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Regioselective and stereoselective sulfonylation of alkynylcarbonyl compounds in water†

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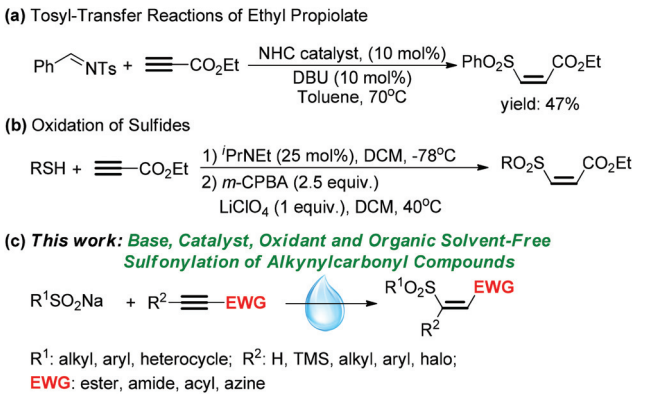
With water as the reaction medium, an efficient protocol has been developed for the synthesis of *Z*-β-sulfonyl-α,β-unsaturated carbonyl products *via* water-promoted sulfonylation of alkynylcarbonyl compounds with sodium sulfinates. This strategy could effectively avoid the use of toxic organic solvents, catalysts and additives. This method features a wide substrate scope with a broad range of functional group tolerance, utilizes easily available starting materials, can be scaled-up, and is operationally simple.

Introduction

β-Sulfonyl-α,β-unsaturated carbonyl compounds are valuable structural units in biologically active molecules[1] and serve as versatile synthetic precursors[2] for a diverse range of chemical transformations that produce pharmaceutical and industrially important organic compounds. New strategies for the facile synthesis of stereo-challenging β-sulfonyl-α,β-unsaturated carbonyl compounds remain a considerable focus of research. Selective access to either the *E*- or *Z*-isomer of a β-sulfonyl-α,β-unsaturated carbonyl compound is often the decisive factor in the success of any β-sulfonyl-α,β-unsaturated carbonyl compound synthesis method. Among the routes for the synthesis of β-sulfonyl-α,β-unsaturated carbonyl compounds, selective preparation of *E*-isomers has been well established,[2c,3] while the corresponding methods to access thermodynamically less favorable *Z*-isomers remain a challenge. One method involves the synthesisof *Z*-β-sulfonyl enoates through $B(OH)_3$-promoted sulfonylation of propargylic esters in the presence of irritant Bu_4NHSO_4 as a phase transfer catalyst in aqueous-tetrahydrofuran.[4] The other route involves the use of *N*-tosylimines to react with propargylic esters by using an expensive NHC catalyst, but only one example (ethyl 3-tosylacrylate) was presented, and alkyl aldimines were not included in this method (Scheme 1a).[5] In the third route, Downey *et al.* treated aryl and aliphatic thiols with propargylic esters to form *Z*-β-thioenoates, which were then treated with *m*-CPBA and $LiClO_4$ to form *Z*-β-sulfonyl enoate compounds (Scheme 1b).[6]



Scheme 1 Synthesis of *Z*-β-sulfonyl-α,β-unsaturated carbonyl compounds.

However, low stereoselectivity and the use of hazardous $LiClO_4$ have limited the application of this method.

Recently, significant progress has been made in the development of catalytic reactions in the aqueous phase.[7] Water promotes or accelerates successfully these organic transformations and also serves as excellent supporting medium with numerous advantages including the ease of product isolation, nontoxicity, non-flammability, high heat capacity and redox stability.[8] Several factors, such as hydrophobicity, hydrogen-bonding, polarity and acidity contribute to the rate-enhancing effect of water. Continuing with our interest in alkyne chemistry,[9] we focused our attention to the development of a new method for the synthesis of *Z*-β-sulfonyl-α,β-unsaturated carbonyl compounds, and we now report the results of our investigation, water-mediated sulfonylation of alkynylcarbonyl compounds with sodium sulfinates (Scheme 1c). This approach offers a valuable alternative compared to the above-mentioned methods: (i) sodium sulfinates are versatile and

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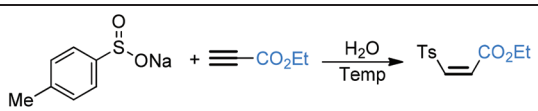
readily available intermediates in organic synthesis;[10] (ii) no catalysts or hazardous reagents are used. A mechanistic study suggests that the sulfonylation reaction proceeds *via* a water-promoted anti-selective addition of alkynylcarbonyl compounds, which leads to high *Z*-selectivity.

Results and discussion

To test the possibility of our envisioned method, commercially available 4-methylbenzenesulfinate **1a** was selected as a SO_2^- source due to the ease of converting sodium 4-methylbenzenesulfinate into sulfonyl anions in water. When **1a** was treated with 1 equiv. of ethyl propiolate **2a** in water at room temperature under air, a 14% yield of 3-tosylacrylate **3aa** based on 16% conversion of the starting material **1a** was obtained after 24 h. We found that the formation of **3aa** was more favorable at elevated temperatures (Table 1, entries 2 and 3). However, increasing the temperature to 80 °C has a negative impact on the reaction, resulting in fast hydrolysis of ethyl propiolate **2a** and 3-tosylacrylate **3aa** (entry 4). Significantly, employment of an excess amount of **2a** was found to provide the desired sulfonylated product **3aa** in good yield within a very short reaction time (entries 5–7). A nearly quantitative sulfonylation yield (98%) was obtained when the amount of ethyl propiolate reached 3.5 equiv. (entry 7). Concentration screening (entries 8 and 9) revealed that when the reaction was carried out at a concentration of 0.2 M, the reaction time could be shortened to 20 min and the yield increased to 100% (Table 1, entry 8). The reaction of **1a** with **2a** in the presence of catalytic amounts of acetic acid had no significant effect on yield, rate or selectivity (entry 10). Conducting the reaction in a Schlenk tube did not affect the reaction yield (entry 11). We were pleased to observe that all of the conditions that we tested resulted in the formation of *Z*-tosylacrylate in high stereoselectivity, establishing the feasibility of our proposed sulfonylation process. Mild reaction conditions, shorter reaction times, cost-effectiveness, operational simplicity, excellent yields and high stereoselectivity make this transformation an alternative method for the straightforward preparation of numerous *Z*-β-sulfonyl enoates. Within the set of previous methods highlighted herein, a solution was offered to this problem in the form of a novel, mild and green alternative for this key transformation.

With the optimal system in hand, we examined the scope of sodium sulfinate substrates with ethyl propiolate **2a** as illustrated in Table 2. To our delight, the current reaction system was suitable for a wide range of aryl sodium sulfinates (Table 2, **3aa–3pa**). No matter whether the benzene ring of aryl sodium sulfinate was substituted with either a sterically hindered, electron-donating or electron-withdrawing group, all of them delivered the desired products in good to excellent yields and with an excellent range of *Z*/*E* ratios from 12 : 1 to 28 : 1 (based on the analysis of ^{1}H NMR spectra). Importantly, a variety of functional groups, such as methyl, alkoxyl (OMe and OCF_3), amide, halide (F, Cl, Br and I), trifluoromethyl, cyano and nitro groups were all well tolerated. The reactions of di- and tri-substituted sodium benzenesulfinates gave the desired products in 89% (**3oa**, *Z*/*E* 10 : 1) and 95% (**3pa**, *Z*/*E* 12 : 1) yields, respectively. Polycyclic and heteroaromatic substituted sodium sulfinates could also be transformed into the corresponding products in good to excellent yields as well as high *Z*/*E* ratios (**3qa** and **3ra**). When aliphatic sodium sulfinate substrates were employed for the transformation, the corresponding products were obtained in 81–83% yields (**3sa–3ua**). More importantly, the synthesis of **3aa** was conducted on a ~2.41 g scale at a higher concentration (95% yield on a

Table 1 Optimization of reaction conditions[a]

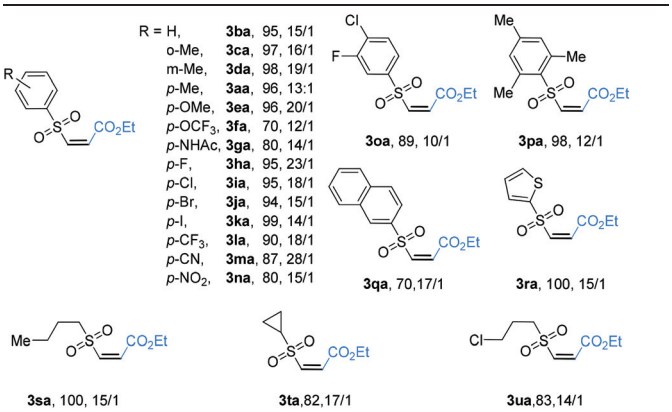


1a **2a** **3aa**

Entry	Equiv. of **2a**	Temp.	Time	Yield[b,c]	*E*/*Z*[b]
1	1	rt	24 h	14	7 : 1
2	1	40	12 h	18	7 : 1
3	1	60	1 h	30	8 : 1
4	1	80	1 h	27	8 : 1
5	2	60	35 min	72	11 : 1
6	3	60	25 min	95	13 : 1
7	3.5	60	20 min	98	13 : 1
8[d]	3.5	60	20 min	100 (96)	13 : 1
9[e]	3.5	60	20 min	97	13 : 1
10[d,f]	3.5	60	20 min	99	12 : 1
11[d,g]	3.5	60	20 min	100	13 : 1

[a] Unless otherwise specified, the reactions were carried out in a sealed tube in the presence of **1a** (0.1 mmol), **2a** and water (1 ml). [b] Estimated by ^{1}H NMR using diethyl phthalate as an internal reference. [c] The number in parentheses shows isolated yield. [d] 0.5 ml water was used. [e] 2 ml water was used. [f] 0.01 mmol acetic acid was used as the catalyst and 0.5 ml water was used as the solvent. [g] The reaction was carried out in a Schlenk tube in the presence of **1a** (0.1 mmol), **2a** (0.35 mmol) and water (0.5 ml). rt = room temperature.

Table 2 Reaction scope of sodium sulfinate[a]



[a] All reactions were carried out in a sealed tube in the presence of **1** (0.2 mmol), **2** (0.7 mmol) and water (1 ml); isolated yields are reported.

10 mmol scale, 0.4 M) without any problem, which would potential economic production on a commercial scale.

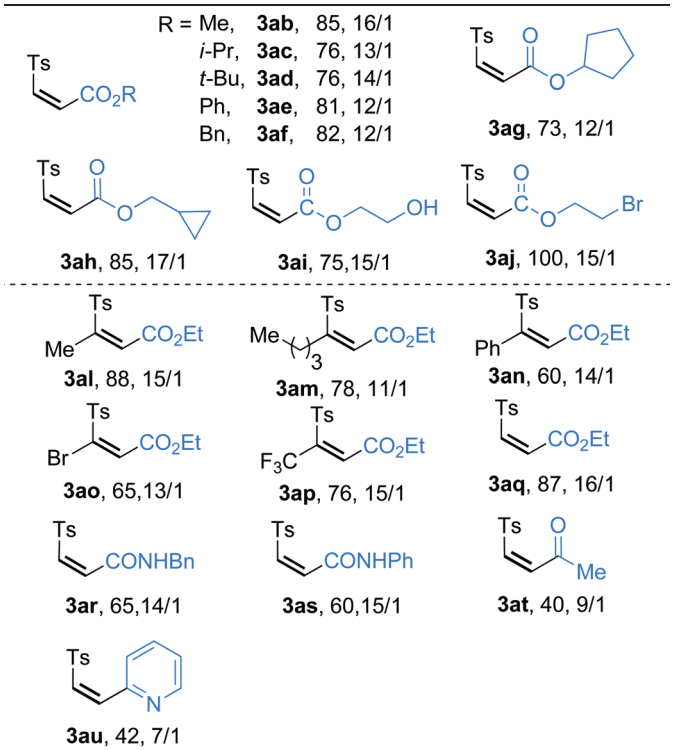
We next turned our attention to the scope of propargylic carboxylate substrates (Table 3). We were pleased to find that the readily available propargylic carboxylate did smoothly react with sodium 4-methylbenzenesulfinate (**1a**) to produce a greatly widened range of tosylacrylates, which clearly exhibited the power of this sulfonylation strategy. Propargylic carboxylates with various chain lengths and isomeric structures did not significantly affect the product yields and *Z*-selectivity (**3ab–3aj**). High functional group compatibility was exhibited, tolerating alkyl (**3ab–3ad**, **3af**), Ph (**3ae**), cyclopentyl (**3ag**), cyclopropylmethyl (**3ah**), free OH (**3ai**), and Br (**3aj**) moieties. The internal propargylic carboxylates, which were usually very less reactive than the terminal propargylic carboxylates, were also tested. Sterically demanding phenyl-substituted ethyl propiolate (**2n**) provided the corresponding product in lower yield than the alkyl-substituted substrates (**3l** and **3m**), indicating that steric congestion around the alkynyl decreases the reaction efficiency. The electron-withdrawing substituted ethyl propiolate showed inferior reaction efficiency to that of the electron-donating ones (**3ao** and **3ap** *vs.* **3al**). Ethyl 3-(trimethylsilyl)propiolate (**2p**) could well react with **1a** to give (*Z*)-ethyl 3-tosylacrylate (**3aa**) in 87% yield. Apparently, the **2p** proceeds *via* an intermolecular nucleophilic substitution reaction with concomitant release of the TMS group. Furthermore, the method could also be applied to other acetylenes substituted with electron-withdrawing groups, including amide (**3aq** and **3ar**), acetyl (**3as**) and azine (**3at**) groups, which gave the corresponding sulfonylation products in moderate to good yields.

β-Sulfonyl enoates are not only useful building blocks in organic synthesis but also important structure motifs commonly found in drugs. Moreover, late-stage modification is a valuable strategy for medicinal chemistry research. Therefore, several complex bioactive molecule derivatives were subjected to the standard reaction conditions (Table 4). Natural alcohol derivatives containing tosylpropiolates, such as indanol (**4aa**), perillyl (**4ab**), benzoin (**4ac**) and farnesol derivatives (**4ad**) worked well in the current transformation, generating the corresponding tosylacrylates in 56–82% yields and with *Z*/*E* ratios ranging from 5 : 1 to 13 : 1. These results demonstrate that the present protocol could be applied in late stage bioactive compound modification.

To gain insight into the possible mechanism of this sulfonylation process, the following competitive experiments were performed. First, the sulfonylation of **2a** in D_2O (0.5 mL) afforded deuterated product **D-3aa** with a small quantity of **D-4a** (Scheme 2a), which indicated that the α-hydrogen atom of ethyl 3-tosylpropiolate was originated from water. In addition, a small quantity of **D-4a** was detected by MS. The preformed **2l** was subjected to the reaction with **1a** in D_2O, and the expected **D-4l** was also detected by MS (Scheme 2b). These results were consistent with those obtained for the sulfonylation reactions. An excess of ethyl propiolate was critical to obtain a high yield of **3aa** (see Table 1, entries 4–6), which suggested that propargylic acid was essential for the success of this transformation. Subsequently, radical trapping experiments were performed (Scheme 2c). The addition of radical scavengers such as TEMPO and BHT (2.0 equiv.) did not retard the sulfonylation of **2a** under standard conditions, which indicated that the reaction might not proceed through a radical pathway.

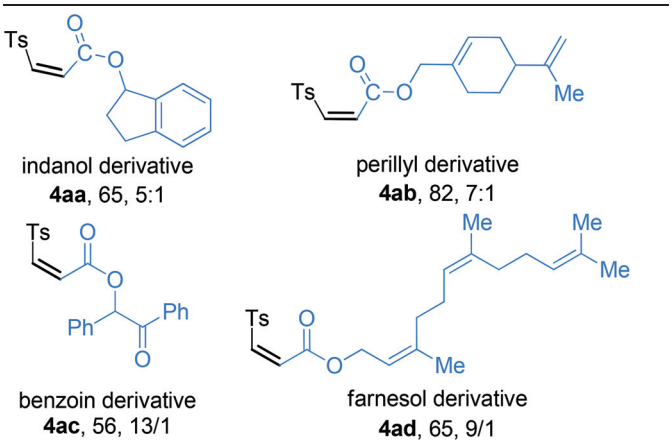
On the basis of the results described above and previous reports, a plausible mechanism is proposed (Scheme 3). First,

Table 3 Reaction scope of propargylic carboxylate[a]

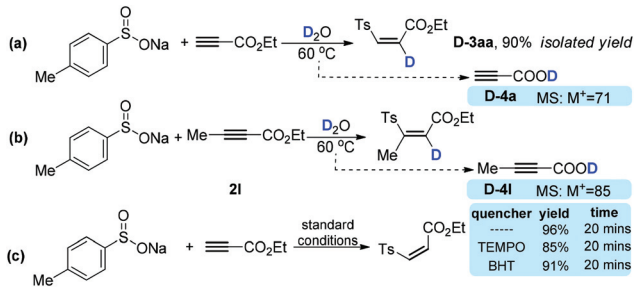


[a] All reactions were carried out in a sealed tube in the presence of **1** (0.2 mmol), **2** (0.7 mmol) and water (1 ml); isolated yields are reported.

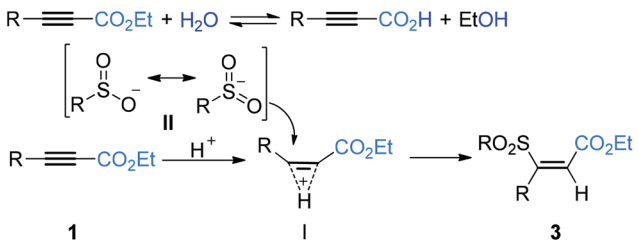
Table 4 Reaction scope of late-stage modification[a]



[a] All reactions were carried out in a sealed tube in the presence of **1** (0.2 mmol), **2** (0.7 mmol) and water (1 ml); isolated yields are reported.



Scheme 2 Control experiments.



Scheme 3 Proposed mechanism.

an ethenium intermediate[11] I is formed through electrophilic addition of a proton to an activated alkyne moiety, which is generated from the hydrolysis of ethyl propiolate under heating conditions. Then, the sulfonyl anion anti-attacked the less steric hindered carbon of intermediate I to produce *Z*-β-sulfonyl enoates **3**.

Conclusions

In conclusion, we report a direct C–S coupling reaction which was promoted by water for the efficient synthesis of various *Z*-β-sulfonyl-α,β-unsaturated carbonyl compounds under environmentally-friendly conditions. The newly developed protocol has advantages over the previous methods: (1) the well-matched reactivity of electron-withdrawing group substituted acetylenes with sodium sulfinates results in simple reaction conditions with easy operationality, where organic solvents, catalysts and additives are not required; (2) in contrast to the previous methods, both terminal and internal alkynylcarbonyl compounds, as well as heteroaromatic alkynes are suitable for the sulfonylation reaction; (3) complete regioselectivity and uniformly high levels of enol vinyl (*Z*)-stereoselectivity are observed; and (4) a slight heating may be used, thus significantly shortening the reaction time to 20 min.

Experimental

General information

Unless otherwise specified, all reagents and solvents were obtained from commercial suppliers and used without further purification. All reagents were weighed and handled in air at room temperature. ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 100 MHz by using a Bruker Avance 400 spectrometer. Chemical shifts were reported in parts per million (δ) relative to tetramethylsilane (TMS). The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and brs = broad singlet. IR spectra were recorded on a Nicolet iS10 FT-IR spectrometer and only major peaks were reported in cm^{-1}. Mass spectra were recorded on a spectrometer operating on ESI-TOF.

General procedure for the synthesis of *Z*-β-sulfonyl enoates

In a sealed tube were placed sodium sulfinate (0.2 mmol), alkynylcarbonyl compound (0.7 mmol) and H_2O (1 mL), and then the contents were stirred at 60 °C. The progress of the reaction was monitored by TLC. The reaction typically took 20 min. Upon completion, the reaction mixture was cooled down to room temperature, mixed with silica gel and concentrated under vacuum. The residue was purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford **3–4**.

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