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Sodium iodide-mediated synthesis of vinyl sulfides and vinyl sulfones with solvent-controlled chemical selectivity†

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Vinyl sulfides and vinyl sulfones are ubiquitous structures in organic chemistry because of their presence in natural and biologically active compounds and are very frequently encountered structural motifs in organic synthesis. Herein we report an efficient synthesis of vinyl sulfides and vinyl sulfones *via* transition metal-free sodium iodide-mediated sulfenylation of alcohols and sulfinic acids with solvent-controlled selectivity.

Introduction

Functionalized olefins are valuable intermediates in organic synthesis, because of their ability to serve as convenient substrates in transition metal-catalyzed cross-coupling reactions and their presence in natural and biologically active compounds.[1] In this respect, sulfur-containing olefins as important building units or intermediates have been applied in many different fields, such as total synthesis, functional materials science and medicinal chemistry.[2] For example, vinyl sulfides are employed as precursors for enol substituents,[3] Michael acceptors,[4] in cycloaddition reactions,[5] in olefin metathesis,[6] as reagents in cross-coupling,[7] in Heck reactions,[8] as equivalents of enolate anions,[9] and in aldehyde/ketone formation.[10] Vinyl sulfones and their derivatives have been reported to be potent inhibitors of enzymes such as sortase,[11] protein tyrosine phosphatases,[12] and cysteine proteases.[13] In view of their significance, developing more practical and efficient synthetic approaches to construct these compounds is of great interest.[14] Two common methods are frequently utilized for the synthesis of vinyl sulfides, including the copper-catalyzed *S*-vinylation of thiols with vinyl halides and the addition of thiols to alkynes.[15] Recently, Zhang and co-workers reported a copper-mediated stereospecific C–H oxidative sulfenylation of terminal alkenes with disulfides.[14] For the synthesis of vinyl sulfones, Wittig reaction of α-sulfinyl phosphonium ylides, β-elimination of halosulfones, condensation of aldehydes with sulfonylacetic, and the oxidation of the corresponding sulfides are perhaps the most common synthesis methods.[16] Recently, Zhan's group reported a copper(II)-catalyzed chemo- and stereocontrolled synthesis of vinyl sulfones from terminal alkynes and arylsulfonyl hydrazides.[2] Kuhakarn and co-workers discovered an efficient method for the synthesis of (*E*)-vinyl sulfones *via* decarboxylative sulfonylation of arylpropiolic acids with sulfinic acids.[14] In spite of the great success achieved so far in this area, there are still certain limitations, such as difficulties in controlling stereoselectivities and chemoselectivities, expensive substrates, moderate scope and functional group tolerance. Therefore, a new general, flexible, high stereoselective and chemoselective approach for the synthesis of vinyl sulfides and vinyl sulfones is still necessary.

Sulfinic acids are readily accessible and have been widely used as sulfur sources in medicinal chemistry.[17] Moreover, sulfinic acids can be reduced to disulfides, which are active intermediates that can be used as sulfenylating agents. So we envisioned that sulfinic acids might be served as potential sulfur sources to react with alcohols under certain reaction conditions. To our knowledge, there are no examples describing the reaction of sulfinic acids and alcohols. Herein we report an efficient synthesis of vinyl sulfides and vinyl sulfones *via* transition metal-free sodium iodide-mediated sulfenylation of alcohols with sulfinic acids.

Results and discussion

To obtain the optimized reaction conditions, several acids (10 mol%) were examined in the model reaction of alcohol **1a** with benzenesulfinic acid **2a** using tetrabutylammonium iodide as an additive in 1,2-dichloroethane at 80 °C (Table 1, entries 1–4). To our delight, TsOH·H_2O was identified as the acid of choice, which promoted the formation of vinyl sulfide **3a** in 61% yield (Table 1, entry 1). Iodine and several iodides such as NaI, KI were investigated to improve the reaction efficiency (Table 1, entries 5–7). Among the above iodides examined, NaI was found to be the most effective additive to give the target product **3a** in 70% yield (Table 1, entry 5). Further solvent screening showed

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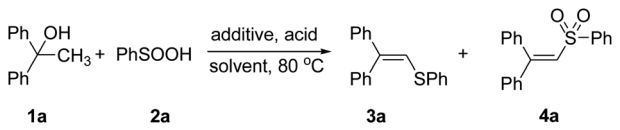
Table 1 Optimization of reaction conditions[a]



1a 2a 3a 4a

Entry	Solvent	Additive (eq.)	Acid (eq.)	Yield[b] (%) **3a**	Yield[b] (%) **4a**
1	DCE	*n*-Bu_4NI (1.0)	$TsOH\cdot H_2O$ (0.1)	61	0
2	DCE	*n*-Bu_4NI (1.0)	HCl (0.1)	57	0
3	DCE	*n*-Bu_4NI (1.0)	TfOH (0.1)	53	0
4	DCE	*n*-Bu_4NI (1.0)	H_2SO_4 (0.1)	58	0
5	DCE	NaI (1.0)	$TsOH\cdot H_2O$ (0.1)	70	0
6	DCE	KI (1.0)	$TsOH\cdot H_2O$ (0.1)	63	0
7	DCE	I_2 (1.0)	$TsOH\cdot H_2O$ (0.1)	0	0
8	MeCN	NaI (1.0)	$TsOH\cdot H_2O$ (0.1)	18	44
9	$MeNO_2$	NaI (1.0)	$TsOH\cdot H_2O$ (0.1)	Trace	59
10	Toluene	NaI (1.0)	$TsOH\cdot H_2O$ (0.1)	42	30
11	DMSO	NaI (1.0)	$TsOH\cdot H_2O$ (0.1)	17	21
12	DMF	NaI (1.0)	$TsOH\cdot H_2O$ (0.1)	Trace	15
13	Dioxane	NaI (1.0)	$TsOH\cdot H_2O$ (0.1)	30	0
14	EtOH	NaI (1.0)	$TsOH\cdot H_2O$ (0.1)	Trace	39
15	DCE	NaI (1.5)	$TsOH\cdot H_2O$ (0.1)	78	Trace
16	DCE	NaI (1.5)	$TsOH\cdot H_2O$ (0.2)	90	Trace
17	$MeNO_2$	NaI (1.5)	$TsOH\cdot H_2O$ (0.2)	Trace	86

[a] Reaction conditions: alcohol **1a** (0.20 mmol), benzenesulfinic acid **2a** (0.30 mmol), additive, acid, solvent (1.0 mL), 80 °C, 24 h. [b] Isolated yield.

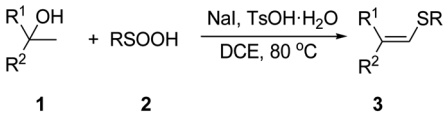
interesting results: (1) we observed the generation of vinyl sulfone **4a** in MeCN (Table 1, entry 8). (2) $MeNO_2$ was the best solvent for the formation of **4a**, and improved the yield to 59% yield (Table 1, entry 9). (3) DCE was the best solvent for the formation of **3a**. These results demonstrate that solvent plays an important role in controlling the chemoselectivity of the reaction, which could be explained by the fact that $MeNO_2$ is beneficial to the production of free radical intermediates. A high yield was obtained when the loading of sodium iodide was increased to 1.5 equivalents (Table 1, entry 15). Further efforts to increase the yield of vinyl sulfide **3a** by increasing the loading of $TsOH\cdot H_2O$ to 0.2 equivalent resulted in a higher yield of 90% (Table 1, entry 16). Similarly, the yield of **4a** was increased to 86% in the presence of 1.5 equivalents of NaI and 20 mol% $TsOH\cdot H_2O$ in $MeNO_2$.

Encouraged by our preliminary findings, the substrate scope of alcohols and sulfinic acids for the synthesis of vinyl sulfides was explored, and the results were shown in Table 2. In the presence of 1.5 equivalents of NaI, 20 mol% $TsOH\cdot H_2O$ and DCE as solvent, a broad range of bisbenzylic, monobenzylic and naphthyl alcohols smoothly underwent this kind of transformation, generating structurally diverse vinyl sulfide **3** in moderate to excellent yields with extremely high stereoselectivity (Table 2, entries 1–11). The reactivity of monoaryl alcohols is lower than diaryl alcohol. Notably, this protocol proved useful for the construction of vinyl sulfides containing polycycles such as **3d–f** (Table 2, entries 4–6). However, this protocol was not applicable to less reactive alkyl alcohols (Table 2, entry 9) substrate scope is also broad with respect to the sulfinic acids. Various arylsulfinic acids smoothly reacted with alcohol **1a** to give the corresponding vinyl sulfides in good to excellent yields (Table 2, entries 12–22). It is noteworthy that both electron-withdrawing and electron-donating groups were introduced into the vinyl sulfides by employing arylsulfinic acid bearing such groups on the aromatic ring. Furthermore, alkylsulfinic acids could also smoothly react with alcohol **1a** to give the corresponding vinyl sulfides (Table 2, entries 23–25). But the yield is lower than arylsulfinic acids, this may be due to the low activity of alkylsulfinic acids.

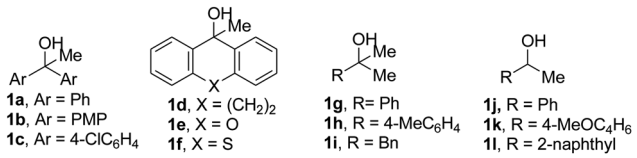
Next, the substrate scope of alcohols and sulfinic acids for the synthesis of vinyl sulfones was explored, and the results were shown in Table 3. In the presence of 1.5 equivalents of NaI, 20 mol% $TsOH\cdot H_2O$ and $MeNO_2$ as solvent, a broad range of bisbenzylic and monobenzylic alcohols were found to react well with benzenesulfinic acids to yield structurally diverse vinyl sulfones derivatives in good to excellent yields with extremely high stereoselectivity (Table 3, entries 1–7). The results represented in Table 3 show that the scope of sulfinic acids is also very general in the sulfonylation of alcohols. A number of arylsulfinic acids bearing either electron-donating groups or electron-withdrawing groups on the aromatic rings were transformed into their corresponding vinyl sulfones at 80 °C in good to excellent yields (Table 3, entries 8–14). Moreover, alkylsulfinic acids could also smoothly react with alcohol **1a** to give the corresponding vinyl sulfones (Table 3, entry 15).

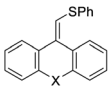
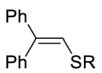
In order to gain further insight into the reaction mechanism, four control experiments were set up under various reaction conditions. Benzenesulfinic acid was reduced to diphenyldisulfane **2a′** in 94% yield in the presence of 1.5 equivalents of NaI, 20 mol% $TsOH\cdot H_2O$ and DCE as solvent (Scheme 1a).

Table 2 Sulfenylation of alcohols with sulfinic acids[a]



1 2 3



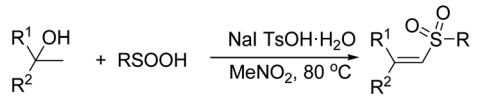
Entry	1	2	Product 3		Yield[b] (%)
1	**1a**	**2a**		**3aa**, Ar = Ph	90
2	**1b**	**2a**		**3ba**, Ar = PMP	83
3	**1c**	**2a**		**3ca**, Ar = 4-ClC_6H_4	89
4	**1d**	**2a**		**3da**, X = $(CH_2)_2$	91
5	**1e**	**2a**		**3ea**, X = O	81
6	**1f**	**2a**		**3fa**, X = S	77
7	**1g**	**2a**		**3ga**, R = Ph	65
8	**1h**	**2a**		**3ha**, R = 4-MeC_6H_4	69
9	**1i**	**2a**		**3ia**, R = Bn	0
10	**1j**	**2a**	RCH = CHSPh	**3ja**, R = Ph	43
11	**1k**	**2a**		**3ka**, R = 2-naphthyl	56
12	**1a**	**2b**		**3ab**, R = 4-MeC_6H_4	91
13	**1a**	**2c**		**3ac**, R = 4-*t*BuC_6H_4	88
14	**1a**	**2d**		**3ad**, R = 4-$MeOC_6H_4$	85
15	**1a**	**2e**		**3ae**, R = 4-FC_6H_4	93
16	**1a**	**2f**		**3af**, R = 4-ClC_6H_4	89
17	**1a**	**2g**		**3ag**, R = 4-BrC_6H_4	86
18	**1a**	**2h**		**3ah**, R = 4-IC_6H_4	81
19	**1a**	**2i**		**3ai**, R = 3-$O_2NC_6H_4$	90
20	**1a**	**2j**		**3aj**, R = 2,4-$Cl_2C_6H_4$	83
21	**1a**	**2k**		**3ak**, 1-naphthyl	98
22	**1a**	**2l**		**3al**, 2-naphthyl	99
23	**1a**	**2m**		**3am**, $Me(CH_2)_7$	72
24	**1a**	**2n**		**3an**, Bn	76
25	**1a**	**2o**		**3ao**, CH_3	67

[a] Reaction conditions: alcohol **1** (0.20 mmol), sulfinic acid **2** (0.30 mmol), NaI (0.30 mmol), TsOH·H_2O (0.040 mmol), DCE (1.0 mL), 80 °C, 24 h. [b] Isolated yield.

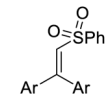
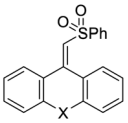
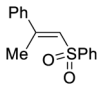
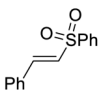
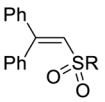
Under the 1.0 equivalents of iodine, diphenyldisulfane **2a′** smoothly reacted with alcohol **1a** to give the corresponding vinyl sulfide **3ab** in 91% yield (Scheme 1b). Under the standard reaction conditions, alcohol **1a** and diphenyldisulfane **2a′** don't react (Scheme 1c). In the presence of 1.5 equivalents of NaI, 20 mol% TsOH and DCE as solvent, alkene **6a** was found to react smoothly with benzenesulfinic acids to give vinyl sulfide **3ab** in 93% yields (Scheme 1d).

On the basis of the above experimental results and previous relevant mechanism studies,[14,18] we proposed the reaction pathway depicted in Scheme 2. Initially, alcohol **1** undergo elimination reaction to form alkene **6** under TsOH and heating conditions. Meanwhile, 1,2-diphenyldisulfane (**2a′**) is generated from sulfinic acid **2** in the presence of NaI and TsOH. Then **2a′** reacts with I_2 to give the sulfenyl iodide **5**, which is attacked by **6**

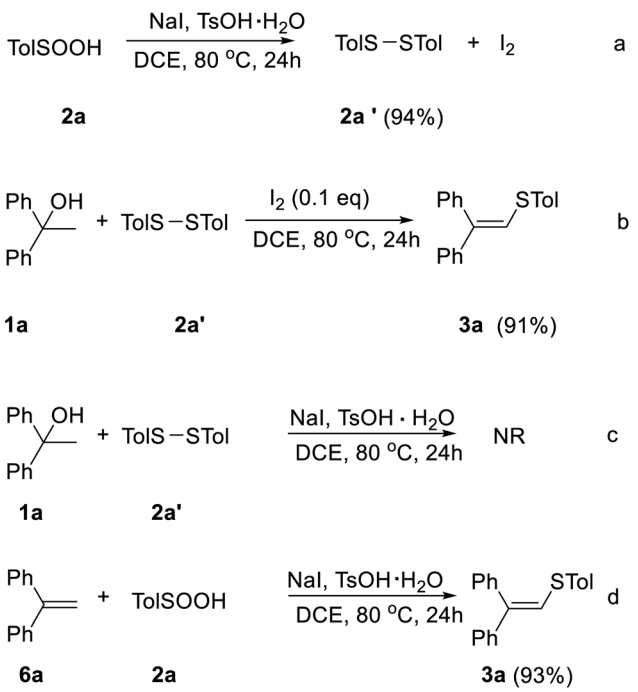
Table 3 Sulfonylation of alcohols with sulfinic acids[a] *tab3fnb*



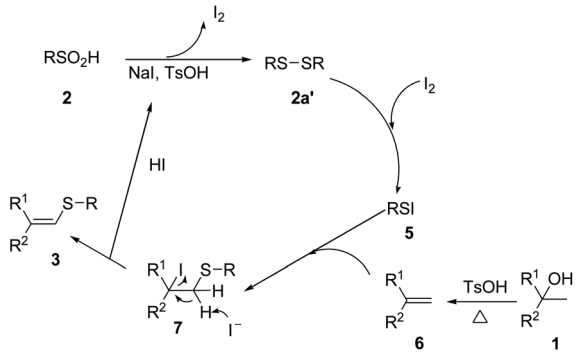
1 2 4

Entry	1	2	Product		Yield[b] (%)
1	**1a**	**2a**		**4aa**, Ar = Ph	86
2	**1b**	**2a**		**4ba**, Ar = PMP	93
3	**1c**	**2a**		**4ca**, Ar = 4-ClC_6H_4	88
4	**1d**	**2a**		**4da**, X = $(CH_2)_2$	90
5	**1f**	**2a**		**4fa**, X = S	81
6	**1g**	**2a**		**4ga**	75
7	**1j**	**2a**		**4ja**	67
8	**1a**	**2b**		**4ab**, R = 4-MeC_6H_4	91
9	**1a**	**2c**		**4ac**, R = 4-*t*BuC_6H_4	85
10	**1a**	**2d**		**4ad**, R = 4-$MeOC_6H_4$	82
11	**1a**	**2e**		**4ae**, R = 4-FC_6H_4	73
12	**1a**	**2f**		**4af**, R = 4-ClC_6H_4	87
13	**1a**	**2k**		**4ak**, 1-naphthyl	90
14	**1a**	**2l**		**4al**, 2-naphthyl	95
15	**1a**	**2m**		**4am**, $Me(CH_2)_7$	63

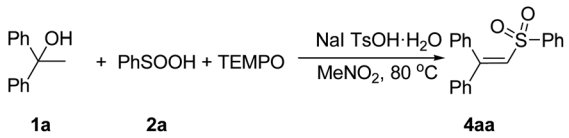
[a] Reaction conditions: alcohol **1** (0.20 mmol), sulfinic acid **2** (0.30 mmol), NaI (0.30 mmol), TsOH·H_2O (0.040 mmol), $MeNO_2$ (1.0 mL), 80 °C, 24 h. [b] Isolated yield.



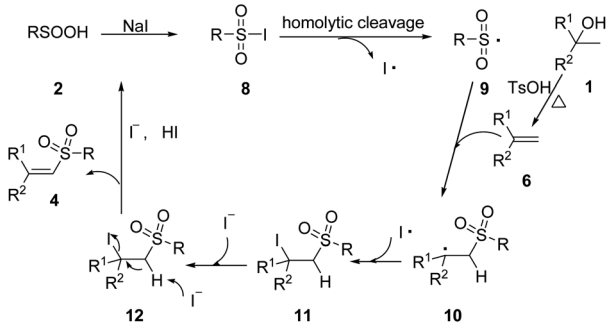
Scheme 1 Control experiments (a–d).



Scheme 2 Proposed reaction pathway for the synthesis of vinyl sulfides.



Scheme 3 Control experiment for the generation of vinyl sulfone.



Scheme 4 Proposed reaction pathway for the synthesis of vinyl sulfones.

to give intermediate **7**. Finally, elimination of HI from **7** affords the corresponding vinyl sulfide **3**.

We performed a relevant control experiment for vinyl sulfones (Scheme 3). When a stoichiometric amount of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy, a well known radical-capturing species) was added to this reaction mixture, the formation of **4a** was completely inhibited in the reaction. Therefore, we reason that a radical process should be involved in this reaction.

On the basis of the preliminary result above and previous relevant mechanism studies,[14] we proposed a plausible mechanism for the generation of vinyl sulfones in Scheme 4. First, alcohol **1** undergo elimination reaction to form alkene **6** under TsOH and heating conditions. Meanwhile, sulfonyl iodide **8** was generated from benzenesulfinic acid in the presence of NaI under air. Then, **8** experienced homolytic cleavage to produce a sulfonyl radical **9**, which interacted with alkene **6** to give intermediate **10**. Next, intermediate **10** reacts with an iodine radical to give intermediate **11**. Finally, elimination of HI from **11** produces the corresponding vinyl sulfone **4**.

Conclusions

In conclusion, we have developed a NaI mediated elimination/coupling reaction of alcohols and sulfinic acids, constructing structurally diverse vinyl sulfides and vinyl sulfones. Solvent is crucial for the chemical selectivity. Solvent-controlled selectivity of the elimination/coupling reaction was realized for divergent synthesis of vinyl sulfides and vinyl sulfones. The described protocol is more convenient for the preparation of vinyl sulfide than vinyl sulfone related skeletons and the starting materials are readily available. Current efforts are directed toward further methodological refinement and synthetic applications.

Experimental

General procedure for the synthesis of vinyl sulfides (Table 2)

To a solution of alcohol **1** (0.20 mmol) in DCE (1.0 mL) under an air atmosphere at room temperature were added sulfinic acid **2** (0.30 mmol), NaI (45.0 mg, 0.30 mmol) and TsOH·H_2O (7.6 mg, 0.040 mmol). The mixture was stirred at 80 °C for 24 h, cooled to room temperature, and directly purified by preparative thin layer chromatography on silica gel, developing with petroleum ether/ethyl acetate (100 : 0 to 20 : 1), to give compound **3**.

General procedure for the synthesis of vinyl sulfones (Table 3)

To a solution of alcohol **1** (0.20 mmol) in $MeNO_2$ (1.0 mL) under an air atmosphere at room temperature were added sulfinic acid **2** (0.30 mmol), NaI (45.0 mg, 0.30 mmol) and TsOH·H_2O (7.6 mg, 0.040 mmol). The mixture was stirred at 80 °C for 24 h, cooled to room temperature, and directly purified by preparative thin layer chromatography on silica gel, developing with petroleum ether/ethyl acetate (20 : 1 to 5 : 1), to give compound **4**.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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