RSC Advances

ROYAL SOCIETY OF CHEMISTRY

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Cite this: *RSC Adv.*, 2020, **10**, 33155

Electrochemical sulfonylation of alkenes with sulfonyl hydrazides: a metal- and oxidant-free protocol for the synthesis of (*E*)-vinyl sulfones in water†

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Received 21st August 2020
Accepted 1st September 2020

DOI: 10.1039/d0ra07212e

rsc.li/rsc-advances

An efficient electrochemical transformation of a variety of alkenes and sulfonyl hydrazides into vinyl sulfones with a catalytic amount of tetrabutylammonium iodide in water is reported. The reaction proceeds smoothly to afford vinyl sulfones with good selectivities and yields at room temperature under air in an undivided cell. Cyclic voltammograms and control experiments have been performed to provide preliminary insight into the reaction mechanism. The key features of this reaction include using pure water as solvent, transition metal- and oxidant-free conditions, and being easily scaled up to gram-scale synthesis.

Introduction

To achieve green and sustainable procedures, metal-free strategies have attracted much attention during the past decade.[1] In particular, transition-metal-free couplings in water could provide great opportunities for more sustainable synthetic chemistry.[2] In addition, the development of transition-metal-free reactions in water enabled by efficient and cleaner techniques could explore novel approaches to construct chemical products in an environmentally benign manner.[3]

Vinyl sulfones are important and useful building blocks for various organic transformations and exhibit a broad range of biological properties.[4] As a consequence, various synthetic routes to vinyl sulfones have been developed.[5,6] In terms of these synthetic methodologies, the cross-coupling of a variety of alkenes with sulfonyl hydrazides has garnered considerable attention for the synthesis of vinyl sulfones.[6] Despite some great advantages of these reactions, the methods still suffered from certain shortcomings, such as requiring strong oxidants,[6a–d] employment of transition metal catalysts,[6e] or high temperature.[6f] Therefore, it is desirable to synthesize vinyl sulfones directly from styrenes and sulfonyl hydrazides under the metal and oxidant-free conditions.

Organic electrosynthesis has been recognized as an atom-economical and eco-friendly benign synthetic strategy, wherein the electric current can be used to replace a stoichiometric amount of a redox agent.[7] Recently, an elegant example has been devoted to the electrosynthesis of vinyl sulfones by Terent'ev and co-workers.[8] However, the protocol still involved excessive KI and organic solvent. Thus, a more green and efficient strategy for the electrosynthesis of (*E*)-vinyl sulfones between styrenes and sulfonyl hydrazides under milder reaction condition is desired. As a benign solvent, water could lead to new reactivity, as well as environmentally.[9] As part of our ongoing activities in developing electrochemical aqueous-phase reactions,[10] we report here an electrochemical cross-coupling of readily available styrenes and sulfonyl hydrazides using iodide salt as the catalyst with an elegant constant current in water at room temperature under air.

Results and discussion

At the beginning of our investigation, we used styrene **1a** and *p*-toluenesulfonyl hydrazide **2a** as the model substrates to screen the optimized conditions. After some experiments, the optimal reaction conditions were defined as electrolyzing **1a** and **2a** in saturated $(NH_4)_2CO_3$ aqueous solution using 10 mol% of *n*-Bu_4NI as the catalyst at room temperature in an undivided cell with Pt foils (1.0×1.5 cm^2). Under these mild conditions, the desired product **3a** was obtained in 88% yield after the reaction mixture had been stirred for 3.0 h (Table 1, entry 1). It was noted that the yield of **3a** increased sharply to 32% when the reaction was run without *n*-Bu_4NI (entry 2). When *n*-Bu_4NI was replaced with some other catalysts, such as NH_4I, $PhI(OAc)_2$, *n*-Bu_4NBr

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/d0ra07212e

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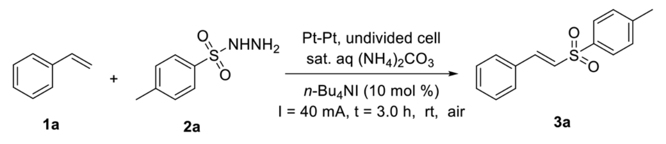
Table 1 Optimization of reaction conditions[a]

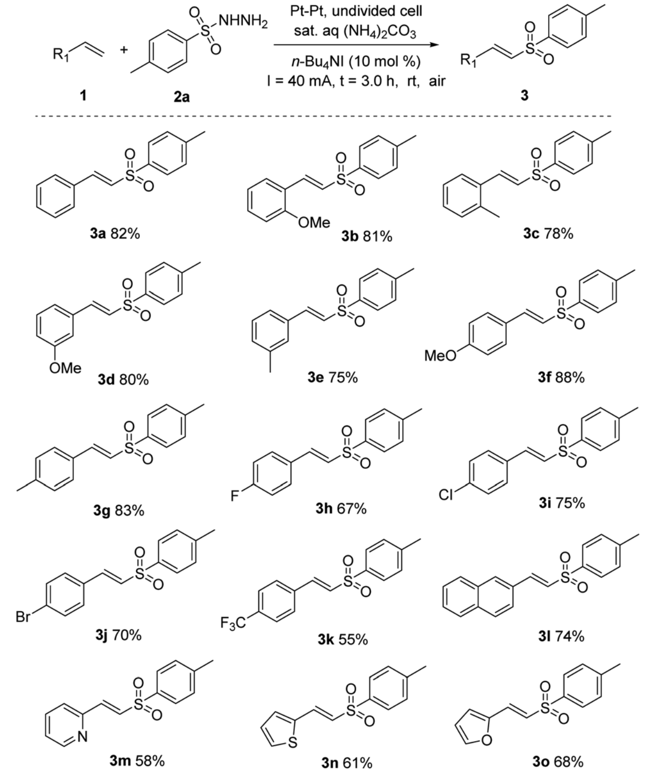


Entry	Variation from the standard conditions	Yield[b] [%]
1	None	88
2	In the absence of *n*-Bu_4NI	32
3	NH_4I instead of *n*-Bu_4NI	77
4	$PhI(OAc)_2$ instead of *n*-Bu_4NI	48
5	*n*-Bu_4NBr instead of *n*-Bu_4NI	68
6	I_2 instead of *n*-Bu_4NI	56
7	Sat. aq. NH_4HCO_3 instead of sat. aq. $(NH_4)_2CO_3$	53
8	Sat. aq. CS_2CO_3 instead of sat. aq. $(NH_4)_2CO_3$	75
9	Graphite rods as electrodes	72
10[c]	Reticulated vitreous carbon RVC as electrodes	70
11[d]	30 mA instead of 40 mA, 4 h	77
12	50 mA instead of 40 mA, 2.4 h	81
13	No electric current	N.R.

[a] Standard conditions: the mixture of **1a** (0.5 mmol), **2a** (1.0 mmol), *n*-Bu_4NI (10 mol%) in saturated $(NH_4)_2CO_3$ aqueous solution (5.0 mL) was electrolyzed at constant current (40 mA) in an undivided cell at room temperature for 3.0 hours, anode and cathode: Pt foil (1.0 × 1.5 cm^2). [b] The yield of the product was determined by ^1H NMR spectroscopy; N.R., no reaction. [c] Graphite rods (diameter: 0.5 cm, height: 1.78 cm). [d] Reticulated vitreous carbon RVC (100 PPI, 1.5 cm × 1 cm × 0.2 cm).

and I_2, the yield of the desired product **3a** was reduced (entries 3–6). Among a series of electrolyte (entries 7–8), sat. aq. $(NH_4)_2CO_3$ gave the optimal result. Subsequently, the electrode material was also screened. When the Pt foil electrodes were replaced by graphite rods or reticulated vitreous carbon rods, the yield of the desired product dropped (entries 9–10). In addition, the electrolysis at lower or higher current density led to a decrease of the yield (entries 11–12). Finally, it was found that no desired product could be obtained without an electric current in this reaction (entry 13).

With the optimized reaction conditions in hand, a series of styrene derivatives were further evaluated. As presented in Scheme 1, the reaction proceeded smoothly with various of styrenes to afford the corresponding vinyl sulfones with moderate to good yields (**3a–o**). Notably, *para*-, *meta*-, or *ortho*-substituted aryl alkenes, bearing either electron-donating groups (Me and OMe, **3b–g**) or electron-withdrawing (F, Br, and Cl, **3h–j**) groups on the aryl ring, gave high yields of the desired products. Strong electron-withdrawing groups (CF_3, **3k**) influenced the reaction and delivered lower yields. Moreover, naphthalene derivative (**3l**) was also accommodated in the reaction and afforded the desired product in a yield of 74%. Heteroarene-based styrenes were also good substrates for this process and gave the desired products in moderate yields (**3m–o**). Importantly, excellent *E* selectivity (*E*/*Z* > 99 : 1) were observed in all product. Notably, alkenes with some functional groups-substituted, such as ester, amides, and silyl ethers are not compatible with this electrochemical transformation.

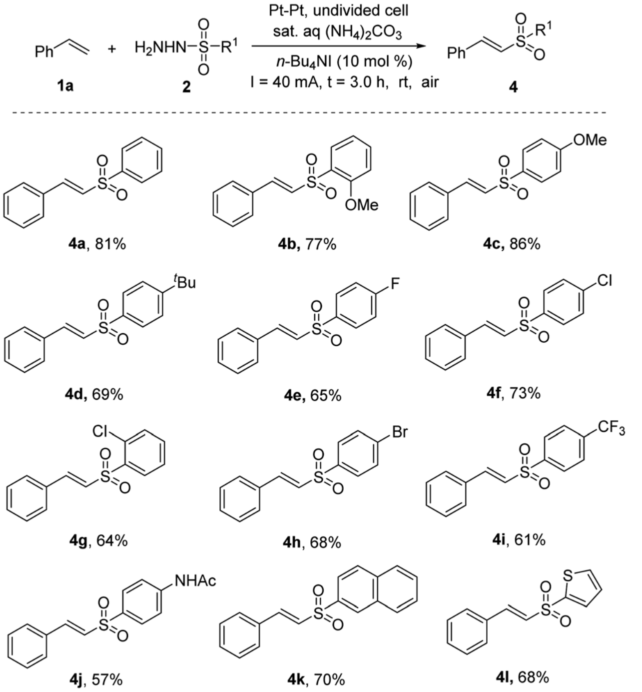


Scheme 1 Scope of the reaction with styrene.[a,b] [a]Reaction conditions: the mixture of **1** (0.5 mmol), **2a** (1.0 mmol), *n*-Bu_4NI (10 mol%) in saturated $(NH_4)_2CO_3$ aqueous solution (5.0 mL) was electrolyzed at constant current (40 mA) in an undivided cell at room temperature for 3.0 hours, anode and cathode: Pt foil (1.0 × 1.5 cm^2). [b]Yields of isolated products.

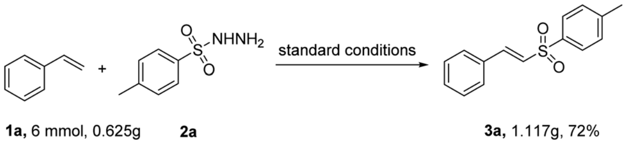
To further examine the scope of this reaction, a range of sulfonyl hydrazides were also used to react with styrene. As shown in Scheme 2, unsubstituted sulfonyl hydrazide afforded the product **4a** with 81% yield. A series of sulfonyl hydrazides bearing electron-donating groups (OMe and ^{t}Bu **4b–d**) and electron-withdrawing (F, Br, Cl, and NHAc, **4e–h**, **4j**) groups produced sulfones in moderate to good yields. The strongly electron-withdrawing group (CF_3, **4i**) led to a slight decrease in yield. Furthermore, sulfonyl hydrazides with a naphthyl group (**4k**) or a thienyl group (**4l**) were examined in this reaction, and the desired products were afforded in yields of 70% and 68%, respectively. It was noteworthy that excellent *E* selectivity (*E*/*Z* > 99 : 1) was observed in all cases.

To demonstrate the synthetic utility of this transformation, electrochemical synthesis of the (*E*)-vinyl sulfones in water was performed at a gram scale (Scheme 3). Product **3a** could be prepared in 72% of yield by prolonging the time and changing the size of platinum electrodes, further highlighting the utility of the electrochemical protocol.

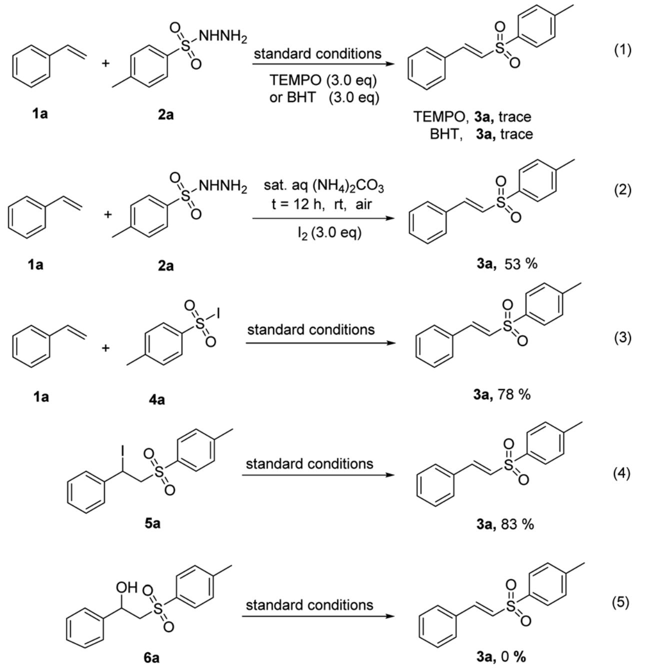
To understand the mechanism of this reaction, a series of preliminary mechanistic experiments were performed (Scheme 4). The reaction of **1a** and **2a** was inhibited in the presence of



Scheme 2 Scope of the reaction with sulfonyl hydrazides.[a,b] [a]Reaction conditions: the mixture of **1a** (0.5 mmol), **2** (1.0 mmol), n-Bu$_4$NI (10 mol%) in saturated (NH$_4$)$_2$CO$_3$ aqueous solution (5.0 mL) was electrolyzed at constant current (40 mA) in an undivided cell at room temperature for 3.0 hours, anode and cathode: Pt foil (1.0 × 1.5 cm^2). [b]Yields of isolated products.



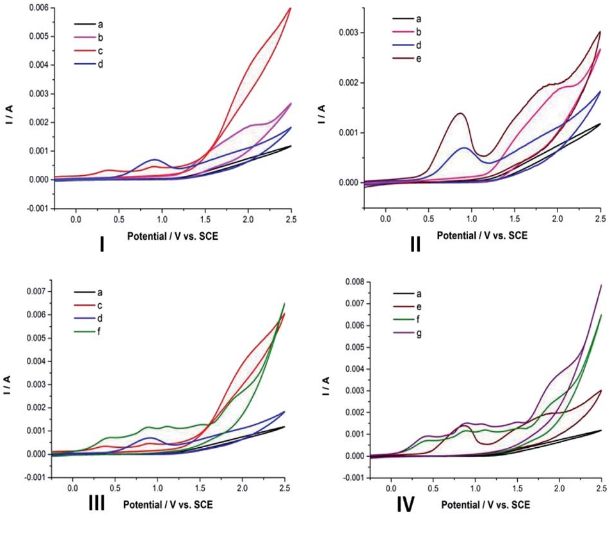
Scheme 3 Gram-scale electrochemical synthesis of **3a**.



Scheme 4 Preliminary mechanistic studies.

radical inhibitors, such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and 2,6-di-*tert*-butyl-4-methylphenol (BHT) (Scheme 4, eqn (1)) under standard conditions, which supported that the reaction presumably involved a radical pathway. To determine the involvement of molecular iodine, the reaction was carried out in the presence of I$_2$, the desired product **3a** was afforded in a 53% yield (Scheme 4, eqn (2)). It was proposed that I$_2$ produced by anode has an effect on the activation of the reaction. In addition, when 4-methylbenzenesulfonyl iodide **4a** was subjected to the reaction with **1a** under standard conditions, a 78% yield of **3a** was obtained (Scheme 4, eqn (3)). Similarly, direct synthesis of desired product **3a** from the β-iodosulfone **5a** under the standard conditions was also successful (Scheme 4, eqn (4)). But when β-hydroxysulfone **6a** was used as the starting material under the standard conditions, no target product **3a** was obtained (Scheme 4, eqn (5)). Thus, it was demonstrated that 4-methylbenzenesulfonyl iodide **4a** and β-iodosulfone **5a** could be active intermediates for this reaction and the involvement of β-hydroxysulfone **6a** as an intermediate was ruled out.

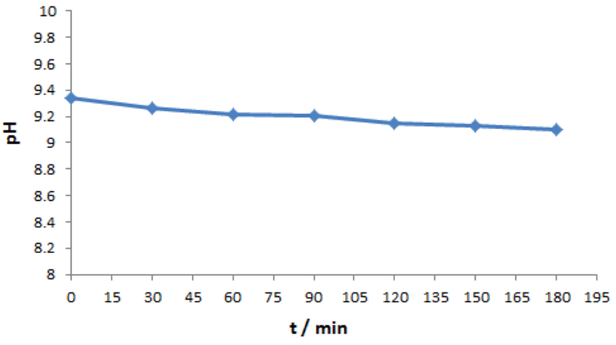
To gain more insight into this reaction mechanism, cyclic voltammetry (CV) experiments were carried out. As shown in Scheme 5, the oxidation peak of **1a** was observed at $E_p = 1.95$ V *vs.* SCE (Scheme 5(I), curve b).[8] Then, the CV of **2a** displayed two



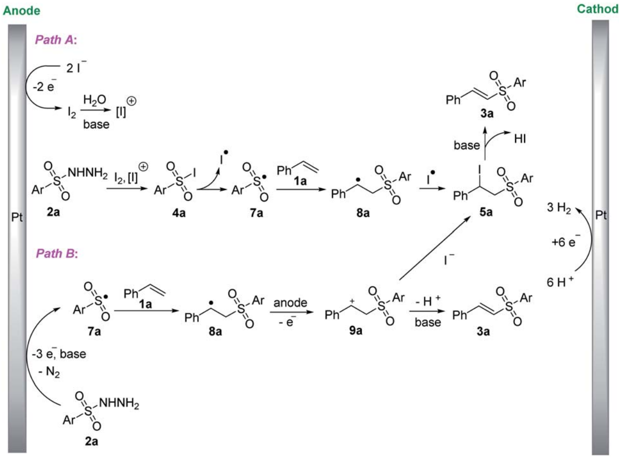
Scheme 5 Cyclic voltammetry experiments.[a] [a]Cyclic voltammograms of related compounds in sat. aq. (NH$_4$)$_2$CO$_3$, using a glassy carbon electrode as working electrode (d = 3 mm), a Pt wire as counter electrode, and a saturated calomel electrode (SCE) as a reference electrode, at 100 mV s^{-1} scan rate: (a) none; (b) **1a** (0.005 M); (c) **2a** (0.005 M); (d) n-Bu$_4$NI (0.001 M); (e) **1a** (0.005 M) and n-Bu$_4$NI (0.001 M); (f) **2a** (0.005 M) and n-Bu$_4$NI (0.001 M); (g) **1a** (0.005 M), **2a** (0.005 M) and n-Bu$_4$NI (0.001 M).

oxidation peaks at 0.36 V *vs.* SCE and 0.91 V *vs.* SCE (Scheme 5(I), curve c).[6b] These results showed that **2a** was oxidized preferentially than **1a** under the standard conditions. Additionally, we found that the pH of the reaction solution remained at 9.34–9.10 throughout the process (Scheme 6), which implied that the oxidation of **2a** could be promoted in basic acidic reaction conditions.[11] Next, the role of *n*-Bu_4NI was also studied. The anode potential of *n*-Bu_4NI was observed at 0.90 V *vs.* SCE (Scheme 5(I), curve d), which indicates that iodine ions (I^-) could be oxidized to molecular iodine (I_2).[6b,8,12] The CV result of **1a** and *n*-Bu_4NI mixtures showed no obvious new oxidation peaks (Scheme 5(II), curve e), which indicated that *n*-Bu_4NI did not affect compound **1a**. Intriguingly, the addition of *n*-Bu_4NI to **2a** led to two new oxidation peaks at 1.11 V *vs.* SCE and 1.52 V *vs.* SCE (Scheme 5(III), curve f), which indicated that sulfonyl hydrazide **2a** could be oxidized by I_2 or its derivatives in the electrolysis process.[13] Furthermore, in the mixture solution of **1a**, **2a**, and *n*-Bu_4NI, it did not significantly change the curve (Scheme 5(IV), curve g). Combined with one of the control experiments (Scheme 3, eqn (2)), it suggested that I_2 produced by the electrochemical process is involved in the reaction.

In light of these experimental results and previous works,[6,8,12–14] two possible mechanisms for this reaction are proposed in Scheme 7. In Path A, the iodide ions were oxidized to molecular iodine at the anode. Under the basic aqueous reaction conditions, molecular iodine can further form electrophilic iodine-containing species $[I]^+$. Then, the iodine-containing species (I_2, $[I^+]$) reacted with hydrazide **2a** to give the sulfonyl iodide **4a**, which was decomposed to generate sulfonyl radical **7a** and iodine radical. Subsequently, the sulfonyl radical **7a** added to styrene **1a** to afford the benzylic radical **8a**, followed by the reaction with iodine radical to form β-iodosulfone intermediate **5a.** Finally, β-iodosulfone intermediate **5a** was converted into the desired product **3a** through elimination of HI. While in Path B, hydrazide **2a** generated the corresponding sulfonyl radical **7a** *via* preferential deprotonation under the basic condition and three electron oxidation together with the release of molecular nitrogen. The sulfonyl radical **7a** then reacted with styrene **1a** to produce the benzylic radical **8a**, which was further oxidized to benzyl cation **9a** on the anode. The benzyl cation **9a** can generate **3a** directly through liberating H^+ or react with iodide anion to form β-iodosulfone **5a**, which can lead to **3a** formation through HI elimination.



Scheme 6 pH value during the process of the reaction.[a] [a]The pH value was measured every 30 minutes.



Scheme 7 Proposed mechanism.

Conclusions

We developed an efficient electrochemical method for the synthesis of (*E*)-vinyl sulfones from a variety of alkenes and sulfonyl hydrazides with a catalytic amount of iodide salt in water. The reaction proceeded smoothly to afford (*E*)-vinyl sulfones with good selectivities and yields in an undivided cell at room temperature under metal- and external oxidant-free conditions. A satisfactory gram-scale reaction showed the synthetic utility of this process. Further exploration of the synthetic applications is undergoing in our lab.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thank the Innovation Projects of Department of Education of Guangdong Province (2018KQNCX236, 2019KTSCX162), the Science and Technology Project of Guangdong Province (408-99000213), the Science and Technology Project of Shaoguang city (2018sn047, 2019sn055), Shaoguan University (408-9900416, 408-99000618), National undergraduate innovation and entrepreneurship project (201810576016), National Natural Science Foundation of China (21961002), and the emergency project of Gannan Medical University (YJ202027) for financial support.

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