



An efficient electrochemical synthesis of vinyl sulfones from sodium sulfinates and olefins



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ABSTRACT

An electrochemical conversion of olefins with sodium sulfinates into vinyl sulfones was described. The in situ electrogenerated I_2 could effectively promote this conversion to afford the target products in good to excellent yields at room temperature. Compared with the traditional thermo-chemical method, this electrochemical route was more convenient and efficient.

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1. Introduction

Vinyl sulfones are very important compounds in organic synthesis and pharmaceutical industry, which have been widely utilized as cysteine proteases inhibitors,¹ antibiotic TAN-1085,² HIV-1 integrase³ as well as other synthetic intermediates.^{4,5} To date, there are a number of available approaches for the synthesis of vinyl sulfones, such as transition-metal (Pd,⁶ Cu,⁷ Ce⁸ or Ag⁹) catalyzed, iodine catalyzed,^{10–12} and other synthetic ways.^{13–15}

Compared with the transition-metal-catalyzed method, iodine catalyzed reactions¹⁶ have their own peculiar advantages and characteristics. Therefore, they have attracted more and more attention in the past few years. Recently, the Lei's group¹¹ has reported a new method for the synthesis of vinyl sulfones from sulfonyl hydrazides and olefins catalyzed by I_2 in the presence of TBHP (*tert*-butylhydroperoxide) and acetic acid. However, the oxidative process requires the use of stoichiometric amount of hazardous oxidant TBHP and other additives. Taking the importance of vinyl sulfones into consideration, it is still a great demand to exploit simple and efficient methods for the synthesis of vinyl sulfones.

An electrochemical method has become a very useful mean in organic synthesis.¹⁷ Electrosynthesis could effectively avoid the use of hazardous or toxic oxidants and achieve oxidation and reduction reactions in mild electron-transfer conditions, demonstrating its advantages and environment friendly characteristics. Recently, we have been interested in organic electrosynthesis.¹⁸ As part of our

continuing study on electrosynthesis, herein we report a convenient and efficient electrochemical route for the synthesis of vinyl sulfones from sodium sulfinates and olefins.

2. Result and discussion

2.1. Influence of supporting electrolytes

In this study, we used styrene (**1a**) and sodium 4-methylbenzene sulfinate (**2a**) as model substrates to optimize electrolytic conditions. According to our previous experience, electrolytic results are related to supporting electrolytes, solvents, and electrode materials. The effect of supporting electrolytes was first examined. As shown in Table 1, supporting electrolytes have a great effect on the electrosynthesis. Under the same anion (I^-), different cations (K^+ , $n\text{-Bu}_4N^+$, NH_4^+ , and Na^+) led to different yields (Table 1, entries 1–4). For example, when KI was used as the supporting electrolyte, the target product 1-methyl-4-(styrylsulfonyl) benzene **3aa** was obtained with 53% yield. In the $n\text{-Bu}_4NI$ case, the electrolysis afforded a lower yield (31%), together with some by-products (such as 1,4-diphenylbutane) and unreacted styrene. Excitingly, the yield of **3aa** was remarkably increased to 85% and 90% when using NH_4I and NaI as the supporting electrolyte (Table 1, entries 3 and 4), respectively. At the present stage, we did not completely understand why the anion of supporting electrolytes could lead to such an unusual result. Moreover, when $NaCl$ or $NaBr$ was used as the supporting electrolyte, trace amount of **3aa** was detected. Particularly, **3aa** was not obtained at all when NaI supporting electrolyte was replaced by $NaOAc$ or $n\text{-Bu}_4NBF_4$ (Table 1,

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Table 1
Influence of supporting electrolytes on the electrosynthesis of vinyl sulfones^a

Entry	Anode–cathode	Supporting electrolyte	Solvent	Yield ^b (%)
1	C–Ni	KI	DMSO	53
2	C–Ni	<i>n</i> -Bu ₄ NI	DMSO	31
3	C–Ni	NH ₄ I	DMSO	85
4	C–Ni	NaI	DMSO	90
5	C–Ni	NaCl	DMSO	Trace
6	C–Ni	NaBr	DMSO	Trace
7	C–Ni	NaOAc	DMSO	0
8	C–Ni	<i>n</i> -Bu ₄ NBF ₄	DMSO	0

^a Reaction conditions: **1a** (1 mmol), **2a** (1.1 mmol), solvent (8 mL), supporting electrolyte (1.0 mol L^{−1}), undivided cell, electrolysis with constant current 50 mA for 1 h and then continuously stirring for 4 h at rt.

^b Yields were determined by GC–MS.

entries 7 and 8). These results indicated that the iodide anion was of great importance for the present electrosynthetic system. Among the examined supporting electrolytes, NaI exhibits the best result (Table 1, entry 4). In the present case, the supporting electrolyte could not only act as conducting salts but also participate in electrochemical reactions to produce reactive species. Therefore, the electrolytic results greatly depend on the property of supporting electrolytes.

2.2. Influence of solvents

Solvent was also a key factor. With DMF as the solvent, **3aa** was obtained in 69% yield, and sulfonamide and unreacted styrene were observed (Table 2, entry 1). The formation of the by-product sulfonamide indicated that DMF solvent took part in the reaction. When H₂O was chosen as the solvent, the yield of **3aa** was only 34% (Table 2, entry 3). This result may be attributed to the fact that H₂O could easily be electrolyzed to lower current efficiency. In the THF solvent, the solubility of NaI is very limited, which is not beneficial to the electrosynthesis (Table 2, entry 4). In addition, the reaction was extremely sluggish with CH₃OH or MeCN as the solvent (Table 2, entries 5 and 6), and styrene (**1a**) was almost quantitatively recovered. From Table 2, it could be seen that DMSO was the most suitable solvent for the present electrosynthetic system (entry 2).

Table 2
Influence of solvents on the electrosynthesis of vinyl sulfones^a

Entry	Anode–cathode	Supporting electrolyte	Solvent	Yield ^b (%)
1	C–Ni	NaI	DMF	69
2	C–Ni	NaI	DMSO	90
3	C–Ni	NaI	H ₂ O	34
4	C–Ni	NaI	THF	12
5	C–Ni	NaI	CH ₃ OH	Trace
6	C–Ni	NaI	MeCN	Trace

^a Reaction conditions as shown in Table 1.

^b Yields were determined by GC–MS.

2.3. Influence of cathode materials

Like Ni cathode, C, Al or Cu cathode could afford the target product **3aa** in excellent yields (Table 3, entries 1–4), indicating that these cathode materials were all suitable for this electrochemical process.

Table 3
Influence of cathode materials on the electrosynthesis of vinyl sulfones^a

Entry	Anode–cathode	Supporting electrolyte	Solvent	Yield ^b (%)
1	C–C	NaI	DMSO	91
2	C–Al	NaI	DMSO	89
3	C–Cu	NaI	DMSO	90
4	C–Ni	NaI	DMSO	92

^a Reaction conditions as shown in Table 1.

^b Yields were determined by GC–MS.

According to the experimental results (Tables 1–3), an electrochemical system, which is composed of NaI supporting electrolyte, DMSO solvent, Ni cathode, and graphite anode should be preferentially considered.

2.4. Electrosynthesis of vinyl sulfones from sodium sulfonates and olefins

In order to test the scope of the reaction, our investigation was extended to different olefins and sodium sulfonates under the optimized conditions. The results were summarized in Table 4.

Table 4
Electrosynthesis of vinyl sulfones from olefins and sodium sulfonates^a

1a-k	2a-f	3
3aa , 85%	3ba , 80%	3ca , 81%
3da , 84%	3ea , 78%	3fa , 83%
3ga , 86%	3ha , 89%	3ia , 80%
3ja , 70%	3ab , 84%	3bb , 81%
3cb , 83%	3db , 82%	3eb , 77%
3fb , 80%	3gb , 84%	3hb , 87%
3ib , 79%	3ac , 85%	3ad , 87%
3ae , 87%	3af , 78%	3ka , 0%

^a Reaction conditions as shown in Table 1. Isolated yields based on olefins.

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