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Electrochemical synthesis of cyclic sulfites using diols and sulfur dioxide†

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We report a simple protocol for the electrochemical synthesis of cyclic sulfites. Starting from diols and easy-to-handle stock solutions of SO_2, the reaction features a quasi-divided cell setup under constant current conditions. The feasibility of this novel electrochemical dehydrative reaction is demonstrated by a broad scope of 20 examples, achieving yields of up to 87%.

Sulfur dioxide emissions, which are closely linked to fossil fuel incineration, pose serious health threats and are known to interfere with Earth's sensitive climate in multiple ways. Desulfurization of industrial flue gases produces low-purity SO_2, which can be easily separated and is often directly converted into gypsum.[1] Most of the high-purity sulfur dioxide originates from the hydrodesulfurization of natural gas or crude oil after oxidative treatment in the Claus process and is subsequently converted into base chemicals like sulfuric acid.[2,3] On the other hand, many pharmaceuticals or other industrially relevant chemicals feature the SO_2 motif within their molecular structure.[4] Utilizing sulfur dioxide directly as an inexpensive feedstock would allow for the construction of complex, value-added products in a single straightforward step.[5] But transformations utilizing this strategy remain limited. In particular on a laboratory scale the safe handling of toxic and noxious SO_2 poses challenges.[6] As an alternative, surrogates, such as DABSO,[7] SOgen,[8] and inorganic sulfites, *e.g.* $K_2S_2O_5$[9] are often used. But these compounds are more expensive than SO_2, exhibit poor atom efficiency and can generate vast amounts of waste. A more sustainable approach is the use of SO_2 stock solutions, which have been demonstrated to allow access to a wide range of structural motifs like sulfones, sulfonyl fluorides,[10] sulfonates,[11–13] sulfonamides,[14,15] and sulfamides.[16] Moreover, solutions of SO_2 become conductive upon the addition of amines and have recently been shown to be recyclable as well,[15] making them particularly suitable for electrolytic conversion.

In this work, we focused on the development of cyclic sulfites. These high-value compounds, which were first described in 1909,[17] have found various applications over the years: sulfites are prone to be attacked by nucleophiles[18] or oxidized to the more reactive sulfates, enabling nucleophilic substitution at the α-carbon.[19] Cyclic sulfites may be polymerized through cationic ring opening. Depending on the ring size of the starting material, the resulting polymer is either a polyoxyethylene[20] or a polysulfite,[21] which are currently being investigated as either biopolymers[20] or biodegradable polymers (Scheme 1a).[22] Due to their exceptional electrochemical stability, cyclic sulfites have found direct application as additives in lithium ion batteries (Scheme 1b).[23] Moreover, these structures are known to exhibit bioactivity, as evidenced by multiple reports demonstrating antitumor[24] (Scheme 1c) and anticonvulsant properties.[25]

The most common method for the preparation of such moieties is the reaction of a diol with thionyl chloride (Scheme 1d), generating stoichiometric amounts of chlorinated waste in the process.[26] An alternative route uses the addition of SO_2 to an epoxide, accessing 5-membered cyclic sulfite esters (Scheme 1e). But either elevated temperatures[27] or metal catalysts are needed.[28] Although this method performs well in terms of atom economy, it restricts the resulting products to 5-membered cycles. Circumventing this major limitation, we now report an electrochemical protocol for the construction of various cyclic sulfites, employing widely available diols and SO_2 directly under mild conditions (Scheme 1f). Utilizing electric current as green redox equivalents, electrosynthesis allows for the construction of complex molecules from simple starting materials,[29,30] accessing new and often complementary reactivities while at the same time being inherently safe.[31–38] Although the envisioned transformation is redox neutral in nature, it has recently been demonstrated that electrosynthesis can be used to dehydrate carboxylic acids.[39,40] Electrochemical dehydration seems to be a general method, but to our surprise only a few cases have been reported.[41–45]

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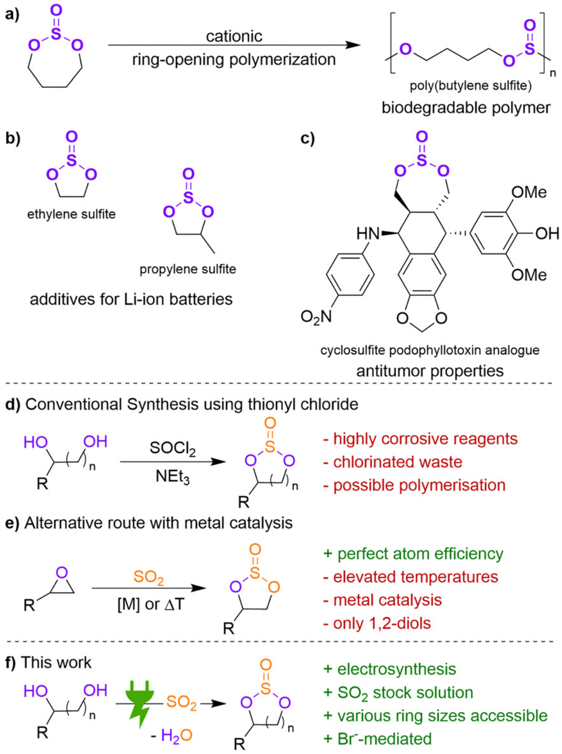
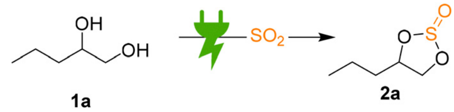


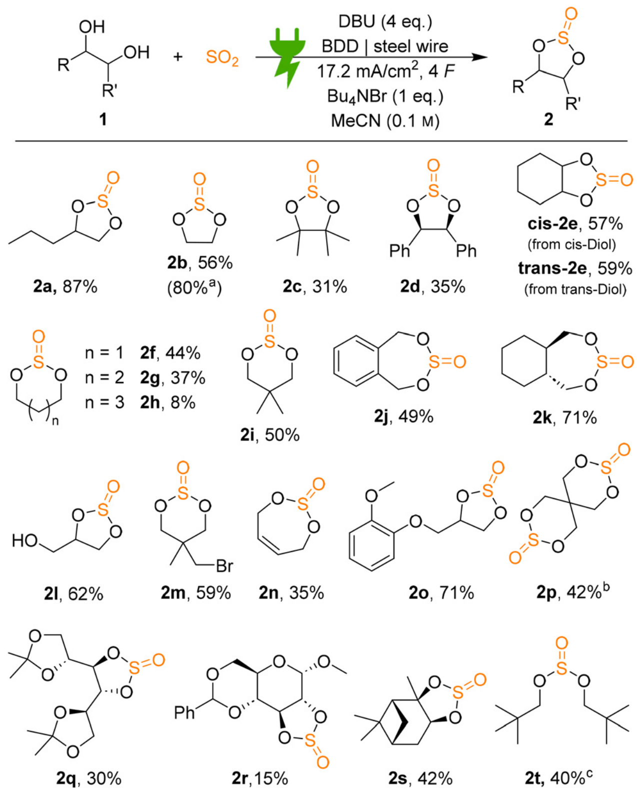
Scheme 1 Overview of the applications, uses, and synthetic access to cyclic sulfites.

Table 1 Optimization of reaction conditions



Entry	Cell	Anode	Supporting electrolyte	Yield[a] (%)
1[b]	Divided	Glassy carbon	None	40
2[c]	Undivided	Glassy carbon	None	28
3[c]	Quasi-divided	Glassy carbon	None	41
4	Quasi-divided	Glassy carbon	Bu_4NSCN	51
5	Quasi-divided	Glassy carbon	Bu_4NI	72
6	Quasi-divided	Glassy carbon	Bu_4NBr	74
7	Quasi-divided	Platinum	Bu_4NBr	50
8	Quasi-divided	Graphite	Bu_4NBr	58
9	Quasi-divided	Graphite foil	Bu_4NBr	77
10	Quasi-divided	BDD	Bu_4NBr	80
11[d]	Quasi-divided	BDD	Bu_4NBr	95 (87)

Conditions: **1a** (500 µmol, 1 eq., 0.1 M), SO_2 (5 eq.), DBU (3.0 eq.), supporting electrolyte (1 eq.), MeCN (5 mL), anode|stainless steel wire, 17.2 mA cm^{-2}, 4 F, rt. [a] Sum of the yields of both diastereomers. Determined by GC. Isolated yield in parentheses. [b] **1a** (600 µmol, 1 eq., 0.1 M), 10 mA cm^{-2}, 2F. [c] 2F. [d] 4 eq. of DBU.



Scheme 2 Scope of sulfites. Conditions: diol **1** (500 µmol, 1 eq., 0.1 M), SO_2 (5 eq.), DBU (4 eq.), Bu_4NBr (1 eq.), MeCN (5 mL), BDD|stainless steel wire, 17.2 mA cm^{-2}, 4 F, rt. [a] qNMR yield. [b] 10 eq. of SO_2, 8 eq. of DBU, 2 eq. of Bu_4NBr and 8 F. [c] Neopentanol (600 µmol, 1 eq., 0.1 M), BDD‖stainless steel.

We selected pentane-1,2-diol as a test substrate for the dehydrative electrolysis to cyclic sulfites. Sulfur dioxide was introduced as a stock solution in acetonitrile, and 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) served as an auxiliary base. After constant-current electrolysis in a divided cell, we were pleased to observe the desired product **2a** in the anodic compartment in 40% yield (GC, Table 1, entry 1). Other organic bases proved to be inferior (see the ESI†). Simplifying the electrochemical cell to an undivided one decreased the yield by 12% (entry 2), most probably due to interferences from reduced SO_2 species formed at the cathode.[12,46,47] The initial yield was reestablished by the use of a stainless steel wire as the cathode, resulting in a setup known as a quasi-divided cell (entry 3).[11] Screening of different supporting electrolytes (see the ESI†) revealed increased yields with redox-active Bu_4NSCN (entry 4, 51%), which is known to dehydrate carboxylic acid to the corresponding anhydrides anodically.[39] Even better results were obtained when using either Bu_4NI (entry 5, 72%) or Bu_4NBr (entry 6, 74%). In a next step, different anode materials were investigated (entries 7–10), with boron-doped diamond (BDD, entry 10, 80%) performing best. Further optimization of the amount of applied charge, current density and the stoichiometry of SO_2 and the base (see the ESI†) resulted in 95% GC yield (entry 11), of which 87% could be isolated.

With the optimized conditions in hand, we explored the scope of our newly discovered reaction using different diols (Scheme 2). Unsubstituted ethylene glycol (**2b**) resulted in an 80% qNMR yield, but due to the high volatility of the product, only 56% could be isolated. Increasing the steric load on the α-carbon by using a tertiary diol (**2c**) or two phenyl groups (**2d**) resulted in lower yields of 31% and 35%, respectively. Starting from either *cis*- or *trans*-cyclohexane-1,2-diol gave satisfying yields of 57% (*cis*-**2e**) and 59% (*trans*-**2e**), demonstrating that relative stereochemistry does not influence the reaction and retention of the stereocenter occurs. By investigating the distance between the two hydroxyl groups, we observed a clear trend: the yield dropped consistently with increasing ring size of the product, from a 5-membered (**2b**, 80% qNMR) over a 6-membered (**2f**, 44%) and a 7-membered (**2g**, 42%) ring to an 8-membered ring (**2h**, 8%). Importantly, the yields could be increased by prearranging the alcohol groups. Introducing two methyl substituents in position 2 leads to the formation of the respective 6-membered ring in 50% yield (**2i**), while prearranging 1,4-diols with phenyl (**1j**) or a cyclohexane (**1k**) moiety increased the yields of the resulting 7-membered rings to 49% (**2j**) and 71% (**2k**), respectively. The preference of the reaction to form smaller rings can be actively exploited. Using glycerol (**1l**), we only observed the formation of the respective 5-membered ring (**2l**, 62%), and no dimerized products could be detected. Next, we tested functional group tolerance. We were pleased to see that a bromo substituent (**2m**, 59%) and an unsaturated diol (**2n**, 35%) both formed the desired products. Even a very easy-to-oxidize (methoxy phenoxy)-substituent resulted in a good yield of 71% (**2o**). Employing pentaerythritol leads to the formation of a difunctionalized spiro-compound (**2p**, 42%). Sulfinylation of an open-chain protected mannitol (**2q**) was successfully achieved in a yield of 30%, while a closed-chain glucose derivative (**2r**) still yielded 15%, but sensitive sugars seem to degrade during the reaction, explaining the lowered yields. The sterically demanding (+)-pinan-2,3-diol was converted to the sulfite (**2s**) in an acceptable yield of 42%. The monoalcohol neopentanol (**1t**) was converted into the linear sulfite (**2t**) in 40% yield, albeit a divided cell had to be used, indicating that reoptimization of reaction conditions is advised for monoalcohols.

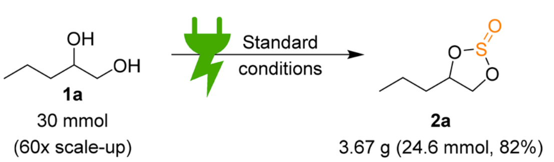
To demonstrate the scalability of our protocol, sulfite ester **2a** was synthesized in a multi-gram scale reaction (Scheme 3, 60-fold scale-up, see the ESI†). After simple isolation by filtration over silica, the product was obtained in 82% yield, showing only a minor decline compared to the micro-molar scale.

To elucidate the mechanism of the dehydration, several control experiments were conducted. Only trace amounts of the desired product could be detected when the electric charge was omitted (Table 2, entry 1), proving that the redox neutral reaction is electrochemically induced. Similarly, no signs of the desired product were detected when the auxiliary base DBU was left out (entry 2). In a divided cell, the cyclic sulfite is only found in the anodic compartment, suggesting that the reaction mechanism works oxidatively. When the reaction is performed under standard conditions, SO_4^{2-} can be detected by ion chromatography (see the ESI†). Unsurprisingly, cyclic voltammetry experiments showed the oxidation of bromide to bromine (E^{ox} = 0.51 V *vs.* FcH/FcH$^+$, see the ESI†) as the initial electrochemical step. To further prove the active role of elemental halogen in the mechanism, the reaction was conducted without passing electric charge, but with the addition of 1 eq. of iodine instead (Table 2, entry 3), affording a 68% yield of the cyclic ester. Performing the electrosynthesis with an ^{18}O-labeled diol resulted in the formation of the sulfite ester having both labeled oxygens incorporated (see the ESI†), proving that the oxygen being lost during the dehydration originates from SO_2. Based on these results, we propose the following mechanism (Scheme 4): first, diol **1** is converted into intermediate **I** by base-assisted addition of one molecule of SO_2. The formation of such monoalkyl sulfite intermediates is well described in the literature and has already been put to synthetic use on multiple occasions.[12,46–48] Electrochemically, bromide is oxidized to bromine, as evidenced by CV studies. Elemental bromine then reacts with **I** to form the bromo sulfinate **II**. The pre-formed hypobromite acts as a leaving group, facilitating the nucleophilic attack of the second alcohol or alkoxide, ultimately forming the desired cyclic sulfite ester **2**. The hypobromite formed during the last step can disproportionate into bromate and bromide. Both hypobromite and bromate are strong oxidizers and are believed to be able to oxidize SO_2 to the detected sulfate under bromide regeneration. On the cathode, the limited surface area of the wire results in a high current density,

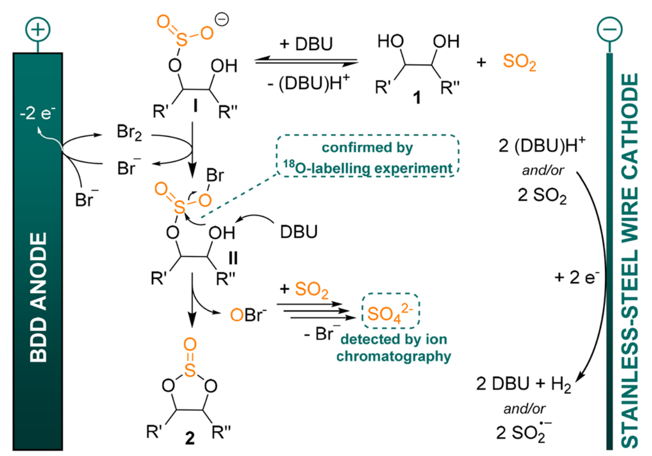
Table 2 Control experiments

Entry	Deviation from standard conditions[a]	Yield[b] (%)
1	None	92
2	No charge	Traces
3	No DBU	0
4	No charge + 1 eq. I_2	68

[a] Conditions: **1a** (500 μmol, 1 eq., 0.1 M), SO_2 (5 eq.), DBU (4 eq.), Bu_4NBr (1 eq.), MeCN (5 mL), BDD | stainless steel wire, 17.2 mA cm^{-2}, 4 F, rt. [b] Yield determined by qNMR.



Scheme 3 Multi-gram scale synthesis. Conditions: diol **1a** (30 mmol, 1 eq., 0.1 M), SO_2 (5 eq.), DBU (4 eq.), Bu_4NBr (1 eq.), MeCN (300 mL), BDD|stainless steel wire, 17.2 mA cm^{-2}, 4 F, rt.



Scheme 4 Proposed reaction mechanism.

leading to reduced SO_2 and proton discharge. Gas evolution as well as coloring at the cathode supports this assumption.

In summary, we established a novel and simple method for synthesizing cyclic sulfite esters starting from diols and sulfur dioxide stock solution under mild electrochemical reaction conditions. The reaction features a quasi-divided setup and proceeds through the formation of a monoalkyl sulfite, followed by its subsequent transformation into a hypobromite leaving group through anodically generated bromine. The reaction scope was demonstrated with 20 examples exhibiting yields of up to 87% and could easily be transferred to a multi-gram scale. Our protocol greatly enhances the sustainability and scope of cyclic sulfite ester synthesis and is a rare and novel example of an electrochemically induced dehydration reaction. This approach avoids the use of thionyl chloride for the activation of SO_2 by electrochemistry.

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Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the ESI.†

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