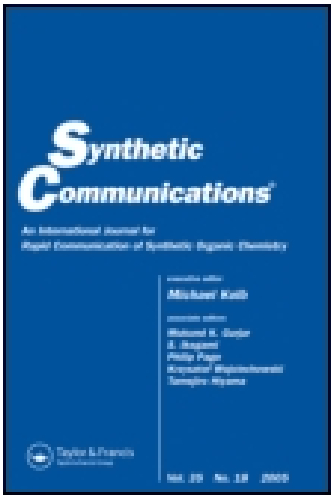

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THREE-COMPONENT REACTIONS OF KETENE DITHIOACETALS, ALDEHYDES, AND ARENESULFINIC ACIDS: FACILE SYNTHESIS OF ALLYLIC SULFONES

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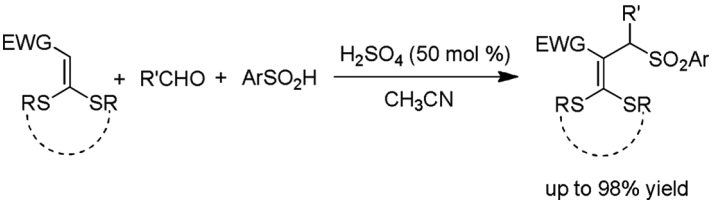
GRAPHICAL ABSTRACT



Abstract *A facile and efficient synthesis of allylic sulfones via sulfuric acid–mediated three-component reactions of easily available ketene dithioacetals, aldehydes, and arenesulfinic acids is presented. The reaction features low cost and good yields.*

Keywords Allylic sulfones; ketene dithioacetals; multicomponent reactions; sulfinic acids

INTRODUCTION

Allylic sulfones are versatile building blocks in a number of carbon–carbon bond-forming reactions owing to the ability of the sulfone moiety to stabilize an adjacent carbanion and serve as a leaving group, which is enhanced by the "allylic" environment.[1] In addition, they are the necessary constituents of some biologically important compounds displaying interesting activities, such as anticancer agents,[2] antibacterial agents,[3] thyroid-stimulating hormone (TSH) receptor antagonists,[4] and weed-control herbicides.[5] Therefore, much attention has been paid to the preparation of allylic sulfones. Traditionally, they can be prepared by the oxidation of the corresponding sulfides, where a stoichiometric amount of hazardous oxidants is often required. An alternative to this is the coupling of sulfonyl nucleophiles (sulfinate salts or sulfinic acids) with various allylic carbon electrophiles, with the elimination of undesirable wastes from prefunctionalized allylic compounds.[6,7]

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Although numerous new approaches have also been reported in recent years, they commonly require expensive reagents and/or catalysts.[8] Hence, the development of mild and cost-effective processes remains a significant challenge.

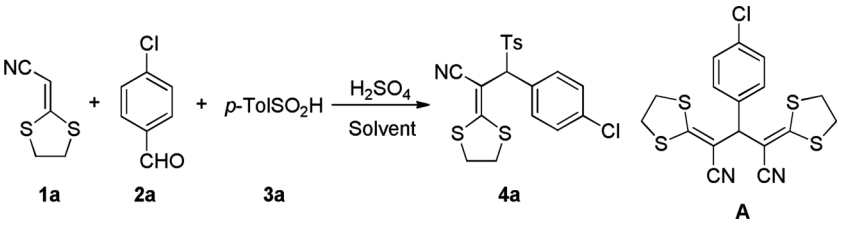
Multicomponent reactions (MCRs) are powerful tools for the rapid construction of molecular complexity because highly elaborated compounds are formed from simple starting materials in an operationally brief and atom-economical manner.[9] Although MCRs of sulfonyl nucleophiles, aldehydes, and reactive nucleophiles could efficiently afford several functionalized sulfones, they are rather limited in the scope of nucleophiles, and up to the present alkenes have never been involved.[10–12] α-Oxo ketene dithioacetals are kinds of polarized alkenes which have been used as versatile synthons for the synthesis of various carbo- and heterocyclic compounds.[13] Our continuing interest in the α-functionalization of ketene dithioacetals[14] prompted us to investigate their reactivity in new MCRs as nucleophiles. Herein, we report a novel sulfuric acid–mediated MCR of ketene dithioacetals, aldehydes, and arenesulfinic acids, furnishing highly functionalized allylic sulfones in good yields.

RESULTS AND DISCUSSION

Initially, a three-component reaction of α-cyanoketene cyclic dithioacetal **1a**, 4-chlorobenzaldehyde **2a**, and *p*-toluenesulfinic acid **3a** was used as a model reaction to screen the reaction conditions (Table 1). To our delight, the three components reacted smoothly in CH_3CN at room temperature to afford the desired product **4a** in good yield (86%) within 24 h, even without any promoter (Table 1, entry 1). However, attempt to improve the yield of **4a** by raising the temperature met with no success (Table 1, entry 2), probably due to the instability of sulfinic acids.[15] To further improve the reaction efficiency, simple Brønsted acid (H_2SO_4) was added. However, no improvement was observed when a catalytic amount (20 mol%) of H_2SO_4 was employed (Table 1, entry 3). By increasing H_2SO_4 loading to 50 mol%, the reaction could reach completion rapidly within **5** h, furnishing **4a** in excellent yield (93%, Table 1, entry 4). With lower amounts of aldehyde **2a** (1.2 equiv, Table 1, entry 5) or sulfinic acid **3a** (2.0 equiv, Table 1, entry 6), satisfactory yields (83% and 80%) were still obtained after a prolonged reaction time, but with the formation of undesired by-product **A**[14c,16] in 8% and 12% yields, respectively. Next, other solvents instead of CH_3CN were tested. It was found that CH_2Cl_2 was a suitable reaction medium as well, albeit with a slightly longer reaction time (Table 1, entry 7). When the reaction was carried out in tetrahydrofuran (THF), a decrease in the yield of **4a** was observed even after 72 h (Table 1, entry 8). The use of dimethylformamide (DMF) or CH_3OH as solvent was proved to be unsuccessful (Table 1, entries 9 and 10).

With optimized conditions in hand (Table 1, entry 4), the generality of this new MCR was examined. As described in Table 2, the desired sulfone **4b** was synthesized smoothly from benzenesulfinic acid, ketene dithioacetal **1a**, and aldehyde **2a** in a slightly decreased yield (87%, Table 2, entry 2), while the reaction of arenesulfinic acid with an electron-withdrawing group was more sluggish, and a significant amount of by-product **A** was isolated (Table 2, entry 3). On the other hand, all selected aldehydes **2** bearing phenyl (Table 2, entry 9), electron-deficient (Table 2, entries 1–5), electron-rich (Table 2, entries 6–8), aromatic and heteroaromatic groups

Table 1. Optimization of reaction conditions[a]



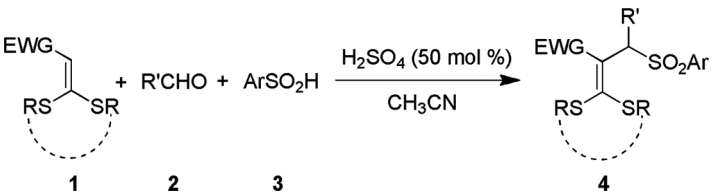
Entry	H_2SO_4 (mol %)	Solvent	Time (h)	Yield of **4a** (%)[b]
1	—	CH_3CN	24	86
2	—	CH_3CN	24	79[c]
3	20	CH_3CN	24	88
4	**50**	**CH_3CN**	**5.0**	**93**
5	50	CH_3CN	12	83[d]
6	50	CH_3CN	12	80[e]
7	50	CH_2Cl_2	8.0	90
8	50	THF	72	71[f]
9	50	DMF	72	nr[g]
10	50	CH_3OH	72	13[h]

[a]Reaction conditions: **1a** (1.0 mmol), **2a** (2.0 mmol), **3a** (3.0 mmol), solvent (5.0 mL), room temperature.
[b]Isolated yields.
[c]Stirring at 35 °C.
[d]1.2 equiv of **2a** was used, and by-product **A** was isolated in 8% yield.
[e]2.0 equiv of **3a** was used, and by-product **A** was isolated in 12% yield.
[f]With recovery of 26% of **1a**.
[g]No reaction.
[h]With recovery of 67% of **1a**.

(Table 2, entry 10) are suitable components for this transformation, and the yield reached up to 98%. Paraformaldehyde, an aliphatic aldehyde, underwent the same reaction to give the corresponding product **4k** in moderate yield at reflux temperature (Table 2, entry 11). Next, a series of reactions of various ketene dithioacetals **1** with paraformaldehyde and *p*-toluenesulfinic acid were carried out. In the cases of α-cyanoketene acyclic dithioacetals, allylic sulfones **4l** and **4m** were separated in nearly quantitative yields by employing $TiCl_4$ as promoter and CH_2Cl_2 as solvent (Table 2, entries 12 and 13). A wide scope of electron-withdrawing groups (EWGs) was also observed. Alkanoyl (Table 2, entry 14) and benzoyl groups (Table 2, entry 15) both proved to be adept in this transformation under optimized conditions. When α-cinnamoyl ketene dithioacetal was used, an unexpected product **4p′** was formed in 70% yield, resulting from the Michael addition of excess sulfinic acid to the cinnamoyl group (Table 2, entry 16). In the presence of NaOH, **4p′** could be readily converted to cinnamoyl-substituted allylic sulfone **4p** (Scheme 1). Unfortunately, the reaction of α-alkoxycarbonyl ketene dithioacetal resulted in a complex mixture (Table 2, entry 17).

On the basis of all the results mentioned together with our previous reports,[14,16,17] a plausible mechanism for this new MCR is outlined in Scheme 2.

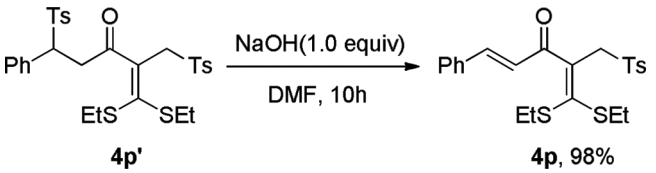
Table 2. Synthesis of allylic sulfones **4** by MCRs of **1, 2**, and **3**[a]



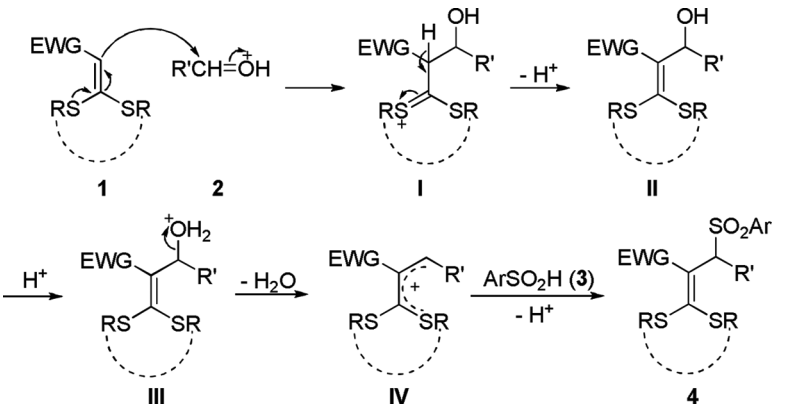
Entry	EWG	R	R′	Ar	*t* (h)	4	Yield (%)[b]
1	CN	-CH_2CH_2-	4-ClPh	4-MePh	5	**4a**	93
2	CN	-CH_2CH_2-	4-ClPh	Ph	6	**4b**	87
3	CN	-CH_2CH_2-	4-ClPh	4-ClPh	12	**4c**	72[c]
4	CN	-CH_2CH_2-	4-NO_2Ph	4-MePh	12	**4d**	66
5	CN	-CH_2CH_2-	2-NO_2Ph	4-MePh	48	**4e**	91
6	CN	-CH_2CH_2-	4-MePh	4-MePh	24	**4f**	98
7	CN	-CH_2CH_2-	4-MeOPh	4-MePh	24	**4g**	98
8	CN	-CH_2CH_2-	3,4-O_2CH_2Ph	4-MePh	48	**4h**	42
9	CN	-CH_2CH_2-	Ph	4-MePh	12	**4i**	91
10	CN	-CH_2CH_2-	2-furyl	4-MePh	18	**4j**	87
11	CN	-CH_2CH_2-	H	4-MePh	18	**4k**	53[d,e]
12	CN	Me	H	4-MePh	12	**4l**	96[e,f]
13	CN	Et	H	4-MePh	12	**4m**	98[e,f]
14	MeCO	Et	H	4-MePh	12	**4n**	73[e]
15	PhCO	Et	H	4-MePh	12	**4o**	61[e]
16	PhCH=CHCO	Et	H	4-MePh	12	**4p′**	70[e]
17	CO_2Et	Et	H	4-MePh	5		Complex[e]

[a]Reaction conditions: **1** (1.0 mmol), **2** (2.0 mmol), **3** (3.0 mmol), H_2SO_4 (0.5 mmol), MeCN (5.0 mL), room temperature.
[b]Isolated yields.
[c]By-product **A** was isolated in 19% yield.
[d]Stirring at reflux temperature.
[e]3.0 equiv of paraformaldehyde was used.
[f]$TiCl_4$ (1.5 mmol) used as promoter and CH_2Cl_2 as solvent.

Initiated by the nucleophilic attack of the electron-rich α-carbon atom of **1** at the carbonyl carbon of acid-activated aldehyde **2**, intermediate **I** is first produced and subsequently converted to allyl alcohol **II**, which readily undergoes acid-promoted elimination of H_2O to give carbocation intermediate **IV** via oxonium salt **III**. Finally, **IV** is captured by arenesulfinic acid **3** and sufone **4** is formed.



Scheme 1. Synthesis of **4p** from Michael adduct **4p′**.



Scheme 2. Plausible mechanism for the MCR leading to allylic sulfone **4**.

CONCLUSIONS

In summary, we have developed a novel, efficient, and cost-effective method for the synthesis of allylic sulfones via sulfuric acid–mediated MCRs of ketene dithioacetals, aldehydes, and arenesulfinic acids. This protocol is associated with readily available starting materials, dense and flexible substitution patterns, and potential synthetic utility of the final products. Further research is ongoing in our laboratory.

EXPERIMENTAL

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. Substrates **1** were prepared by the reported methods.[18,19] ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 °C on Varian 500- and 125-MHz instruments, respectively, and TMS as internal standard. High-resolution mass spectra (HRMS) were obtained using a Bruker MicroTOF II Focus spectrometer (electrospray ionization, ESI). Melting points were uncorrected.

General Procedure for Synthesis of Allylic Sulfones 4 (4a as Example)

A 25-mL flask, equipped with a magnetic stirring bar, was charged with ketene dithioacetal **1a** (143 mg, 1.0 mmol) and *p*-toluenesulfinic acid **3a** (469 mg, 3.0 mmol), followed by addition of acetonitrile (5.0 mL). The mixture was stirred at room temperature for 5 min to fully dissolve the substrates. Then benzaldehyde **2a** (281 mg, 2.0 mmol) and concentrated sulfuric acid (0.027 mL, 0.5 mmol) were added, and the solution was stirred at ambient temperature for another 5 h. After **1a** was consumed, as indicated by thin-layer chromatography (TLC), the reaction mixture was quenched with water, neutralized by saturated aqueous $NaHCO_3$ solution, and extracted with CH_2Cl_2 three times. The extract was dried over anhydrous $MgSO_4$. After removal of solvents, the residue was purified by column chromatography (silica gel, petroleum ether–dichloromethane–ethyl acetate = 8:2:1, v/v) to afford allylic sulfone **4a** as a white solid (392 mg, 93% yield).

Spectral Data

3-(4-Chlorophenyl)-2-(1,3-dithiolan-2-ylidene)-3-tosylpropanenitrile **4a**: White solid: mp 218–219 °C. ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 2.43$ (s, 3H), 3.40–3.44 (m, 1H), 3.46–3.53 (m, 3H), 4.92 (s, 1H), 7.28 (d, $J = 8.5$ Hz, 2H), 7.33 (d, $J = 8.5$ Hz, Hz, 2H), 7.52 (d, $J = 8.0$ Hz, 2H), 7.68 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 172.1$, 145.4, 135.7, 134.0, 131.1 (2C), 129.7 (2C), 129.3 (2C), 129.1 (2C), 128.8, 117.0, 89.7, 73.7, 39.8, 38.7, 21.7. HRMS (ESI-TOF) calcd. for $C_19H_17ClNO_2S_3^+$ ($[M+H]^+$) 422.0104. Found 422.0107.

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SUPPORTING INFORMATION

Full experimental details, spectral data of the products, and ^{1}H NMR and ^{13}C NMR spectra of new compounds can be accessed on the publisher's website.

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