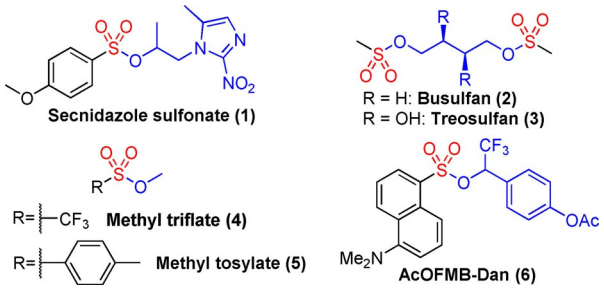
Electrochemistry

Metal- and Reagent-Free Electrochemical Synthesis of Alkyl Arylsulfonates in a Multi-Component Reaction

Stephan P. Blum,[a] Dieter Schollmeyer,[a] Maris Turks,*[b] and Siegfried R. Waldvogel*[a]

Abstract: This work presents the first electrochemical preparation of alkyl arylsulfonates by direct anodic oxidation of electron-rich arenes. The reaction mechanism features a multi-component reaction consisting of electron-rich arenes, an alcohol of choice and excess SO_2 in an acetonitrile-HFIP reaction mixture. In-situ formed monoalkyl sulfites are considered as key intermediates with bifunctional purpose. Firstly, this species functions as nucleophile and secondly, excellent conductivity is provided. Several primary and secondary alcohols and electron-rich arenes are implemented in this reaction to form the alkyl arylsulfonates in yields up to 73% with exquisite selectivity. Boron-doped diamond electrodes (BDD) are employed in divided cells, separated by a simple commercially available glass frit.

Sulfonate esters are omnipresent in synthetic chemistry,[1] dyes,[2] materials,[3] drugs and various other bioactive compounds.[4] One example is the secnidazole sulfonate (**1**) (Scheme 1), which proved to exhibit unique antibacterial and antifungal properties.[5] The drug Busulfan (**2**) and Treosulfan (**3**), are bifunctional DNA alkylating agents and therefore used in chemotherapy.[6] Additionally, the versatile reagents methyl triflate (**4**) and methyl tosylate (**5**) are employed as methylation agents.[7] Para-substituted 2,2,2-trifluoro-1-phenyl-ethyl esters, such as AcOFMB-Dan (**6**), have been developed for cytoplasmic delivery of dansyl acid and other dyes into living cells with subsequent unmasking of the chemically stable sulfonate ester



Scheme 1. Relevant examples of alkyl sulfonates.

protecting group by an enzymatic pathway.[2,8] Furthermore, neopentyl and isopropyl sulfonates in particular have been successfully applied in multistep synthesis as protection groups for sulfonic acids and can be cleaved under acidic conditions. Thus, sulfonate esters can be introduced at an early stage without dealing with solubility issues in organic solvents, implicated by the sulfonic acid group.[9] In addition, neopentyl sulfonates are capable as leaving groups for Ni-catalyzed cross-coupling reactions.[10]

Traditional strategies in the synthesis of alkyl arylsulfonates feature the treatment of an arene with chlorosulfonic acid to obtain the corresponding sulfonyl chloride with subsequent esterification (Scheme 2).[11] However, this two-step synthesis requires harsh reaction conditions and sulfonyl chlorides are considered sensitive towards moisture.[12] Furthermore, the regioselectivity is determined by the inherent reactivity of the substrate, which often results in mixtures of regioisomers.[11,13] Lei and co-workers obtained alkyl arylsulfonates directly from the corresponding thiols by photochemical oxidation. Nevertheless, this approach comprises several limitations, such as the required prefunctionalization, the application of an oxygen atmosphere and the need of a photocatalyst.[14] Another recent approach was reported by Han and co-workers comprising a Cu-catalyzed radical reaction of aryl diazonium salts with 1,4-diazabicyclo[2.2.2]octane bis(sulfur dioxide) adduct (DABSO) as SO_2 source and the desired alcohol in a multi-component reaction.[15] However, diazonium salts are difficult to handle due to their sensitivity and explosive nature in their solid state.[16]

Our work implements the metal- and reagent-free electrochemical synthesis of alkyl arylsulfonates from unfunctionalized electron-rich arenes with excellent selectivity. Key feature in this one-pot synthesis is the use of a stock solution of SO_2 in acetonitrile with known concentration, so that no expensive DABSO is required.[17] Inexpensive electricity is used as oxidant. Electrochemical reactions comprise the principles of modern

[a] S. P. Blum, Dr. D. Schollmeyer, Prof. Dr. S. R. Waldvogel
Department of Chemistry
Johannes Gutenberg-University Mainz
Duesbergweg 10-14, 55128 Mainz (Germany)
E-mail: waldvogel@uni-mainz.de

[b] Prof. Dr. M. Turks
Institute of Technology of Organic Chemistry
Faculty of Materials Science and Applied Chemistry
Riga Technical University
P. Valdena 3, Riga, 1048 (Latvia)
E-mail: maris.turks@rtu.lv

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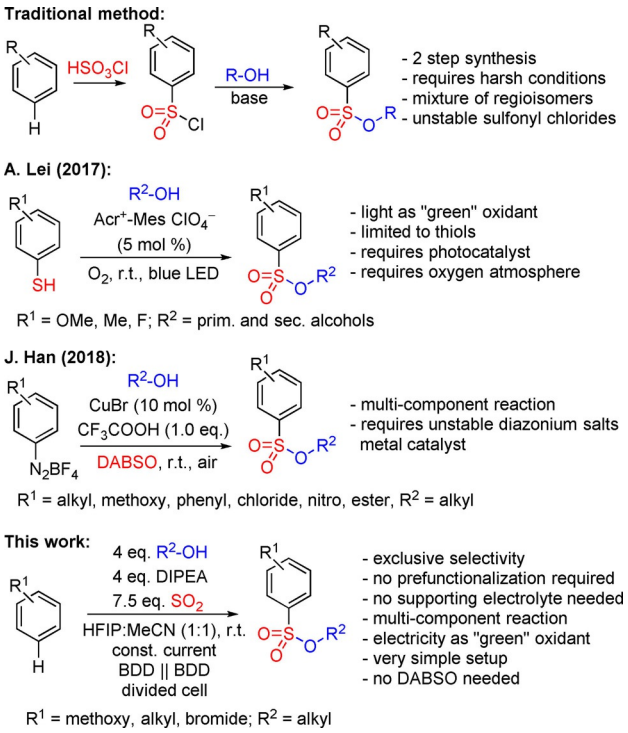
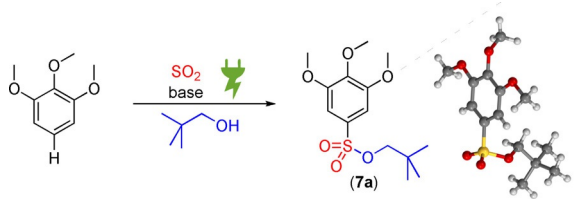


Scheme 2. Comparison and evaluation of different strategies to synthesize alkyl arylsulfonates. DIPEA = *N*,*N*-Diisopropylethylamine.

green chemistry and are inherently safe.[18] The benefits of electrosynthesis are further highlighted in numerous of our research works.[19] The fluorinated solvent 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)[20] and boron-doped diamond (BDD) electrodes[21] play a key role in the implementation of new electrochemical reactivity. Recently, a general protocol for the sulfonylation of arenes, phenols and aniline derivatives was published.[22]

Sulfur dioxide is utilized as feedstock in chemical industry and food industry.[23] Synthetic chemistry with SO_2 has experienced a significant boost since the discovery of the reagent DABSO, which is an easy-to-handle SO_2 surrogate.[23a,24] Nevertheless, it is quite costly and lowers the total atom economy.[25] The usage of a SO_2 stock solution is a superior alternative. In fact, SO_2 solutions in aprotic solvents have been applied in electrochemical transformations featuring the cathodic reduction of SO_2.[26] To the best of our knowledge, anodic reactions involving nonaqueous SO_2 as substrate[12b] have not been reported, yet.

The electrochemical synthesis of alkyl arylsulfonates according to Scheme 3 was initially discovered with 1,2,3-trimethoxybenzene and neopentyl alcohol as substrates in presence of a base and SO_2. At first, the nature of the base was screened.[27] Tertiary amines, such as TEA or DIPEA turned out to give improved yields in comparison to heterocyclic bases like DBU. Experimental details can be retrieved from the supporting information. It is noteworthy that Olah et al. reported the formation of a tertiary amine-SO_2 complex and the subsequent reaction with oximes,[28] nitro compounds[29] and pyridine-*N*-oxide.[30] As mentioned above, the SO_2 source was a freshly prepared stock



Scheme 3. General reaction Scheme for the electrochemical multi-component synthesis of alkyl arylsulfonates. On the right side: molecular structure of **7a** (determined by X-ray analysis of a suitable single crystal).

solution in acetonitrile. The concentration was determined iodometrically (see Supporting Information). Neopentyl alcohol was selected due to the enhanced stability of sulfonate neopentyl esters.[9b,c]

Due to the simple experimental set-up, reaction optimization was first conducted in undivided cells (Table 1). Conductivity of the electrochemical reaction was improved in an HFIP/MeCN solvent mixture. Four equivalents of DIPEA and neopentyl alcohol turned out to be best (Table 1, entry 1). BDD electrodes proved to be superior in comparison to other electrode materials (entries 4–7). Interestingly, the product yield did not improve significantly (entries 8–10) by application of higher amount of charge.

Higher product yields were obtained by application of a divided cell (Table 2) with a simple commercially available glass frit. The optimum current density was at 11.25 mA cm^{-2} (Table 2, entries 12–15). 3.5 F as amount of charge also gave best results (entries 11, 16, 17). Omitting of an organic base, HFIP, or no application of electric current (entries 18–20) resulted in no product formation.

Thereupon, the substrate scope was extended with different alcohols according to the general reaction shown in Scheme 4. Highest yields were obtained with neopentyl alcohol and 2-methylpropanol giving substrate **7a** with 73% yield and **7b** with 69% yield. The molecular structure of **7a** was confirmed (Scheme 3) for final structural isomer determination. Usage of the simplest primary alcohols, ethanol and methanol, gave slightly lower yields (**7c**, 65% and **7d**, 48%). Potential decom-

Table 1. Optimization of the reaction in undivided cells.

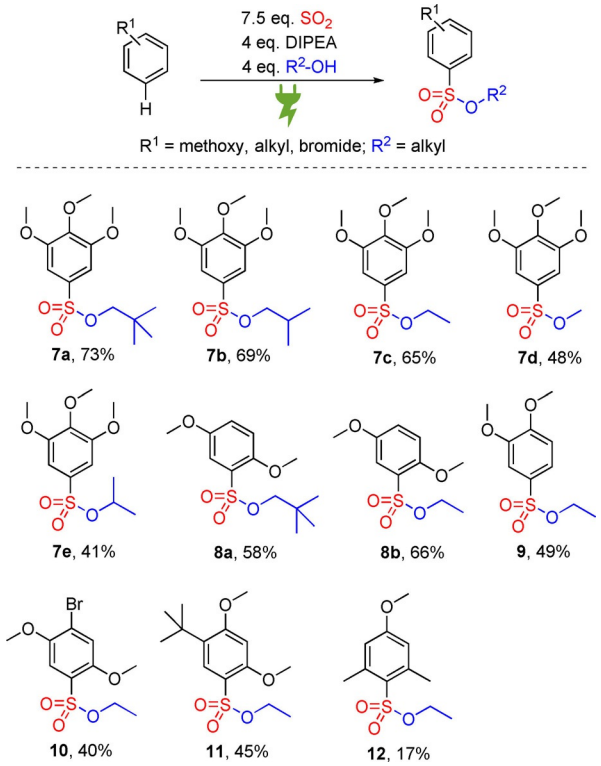
Entry	Deviation from the standard conditions[a]	Yield [%][b]
1	None	39
2	2.0 equiv. DIPEA and neopentyl alcohol	32
3	5.0 equiv. DIPEA and neopentyl alcohol	24
4	Pt electrodes	30
5	Pt cathode, BDD anode	40
6	Glassy carbon electrodes	23
7	Graphite electrodes	18
8	3.00 F	45
9	**6.00 F**	**53**
10	8.00 F	46

[a] Standard conditions: 0.1 M 1,2,3-trimethoxybenzene, 4 equiv. neopentyl alcohol, 4 equiv. DIPEA, 7.5 equiv. SO_2, HFIP:MeCN = 1:1, r.t., undivided cell, BDD electrodes, constant current, j = 12 mA cm^{-2}, 2.50 F. [b] Yield determined by internal NMR standard (1,3,5-trimethoxy-benzene).

Table 2. Optimization of the reaction in divided cells.

Entry	Deviation from the standard conditions[a]	Yield [%][b]
11	**None**	**73**
12	$j = 4.00$ mA cm^{-2}, 2.50 F	56
13	$j = 7.00$ mA cm^{-2}, 2.50 F	64
14	$j = 11.25$ mA cm^{-2}, 2.50 F	66
15	$j = 14.00$ mA cm^{-2}, 2.50 F	55
16	3.25 F	70
17	4.00 F	66
18	No base, 0.2 M $[NBu_4]^+[BF_4]^-$	0
19	No electric current	0
20	Only MeCN (no HFIP)	0

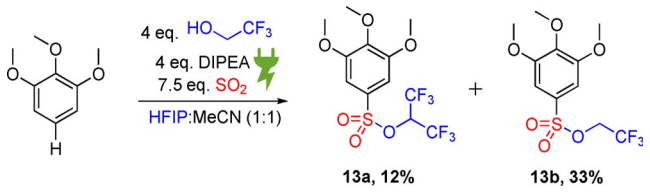
[a] Standard conditions: 0.1 M 1,2,3-trimethoxybenzene, 4 equiv. neopentyl alcohol, 4 equiv. DIPEA, 7.5 equiv. SO_2, HFIP:MeCN = 1:1, r.t., divided cell (frit), BDD electrodes, constant current, $j = 11.25$ mA cm^{-2}, $Q = 3.50$ F. [b] Yield determined by internal NMR standard (1,3,5-trimethoxy-benzene).



Scheme 4. General reaction Scheme for the synthesis of alkyl arylsulfonates. Conditions: HFIP:MeCN = 1:1, r.t., divided cell (frit), BDD electrodes, constant current, $j = 11.25$ mA cm^{-2}, $Q = 3.50$ F. The scope of the reaction including isolated yield are displayed.

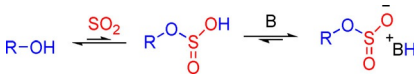
position of the products could occur during the work-up process due to their minor stability.[9c] The secondary alcohol isopropanol as reactant resulted in lower yields (**7e**, 41%), which can be explained by the higher steric demand of the isopropyl group. Next, we investigated the substrate scope of different arenes. The reactivity of 1,4-dimethoxybenzene was in similar fashion with neopentyl alcohol and ethanol giving **8a** with 58% and **8b** with 66% yield. Thus, further arenes were examined with ethanol as reactant. Substrate **9**, **10**, and **11** provided comparable yields ranging from 40% to 49%. It is noteworthy to mention, that **10** has a bromo substituent, which is of high synthetic interest due to potential follow-up reactions for further functionalization.[31] In general, arenes bearing methyl groups suffered from lower conversion. Nevertheless, **12** was isolated with 17% yield. Arenes with higher oxidation potential resulted in no or very low product formation.

Interestingly, a competition reaction between 2,2,2-trifluoroethanol and HFIP was observed (Scheme 5). A product mixture of **13a** (12%) and **13b** (33%) was isolated. Therefore, we assume that the nucleophilicity of 2,2,2-trifluoroethanol was not sufficient so that HFIP was competing to some extent in the reaction.



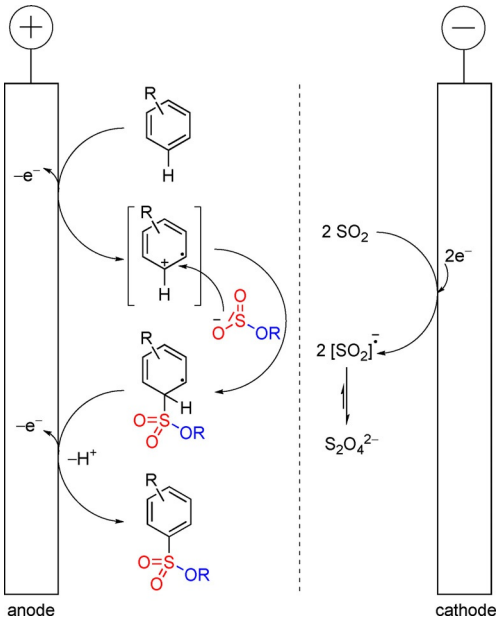
Scheme 5. Competition experiment between 2,2,2-trifluoroethanol and HFIP. Conditions: HFIP:MeCN = 1:1, r.t., divided cell (frit), BDD electrodes, constant current, $j = 11.25$ mA cm^{-2}, $Q = 3.50$ F.

Due to these results, we conclude that the reaction mechanism proceeds by an in situ formed monoalkyl sulfite (Scheme 6). Excess SO_2 in presence of an alcohol forms the sulfurous acid intermediate. Addition of an organic base shifts the equilibrium towards the monoalkyl sulfite side. Therefore, the presence of a base is essential for the reaction. However, no additional supporting electrolyte for the reaction is needed, as the conductivity given is already sufficient. In fact, a few publications about monoalkyl sulfites have already been reported,[32] but to our knowledge it is the first time that this species is employed as reactant in organic synthesis.



Scheme 6. Proposed mechanism for the generation of monoalkyl sulfites by addition of an organic base.

According to cyclic voltammetry results (Supporting Information), the arene is considered to undergo electrochemical oxidation to form the radical cation transition state. The monoalkyl sulfite then undergoes nucleophilic addition as illustrated in Scheme 7 to form the corresponding intermediate adduct. A second oxidation step then finally provides the alkyl arylsulfonates. SO_2 is considered to be reduced to the SO_2 anion radical at the cathode, which was confirmed via cyclovoltammetry studies (supporting information). This species is reported to dimerize to dithionite or to undergo the formation of complex ions with SO_2 molecules.[26] Therefore, divided cells compose the better alternative towards undivided cells in order to prevent anodic oxidation of these species, which could explain



Scheme 7. Proposed mechanism for the electrochemical synthesis of alkyl arylsulfonates. Cathodic and anodic reactions are separated by a dotted line, which represents the division of the cell by a frit.

the low current efficiencies obtained in undivided cells (Table 1, entries 8–10).

In summary, we established a new concise electrochemical methodology to synthesize alkyl arylsulfonates starting from arenes by a multi-component reaction. A highlight is the in situ formation of the monoalkyl sulfite intermediate, which takes the role as nucleophile and supporting electrolyte. Direct anodic oxidation of the arene initiates a dehydrogenative reaction mechanism. More than 11 examples up to 73% yield with a variety of arenes and different alcohols were implemented.

Experimental Section

The anode compartment was charged with the arene substrate (0.60 mmol). Acetonitrile, SO_2 in acetonitrile (15.0 equiv.) and the alcohol (4.80 mmol, 8.0 equiv.) were combined in a pear-shaped flask. The mixture was cooled to 0 °C and *N*-ethyl-*N*-isopropylpropan-2-amine (4.80 mmol, 8.0 equiv.) was added dropwise through a septum. The reaction mixture was stirred for 5 min and HFIP was added slowly at 0 °C under stirring, so that a total volume of 12.0 mL and a solvent ratio of HFIP:MeCN = 1:1 was obtained. 6 mL of the reaction mixture was transferred into the cathode compartment and the other half of the electrolyte was then immediately transferred to the anode compartment of the divided cell. The electrolysis was conducted at r.t. at galvanostatic conditions. The reaction mixture was stirred for 14 h in total. The anolyte and catholyte were combined and the solvents were distilled at reduced pressure for reutilization. Cold distilled water (30.0 mL) was added to the remaining reaction mixture, which was then extracted in ethyl acetate (3 × 30.0 mL). The combined organic fractions were dried over Na_2SO_4. The organic solvent was removed at reduced pressure and the crude product was purified via column chromatography on silica with a cyclohexane/ethyl acetate solvent gradient.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: C–H activation · electrochemistry · green chemistry · oxidation · radical ions

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