Organic & Biomolecular Chemistry

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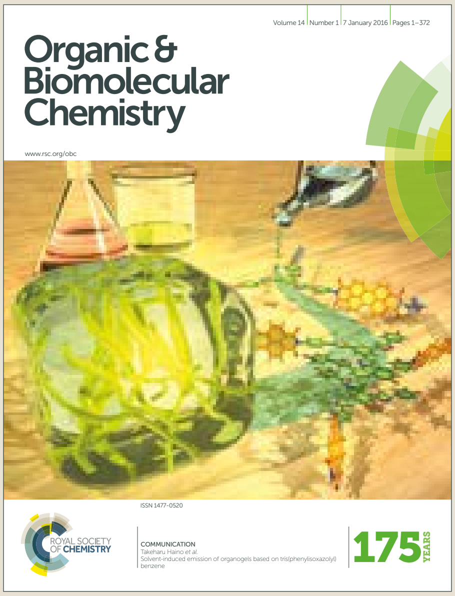

View Article Online
DOI: 10.1039/C8OB03162B

Journal Name

ARTICLE

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Electrochemically induced oxidative S-O coupling: synthesis of sulfonates from sulfonyl hydrazides and *N*-hydroxyimides or *N*-hydroxybenzotriazoles

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The process of oxidative S-O coupling under the action of electric current was developed. Aryl, hetaryl and alkyl sulfonyl hydrazides and *N*-hydroxy compounds (*N*-hydroxyimides and *N*-hydroxybenzotriazoles) are applied as starting reagents for the preparation of sulfonates. The reaction is carried out under constant current conditions in an experimentally convenient undivided electrochemical cell equipped with graphite anode and stainless steel cathode under high current density (60 mA/cm^2). NH_4Br in this process acts as a supporting electrolyte and participates in oxidation of starting compounds to form coupling product. Developed strategy represents a quite atom-efficient approach: one partner loses two nitrogen and three hydrogen atoms, while another one only one hydrogen atom. Cyclic voltammetry and control experiment allowed to propose possible reaction pathways: generated through anodic oxidation molecular bromine or its hypervalent derivatives oxidize starting compounds to form reactive species, which couple to form S-O bond.

Introduction

For the last decades transition metals-catalyzed cross-coupling has become one of the most powerful tools in organic synthesis for the construction of carbon-carbon and carbon-heteroatom bonds.[1] The rise of interest to the oxidative coupling methodology is a logical continuation of traditional cross-coupling strategy. It doesn't require prefunctionalization of starting compounds and as a result is more ecologically and economically attractive.[2] Besides, application of these transformations in modern organic chemistry often provides compounds inaccessible through other ways. Among numerous oxidative coupling processes the reactions with sulfur and oxygen components are less studied due to their easy overoxidation and fragmentation.[3] Only few examples of oxidative S-O coupling have already been reported.[4]

Among oxidants used for the oxidative coupling processes electric current is one of the cheapest, most available and environment-friendly.[5] Reactions of oxidative C-C,[6] C-N,[7] C-O,[8] C-S,[9] C-P,[10] C-Hal,[11] S-N[12] coupling have already been conducted electrochemically and this strategy is becoming more and more popular.[13] Organic electrosynthesis in undivided cell is the most promising, because in this case no special equipment is required.

Here we report electrochemically induced oxidative S-O coupling process. Sulfonyl hydrazides and *N*-hydroxy compounds, such as *N*-hydroxyimides and *N*-hydroxybenzotriazoles, are applied as starting reagents. As a result, various sulfonates are formed. Developed strategy represents a quite atom-efficient approach: one partner loses two nitrogen and three hydrogen atoms, while another partner loses only one hydrogen atom. Sulfonates analogous to synthesized structures are known as effective serine protease inhibitors. [14] They are also applied in organic synthesis:[15] combination of sulfonyl and *N*-hydroxy moieties in one molecule permits to activate both of these groups in order to obtain sulfonamides,[16] arylamides,[17] quinazolinedione and urea derivatives.[18] Similar structures with carboxylate fragment instead of sulfonate, are widely used as precursors of alkyl radicals under visible light irradiation.[19]

Results and discussion

Electrosynthesis of sulfonates **3aa**-**3ma**, **3ab**-**3af** from sulfonyl hydrazides **1a**-**1m** and *N*-hydroxy compounds **2a**-**2f** was conducted in H_2O-THF, H_2O-MeCN, MeOH-THF and MeOH solution with NH_4I, NH_4Br, NH_4Cl, KBr, NaBr and $NH_4Br/LiClO_4$ as supporting electrolytes (Scheme 1).

p-Toluenesulfonyl hydrazide **1a** and *N*-hydroxysuccinimide **2a** were chosen as starting reagents for the search of optimal conditions for the electrosynthesis of sulfonate **3aa**. The influence of nature of supporting electrolyte and its molar ratio with starting compounds, the amount of electricity passed, temperature and solvent nature on the yield of **3aa** was investigated (Table 1).

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Electronic Supplementary Information (ESI) available: general reaction procedures, characterization data, copies of NMR spectra. See DOI: 10.1039/x0xx00000x

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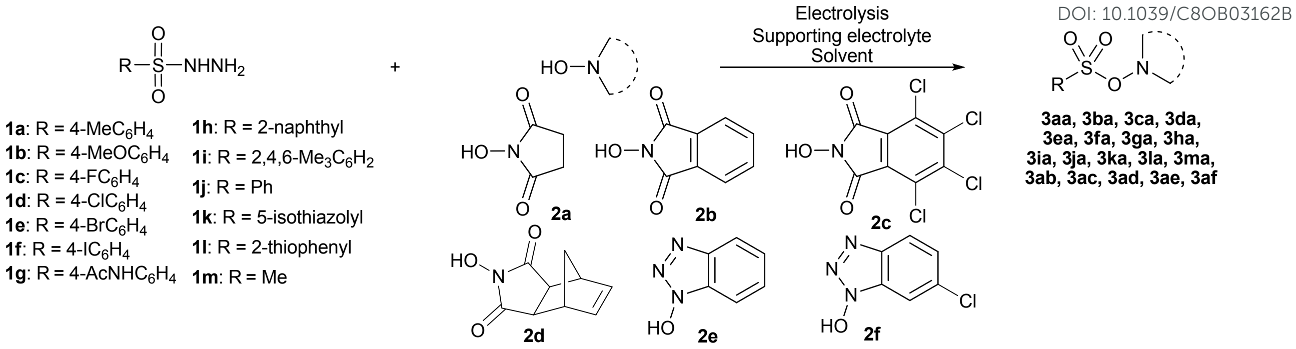
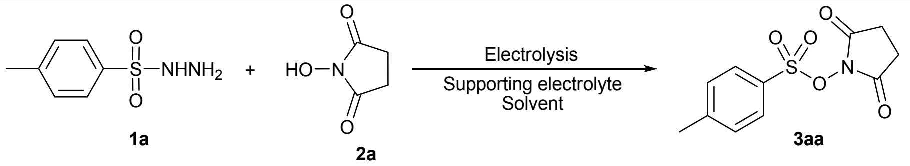


Scheme 1. Electrosynthesis of sulfonates **3aa**-**3ma**, **3ab**-**3af** from sulfonyl hydrazides **1a**-**1m** and *N*-hydroxy compounds **2a**-**2f** *via* oxidative S-O bond formation (in the codification of **3** the first letter index refers to the hydrazide **1** moiety, the second letter index to the *N*-hydroxy compound **2** moiety).

Electrode materials and solvents were chosen for their inertness under the action of electric current, solvents used should also possess high conductivity. Halogen-containing salts are widely applied as supporting electrolytes in organic electrosynthesis, because they can also act as redox mediators.[20] From a formal point of view, for the oxidation of nitrogen-containing part of sulfonyl hydrazides, including **1a**, four electrons are required. Thus, in our first experiments (Table 1, entries 1-5) theoretically calculated amount of electricity was passed. Reaction temperature and current density values were chosen to avoid too many side processes and at the same time carrying out the electrosynthesis fast enough.

The nature of supporting electrolyte was demonstrated to be quite important for the effectiveness of S-O coupling process (Table 1, entries 1-5). NH_4Br turned out to be the best one affording **3aa** in 68% yield (entry 2). After that effect of amount of electricity passed was investigated. Its increase to 7 F/mol led to slight rise in **3aa** yield (entry 6), passing of 10 F/mol resulted in target product **3aa** in 84% yield (entry 7). Further growth of electricity amount did not give better results (entry 8). Usage of less than 3 equivalents of NH_4Br or application of a mixture of $LiClO_4$ as an inert electrolyte and the catalytic amounts of NH_4Br caused a drop of coupling product yields (entries 9-11). As shown in entries 12-14, performance of electrosynthesis in the solvents different from H_2O-THF did not result in considerable changes in the reaction efficiency. Increase of reaction temperature to 40 °C provided target product **3aa** in 95% yield (entry 15), however further heating led to **3aa** only in 62% (entry 16). Thus on the basis of obtained experimental data the reaction best of all goes at 40 °C with 3 equivalents of NH_4Br as a supporting electrolyte, 10 F/mol electricity passed and H_2O-THF as a solvent.

Table 1. Optimization of the conditions for the electrochemically induced S-O coupling starting from *p*-toluenesulfonyl hydrazide **1a** and *N*-hydroxysuccinimide **2a**. [a]



Entry	Electrolyte (equiv)	Electricity passed, F/mol **1a**	Temperature, °C	Solvent	Yield **3aa,** % [b]
1	NH_4I (3)	4	25	H_2O-THF	45
2	NH_4Br (3)	4	25	H_2O-THF	68
3	NH_4Cl (3)	4	25	H_2O-THF	66
4	KBr (3)	4	25	H_2O-THF	31
5	NaBr (3)	4	25	H_2O-THF	26
6	NH_4Br (3)	7	25	H_2O-THF	75
7	NH_4Br (3)	10	25	H_2O-THF	84
8	NH_4Br (3)	15	25	H_2O-THF	78
9	NH_4Br (2)	10	25	H_2O-THF	56
10	NH_4Br (1)	10	25	H_2O-THF	60
11	NH_4Br (0.2)+$LiClO_4$ (3)	10	25	H_2O-THF	18
12	NH_4Br (3)	10	25	H_2O-MeCN	70
13	NH_4Br (3)	10	25	MeOH-THF	65
14	NH_4Br (3)	10	25	MeOH	57
15	NH_4Br (3)	10	40	H_2O-THF	95
16	NH_4Br (3)	10	60	H_2O-THF	62

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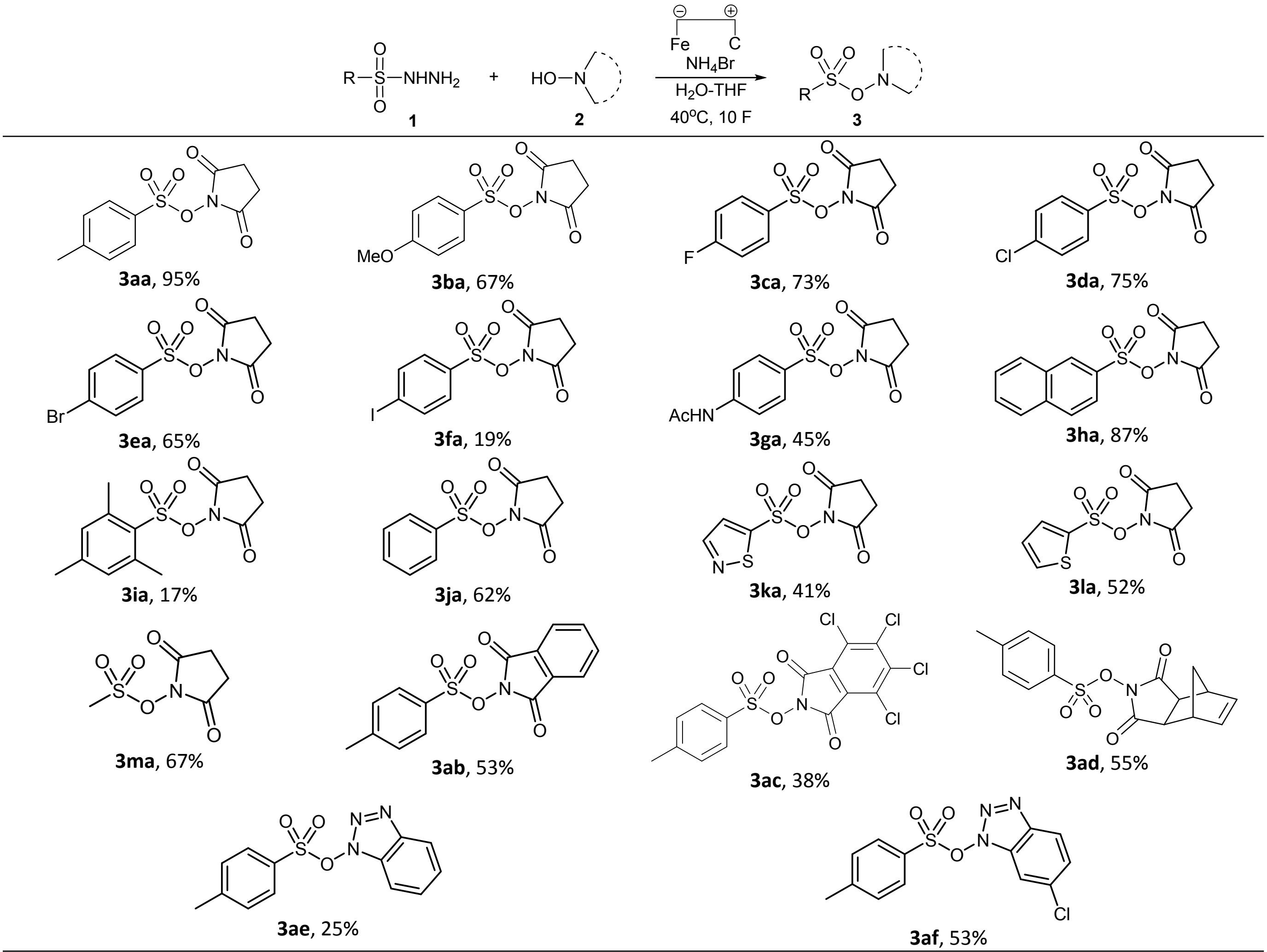
[a] **General procedure:** the solution of *p*-toluenesulfonyl hydrazide **1a** (1 mmol, 186 mg), *N*-hydroxysuccinimide **2a** (1 mmol, 115 mg) and supporting electrolyte (0.2-3 mmol, 20-435 mg) in 30 mL of H_2O-THF (1:1), H_2O-MeCN (1:1), MeOH-THF (1:1) or MeOH was electrolyzed under constant current conditions (60 mA / cm^2 at 25-60 °C) under magnetic stirring with the use of graphite anode and stainless steel cathode. [b] Isolated yield.

After that we tested optimal reaction conditions on a wide scope of sulfonyl hydrazides **1a**-**1m** and various *N*-hydroxy compounds **2a**-**2f** (Table 2). Arylsulfonyl hydrazides **1a**-**1i** entered the reaction of oxidative S-O coupling with *N*-hydroxysuccinimide **2a** affording target molecules with yields from moderate to high except **1f** and **1i** cases. Low yield in the case of **3fa** product can be explained by a number of side oxidative processes involving iodine or its derivatives.[21] Presumably, steric hindrance of mesitylenesulfonyl hydrazide **1i** was a key factor in low efficiency of **3ia** product formation. Reaction of nitro-substituted arylsulfonyl hydrazides resulted in inseparable mixture, probably, of nitro-group reduction products. Hetaryl substituted sulfonyl hydrazides **1k** and **1l** gave target products in moderate yields. Methylsulfonyl hydrazide **1m** provided coupling product **3ma** with high yield demonstrating the compatibility of this methodology with alkyl substrates too. Not only *N*-hydroxysuccinimide **2a** can serve as O-component in developed process: other *N*-hydroxyimides **2b**-**2d** and *N*-hydroxybenzotriazoles **2e** and **2f** led to the formation of coupling products with moderate yields.

Under optimized conditions we also applied sodium sulfinates **4a, 4d, 4j** in our approach. These compounds are widely used in various oxidative coupling processes for the formation of carbon-sulfur and sulfur-heteroatom bonds.[22] As shown in Scheme 2, sodium sulfinates **4a, 4d, 4j** react with *N*-hydroxysuccinimide **2a** less efficient than sulfonyl hydrazides **1**: target coupling products **3aa, 3da, 3ja** were formed in 29-40% yield.

Table 2. Scope of sulfonates **3aa**-**3ma**, **3ab**-**3af** synthesis from sulfonyl hydrazides **1a**-**1m** and *N*-hydroxy compounds **2a**-**2f** *via* electrochemically induced oxidative S-O coupling. [a, b]



3aa, 95% **3ba**, 67% **3ca**, 73% **3da**, 75%

3ea, 65% **3fa**, 19% **3ga**, 45% **3ha**, 87%

3ia, 17% **3ja**, 62% **3ka**, 41% **3la**, 52%

3ma, 67% **3ab**, 53% **3ac**, 38% **3ad**, 55%

3ae, 25% **3af**, 53%

[a] General procedure: the solution of sulfonyl hydrazide **1a**-**1m** (1 mmol), *N*-hydroxy compound **2a**-**2f** (1 mmol) and NH_4Br (3 mmol,) in 30 ml of H_2O-THF (1:1) was electrolyzed under constant current conditions (60 mA / cm^2 at 40 °C) under magnetic stirring with the use of graphite anode and stainless steel cathode. [b] Isolated yields are given.

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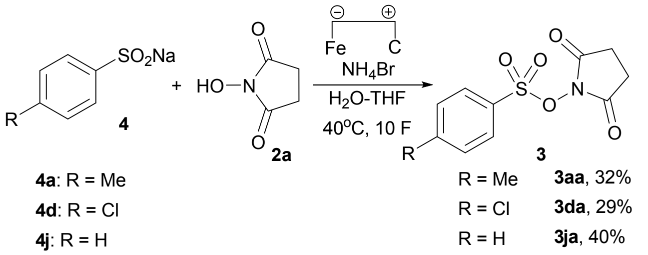
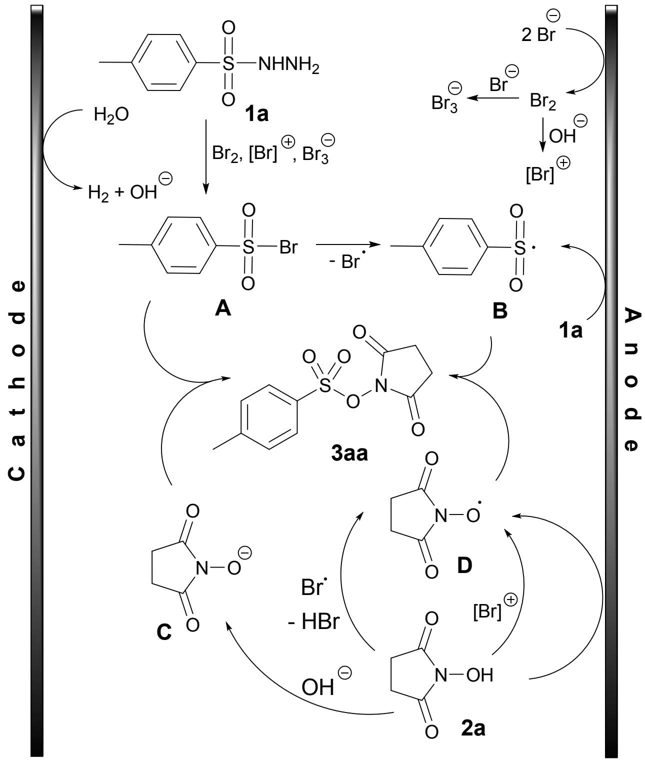


Scheme 2. Electrosynthesis of sulfonates **3aa**, **3da**, **3ja** from sodium sulfinates **4a, 4d, 4j** and *N*-hydroxysuccinimide **2a** (yield based on NMR; 1,4-dinitrobenzene as internal standard).

On the basis of our previous experience[9a, 12a] and literature data we proposed two different ways for this reaction: ionic and radical ones (Scheme 3). Some extra experiments including cyclic voltammetry were conducted. Cyclic voltammetry experiments were implemented on a working glassy-carbon electrode with H_2O-THF (1:1) system as a solvent and tetrabutylammonium perchlorate as a supporting electrolyte.

Anyway the initial step of the process is anodic oxidation of bromide anion resulting in molecular bromine. Cyclic voltammetry data demonstrated that bromide-anion is oxidized under the earliest potentials (Figure 1, + 1.13 V) among all reaction participants.



Scheme 3. Proposed reaction pathways.

It is well-known[23] that molecular bromine can oxidize *p*-toluenesulfonyl hydrazide **1a** affording *p*-toluenesulfonyl bromide **A**. In the processes of bromide-anion oxidation and formation of *p*-toluenesulfonyl bromide **A** hypobromites, bromates, perbromates ($[Br]^+$)[24] or tribromide anion Br_3^- [25] can also participate. Hypobromites, bromates and perbromates are mainly generated as a result of the reaction between molecular bromine and hydroxide-anion forming by the cathodic reduction of H_2O.[26] Tribromide anion can be formed through the reaction of molecular bromine with bromide-anion.[27] Starting *N*-hydroxysuccinimide **2a** can be deprotonated by forming hydroxide-anion with the generation of anion **C**. Ionic interaction between *p*-toluenesulfonyl bromide **A** as an electrophile and *N*-hydroxysuccinimide anion **C** as a nucleophile leads to the coupling product **3aa**. The reaction between individually prepared *p*-toluenesulfonyl bromide **A** and potassium salt of *N*-hydroxy succinimide **C'** gave the coupling product **3aa** in 68% yield in H_2O-THF solution at 40 °C (Scheme 4). This fact demonstrated the possibility of formation of sulfonate **3aa** from intermediates **A** and **C** under reaction conditions.

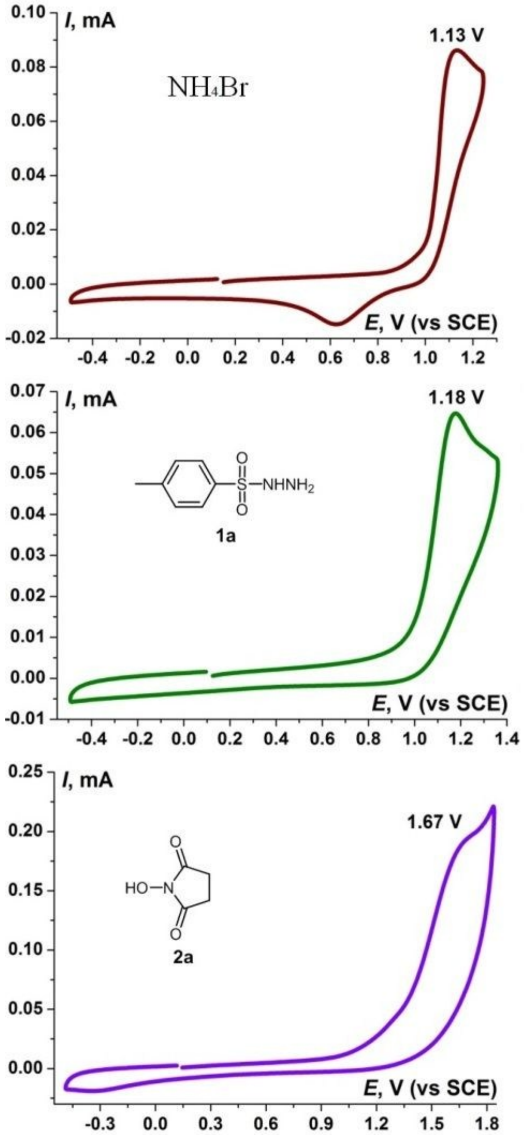


Figure 1. The CV curves obtained for 3.0 mmol·L^{-1} solutions of NH_4Br, *p*-toluenesulfonyl hydrazide **1a** and *N*-hydroxysuccinimide **2a** in 0.1 M Bu_4NClO_4 in H_2O-THF (1:1) on a working glassy-carbon electrode (d = 2.9 mm) at a scan rate of 100 mV·s^{-1}.

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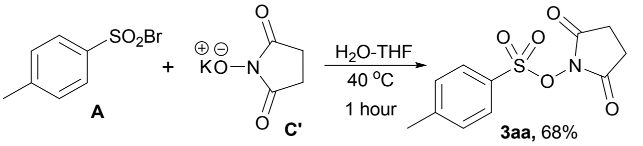

Scheme 4. Synthesis of sulfonate **3aa** from individually prepared *p*-toluenesulfonyl bromide **A** and potassium salt of *N*-hydroxy succinimide **C’** (control experiment).

Turning back to possible radical pathway, *p*-toluenesulfonyl bromide **A** can decompose with the formation of *p*-toluenesulfonyl radical **B** and bromo radical.[28] Radical **B** can be also formed through the direct anodic oxidation of sulfonyl hydrazide **1a**.[29] *N*-oxyimide radical **D** can be formed through different pathways. The first one is a direct anodic oxidation of *N*-hydroxysuccinimide **2a** (Figure 1, +1.67 V)[30] or *N*-oxysuccinimide anion **C**. The second one is the reaction between **2a** and bromo radical or hypobromites, bromates or perbromates. Recombination of *p*-toluenesulfonyl radical **B** and *N*-oxyimide radical **D** provides target product **3aa**.

Conclusions

In summary, we have demonstrated atom-efficient electrochemically induced oxidative S-O coupling, which permits to avoid usage of stoichiometric amounts of chemical oxidants. Sulfonyl hydrazides and *N*-hydroxy compounds were applied as starting materials. The process is carried out under constant current conditions in an experimentally convenient undivided electrochemical cell equipped with graphite anode and stainless steel cathode. Application of NH_4Br as a supporting electrolyte and a redox catalyst allows oxidizing starting sulfonyl hydrazides and *N*-hydroxy compounds selectively resulting in coupling products in yields from moderate to high. On the basis of reported literature, cyclic voltammetry data and control experiment possible reaction pathways were proposed: molecular bromine, which is generated through anodic oxidation of NH_4Br, or hypobromite, bromate, perbromate, tribromide anions oxidize starting compounds to form reactive intermediates, which couple to form S-O bond.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Russian Science Foundation (Grant № 18-13-00027).

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