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Transition Metal-Free Difunctionalization of C−C Bond with Sodium Sulfinates and Water Leading to (*E*)-1-Phenyl-4-sulfonylbut-1-enes

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Abstract. Without using any transition metal and base, an eco-friendly, practical and economical protocol has been established for the one-pot synthesis of diverse (*E*)-1-phenyl-4-sulfonylbut-1-enes from easily accessible starting materials. This strategy features a wide substrate scope, tolerates a broad range of functional groups, employs a less expensive oxidant, is operationally simple, and can be easily scaled-up.

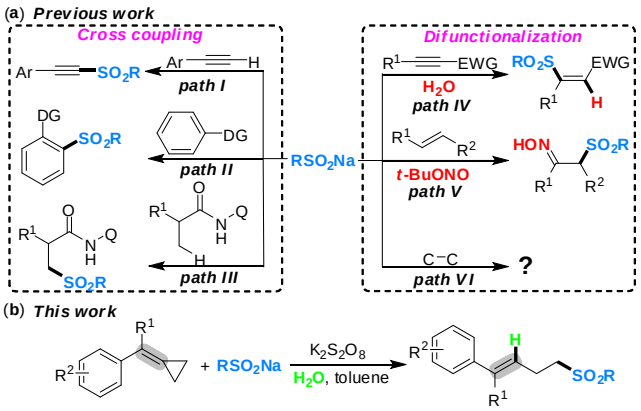
Keywords: difunctionalization; transition metal-free; sodium sulfinates; MCPs; (*E*)-1-phenyl-4-sulfonylbut-1-enes

Introduction

Carbon−carbon σ-bonds (C−C) are a class of common chemical bonds with high stability. Recently, the activation of carbon−carbon σ bonds has emerged as a useful strategy for constructing complex molecular skeletons in a facile manner,[1] and numerous elegant carbon−carbon σ-bond activation strategies have been developed for building new carbon−carbon bonds or carbon−heteroatom bonds. Recently, a variety of effective carbon−carbon σ-bond activation strategies, including oxidative cleavage,[2] the use of directing chelating groups,[3] and the cleavage of functional substrates bearing ester,[4] carboxyl,[5] carbonyl,[6] hydroxyl,[7] cyano,[8] or oxime[9] groups, have been developed, and most of these strategies require the use of transition metals (TMs), such as Ir, Pd, Ru and Rh. However, it would be highly attractive if these transformations could be achieved under transition metal-free conditions, as this would provide a simpler and greener option.

Three-membered carbocyclic compounds, especially methylenecyclopropanes (MCPs), are highly strained rings with high reactivity, but they are easily accessible (See S2.1 in Supporting Information), and are thus important raw materials in organic synthesis.[10] Herein, we develop a new carbon−carbon σ-bond activation strategy for the selective synthesis of (*E*)-1-phenyl-4-sulfonylbut-1-ene architectures by the transition metal- and base-free hydroxysulfonylation of carbon−carbon σ-bonds in methylenecyclopropanes with sodium sulfinates and water.

Sodium sulfinates, as readily accessible salts with high activity, are widely used in organic synthesis and pharmaceutical chemistry.[11-16] Therefore, a series of interesting transformations were developed by using sodium sulfinates as the sulfonyl source or alkyl source (usually aryl groups were afforded by desulfinylation).[11] Recently, many chemists have reported sulfonylation methods for cross-coupling reactions and difunctionalization reactions by utilizing sodium sulfinates as the sulfonyl source. For couplings with C−X,[12] a variety of C−X species, such as C−halogen, C−N_2BF_4, C−OTf, C−COOH and C−$B(OH)_2$, have been utilized. In 2011, Maloney and co-workers[12a] reported the cross-coupling reaction between chloropyridines and sodium sulfinates for accessing sulfonylated pyridine moieties. For couplings with C−H, a variety of diverse C−H bonds, including C(sp)−H bonds,[12b] C(sp^2)−H bonds[13] and C(sp^3)−H bonds,[14] could smoothly undergo the cross-coupling sulfonylation (Scheme 1a, paths I−III). Interestingly, sodium sulfinates could also be employed for the sulfonylation and difunctionalization of unsaturated bonds, including carbon−carbon triple bonds[15] and carbon−carbon double bonds.[16] In 2016, He's group[15a] presented the 1,2-difunctionalization of alkyne with sodium sulfinates and water under transition metal-free and additive-free conditions (Scheme 1a, path IV). Li's group[16a] reported the copper-catalysed 1,2-difunctionalization of alkenes with *tert*-butyl nitrite and sodium sulfinates for the synthesis of α-sulfonylethane oximes (Scheme 1a, path V). However, the difunctionalization of saturated carbon−carbon σ-bonds with sodium sulfinates is lacking (Scheme 1a, path VI).[17]



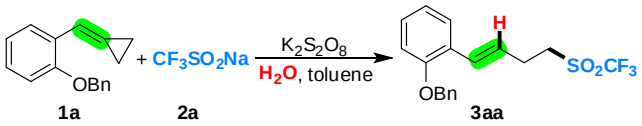
Scheme 1. Sulfonylation Reactions of Sodium Sulfinates

Results and Discussion

Firstly, the reaction between 1-(benzyloxy)-2-(cyclopropylidene-methyl)benzene (**1a**) and sodium trifluoromethanesulfinate (**2a**) was selected to screen the best conditions. After a series of investigations, the best yield of (*E*)-1-(benzyloxy)-2-(4-(trifluoromethylsulfonyl)but-1-enyl)benzene **3aa** (82%) was achieved using **1a** (0.2 mmol), **2a** (0.4 mmol, 2 equiv), and $K_2S_2O_8$ (0.4 mmol, 2 equiv) in toluene (2 mL) under 80 °C for 48 hours. To our surprise, the oxidants played an important role in assembling 4-sulfonylbut-1-enes **3aa**, as only trace yields were obtained in the presence of 1,4-benzoquinone (BQ) (entry 2), potassium peroxomonosulfate (oxone) and *tert*-butyl hydroperoxide (TBHP, 5.0 M in decane) (entry 3 and entry 4). Reducing the amount of $K_2S_2O_8$ from 2 equiv to 1 equiv resulted in a significantly lower yield of target product **3aa** (entry 5). No obvious increase in the product yield was obtained when 3 equiv of $K_2S_2O_8$ was utilized (entry 6). Subsequently, a series of other solvents, including dioxane, THF, CH_3CN, DMF and DMSO, were tested in the transformation, and the results showed that toluene was the best solvent. Next, the reaction temperature was investigated. The reaction yields decreased when the difunctionalization was performed at 60 °C or 100 °C (entries 12-13). Not all of **3aa** was consumed at a lower temperature, and a small portion of **3aa** decomposed at a higher temperature. Only a 59% yield of the ring-opened product was obtained when the transformation proceeded for 24 h (entry 14). Gratifyingly, the difunctionalization could occur smoothly in an air atmosphere and afforded (*E*)-4-sulfonylbut-1-ene **3aa** in 78% yield (entry 15). We also tested effect of the amount of H_2O, and the results showed that 4 equiv. of H_2O afforded the best result (entry 1 *vs.* entries 16−17). Subsequently, we were pleased to find that the reaction on a 1 g (4.24 mmol) scale of MCP **1a** successfully afforded the desired product in good yield (entry 18).

With the standard reaction conditions in hand, the scope of the substrates was investigated with respect to both MCPs **1** and sodium sulfinates **2a** (Table 2).

Table 1. Screening of optimal reaction conditions[a)]



Entry	Variation from the standard conditions	Isolated yield (%)
1	none	82
2	BQ instead of $K_2S_2O_8$	10
3	Oxone instead of $K_2S_2O_8$	12
4	TBHP instead of $K_2S_2O_8$	0
5	$K_2S_2O_8$ (1 equiv)	55
6	$K_2S_2O_8$ (3 equiv)	83
7	Dioxane instead of toluene	75
8	THF instead of toluene	31
9	CH_3CN instead of toluene	15
10	DMF instead of toluene	trace
11	DMSO instead of toluene	trace
12	At 60 °C	68
13	At 100 °C	77
14	For 24 h	59
15	Under air atmosphere	78
16	H_2O (2 equiv)	75
17	H_2O (6 equiv)	60
18[b)]	none	74

[a)] Unless otherwise specified, the reactions were carried out in the presence of **1a** (0.2 mmol), **2a** (2 equiv, 0.4 mmol), $K_2S_2O_8$ (2 equiv, 0.4 mmol), water (4 equiv, 0.8 mmol) and toluene (2 mL) at 80 °C under Ar atmosphere for 48 h. [b)] (1.0 g, 4.24 mmol) and solvent (10 mL) for 96 h.

A variety of substituted MCPs were first reacted with sodium trifluoromethanesulfinate (**2a**). To our delight, a series of MCPs (**1a**−**k**) with one aryl group at the terminal carbon of the double bond (R^1 = H) could successfully undergo the difunctionalization and give corresponding products **3** in moderate to good yields (products **3aa**−**ka**). The transformation tolerated both electron-donating and electron-withdrawing substituents on the aryl rings. The electronic and steric effects had almost no influence on the difunctionalization according to the reaction yields. To our surprise, MCPs with an unsubstituted Ph group were also suitable for this reaction and gave the difunctional product in 65% yield (**3ka**). However, the reaction did not take place as it did when using methylenecyclobutane **1l** (a four-membered carbocyclic substrate) as the substrate under standard conditions (**3la**). The MCP (**1m**) with an aryl group and a methyl group at the terminal carbon of the double bond (R^1 = Me) failed to generate target product **3ma**. Interestingly, the MCPs **1n**−**s** with two aryl groups at the terminal carbon of the double bond (R^1 = Ar) were suitable substrates under the optimal conditions in the presence of sodium sulfinates **2a**. The MCPs with the same two aryl groups, including aryl rings with

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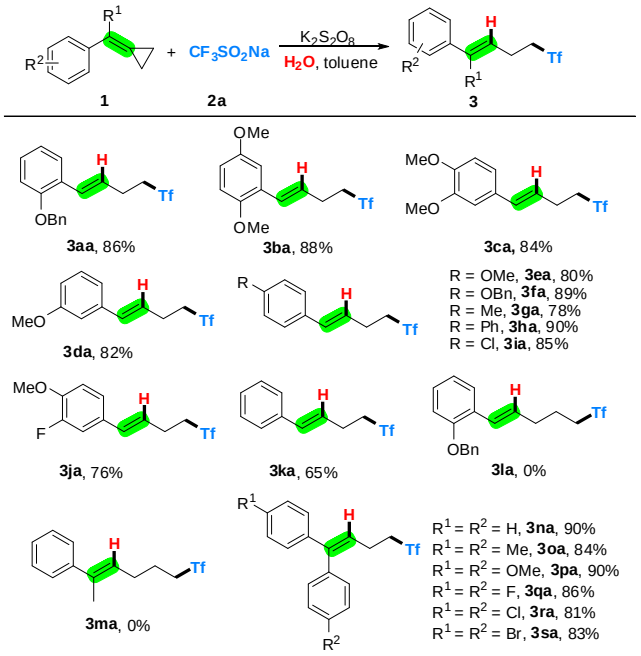
methyl, methoxy, fluoro, chloro and bromo substituents at the *para*-positions, were compatible with this reaction system (products **3na**–**sa**).

Table 2. Difunctionalization of MCPs (**1**) with sodium trifluoromethanesulfinate (**2a**) and water [a)]

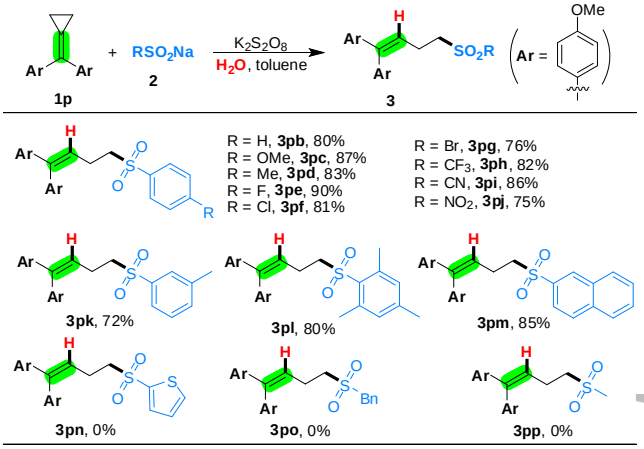


[a)] All reactions were carried out in the presence of **1** (0.2 mmol), **2a** (2 equiv, 0.4 mmol), oxidative (2 equiv, 0.4 mmol), water (4 equiv, 0.8 mmol) and solvent (2 mL) at 80 °C under Ar atmosphere for 48 h; isolated yields are reported.

As shown in Table 3, we next set out to investigate the scope of sodium sulfinates (**2**) in the presence of MCP **1p**, $K_2S_2O_8$, H_2O, and toluene. We were pleased to find that this difunctionalization could be applied to a wide range of sodium sulfinates **2b**–**m**, including substituted sodium arylsulfinates (**2b**–**l**) and sodium naphthylsulfinate (**2m**). Notably, sodium sulfinates **2** bearing an electron-donating group or an electron-withdrawing group on the aromatic ring were all suitable for the difunctionalization reaction (**3pc**–**pk**). Moreover, sodium mesitylsulfinate (**2l**), a tri-substituted aryl sulfinate, also afforded the corresponding product in good yield (**3pl**). Sodium 2-naphthylsulfinate (**2m**), a sterically hindered sodium sulfinate, also reacted smoothly with MCPs **1p** to provide the target product in 85% yield (**3pm**). Unfortunately, sodium heteroaromatic sulfinate **2n** and sodium aliphatic sulfinates **2o**–**p** did not afford the corresponding products (**3pn**–**pp**).

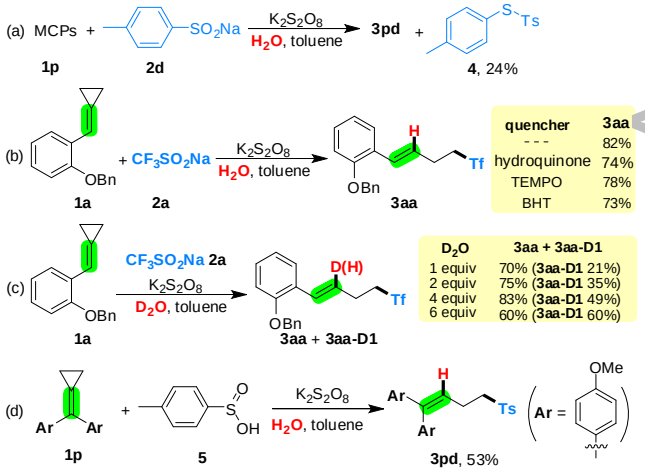
To investigate the mechanism of this difunctionalization reaction, a series of control experiments were performed (Scheme 2). Subjecting of **1p** with **2d** to the standard conditions could produce the desired product **3pd** along with 4- methylbenzenesulfonothioate **4** in 24% yield (Scheme 2a).[13f] The ring-opening reactions carried

Table 3. Difunctionalization of MCP (**1p**) with sodium sulfinates (**2**) and water [a)]



[a)] All reactions were carried out in the presence of **1p** (0.2 mmol), **2** (2 equiv, 0.4 mmol), oxidative (2 equiv, 0.4 mmol), water (4 equiv, 0.8 mmol) and solvent (2 mL) at 80 °C under Ar atmosphere for 48 h; isolated yields are reported.

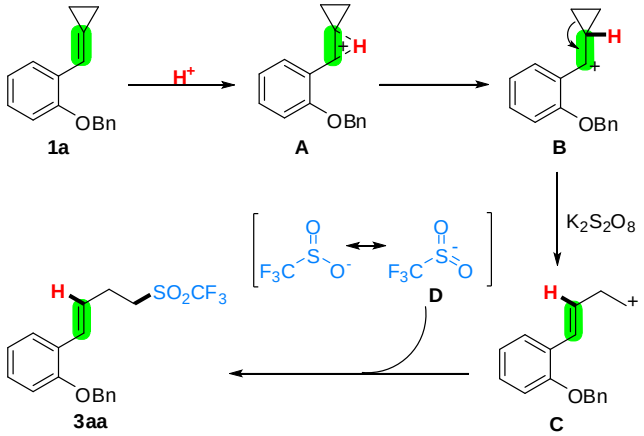
out in the presence of hydroquinone, TEMPO (2,2,6,6-tetramethylpiperidine nitroxide) or BHT (butylated hydroxytoluene) as radical scavengers provided the target product in good yields (Scheme 2b). These results suggested that the difunctionalization did not proceed through a free radical pathway. Next, control experiments to determine the source of the newly introduced hydrogen atoms were conducted. The difunctionalization of **1a** in the presence of 1 equiv of D_2O gave ring-opened product **3aa** in 70% yield with 21% of the newly introduced hydrogen atom being deuterated. The deuterium incorporation increased as the amount of D_2O was increased, which indicated that the hydrogen atom of the newly formed C–H bond was from the water (Scheme 2c). The reason for only partial deuterium incorporation was that the sodium sulfinate and the solvent containing residual water. The reaction between MCP **1p** and 4-methylbenzenesulfinic acid **5** carried out under



Scheme 2. Control Experiments.

standard conditions resulted in a lower yield of product **3pd** compared to the reaction using sodium *p*-tolylsulfinate **2d**. The reason was maybe that the acidity was inappropriate for this reaction (Scheme 2d).

Based on related reports and presented experimental results,[10,15a,16,17] we propose a possible mechanistic pathway (Scheme 3). First, the electrophilic addition of a proton (generated from hydrolysis of H_2O under the action of $K_2S_2O_8$) to the C–C double bond in MCP **1a** provides onium ion intermediate **A**, which generated first when the cation attacks the carbon-carbon double bond or carbon-carbon triple bond.[15a,17] Then, benzyl carbocation intermediate **B**, which is stablized by the aryl group, is formed through the ring opening of onium ion **A**. Next, intermediate **B** undergoes a ring-opening process to give (*E*)-4-(2-(benzyloxy)phenyl)but-3-en-1-ylium **C** under the oxidative action of $K_2S_2O_8$. Based on the steric hindrance of the aryl group, the *trans* double bond is more stable and more easily formed. Finally, sulfonyl anion **D**, generated from sodium sulfinate **2a**, nucleophilically attacks alkyl carbocation intermediate **C** to afford (*E*)-4-sulfonylbut-1-ene **3aa**. Because the nucleophilicity of the sulfonyl anion is much higher than that of the aryl group, alkyl carbocation intermediate **C** undergoes sulfonylation instead of intramolecular cyclization with the aryl group.



Scheme 3. Possible Mechanism.

Conclusion

In summary, we have developed the first example of the difunctionalization of C–C *σ*-bonds in MCPs with sodium sulfinates and H_2O for the efficient synthesis of various functionalized (*E*)-4-sulfonylbut-1-enes. This strategy proceeds through a proton addition, ring-opening and sulfonylation sequence and is a green and simple method for constructing (*E*)-4-sulfonylbut-1-ene skeletons with a broad substrate scope. Additionally, the results of the kinetics experiments revealed that the hydrogen atom of the newly formed C–H bond comes from the water. Further studies on the development of a difunctionalization strategy for C–C *σ*-bonds are currently underway in our laboratory.

Experimental Section

Typical Experimental Procedure for the the Radical Coupling Reaction:

To a Schlenk tube were added MCPs **1** (0.2 mmol), sodium sulfinates **2** (2 equiv, 0.4 mmol), $K_2S_2O_8$ (2 equiv, 0.4 mmol) and toluene (2 mL). Then the tube was stirred at 80 °C under Ar atmosphere for the indicated time until complete consumption of starting material as monitored by TLC analysis. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by silica gel flash column chromatography (hexane/ethyl acetate = 20 : 1 to 10 : 1) to afford the desired products **3**.

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