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Rhodium(III)-Catalyzed *Ortho*-Alkenylation through C−H Bond Cleavage Directed by Sulfoxide Groups

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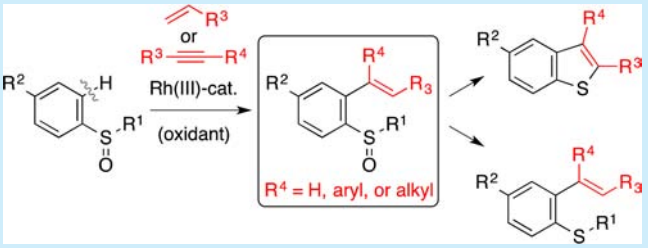
Supporting Information

ABSTRACT: The rhodium-catalyzed *ortho*-alkenylation of phenyl sulfoxides using alkenes or alkynes as substituent sources proceeds efficiently through sulfoxide group directed C−H bond cleavage to produce the corresponding *o*-alkenylphenyl sulfoxides. The products readily undergo interrupted Pumerer cyclization as well as reduction to afford benzothiophenes and *o*-alkenylphenyl sulfides.

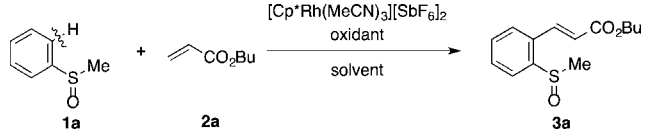


Transition-metal-catalyzed aromatic C−H functionalization has been recognized to be a highly important synthetic tool because it provides step- and atom-economical routes to functionalized aromatic molecules.[1] With the aim of the regioselective cleavage of C−H bonds existing ubiquitously in organic molecules, directing groups are usually employed. Coordination of such groups toward a transition-metal center leads to *ortho*-selective C−H bond cleavage and functionalization.[2] A variety of oxygen- and nitrogen-containing directing groups such as hydroxyl, carboxyl, carbonyl, amide, imino, and pyridyl groups have been utilized in a wide range of reactions. Recently, phosphorus-containing functions have also come into general use.[3]

Meanwhile, it is generally considered that sulfur-containing functional groups such as sulfides and sulfoxides that have lone pairs on the sulfur coordinate metal centers too strongly to suppress their catalytic activities. However, mainly under palladium catalysis, sulfoxide group directed C−H functionalization has recently been developed.[4,5] During our continuous studies on Rh(III)-catalyzed C−H functionalization,[6,7] we succeeded in finding that phenyl sulfoxides undergo *ortho*-alkenylation using alkenes and alkynes as substituent sources. The products, *o*-alkenylated phenyl sulfoxides, are of importance because they can be readily converted to the corresponding benzothiophenes via deoxygenative cyclization (interrupted Pummerer cyclization).[8] The sulfoxide groups are also known to be transformed to other functional groups such as sulfides by reduction treatment.[9] Besides such utilities for further derivatization, *o*-alkenylphenyl sulfoxides themselves are applicable as useful ligands for transition metals.[10] Herein, the new findings concerning the *ortho*-alkenylation of phenyl sulfoxides and preliminary examinations for further transformation of the alkenylated products are described.

In an initial attempt, methyl phenyl sulfoxide (**1a**) (0.5 mmol) was treated with butyl acrylate (**2a**) (0.25 mmol) in the presence of $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.02 mmol) and $Cu(OAc)_2·H_2O$ (0.5 mmol) as catalyst and oxidant, respectively, in chlorobenzene (PhCl) (3 mL) at 120 °C for 6 h under N_2. As a result, an *ortho*-alkenylated product, butyl (*E*)-3-(2-(methylsulfinyl)phenyl)acrylate (**3a**), was formed in 39% yield (based on the amount of **2a** used) (entry 1 in Table 1). In other solvents such as *t*-AmOH, *α,α,α*-trifluorotoluene

Table 1. Reaction of Methyl Phenyl Sulfoxide (1a) with Butyl Acrylate (2a)[a]



entry	oxidant (mmol)	solvent	yield of **3a**[b] (%)
1	$Cu(OAc)_2·H_2O$ (0.5)	PhCl	39
2	$Cu(OAc)_2·H_2O$ (0.5)	*t*-AmOH	34
3	$Cu(OAc)_2·H_2O$ (0.5)	$PhCF_3$	32
4	$Cu(OAc)_2·H_2O$ (0.5)	diglyme	26
5	Ag_2CO_3 (0.25)	PhCl	69
6[c]	Ag_2CO_3 (0.25)	PhCl	0
7[d]	Ag_2CO_3 (0.25)	PhCl	41
8[e]	Ag_2CO_3 (0.25)	PhCl	80 (77)
9[e]	Ag_2CO_3 (0.25)	$PhCF_3$	89 (77)
10[f]	Ag_2CO_3 (2.5)	$PhCF_3$	(72)

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.25 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.02 mmol) in solvent (3 mL) at 120 °C for 6 h under N_2, unless otherwise noted. [b]GC yield based on the amount of **2a** used. Value in parentheses indicates yield after purification. [c]Without $[Cp^*Rh(MeCN)_3][SbF_6]_2$. [d]With **1a** (0.25 mmol). [e]With **1a** (0.75 mmol). [f]With **1a** (7.5 mmol), **2a** (2.5 mmol), an $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.2 mmol), in solvent (30 mL).

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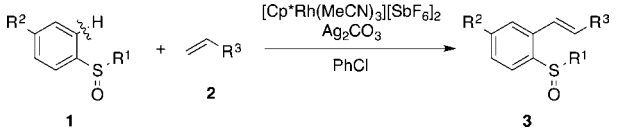
($PhCF_3$), and diglyme, the product yield slightly decreased (entries 2–4). To our delight, the **3a** yield was significantly improved by using Ag_2CO_3 (0.25 mmol) as oxidant (entry 5). The control experiment without Rh-catalyst did not give **3a** at all (entry 6). Decreasing the amount of **1a** to 0.25 mmol caused the reduction of the **3a** yield (entry 7), while using 0.75 mmol of **1a** enhanced it up to 80% (entry 8). In $PhCF_3$, the reaction also proceeded smoothly to give **3a** in the same isolated yield (entry 9). It should be noted that the present reaction could be readily scaled up to 10 times. Thus, from **1a** (7.5 mmol) and **2a** (2.5 mmol), **3a** was obtained in 72% isolated yield (0.48 g, entry 10).

With the optimized conditions in hand, the reactions of variously substituted phenyl sulfoxides with alkenes were examined next (Table 2). A series of acrylates, iso and *tert*-butyl, cyclohexyl, and ethyl acrylates (**2b–e**) coupled with **1a** to produce the corresponding *o*-alkenylated phenyl sulfoxides **3b–e** (entries 1–4). In the case using sterically hindered ester **2c**, a better result was obtained in $PhCF_3$ (entry 2). The reaction with relatively volatile **2e** was conducted at 100 °C (entry 4). On the other hand, *p*-methyl- and *p*-methoxyphenyl sulfoxides **1b** and **1c** underwent the reaction with **2a** in $PhCF_3$ to form **3f** and **3g**, respectively (entries 5 and 6). The reaction of electron-deficient **1d** was found to be sluggish. Thus, even at 140 °C, the product yield was moderate (entry 7). Diphenyl sulfoxide (**1e**) reacted with **2a** smoothly under standard conditions to give **3i** in 62% yield (entry 8).

Table 2. Reaction of Phenyl Sulfoxides 1 with Alkenes 2[a]



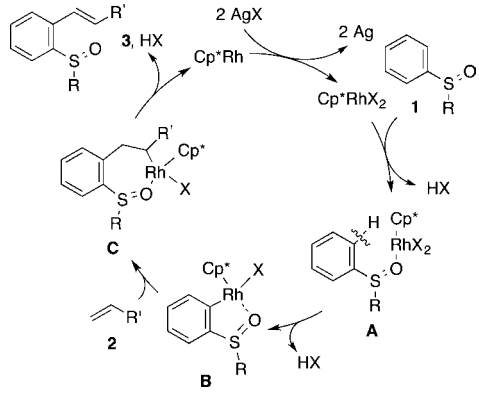
1 + 2 → 3

entry	1	2	product, % yield[b]
1	**1a**	**2b**: R = CO_2Bu^i	**3b**: R = CO_2Bu^i, 68
2[c]		**2c**: R = CO_2Bu^t	**3c**: R = CO_2Bu^t, 48
3		**2d**: R = CO_2Cy	**3d**: R = CO_2Cy, 81
4[d]		**2e**: R = CO_2Et	**3e**: R = CO_2Et, 57
5[c]	**1b**: R = Me	**2a**	**3f**: R = Me, 68
6[c]	**1c**: R = OMe		**3g**: R = OMe, 42
7[e]	**1d**: R = Cl		**3h**: R = Cl, 35
8[c]	**1e**	**2a**	**3i**, 62

[a]Reaction conditions: **1** (0.75 mmol), **2** (0.25 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.02 mmol), Ag_2CO_3 (0.25 mmol), in PhCl (3 mL) at 120 °C for 6 h under N_2, unless otherwise noted. [b]Isolated yield based on the amount of **2** used. [c]In $PhCF_3$. [d]At 100 °C. [e]At 140 °C.

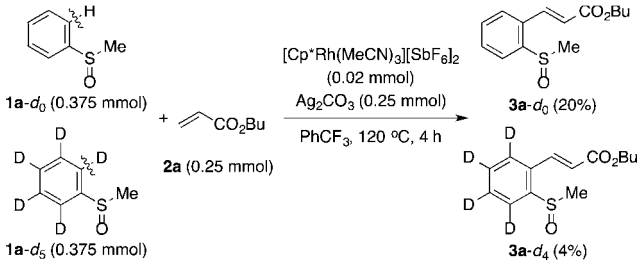
A plausible mechanism for the reaction of phenyl sulfoxide **1** with alkene **2** is illustrated in Scheme 1. Coordination of the sulfoxide group[11] of **1** to a Rh^{III} center and subsequent cyclorhodation on the phenyl group of a resulting intermediate **A** take place to form a five-membered rhodacycle intermediate **B**. Then, alkene insertion to form **C** and β-hydrogen elimination may occur to release **3** and HX. The resulting Rh^{I} species seems to be oxidized by Ag^{I} to regenerate Rh^{III}.

Scheme 1. Plausible Mechanism for the Reaction of 1 with 2



For providing additional mechanistic information, a deuterated substrate, methyl d_5-phenyl sulfoxide (**1a**-d_5), was treated with **2a** under standard conditions (see the Supporting Information). After 3 h, no significant D–H exchange at the *ortho* positions of recovered **1a**-d_5 as well as at the 6-position of produced **3a**-d_4 was observed. This result indicates that the initial C–H(D) bond-cleavage step to form **B** is likely irreversible. Next, an intermolecular competition reaction of **1a**-d_0/**1a**-d_5 with **2a** was examined. As shown in Scheme 2, the alkenylated products **3a**-d_0 and **3a**-d_4 were obtained in a ratio of 5:1 (k_H/k_D), suggesting that the rate-determining step involves the C–H(D) bond cleavage at the *ortho*-position of **1a** (**A** to **B** in Scheme 1). Two parallel reactions using **1a**-d_0 and **1a**-d_5 were also performed separately and showed a similar KIE value of 5.7 (see the Supporting Information).

Scheme 2. Plausible Mechanism for the Reaction of 1 with 2



Next, the *ortho*-alkenylation of phenyl sulfoxides **1** with alkynes **4**[3g,12] was examined under various conditions (see the Supporting Information). Consequently, it was found that **1a** (0.75 mmol) coupled with diphenylacetylene (**4a**) (0.25 mmol) efficiently in the presence of $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.02 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.025 mmol), and 1-adamantanecarboxylic acid (1-$AdCO_2H$) (1 mmol) in diglyme (1 mL) at 120 °C under N_2 to produce (*E*)-1-[2-(methylsulfinyl)phenyl]-1,2-diphenylethene (**5a**) stereoselectively in 68% yield (entry 1 in Table 3). In the absence of the copper cocatalyst, the product

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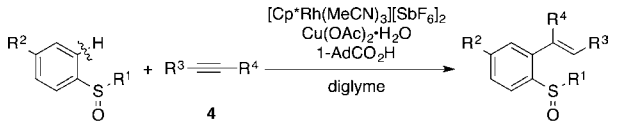
Table 3. Reaction of Phenyl Sulfoxides 1 with Alkynes 4[a]



1 4 5

entry	1	4	time (h)	product, % yield[b]
1	1a	4a: Ar = Ph	6	5a: Ar = Ph, 68
2[c]		4a: Ar = Ph	5	5a: Ar = Ph, 60
3		4b: Ar = 4-MeC_6H_4	7	5b: Ar = 4-MeC_6H_4, 75
4		4c: Ar = 4-ClC_6H_4	7	5c: Ar = 4-ClC_6H_4, 84
5		4d: Ar = 4-$CF_3C_6H_4$	7	5d: Ar = 4-$CF_3C_6H_4$, 76
6[d]		4e: Ar = 4-$MeOC_6H_4$	7	5e: Ar = 4-$MeOC_6H_4$, 48
7	1a	4f: R = Me	4	5f: R = Me, 53
8		4g: R = Bu	5	5g: R = Bu, 50
9	1b: R = Me	4a	7	5h: R = Me, 89
10	1c: R = OMe		7	5i: R = OMe, 50
11[d]	1d: R = Cl		9	5j: R = Cl, 23
12	1e: R = Ph	4a	7	5k: R = Ph, 63
13	1f: R = Et		7	5l: R = Et, 40

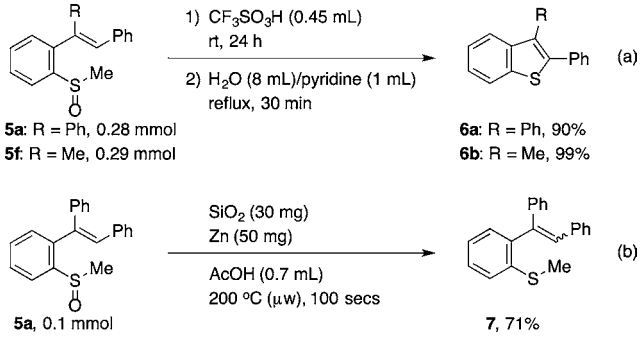
[a]Reaction conditions: **1** (0.75 mmol), **4** (0.25 mmol), [Cp*Rh-$(MeCN)_3$][SbF_6]$_2$ (0.02 mmol), $Cu(OAc)_2$ (0.025 mmol), 1-$AdCO_2H$ (1 mmol), in diglyme (1 mL) at 120 °C under N_2, unless otherwise noted. [b]Isolated yield based on the amount of **4** used. [c]With **1a** (7.5 mmol), **4a** (2.5 mmol), [Cp*Rh$(MeCN)_3$][SbF_6]$_2$ (0.2 mmol), $Cu(OAc)_2$ (0.25 mmol), 1-$AdCO_2H$ (10 mmol), in diglyme (10 mL). [d]At 100 °C.

was contaminated by an unidentified, inseparable impurity. A 10-fold scaled-up reaction using **1a** (7.5 mmol) and **4a** (2.5 mmol) could be conducted smoothly to form **5a** in 60% yield (0.48 g, entry 2). Methyl-, chloro-, trifluoromethyl-, and methoxy-substituted diphenylacetylenes **4b−e** also reacted with **1a** under similar conditions to give products **5b−e** (entries 3−6). In the case with **4e**, a better result was obtained at 100 °C (entry 6). Interestingly, the reactions of unsymmetrical alkynes **4f** and **4g** proceeded stereo- and regioselectively to produce **5f** and **5g** as single major products (entries 7 and 8). The reaction of a dialkylacetylene, 4-octyne, was sluggish to form the corresponding *ortho*-alkenylated product in a low yield (~20%), along with inseparable unidentified byproducts. Treatment of a terminal alkyne, phenylacetylene, gave only a trace amount of coupling product.

On the other hand, *para*-substituted phenyl sulfoxides **1b−d** underwent the reaction with **4a** to form **5h−j**, respectively (entries 9−11). Diphenyl sulfoxide (**1e**) and ethyl phenyl sulfoxide (**1f**) coupled with **4a** in similar ways to give **5k** and **5l** (entries 12 and 13).

Further derivatization of *ortho*-alkenylated phenyl sulfoxides was then examined. Treatment of **5a** and **5f** with TfOH induced interrupted Pummerer cyclization to produce 2,3-diphenylbenzothiophenes **6a,b** in good yields (eq (a) in Scheme 3).[8a] Meanwhile, treatment of **5a** under reductive

Scheme 3. Transformation of *o*-Alkenylphenyl Sulfoxides



conditions using Zn/AcOH on silica gel[9a] gave the corresponding *o*-alkenylphenyl sulfide **7** (eq (b) in Scheme 3). The *o*-alkenylphenyl sulfide structures can be seen in a range of bioactive compounds.[13]

In summary, we have demonstrated that the rhodium-catalyzed alkenylation of phenylsulfoxides occurs smoothly through a sulfoxide group directed C−H bond cleavage. Produced *o*-alkenylphenyl sulfoxides can be transformed to the corresponding sulfide as well as benzothiophenes via reduction and cyclization, respectively.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, additional results, and characterization data of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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