

# Air-Induced Disulfenylation of Alkenes: Facile Synthesis of Vicinal Dithioethers

Guodan Yu

Yingcong Ou

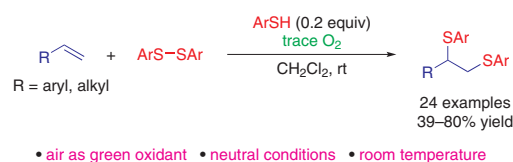
Danyao Chen

Yuanting Huang

Yan Yan

Qian Chen\* 

School of Chemical Engineering and Light Industry,  
Guangdong University of Technology, Guangzhou  
510006, P. R. of China  
qianchen@gdut.edu.cn



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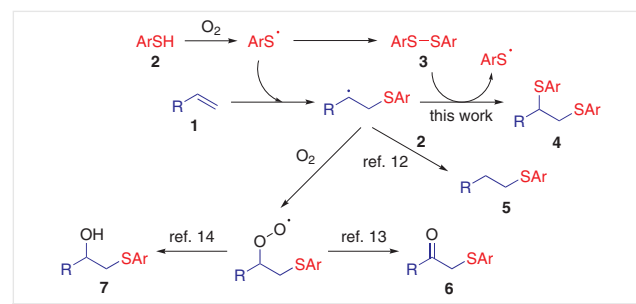
**Abstract** A novel disulfenylation of alkenes with thiophenols and their corresponding disulfides by using air as the oxidant has been achieved. This transformation provides a facile and practical protocol for the synthesis of vicinal dithioethers under mild conditions.

**Key words** disulfenylation, alkenes, thioethers, aerial oxidation

Organosulfur compounds bearing carbon–sulfur bonds are of great importance in organic synthesis and biological chemistry.<sup>1,2</sup> As a result, the development of novel methods for the construction of carbon–sulfur bonds under mild conditions has attracted enormous attention.<sup>3</sup> Among these methods, the disulfenylation of carbon–carbon unsaturated bonds is a facile and practical protocol for the preparation of vicinal dithioethers,<sup>4</sup> which have been widely used as bidentate ligands and in pharmaceutical chemistry as synthetic intermediates.<sup>5</sup> Previous disulfenylations of alkenes with disulfides typically require a Lewis acid (e.g., GaCl<sub>3</sub> or FeCl<sub>3</sub>)<sup>4a,4b</sup> or molecular iodine<sup>4f</sup> as a catalyst. In particular, Li and Chen reported an NH<sub>4</sub>I-promoted bismethylthiolation of terminal alkenes by using dimethyl sulfoxide (DMSO) as the thioetherification reagent.<sup>4h</sup> Our group recently developed a catalyst-free direct C(sp<sup>3</sup>)–H sulfenylation of xanthenes by using air as the oxidant.<sup>6</sup> Consequently, we became interested in studying an air-induced disulfenylation of alkenes for the synthesis of vicinal dithioethers under mild conditions.

Thiyl radicals are known to add efficiently to a wide range of unsaturated compounds such as alkenes, alkynes, or isonitriles.<sup>7</sup> The most useful synthetic applications of thiyl radicals are based on their ability to add to carbon–carbon unsaturated bonds for the construction of carbon–sul-

fur bonds.<sup>8</sup> Notably, thiyl radicals can be easily generated by the autoxidation of thiols in the presence of oxygen.<sup>8c,9</sup> In addition, we have also recently developed a variety of metal-free methods for the construction of carbon–sulfur, phosphorus–sulfur, sulfone–sulfur, and sulfur–oxygen bonds by pathways involving thiyl radicals.<sup>10</sup> On this basis, we surmised that vicinal dithioethers might be formed by disulfenylation of alkenes with thiols and disulfides in the presence of air (oxygen). As shown in Scheme 1, under an air atmosphere, the autoxidation of thiol **2** generates a thiyl radical that can undergo subsequent homocoupling to produce the corresponding disulfide **3**.<sup>9</sup> The thiyl radical can also add across alkene **1** with anti-Markovnikov selectivity to form a carbon-centered radical.<sup>7b</sup> This radical can then react with disulfide **3** to produce the desired vicinal dithioether **4** through radical propagation, with regeneration of the thiyl radical.<sup>11</sup> Moreover, additional reaction pathways would be competitive and would give the corresponding byproducts. Thus, the carbon-centered radical could abstract a hydrogen atom from another molecule of thiol **2** to give the hydrothiolated product **5**<sup>12</sup> or it might react with oxygen to form a peroxy radical that might afford the β-keto sulfide **6**<sup>13</sup> or β-hydroxy sulfide **7**.<sup>14</sup> Here, we report



**Scheme 1** Additions of thiyl radicals to alkenes

that air can efficiently induce the addition of thiols and disulfides to alkenes and provide good yields of vicinal dithioethers through a radical pathway under neutral conditions.

The reaction conditions were tested by using a model reaction of styrene (**1a**) with 4-methylbenzenethiol (**2a**) and bis(4-methylphenyl) disulfide (**3a**) under air (Table 1). First, we carried out the reaction of **1a** with **2a** (0.5 equiv) and **3a** (3 equiv) in CH<sub>3</sub>CN at room temperature under air for 24 hours (Table 1, entry 1). To our delight, the reaction afforded the desired vicinal dithioether **4a** in 52% yield, together with  $\beta$ -keto sulfide **6a** and  $\beta$ -hydroxy sulfide **7a** in yields of 17 and 24%, respectively. A screening of solvents (entries 2–8) showed that CH<sub>2</sub>Cl<sub>2</sub> is the optimal solvent, leading to the formation of **4a** in 59% yield (entry 8). When two equivalents of disulfide **3a** were employed, **4a** was still obtained in the same yield (entry 9), whereas the use of one equivalent of **3a** significantly decreased the product yield (entry 10). When a catalytic amounts of thiol **2a** (0.2 equiv) was used, the yield of **4a** remained unchanged (entry 11), suggesting that the propagation of thiyl radicals might be involved in the reaction. In an attempt to prevent the formation of byproducts **6a** and **7a**, we carried out the reaction under various air–N<sub>2</sub> atmospheres (entries 12–15). Pleasingly, when the amount of oxygen in the reaction atmosphere was about 5%, the reaction proceeded smoothly to afford **4a** in 76% yield (entry 13), and the formation of byproducts was significantly reduced by the use of the lower concentration of oxygen. In addition, a further decrease in the amount of thiol **2a** led to a poor yield of **4a**, probably due to the difficulty in the formation of thiyl radicals in the presence of catalytic amounts of both the thiol and oxygen (entries 16 and 17). Finally, we concluded that the optimal conditions for the disulfenylation of alkenes involve the use 0.2 equivalents of the thiol and two equivalents of the disulfide as a sulfur source with a trace amount of oxygen as the oxidant and CH<sub>2</sub>Cl<sub>2</sub> as the solvent at room temperature (entry 13).

We then set out to explore the generality of the disulfenylation of alkenes.<sup>15</sup> We first applied the optimized conditions to the reaction of styrene (**1a**) with a variety of thiols **2** and their corresponding disulfides **3** (Table 2). Thiophenols and disulfides substrates bearing various substituents such as electron-donating groups (Me or OMe) or weakly electron-withdrawing groups (Br, Cl, or F) on the *para*- or *meta*-positions of the aromatic rings were all well tolerated, and the corresponding vicinal dithioethers **4a–j** were isolated in good yields (60–80%). Unfortunately, the disulfenylation of **1a** with (2-methylphenyl)thiol and the corresponding disulfide failed to give the desired product **4k**, probably due to the steric hindrance by the *ortho*-substituent. We then turned our attention to aliphatic thiols. Phenylmethanethiol and its corresponding disulfide did not afford the dithioether **4l**, possibly because aliphatic thiols fail to generate thiyl radicals under air.<sup>6</sup> In addition, a

**Table 1** Optimization of Reaction Conditions<sup>a,b</sup>

Entry	<b>2a</b> (equiv)	<b>3a</b> (equiv)	Solvent	Yield <sup>b</sup> (%) of <b>4a</b>	Yield <sup>b</sup> (%) of <b>6a</b>	Yield <sup>b</sup> (%) of <b>7a</b>
1	0.5	3	CH <sub>3</sub> CN	52	17	24
2	0.5	3	THF	22	24	35
3	0.5	3	1,4-dioxane	trace	trace	trace
4	0.5	3	DMF	trace	trace	65
5	0.5	3	EtOH	trace	trace	trace
6	0.5	3	DCE	22	trace	trace
7	0.5	3	toluene	trace	trace	27
8	0.5	3	CH <sub>2</sub> Cl <sub>2</sub>	59	15	19
9	0.5	2	CH <sub>2</sub> Cl <sub>2</sub>	59	15	20
10	0.5	1	CH <sub>2</sub> Cl <sub>2</sub>	43	24	30
11	0.2	2	CH <sub>2</sub> Cl <sub>2</sub>	59	15	19
12 <sup>c</sup>	0.2	2	CH <sub>2</sub> Cl <sub>2</sub>	68	10	14
13 <sup>d</sup>	0.2	2	CH <sub>2</sub> Cl <sub>2</sub>	76	trace	9
14 <sup>e</sup>	0.2	2	CH <sub>2</sub> Cl <sub>2</sub>	70	trace	11
15 <sup>f</sup>	0.2	2	CH <sub>2</sub> Cl <sub>2</sub>	52	trace	trace
16 <sup>d</sup>	0.15	2	CH <sub>2</sub> Cl <sub>2</sub>	42	trace	trace
17 <sup>d</sup>	0.1	2	CH <sub>2</sub> Cl <sub>2</sub>	trace	trace	trace

<sup>a</sup> Reaction conditions: a 25 mL vial was charged with **1a** (0.2 mmol), **2a**, and **3a** in the appropriate solvent (2 mL) and sealed under an air atmosphere (1 atm). The mixture was stirred at rt for 24 h.

<sup>b</sup> Yield based on **1a** as determined by <sup>1</sup>H NMR analysis of the crude product using an internal standard.

<sup>c</sup> Air (9 mL) was introduced into the sealed vial under N<sub>2</sub>.

<sup>d</sup> Air (7 mL) was introduced into the sealed vial under N<sub>2</sub>.

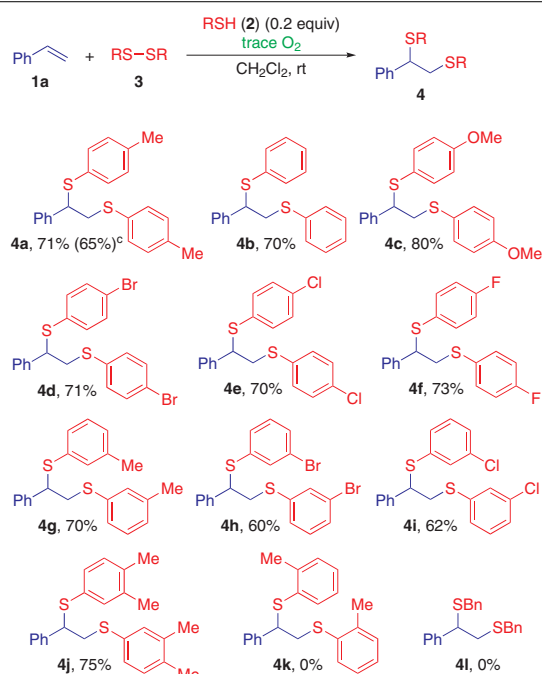
<sup>e</sup> Air (5 mL) was introduced into the sealed vial under N<sub>2</sub>.

<sup>f</sup> Air (3 mL) was introduced into the sealed vial under N<sub>2</sub>.

scaled-up reaction was attempted and, when we increased the scale of the reaction of **1a** with **2a** and **3a** from 0.2 to 7 mmol, we obtained **4a** in 65% yield (1.6 g).

To further define the scope of our protocol, the substrate scope was extended to various alkenes **1** under the optimized conditions (Table 3). Terminal aromatic alkenes with various groups (Me, Br, Cl and F) in the *para*-, *meta*-, or *ortho*-position of aromatic rings underwent the reaction, delivering the desired products **4m–w** in good yields. Significantly, the disulfenylation of terminal aliphatic alkenes gave **4x** and **4y** in yields of 39 and 67%, respectively. Furthermore, cyclohexene, an internal aliphatic alkene, stereoselectively afforded the *trans*-vicinal dithioether **4z** in 45% yield.

To gain more insight into the mechanism of the reaction, we conducted a series of control experiments (Scheme 2). The disulfenylation of styrene (**1a**) with disulfide **3a** failed to give the desired **4a** in the absence of thiol **2a** under otherwise standard conditions (Scheme 2a), suggesting that the reaction is initiated by thiol **2a**. When the reaction

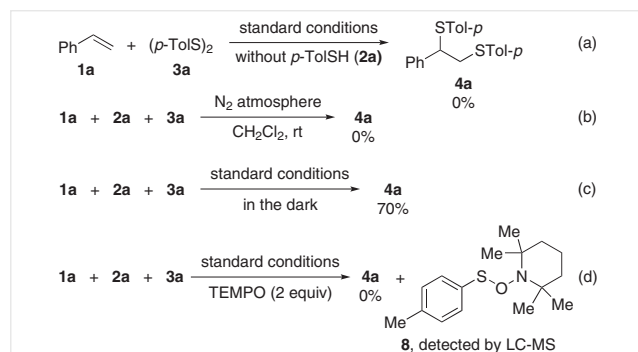
Table 2 Scope of Thiols and Disulfides<sup>a,b</sup>

<sup>a</sup> Reaction conditions: a 25 mL vial was charged with **1a** (0.2 mmol), **2** (0.04 mmol), and **3** (0.4 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL) and sealed under an air- $\text{N}_2$  atmosphere (~5%  $\text{O}_2$ ). The mixture was stirred at rt for 24 h.

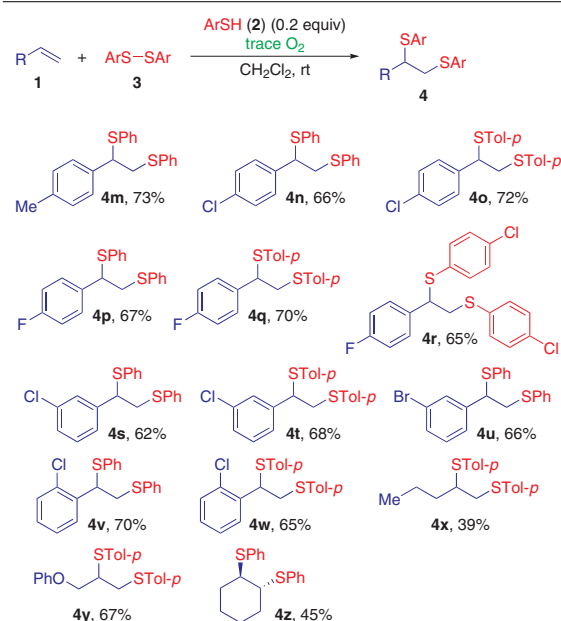
<sup>b</sup> The isolated yields based on **1a** are reported.

<sup>c</sup> Scaled-up reaction (7 mmol).

was carried out under  $\text{N}_2$ , **4a** was not detected (Scheme 2b), suggesting that an aerobic oxidation might be involved in the reaction. The yield of **4a** remained unchanged when the reaction was performed in the dark (Scheme 2c), suggesting that visible light is unnecessary for this transformation. When the radical scavenger TEMPO (2,2,6,6-tetramethylpiperidine *N*-oxyl) was employed under the standard conditions, the desired reaction of **1a** with **2a** and **3a** was com-



Scheme 2 Mechanistic studies

Table 3 Scope of Alkenes<sup>a,b</sup>

<sup>a</sup> Reaction conditions: a 25 mL vial was charged with **1a** (0.2 mmol), **2** (0.04 mmol), and **3** (0.4 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL) and sealed under an air- $\text{N}_2$  atmosphere (~5%  $\text{O}_2$ ). The mixture was stirred at rt for 24 h.

<sup>b</sup> Isolated yields based on **1** are reported.

pletely inhibited, and the TEMPO adduct **8** was detected by LC-MS (Scheme 2d), indicating that this reaction might involve an addition of a thiyl radical to the alkene. Overall, the results of these control experiments are in good agreement with the mechanism proposed in Scheme 1.

In summary, we have developed a green and efficient disulfenylation of alkenes with thiophenols and their corresponding disulfides induced by a trace amount of oxygen, thereby providing a facile and practical protocol for the synthesis of vicinal dithioethers. The good yields and mild reaction conditions showcase the potential of this approach in chemical synthesis.

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## Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/s-0039-1691493>.

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- (15) **1,1'-[(1-phenylethane-1,2-diyl)di(sulfanediyl)]bis(4-methylbenzene) (4a): Typical Procedure**  
A 25 mL vial was charged with styrene (**1a**) (21 mg, 0.2 mmol), thiol **2a** (5 mg, 0.04 mmol), and disulfide **3a** (99 mg, 0.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL), then sealed under a N<sub>2</sub> atmosphere. Air (7 mL) was introduced into the sealed vial and the mixture was stirred at rt for 24 h. After removal of the solvent, the residue was purified by flash column chromatography (silica gel, PE) to give a white solid; yield: 50 mg (71%); mp 67.2–68.5 °C.  
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.29–7.17 (m, 5 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 7.07–6.97 (m, 6 H), 4.15 (dd, *J* = 10.1, 4.9 Hz, 1 H), 3.42 (dd, *J* = 13.5, 4.9 Hz, 1 H), 3.27 (dd, *J* = 13.5, 10.2 Hz, 1 H), 2.29 (s, 3 H), 2.29 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 140.0, 137.9, 136.6, 133.5, 131.9, 130.7, 130.5, 129.80, 129.77, 128.6, 128.2, 127.8, 52.7, 40.2, 21.3, 21.2.