Advanced Synthesis & Catalysis

Accepted Article

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To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201801620

Link to VoR: http://dx.doi.org/10.1002/adsc.201801620

10.1002/adsc.201801620

COMMUNICATION

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

Cs_2CO_3–Mediated Vicinal Thiosulfonylation of 1,1-Dibromo-1-Alkenes with Thiosulfonates: An Expedient Synthesis of (*E*)-1,2-Thiosulfonylethenes

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Received: ((will be filled in by the editorial staff))

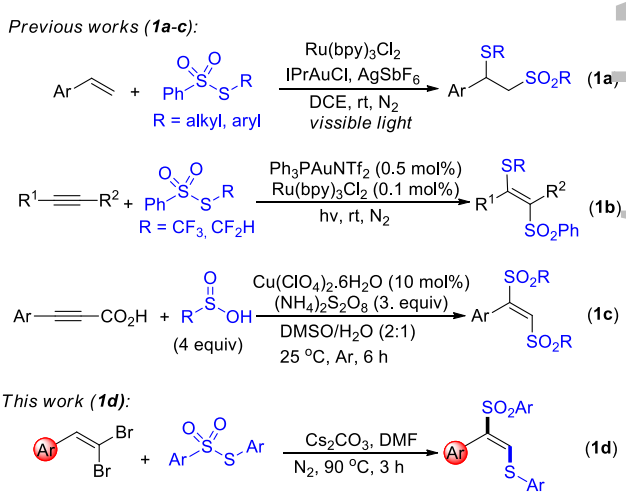
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.((Please delete if not appropriate))

Abstract. A new and highly efficient vicinal thiosulfonylation of 1,1-dibromo-1-alkenes with thiosulfonates in the presence of cesium carbonate has been developed. The metal-free diheterofunctionalization is an operationally simple to access a wide range of (*E*)-1,2-thiosulfonylethenes (α-aryl-β-thioarylvinyl sulfones) in moderate to high yields with high levels of stereoselectivities. Further, scalable reactions have been demonstrated for this transformation, thus illustrating its efficiency and practicality.

Keywords: Diheterofunctionalization; *gem*-Dibromoalkenes; Thiosulfonylation; Thiosulfonates; Vinyl sulfones

Difunctionalization of alkenes and alkynes offers a powerful platform for the rapid construction of molecular complexity from simple starting materials.[1] Significant attention has been devoted for the installation of diverse functional groups onto vicinal carbons of alkene moieties to form two new chemical bonds in a single operation.[2-4] Despite substantial progress has been made toward vicinal difunctionalization of olefins, the reactions toward 1,2-diheterofunctionalizations of alkenes and successively persist of the alkene moiety has not been explored.

Among a variety of organosulfur compounds,[5] thiosulfonates ($RS–SO_2R^1$) are the privileged class of compounds in synthetic organic chemistry.[6-8] Generally, thiosulfonates were demonstrated as a electrophilic sulfenylating reagent, which often discard the sulfonyl moiety as a waste.[4a,7] Recently, the diverse reactivity of thiosulfonates have been discovered as a 1,1- or 1,2-thiosulfonylating agent.[8] However, the installation of two distinct C–S bonds *via* 1,2-thiosulfonylation has rarely been explored.[8a,b] In this context, Xu and co-workers developed a combination of gold and photoredox catalytic approach for an intermolecular atom transfer thiosulfonylation of alkenes in an atom-economical manner (Scheme **1a**).[8a] Later on, Li et al. elegantly reported a gold/photoredox-cocatalyzed vicinal thiosulfonylation of alkynes using $PhSO_2SR$ (R = CF_3 and CF_2H) as a diheterofunctionalization reagent (Scheme **1b**).[8b] Very recently, Li group employed a copper-catalyzed decarboxylative disulfonylation of alkynyl carboxylic acids with sulfinic acids to form (*E*)-1,2-disulfonylethenes (Scheme **1c**).[4b] These approaches usually require an expensive metal catalyst(s), excess use of oxidants and inaccessible starting materials.



Scheme 1. Pattern for vicinal C–S bonds construction.

In spite of these achievements, assembling highly substituted alkenes in a rapid, flexible and efficient manner that also accommodates diverse functional groups remains a challenge. We envisioned that 1,1-dibromo-1-alkene could be right starting material for installation of two different C–S bonds and concurrently retaining the C–C double bond in a single synthetic operation. Therefore, we wanted to

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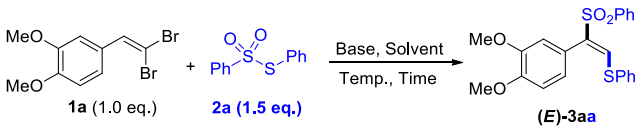
investigate the vicinal thiosulfonylation of 1,1-dibromo-1-alkenes with thiosulfonates to construct 1,2-thiosulfonylethenes (Scheme 1d). In fact, *gem*-dihaloolefins are often used as alkyne precursors and their rich chemistry has been extensively explored.[9] In continuous of our interest on organosulfur chemistry,[10] herein, we report an efficient and unprecedented Cs_2CO_3-mediated intermolecular vicinal thiosulfonylation of 1,1-dibromo-1-alkenes with thiosulfonates to give (*E*)-1,2-thiosulfonylethenes.

At outset, our investigations commenced with 4-(2,2-dibromovinyl)-1,2-dimethoxybenzene **1a** and *S*-phenyl benzenesulfonothioate **2a** as a model substrates. Initial experiments were performed with copper-catalyzed thiosulfonylation of **1a** with **2a** in the presence of Cs_2CO_3 to give moderate to good yields for the desired product **3aa** (see the SI for a detailed survey of reaction conditions). Surprisingly, Cs_2CO_3 alone afforded the thiosulfonylated product **3aa** (Table 1). The reaction of **1a** with 1.5 equiv of **2a** in the presence of Cs_2CO_3 (2 equiv) in DMF, DMSO and DMA (Dimethylacetamide) at 90 °C afforded modest conversion (entries 1-3) and a low conversion in toluene (entry 4) was observed. A substantial progress was seen by increasing the amount of Cs_2CO_3 (entries 5 and 6); the best conversion and high stereoselectivity was achieved with 4 equiv of Cs_2CO_3 (entry 6). Our attempts were failed to improve the conversion by varying the amounts of Cs_2CO_3, concentration and temperature (entries 7-9). No reaction took place in the presence of K_2CO_3 and DBU (entries 10 and 11), however, a low conversion was observed with DABCO (entry 12).

Encouraged by these results, we next proceeded to explore the generality of the reaction under the optimized reaction conditions (Table 2). A series of *gem*-dibromoalkenes (**1a-p**) employed for 1,2-thiosulfonylation with *S*-phenyl benzenesulfonothioate **2a** to afford the corresponding (*E*)-1,2-thiosulfonylethenes **3(a-p)a** in 42-91% yields with excellent stereoselectivities. Notably, both electron-withdrawing and electron-donating groups on the aromatic ring of **1** were compatible under same reaction conditions. However, the nature and position of the substituents had little influence on the outcome (*cf.* **3ca**, **3da**, **3ga-ja**) of the transformation. The structure and alkene geometry of **3ca** was further confirmed by single crystal X-ray data analysis (see SI).[11,12] Remarkably, heteroaryl derived dibromoalkenes **1k** and **1l** were also well-tolerated under the standard conditions, leading to the desired products **3ka** and **3la** in 74% and 67% yields, respectively. The naphthyl derived products (**3ma** and **3na**) were obtained in high yields under the reaction conditions, whereas sterically bulky dibromoalkene **1o** afforded the desired vinyl sulfone in 42% yield only. In contrast, cinnamyl derived dibromoolefin **1p** gave the corresponding product with an inseparable mixture of other unidentified products.

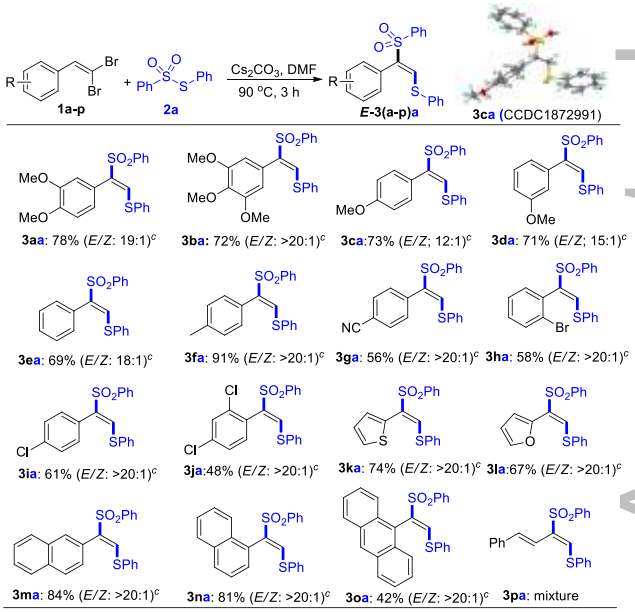
Table 1. Optimization of vicinal thiosulfonylation using 1,1-dibromoalkene **1a** with *S*-phenyl thiosulfonate **2a**.[a]



Entry	Solvent	Base (eq.)	Time	Conv[b]	*E*/*Z*[c]
1	DMF	Cs_2CO_3 (2 eq.)	5 h	59%	16/1
2	DMSO	Cs_2CO_3 (2 eq.)	5 h	49%	15/1
3	DMA	Cs_2CO_3 (2 eq.)	5 h	53%	16/1
4	Toluene	Cs_2CO_3 (2 eq.)	5 h	10%	---
5	DMF	Cs_2CO_3 (3 eq.)	4 h	75%	18/1
6	**DMF**	**Cs_2CO_3 (4 eq.)**	**3 h**	**81%**	**18/1**
7	DMF	Cs_2CO_3 (5 eq.)	3 h	78%	18/1
8[d]	DMF	Cs_2CO_3 (4 eq.)	4 h	70%	18/1
9[e]	DMF	Cs_2CO_3 (4 eq.)	3 h	72%	16/1
10	DMF	K_2CO_3 (4 eq.)	5 h	trace	---
11	DMF	DBU (4 eq.)	5 h	trace	---
12	DMF	DABCO (4 eq.)	5 h	23%	16/1

[a] All reactions performed on a 0.2 mmol scale of **1a** (1.0 eq.), **2a** (1.5 eq.) and base (2 to 5 eq.) in 1.0 mL of solvent at 90 °C. [b,c] Yields and *E*/*Z* mixture based on ^{1}H NMR analysis using 1,2,4,5-tetramethyl benzene as an internal standard. [d] The reaction carried out in 2 mL of DMF. [e] At 110 °C.

Table 2. Substrate scope for vicinal thiosulfonylation.[a,b]



[a] All reactions were performed a 0.5 mmol scale of **1a-p** (1.0 eq.), **2a** (1.5 eq.) and Cs_2CO_3 (4.0 eq.) in anhydrous DMF (2.5 mL) under N_2 at 90 °C for 3 h. [b] Isolated yield. [c] *E*/*Z* mixture based on ^{1}H NMR analysis.

Furthermore, we sought to evaluate the scope of symmetrical and unsymmetrical thiosulfonates (**2b-g**).

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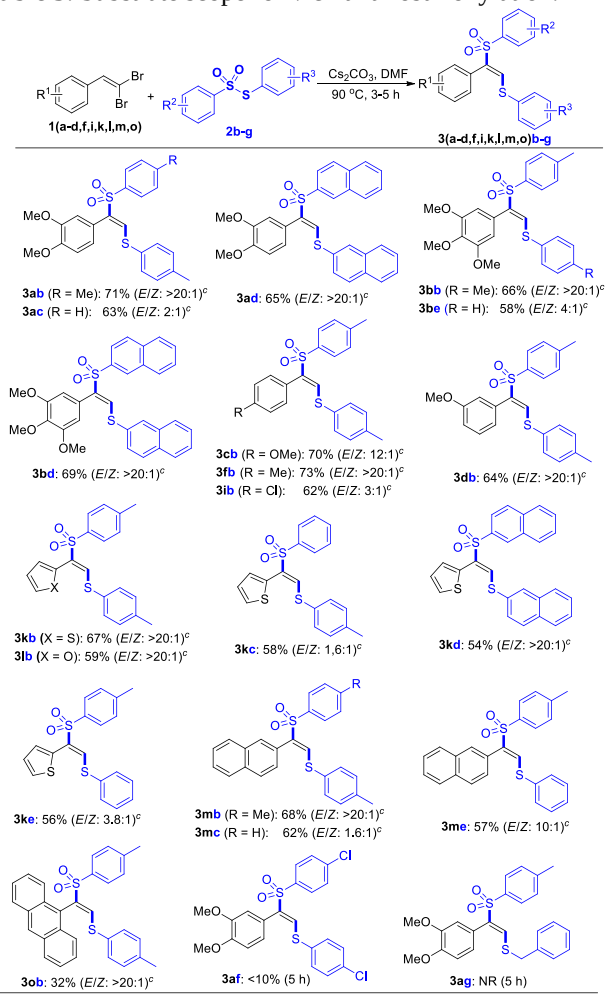
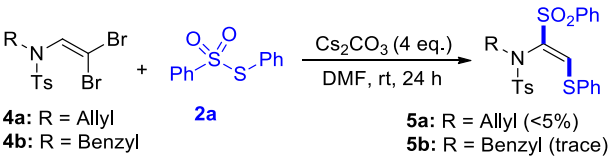
Various thiosulfonates were explored in vicinal thiosulfonylation and smoothly furnished the (*E*)-1,2-thiosulfonylethene products in good to high yields (Table 3). As expected symmetrical thiosulfonates (**2b** and **2d)** reacted well with representative *gem*-dibromoolefins with no apparent effect on the resulted products. The use of unsymmetrical thiosulfonates (**2c** and **2e**) has a considerable influence on the stereoselectivity, which provided thiosulfonylated products (*cf*: **3ac**, **3be**, **3kc**, **3ke**, **3mc** and **3me**) in satisfactory yields. The reaction of **1a** with 4-chloro derived thiosulfonate **2f** gave the corresponding product **3af** in a trace amount, albeit thiosulfonate **2g** was not a suitable substrate for this transformation. It is worth to note that these multifunctional vinyl sulfones are potentially valuable compounds in organic and medical chemistry.[13]

Table 3. Substrate scope for vicinal thiosulfonylation.[a,b]



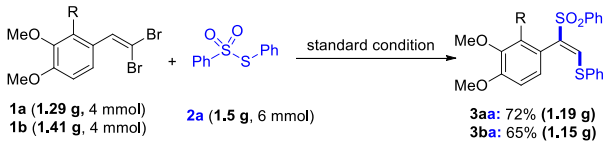
[a] All reactions were performed on a 0.5 mmol scale of **1** (1.0 eq.), **2b-g** (1.5 eq.) and Cs_2CO_3 (4.0 eq.) in anhydrous DMF (2.5 mL) under N_2 at 90 °C for 3-5 h. [b] Isolated yield. [c] *E*/*Z* mixture based on ^{1}H NMR analysis.

Next, the scope of vicinal thiosulfonylation reaction can extend to more valuable substrates. Accordingly, we verified vinyl dibromoenamides (**4a**/**b**) with thiosulfonate **2a** for diverse substitution pattern on the products. Disappointingly, these dibromoenamides were degraded under the optimal reaction conditions. However, the reactions at room temperature proceeded sluggishly to form the desired products **5a** and **5b** in trace amounts (Scheme 2).



Scheme 2. Reactions were performed on a 0.5 mmol scale of **4a/b** (1.0 eq.), **2a** (1.5 eq.) and Cs_2CO_3 (4.0 eq.) in anhydrous DMF (2.5 mL) at 90 °C or at room temperature.

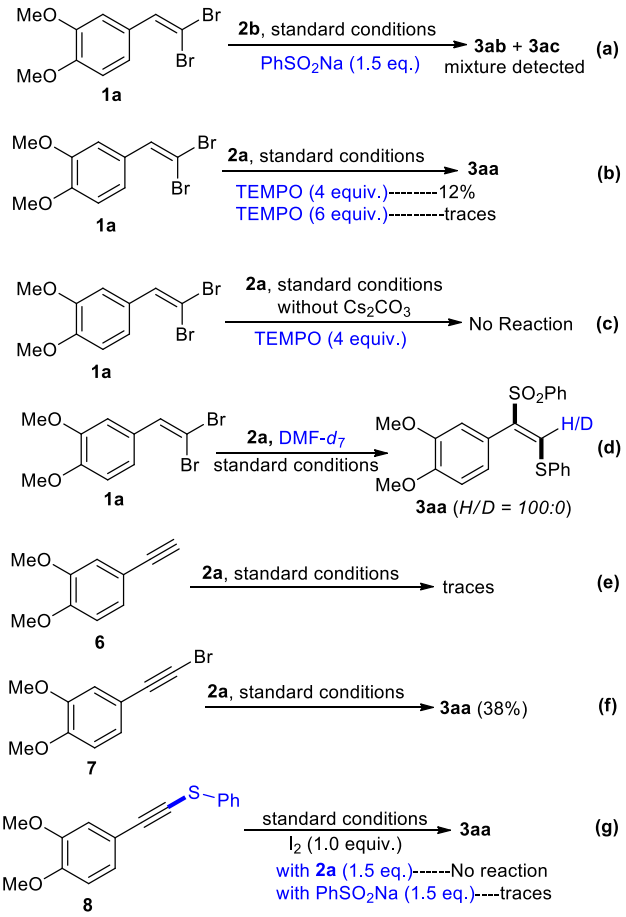
To demonstrate the synthetic utility of this protocol, a gram-scale reaction was carried out under the optimization reaction conditions. As shown in Scheme 3, a 4 mmol scale reactions of 1,1-dibormoalkenes (**1a/b**) with *S*-phenyl benzenesulfonothioate **2a** were performed to produce 1.19 g (72%) of **3aa** and 1.15 g (65%) of **3ba**, thus demonstrated the thiosulfonylation could be readily scalable with a slight deviation on efficiency.



Scheme 3. Gram-scale reaction for thiosulfonyaltion.

To gain valuable insight to understanding the reaction mechanism, several control experiments were performed for 1,2-thiosulfonylation (Scheme 4). A mixture of products **3ab** and **3ac** were detected by ^{1}H NMR, when standard reaction employed with **2b** and sodium benzenesulfinate, thus implying both the thiosulfonates might be competing in the transformation (Scheme 4a). The thiosulfonate **1c** ($PhSO_2STolyl$) would be generated *in situ* by the reaction between **2b** with sodium benzenesulfinate, which might be accountable in the formation of **3ac**. A radical scavenger TEMPO (*2,2,6,6-tetramethyl-1-piperidinyloxy*) was added to the standard reaction. With 4.0 equiv. of TEMPO inhibition of the reaction was observed and **3aa** was obtained in only 12% yield (Scheme 4b). However, the reaction was totally inhibited with 6.0 equiv. of TEMPO (Scheme 4b). Further, no reaction was found without Cs_2CO_3 and also both the reactants were not affected in the presence of TEMPO (Scheme 4c). Next, the reaction between **1a** and **2a** under standard conditions in deuterated DMF (DMF-*d7*) afforded **3aa** in 52% yield without any deuterium incorporation at olefin carbon (Scheme 4d). The terminal alkyne (**6**) yielded the desired product **3aa** in traces (Scheme 4e), however, the 1-bromoalkyne (**7**)[9a] was smoothly transformed into the corresponding product **3aa** in 38% yield under the standard condition (Scheme 4f). Additionally, thioalkyne (**8**)[9h,14] failed to react with

either with **2a** or with sodium benzenesulfinate in the presence of iodine to give **3aa** (Scheme 4g). Overall, these results suggested that the 1-bromoalkyne **7** might be responsible for this transformation.



Scheme 4. Control experiments.

On the basis of above results and the literature precedents[4c,8a,b,9e-j], the transformation should proceed through a radical pathway. On the other hand, the thermal homolytic cleavage of thiosulfonate **2a** was known to generate a sulfonyl and a sulfenyl radical species.[15,16] Although several control experiments have been performed for vicinal thiosulfonylation, yet the reaction mechanism is still not clear. However, a very plausible (tentative) mechanism was proposed in the supporting information to rationalize the experimental outcome and the control experiments.

In conclusion, we have successfully developed a novel Cs_2CO_3–mediated vicinal thiosulfonylation of 1,1-dibromo-alkenes with thiosulfonates under mild reaction conditions. Utilization of readily available starting materials provided an efficient and practical approach to form a variety of (*E*)-1,2-thiosulfonylethenes with high levels of stereoselectivities. The transformation is established by its wide substrate scope and reliable at the gram-scale reactions. The synthetic applications of 1,2-thiosulfonylethenes and more mechanistic studies are currently underway.

Experimental Section

A heat gun-dried Schlenk tube was charged 1,1-dibromo-1-alkenes **1** (0.5 mmol, 1.0 eq.), thiosulfonates **2** (0.75 mmol, 1.5 eq.) and Cs_2CO_3 (2.0 mmol, 4.0 eq.) in DMF (2.5 mL). The reaction mixture was stirred at 90 ^oC for 3 h and monitored by TLC either complete or appeared to be proceeding no further progress. The mixture was quenched by addition of water (10 mL) followed by extraction with EtOAc (3x10 mL). The combined organic layers was washed with brine (2x10 mL), dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The resulting residue was subjected to silica gel flash chromatography to afford the desired (*E*)-1,2-thiosulfonylethenes **3**.

Acknowledgements

We thank SERB-ECR (File No. ECR/2015/000053) and UGC-Start-up grant (F.4-5/2006/BSR), New Delhi for financial assistance. RJR thanks to UGC for faculty position under Faculty Recharge Programme. JJK thanks to DST Inspire, New Delhi for his research fellowship.

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[11] The single X-ray crystal structure (CCDC 1872991) contain the supplementary crystallographic data for compound **3ca**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

[12] A few crystals were picked up carefully and characterised by ^{1}H NMR analysis. The mixture substantially improved to 18:1 (original ratio is 12:1), which revealed the crystals should be major (*E*-isomer) isomer (see SI).

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10.1002/adsc.201801620

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