hemi-aminal followed by the elimination of an aldehyde, results in the production of a secondary amine. Extrusion of aldehyde is confirmed by an experiment using *N,N*-dimethylbenzylamine as the starting material. In the foregoing reaction, benzaldehyde was separated as a by-product from the reaction mixture. In an independent way, inspired by Wei's [22] and Jiang's [23] work, it seems that oxidation of arenesulfonyl hydrazide to the highly reactive arenesulfonyl cation is viable through another anodic oxidation process. In the end, this arenesulfonyl cation reacts with secondary amine and generates the desired sulfonamide.

According results of mechanistic study, it was proposed that in the case of reaction of *tert*-amine and arenesulfonyl chlorides the same anodic oxidation of *tert*-amine take place but here arenesulfonyl chlorides is not electroactive. After production of secondary amine, it reacts with arenesulfonyl chlorides to produce the desired sulfonamide product.

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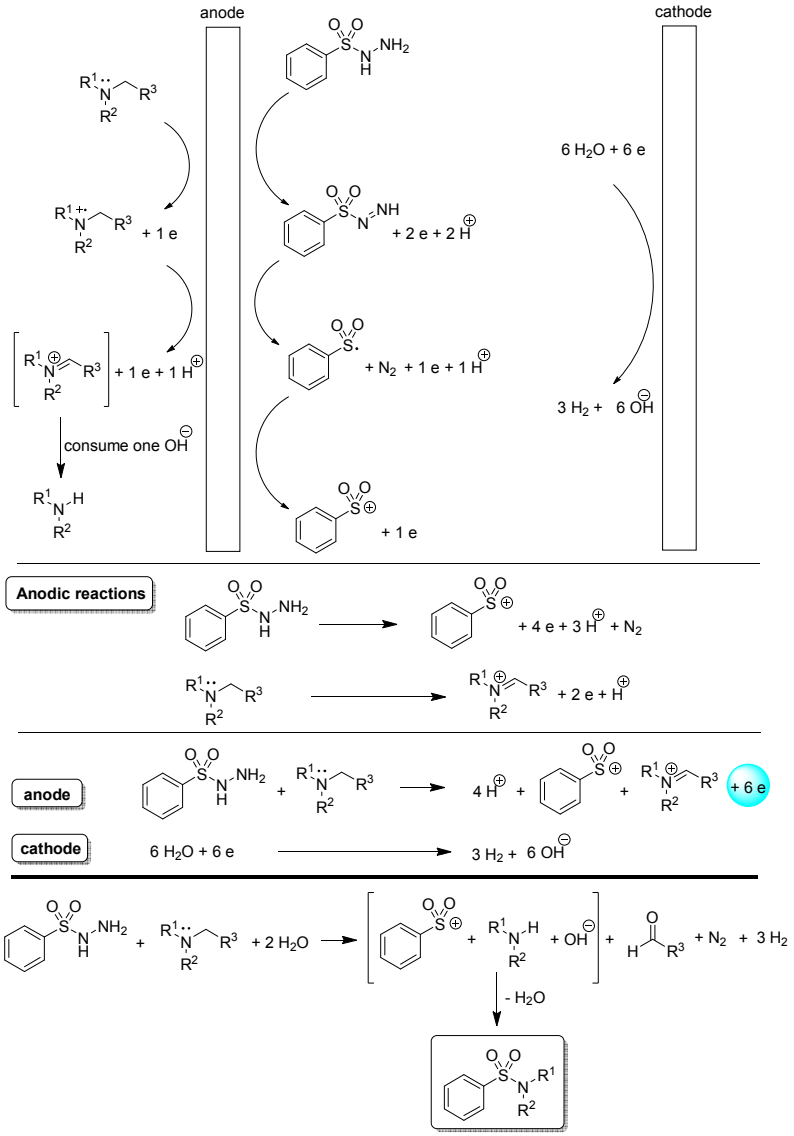

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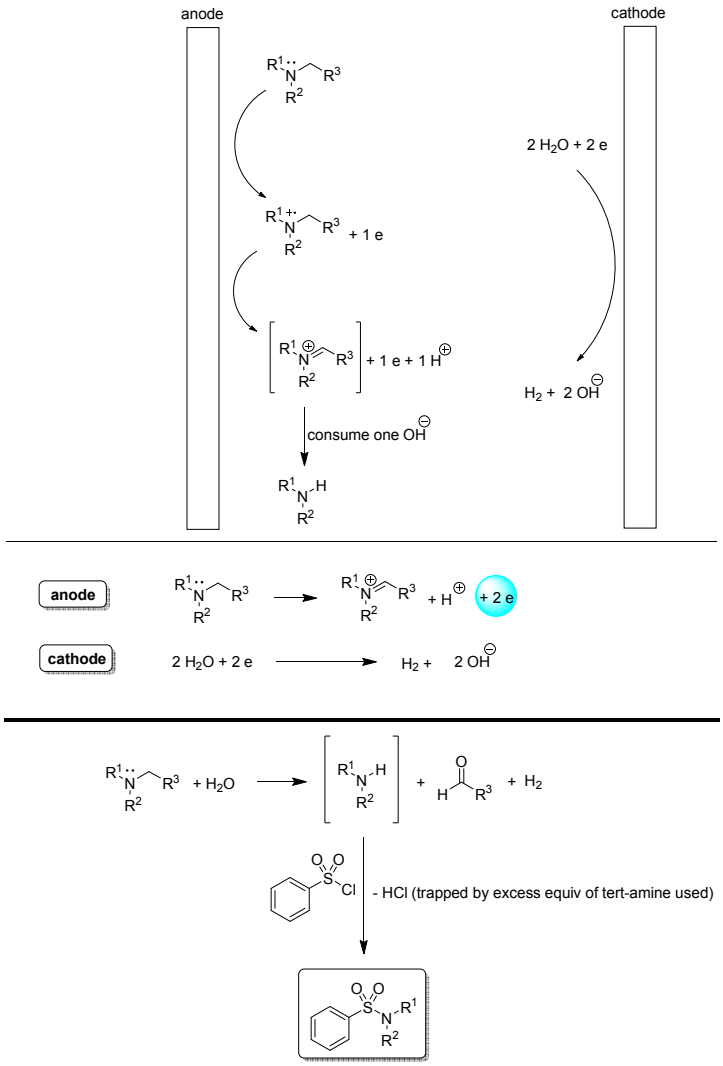
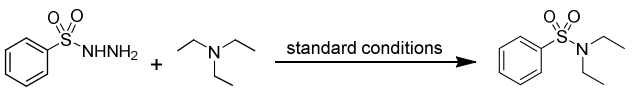


Figure 5. Plausible mechanism for the direct sulfonamidation of *tert*-amines

Also, to confirm the radicalic pathway proposed, an experiment designed in which the reaction of benzenesulfonyl hydrazide with triethylamine performed under optimized conditions and in the presence of 1 equiv. BHT as a radical scavenger. The reaction was completely quenched under this condition. Experiment confirmed the radicalic pathway proposed.

To demonstrate scalability of the invented electrochemical anodic coupling as an important privilege of the process, the reaction of benzenesulfonyl hydrazide with triethylamine was tested in 25 mmol, 30 mmol and 40 mmol scales. As shown in Figure 6, reactions proceeded with no appreciable loss in product yield in comparison with the same reaction conducted on 0.5 mmol scale.



25 mmol	3.4 g (65%)
30 mmol	4.3 g (67%)
40 mmol	5.3 g (62%)

Figure 6. Gram-scale synthesis of sulfonamide **3c**

Because the graphite pencil electrodes may be irreproducible with other country pencils perhaps due to the possible impurities, the 2B pencil electrode used was washed with an aqueous solution of 10% sulfuric acid (2M) to remove all probable present halogenated fillers and then the reaction of benzenesulfonyl hydrazide and triethylamine was repeated with the washed electrodes. The same yield of **3c** was

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obtained. The result showed that it is the pure graphites which act as electrodes not the impurities. In an independent experiment, graphite electrodes were provided from four different 2B pencils to examine reproducibility of the reaction. To this end, the reaction of benzenesulfonyl hydrazide and triethylamine was tested using these electrodes in a 0.5 mmol scale. Analyses proved that all four reactions led to the desired sulfonamide **3c** in the same or comparable yields as the first one. Experiments confirmed the invented method is thoroughly reproducible in other laboratories.

Conclusion

In summary, we have developed the first example of anodic sulfonamidation of *tert*-amines. Electrochemical C-N activation of *tert*-amines finely coupled with a novel electrochemical activation of arenesulfonyl hydrazides and arenesulfonyl chlorides resulted in the synthesis of sulfonamides. This reaction proceeded via cheap pencil graphite electrodes and in the absence of any transition metal or oxidant thus renders it outstandingly sustainable. In contrast to the existing methods which entirely hinges on the use of either quaternary ammonium halides or halogen-containing solvents/electrolytes, this protocol works without intervention of any halide ions. The explained procedure owing to the exploitation of an undivided cell, is satisfactorily facile, thus meeting the demands of contemporary syntheses and suitable to be used as an alternative to the prior methods. The reaction benefits from inexpensive and accessible substrates along with a non-halogenated, cheap and nonhazardous electrolyte. It merits mentioning that no elevated temperature is needed to promote this C-N activation.

Experimental section

Typical procedure for the synthesis of arenesulfonyl hydrazides [24]

Into a 25 mL round-bottomed flask, are added 10 mmol of arenesulfonyl chloride and 3.5 mL of tetrahydrofuran. The mixture is cooled to 10 °C and 1.5 mL hydrazine hydrated (85% hydrazine hydrate, 20 mmol) is added. Stirring is continued for further 15 minutes and then the reaction mixture is transferred to a separatory funnel. The organic layer is filtered and washed with 2.5 mL tetrahydrofuran. The colorless filtrates are stirred during the drop-wise addition of 12 mL of distilled water. Arenenesulfonyl hydrazide separates as fluffy crystalline needles. The product is washed several times with distilled water, and air-dried.

Electrochemical synthesis of sulfonamides from arenesulfonyl hydrazides

An undivided cell was equipped with two pencil graphite electrodes (2.0 mm, 2B) and connected with a DC power supply (Figure S1). A mixture of arenesulfonyl hydrazide (0.5 mmol), *tert*-amine (1 mmol), and Na_2SO_4 (1.25 mmol, 0.5 M) in water/ACN (1:1, 2.5 mL) was added to the cell and stirred at room temperature for 9 h. The mixture was electrolyzed under constant current conditions (6 mA/cm^2) at room temperature while stirring. The electrolysis was terminated when 6.7 F/mol of charge had been consumed. After the electrolysis, the solvent was removed under reduced pressure. After washing the mixture with 10% brine solution and extraction with ethyl acetate, the organic layer was dried over sodium sulfate and evaporated under reduced pressure. The organic residue was purified by a silica loaded column chromatography with 1:20 ethyl acetate in hexane as eluent.

Electrochemical synthesis of sulfonamides from arenesulfonyl chlorides

An undivided cell was equipped with two pencil graphite electrodes (2.0 mm, 2B) and connected with a DC power supply (Figure S1). A mixture of arenesulfonyl chloride (0.5 mmol), *tert*-amine (1 mmol), and Na_2SO_4 (1.25 mmol, 0.5 M) in water (2.5 mL) was added to the cell and stirred at room temperature for 3.2 h. The mixture was electrolysed under constant current conditions (6 mA/cm^2) at room temperature while stirring. The electrolysis was terminated when 2.4 F/mol of charge had been consumed. After the electrolysis, the solvent was removed under reduced pressure. After washing the mixture with 10% brine solution and extraction with ethyl acetate, the organic layer was dried over sodium sulfate and evaporated under reduced pressure. The organic residue was purified by a silica loaded column chromatography with 1:20 ethyl acetate in hexane as eluent.

Conflicts of interest

There are no conflicts to declare.

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