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Electrochemical Decarboxylative Trifluoromethylation of *α, β*-Unsaturated Carboxylic Acids with CF_3SO_2Na

Fang-Yuan Li[a], Dian-Zhao Lin[a], Tian-Jun He[a], Wei-Qiang Zhong[a] and Jing-Mei Huang*[a]

Abstract: A new method for the synthesis of vinyl trifluoromethyl compounds from *α, β*-unsaturated carboxylic acids and CF_3SO_2Na has been developed. This electrochemical decarboxylative trifluoromethylation was found to be highly stereoselective and afforded products in good yields with wide substrate scope under metal-free and external chemical oxidant-free conditions.

Introduction

The incorporation of trifluoromethyl（CF_3）moiety into organic molecules can dramatically influence the latter's characteristics, owing to the unique properties of the trifluoromethyl group, such as the electronic properties, special size, lipophilicity, and metabolic stability.[1] As a consequence, CF_3-containing compounds widely exist in pharmaceuticals, agrochemicals, and materials.[2] Great synthetic interest has been devoted to developing efficient methods for the introduction of the CF_3 group into organic substrates. However, for the construction of C_{sp2}-CF_3 bonds, especially for the C_{vinyl}-CF_3 bonds,[3] fewer approaches are available compared with a variety of processes for the construction of C_{sp3}-CF_3 bonds. In addition, several CF_3 sources, for instance, Togni reagent,[4] Umemoto reagent,[5] Ruppert−Prakash reagent,[6] and the trifluoromethyl sulfinates (e.g. Langlois /Baran reagent),[7] have been explored for trifluoromethylation process. Due to their stabilities and commercial availabilities on a large scale, the trifluoromethyl sulfinates have been proved to be ideal trifluoromethyl donors for the protocol.

Countless methods have been applied to oxidize the trifluoromethyl sulfinates (CF_3SO_2M) to release trifluoromethyl radical ($\bullet CF_3$).[8] In particular, the application of the electrochemical technology to initiate trifluoromethyl radical is appealing due to its green and controllable characteristics. In 2002, Tommasino's group introduced their work on the trifluoromethylation of electron-rich aromatics and alkenes via electrochemical technology.[9] In this study, CF_3 radical was generated from the anodic oxidation of CF_3SO_2K. Subsequently, Baran's group chose $Zn(SO_2CF_3)_2$ as a source of trifluoromethyl radical and accomplished the trifluoromethylation of heteroarenes under electrochemical conditions in 2014 .[10] Further, the works on trifluoromethylative difunctionallization of alkenes by electrolysis of CF_3SO_2Na were disclosed by Cantillo,[11] Lin,[12] Lei,[13] Xu,[14] Pan,[15] and Kim,[16] respectively. Meanwhile, the electrochemical trifluoromethyl/cyclization of *N*-arylacrylamides with CF_3SO_2Na have also been demonstrated by Zeng, [17] Mo, [18] and Ackermann, [19] respectively.

Nowadays, decarboxylative cross-coupling reactions have emerged as an attractive approach for the construction of carbon−carbon bonds.[20] The decarboxylative cross-coupling of vinyl carboxylic acids with the Langlois reagent is envisioned as a promising process for the construction of C_{vinyl}-CF_3 bonds. In 2013, Maiti's group[21] reported a decarboxylative trifluoromethylation of cinnamic acids with Langlois reagent in the presence of $FeCl_3$ and $K_2S_2O_8$. Meanwhile, copper/silver-catalyzed or copper-catalyzed decarboxylative trifluoromethylation reaction using TBHP as an oxidant was disclosed by Duan[22] and Liu,[23] respectively. Later, I_2O_5-treated C_{vinyl}-CF_3 bonds construction was demonstrated by Liu and his co-workers[24] in 2014. It is noticed that all the reported methods had employed excess equivalents of oxidants, and heating was necessary to furnish the reaction. Therefore, the development of an environmentally benign method under the metal-free, external chemical oxidant-free conditions for this transformation is highly desirable.

In the past decade, electrochemistry has experienced a renaissance in the synthetic chemistry.[25, 26] However, the research reports on electrochemical decarboxylation cross-coupling of vinyl carboxylic acids to form new compounds are limited.[27] To the best of our knowledge, the electrochemical trifluoromethylation through decarboxylative cross-coupling of vinyl carboxylic acids and CF_3SO_2Na to form a new C_{vinyl}-CF_3 bond is still unknown. Based on our previous works in the organic electrochemistry,[27b, 28] herein we report the first efficient electrochemical decarboxylative trifluoromethylation of cinnamic acids with the Langlois reagent.

Results and Discussion

To start our investigation, *p*-methoxycinnamic acid (**1a**) and CF_3SO_2Na (**2**) were chosen as model substrates. Under constant current at 5 mA and using $LiClO_4$ as supporting electrolyte in an undivided cell, the reaction of **1a** and **2** afforded 81% yield of the desired product **3a** (Table 1, entry 1). In the absence of trifluoroethanol (TFE) or increase the amount of TFE to one equivalent in the reaction, a decreased yield was obtained (entries 2 and 3). Meanwhile, other additives, such as pivalic acid (PA), K_2CO_3, and $NaHCO_3$, gave the corresponding products in slightly

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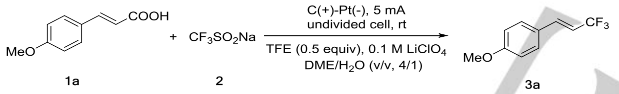
decreased yield (entries 4 and 5), while quite a similar yield was produced with HOAc as a reaction additive (entry 4). The yield decreased sharply to 16% in the absence of H_2O, as the solubility of sodium trifluoromethanesulfinate that is crucial for the reaction conversion is decreased (entry 6). Change of the proportion of H_2O and 1,2-dimethoxyethane (DME) disfavored this protocol (entries 7 and 8). The studies on the effect of solvent revealed that the yield of the product decreased sharply when DMSO or MeCN was used to replace DME (entries 9 and 10), while MeOH disfavored this reaction (entry 11). Only a slight decrease in the yield was observed in the solution of the mixture of THF and H_2O (entry 12). When a series of electrolytes (entries 13-16) were examined, it was found that the $LiClO_4$ was optimal for this transformation. Next, the effect of the electrode material was demonstrated. A comparable yield was obtained by replacing the carbon felt anode with carbon rod anode (entry 17), while a trace amount of target product was collected with the usage of platinum plate anode (entry 18). Both Ni foam cathode and carbon felt cathode showed lower reaction reactivity than the platinum plate cathode (entries 19 and 20). In the end, the endeavors to increase or decrease the operating current, such as 3 mA or 10 mA, caused a decrease in the product yield (entries 21 and 22). Predictably, no desired product could be detected without an electric current (entry 23).

Table 1. Optimization of the Reaction Conditions[a]



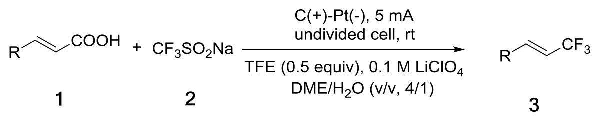
Entry	Variation from the standard conditions	Yield(%)[b]
1	none	81
2	in the absence of TFE	63
3	TFE (1.0 equiv)	68
4[c]	PA or HOAc instead of TFE	64 or 80
5	$NaHCO_3$ or K_2CO_3 instead of TFE	58 or 46
6	without H_2O	16
7	DME/H_2O (v/v, 5/1)	54
8	DME/H_2O (v/v, 3/1)	66
9	DMSO instead of DME	34
10	MeCN instead of DME	43
11	MeOH instead of DME	trace
12	THF instead of DME	72
13	n-Bu_4NClO_4 instead of $LiClO_4$	52
14	$NaClO_4$ instead of $LiClO_4$	69
15	n-Bu_4NBF_4 instead of $LiClO_4$	52
16	NH_4BF_4 instead of $LiClO_4$	56
17[d]	graphite rod anode	77
18[e]	platinum plate anode	trace
19[f]	Ni foam cathode	58
20	carbon felt cathode	43
21	10 mA instead of 5 mA, 4 h	56
22	2.5 mA instead of 5 mA, 16 h	62
23	no electric current	N.R.

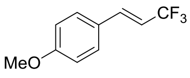
[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.6 mmol), DME/H_2O (v/v = 4/1, 5 mL), TFE (0.1 mmol), 0.1 M $LiClO_4$ as supporting electrolyte, anode: carbon felt (1 × 1.5 cm^2), cathode: Pt foil (1 × 1.5 cm^2), constant current (5 mA), undivided cell, room temperature, 8 h. TFE = Trifluoroethanol, DME = 1,2-dimethoxyethane. [b] Yield determined by ^1H NMR analysis using CH_3NO_2 as the internal standard, N.R. = no reaction. [c] Pivalic acid = PA. [d] Graphite rod (diameter: 0.5cm, height: 1.5 cm). [e] Platinum plate (1 × 1.5 cm^2). [f] Ni foam electrode (0.01 x 1 × 1.5 cm^3).

With the optimized conditions in hand, we proceeded to investigate the substrate generality and limitation of our reaction. As shown in Table 2, the reactions of a series of *α, β*-unsaturated carboxylic acids with CF_3SO_2Na proceeded smoothly and the desired products were obtained in moderate to good yields in most cases. For substrates bearing electron-donating groups on the aryl ring, such as OMe, 3,4-(-OCH_2O-), OC(=O)CH_3, and CH_3, this coupling reaction worked well to give the corresponding Products in the yields of 52-82% (**3a-3h**). A decrease in the yield was observed for the substrate bearing a *m/o*-OMe or *m/o*-CH_3 substituent compared to the substrate bearing a *p*-OMe or *p*-CH_3 substituent on the aryl ring, which implied that the steric effect has an influence on this protocol. It is found that halogen substituents could be well tolerated under the electrochemical conditions (**3i-3l**), which provides the opportunity for further derivatizations of the products. Meanwhile, cinnamic acids with electron withdrawing groups (COOH, CN, CF_3) on the phenyl ring were still suitable for this process and gained desired products in moderate yields (**3m-3p**).It was noteworthy that the substrate with *p*-CHO on the aromatic ring could avoid excessive oxidation under the electrochemical conditions and provided the desired product in 48% of yield (**3q**). However, only a trace amount of the desired product for the substrate containing NO_2 group could be detected in the reaction (**3r**), which was rationalized by the reduction of the nitro group on the cathode. In addition, nitrogen- and sulfur-containing heterocyclic analogues gave desired products in the yields of 43% (**3s**) and 53% (**3t**), respectively. Finally, the 1.2 mmol-scale reaction was implemented. When the reaction with **1e** (1.2 mmol) was carried out, the corresponding product **3e** was collected in the yield of 70% (see the Supporting Information for details). Notably, the trifluoromethylation reaction was also found to be highly stereoselective, and in most cases, the *E/Z* ratios of the CF_3-functionalized alkenes were determined as 99:1 or even higher.

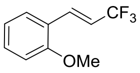
In an attempt to understand the reaction mechanism, some control experiments were carried out (Scheme 1). First, with the addition of a radical scavenger, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), 1,1-diphenylethene or 2,6-di-tert-butyl-4-methylphenol (BHT) (Scheme 1, eq 1 and eq 2), only a trace amount of desired product was obtained, indicating the reaction presumably involved a radical pathway. To our delight, in the reaction with BHT (Scheme 1, eq 2) as a radical scavenger, the BHT−CF_3 adduct was detected by GC-MS (see the Supporting Information for details), which implied that CF_3 radical intermediate was prod-

Table 2. Substrate Scope of *α, β*-Unsaturated Carboxylic Acids [a]

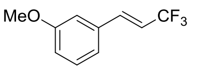




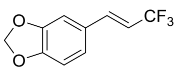
3a 80% 8h[b] 99/1[c]



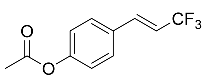
3b 68% 8h 99/1



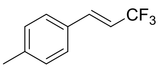
3c 52% 9h 97/3



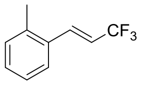
3d 70% 8h >99/1



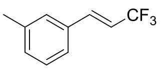
3e 82% 9h >99/1



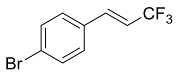
3f 72% 9h >99/1



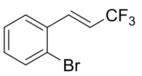
3g 68% 9h 98/2



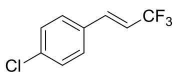
3h 61% 9h 95/5



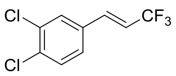
3i 69% 9h 99/1



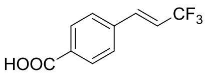
3j 54% 9h 97/3



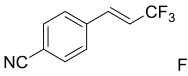
3k 51% 8h >99/1



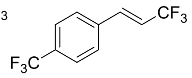
3l 45% 9h 97/3



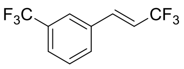
3m 50% 9h >99/1



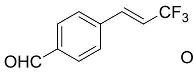
3n 66% 9h >99/1



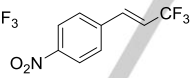
3o 42% 12h >99/1



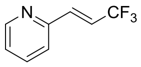
3p 51% 12h >99/1



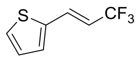
3q 48% 11h 99/1



3r trace



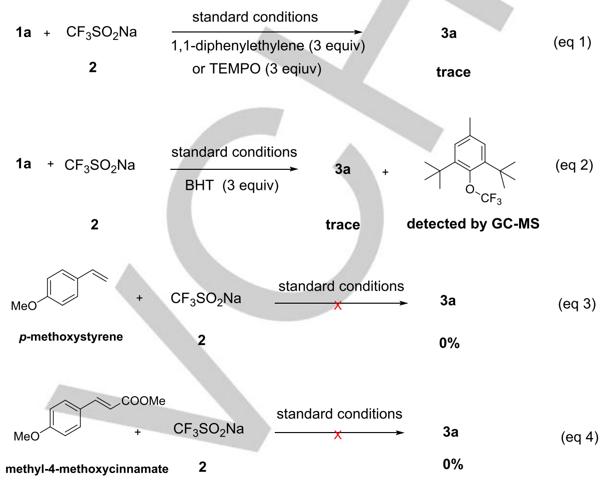
3s[d] 43% 11h 99/1



3t 53% 6.5h 85/15

[a] Reaction conditions: **1** (0.2 mmol), **2** (0.6 mmol), DME/H_2O (v/v = 4/1, 5 mL), TFE (0.1 mmol), 0.1 M $LiClO_4$ as supporting electrolyte, anode: carbon felt (1 × 1.5 cm^2), cathode: Pt foil (1 × 1.5 cm^2), constant current (5 mA), undivided cell, room temperature, isolated yield. [b] Reaction time, indicated by TLC. [c] Ratio of *E/Z* was determined by ^{19}F NMR and ^1H NMR of the crude product mixture. [d] THF instead of DME, NH_4BF_4 instead of $LiClO_4$.

uced in this transformation. Meanwhile, when *p*-methoxy-styrene took the place of *p*-methoxycinnamic acid as the coupling partner under the standard conditions (Scheme 1, eq 3), no desired product was produced, suggesting that *p*-methoxystyrene was not the reaction intermediate. Moreover, when methyl-4-methoxy-cinnamate and **2** were subjected to this protocol, (Scheme 1, eq 4), the expected product was not detected, which demonstrated that the carboxylic group was necessary for the reaction. Cyclic voltammetry (CV) experiments were also implemented. As shown in Figure 1, the oxidation peak of CF_3SO_2Na was observed at 0.98 V vs SCE, while the oxidation peak of the cinnamic acid **1a** was observed at 1.32 V vs SCE. These results indicated that CF_3SO_2Na might be oxidized by anode before **1a** to produce a CF_3 radical.



Scheme 1. Control Experiments

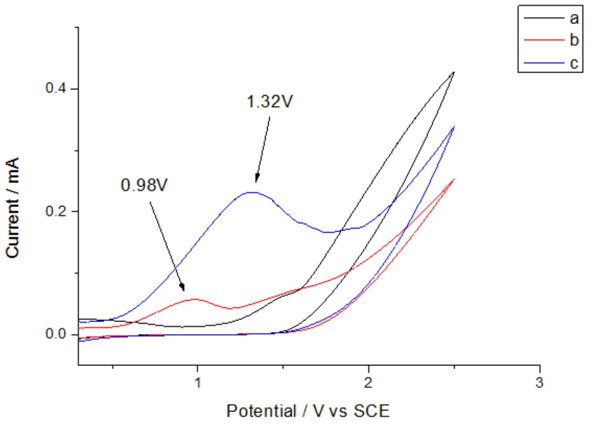
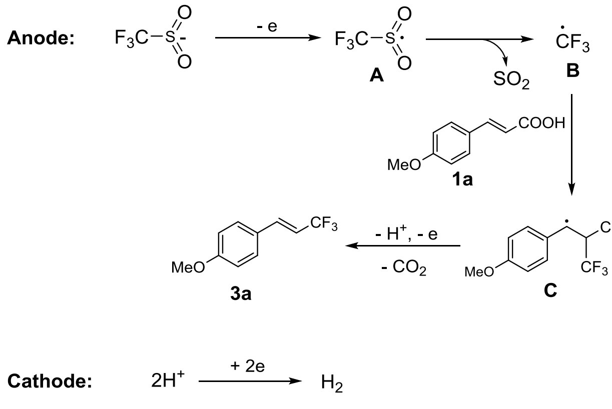


Figure 1. Cyclic voltammograms of 0.1 M $LiClO_4$ solution in DME/H_2O (v/v, 4:1), at room temperature. (a) none; (b) sodium trifluoromethanesulfinate (0.005 M); (c) *p*-methoxycinnamic acid (0.005 M). The voltammogram was obtained with Pt wire as auxiliary electrode and a saturated calomel electrode (SCE) as a reference electrode. The scan rate was 0.1 V/s on a platinum disk electrode (d = 2 mm).

Based on the mechanistic investigations above and the precedent reports,[10, 27a] a plausible radical-based pathway for this process is proposed, as depicted in Scheme 2. The intermediate **A** is generated by the oxidation of sodium trifluoromethanesulfinate on the anodic electrode and goes through rapid cleavage to form the fluoroalkyl radical **B**. Subsequently, this highly active radical **B** reacts with **1a** to give the radical species **C**, which is easy to be decarboxylated to furnish the desired product **3a** under the reaction conditions.



Scheme 2. Proposed Reaction Mechanism

Conclusions

In summary, an electrochemical decarboxylative trifluoromethyllation of cinnamic acids with the Langlois reagent to synthesize vinyl trifluoromethyl compounds has been developed. With a wide substrate scope and an excellent functional-group tolerance, this protocol proceeds smoothly under ambient conditions and refrains from using any metal and chemical oxidants. Mechanism insights reveal that this reaction goes through a radical pathway.

Experimental Section

Synthesis of (*E*)-1-methoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (3a)

Into a round bottom flask, *p*-methoxycinnamic acid **1a** (0.2 mmol, 1.0 equiv), Langlois reagent **2** (0.6 mmol, 3.0 equiv), and trifluoroethanol (TFE) (0.1 mmol, 0.5 equiv) were dissolved in 5 mL 1,2-dimethoxyethane/H_2O (v:v = 4:1) with $LiClO_4$ (0.1 M) as an electrolyte. The resulting solution was electrolyzed with a carbon felt anode (1 × 1.5 cm^2) and a Pt foil cathode (1 × 1.5 cm^2) under a constant current (5 mA) at room temperature for 8 h. After the electrolysis, the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated in *vacuo*. The resulting mixture was purified by silica gel column chromatography to afford the desired product **3a**.

Acknowledgements

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Keywords: decarboxylation • electrochemistry • external chemical oxidant-free • metal-free• trifluoromethylation

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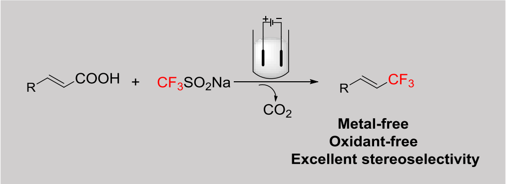

The electrochemical decarboxylative trifluoromethylation of *α, β*-unsaturated carboxylic acids with Langlois reagent was disclosed. The reaction refrained from using metal and external oxidants and afforded the corresponding products in moderate to good yields with a wide range of functional groups tolerated under ambient conditions. In most cases, the *E/Z* ratios of the CF_3-functionalized alkenes were determined as 99:1 or even higher.

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Electrochemical Decarboxylative Trifluoromethylation of *α, β*-Unsaturated Carboxylic Acids with CF_3SO_2Na