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Highly regio- and stereoselective $PdCl_2(MeCN)_2$-catalyzed cross coupling of 1,2-allenylic sulfoxides with allyl bromide

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Abstract—2-Allyl-1(*E*),3(*E*)-dienyl sulfoxides were prepared highly stereoselectively via the $PdCl_2(MeCN)_2$-catalyzed coupling reaction of 1,2-allenylic sulfoxides and allyl bromide. A rationale was proposed for this transformation.
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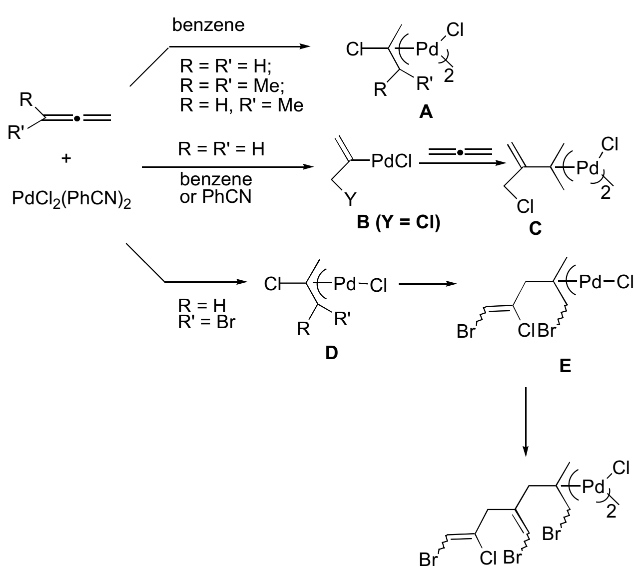
It was reported that the reaction of an allene with $PdCl_2(PhCN)_2$ usually afforded dinuclear monomeric 2-chloro-π-allylic Pd **A**, dimeric π-allylic Pd complex **C**, or even trimeric π-allylic Pd complex **F** (Scheme 1).[1–3] It is quite interesting to note that similar to carbopalladation of allenes[4] the initial halopalladation would also favor the formation of a π-allylic Pd complex of type **D** via the attack of the halogen atom at the center carbon atom. An exception was observed when $PdCl_2(PhCN)_2$ was added as a solid to propadiene, in which the chlorine atom attacked the terminal carbon atom of propadiene forming a vinylic palladium species **B**.[1a] Another example is the catalytic carbonylation of allenes with $PdCl_2$ and $CuCl_2$ in MeOH, which afforded 2-ethoxymethylacrylates via the intermediacy of **B** (Y = OMe) (Scheme 1).[5]



Scheme 1.

In principle, these two types of Pd intermediates, for example, **B** or **D**, may undergo further transformation with a variety of other reagents to afford useful synthetic intermediates providing that the regio- and stereoselectivity can be controlled. To the best of our knowledge, besides the carbonylation,[5,6] no report has been disclosed on the catalytic halopalladation-initiated coupling of an allene with a second partner. In this communication, we wish to disclose our recent observation on the Pd-catalyzed highly regio- and stereoselective coupling reaction of allyl bromide and 1,2-allenylic sulfoxides forming 2-allyl-1(*E*),3(*E*)-dienyl sulfoxides, in which the chlorine atom may attack the 3-position of 1,2-allenyl sulfoxides forming a vinylic Pd intermediate highly stereoselectively.

Recently during the course of systematic study of allene chemistry,[7] we are interested in the chemistry of 1,2-allenyl sulfoxides.[8–10] We observed that the stereoselectivity in the halohydroxylation of 1,2-allenyl sulfoxides was controlled by the participation of the sulfinyl group.[9,10] Based on these results we were interested to

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see the effect of the sulfinyl group on the regio- and stereoselectivity of halometalation of 1,2-allenyl sulfoxides. We initiated this study by using 3-methyl-1,2-butadienyl phenyl sulfoxide **1a** with allyl bromide. Some typical results are summarized in Table 1. With $RuCl_3$ in the presence of LiOAc, the reaction afforded 3-methyl-2-allyl-1(*E*),3(*E*)-butadienyl sulfoxide **3a** in 16% yield (Table 1, entry 1). The stereochemistry was established by the NOESY spectra of **3a**. It is interesting that the reaction with 5 mol% of $PdCl_2$ afforded the product **3a** in 69% yield (Table 1, entry 2). The result with 5 mol% of $PdCl_2(MeCN)_2$ and anhydrous LiOAc is slightly better (compare Table 1, entries 2–4). However, the presence of LiOAc is critical since the reaction in absence of LiOAc or in the presence of $NaHCO_3$ afforded **3a** only in very low yields (Table 1, entries 5 and 6). Furthermore it should be noted that no **3a** was formed under the catalysis of a Pd(0) complex (Table 1, entries 7 and 8).

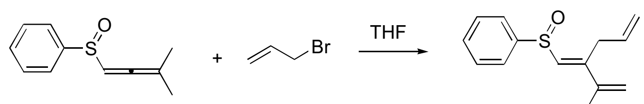
With the standard reaction conditions, some typical examples are shown in Table 2 with the following points noteworthy:

(1) the stereoselectivity of 1,2-carbon–carbon double bond in product **3** ranges from 92:8 to 97:3 (*E*/*Z*);
(2) the stereoselectivity of 3,4-carbon–carbon double bond in **3** is 100% *E*.

In the reaction of **1a** with allyl bromide, besides the formation of **3a** in 72% yield, 4% of 2-(3′-bromo-1′-propenyl)-3-methylbuta-1,3-dienyl phenyl sulfoxide **4a** was also formed, indicating that the reaction may involve a sp^2 carbon–palladium intermediate **5a** (Scheme 2).

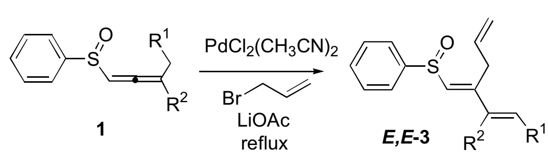
A rationale shown in Scheme 3 was proposed for the $PdCl_2(MeCN)_2$-catalyzed reaction of 1,2-allenyl sulfoxides with allyl bromide. In the first step the divalent palladium would undergo highly regioselective halopalladation reaction with the allene moiety of 1,2-allenylic sulfoxides to form *the vinylic intermediate* **7**. A LiOAc-mediated elimination reaction of *Z*-**7** may lead to the formation of intermediate *Z*-**5**, which may undergo sequential carbopalladation and β-debromopalladation with allyl bromide to afford the final product **3**.[11] The minor product **4a** would be formed by the

Table 1. Transition metal-catalyzed coupling reaction of 1,2-allenyl sulfoxide **1a** with allyl bromide



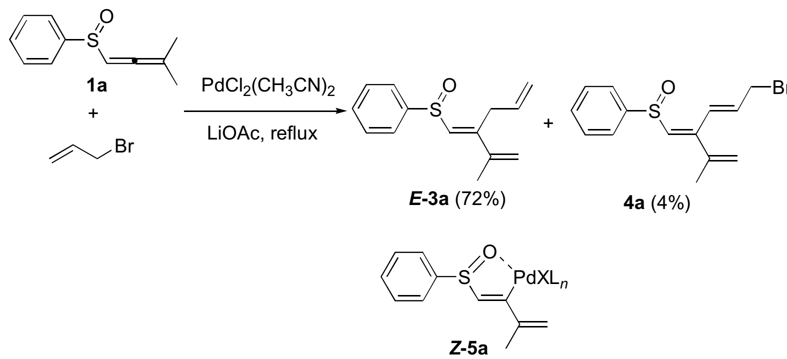
Entry	Catalyst	Base	Solvent (**2**/THF)	Yield of **3a** (%)	Compound **1a** recovered (%)
1	$RuCl_3$	LiOAc	1:1	16	—
2	$PdCl_2$	LiOAc	1:1	69	—
3	$Pd(CH_3CN)_2Cl_2$	$LiOAc·2H_2O$	1:1	70	—
4	$Pd(CH_3CN)_2Cl_2$	LiOAc	1:1	77	—
5	$Pd(CH_3CN)_2Cl_2$	$NaHCO_3$	1:0	Trace	—
6	$Pd(CH_3CN)_2Cl_2$	—	1:2	9	—
7	$Pd_2(dba)_3·CHCl_3$, PPh_3	LiOAc	1:2	—	73
8	$Pd(PPh_3)_4$	LiOAc	1:2	—	67

Table 2. $Pd(MeCN)_2Cl_2$-catalyzed coupling reaction of 1,2-allenyl sulfoxides **1** with allyl bromide[a]

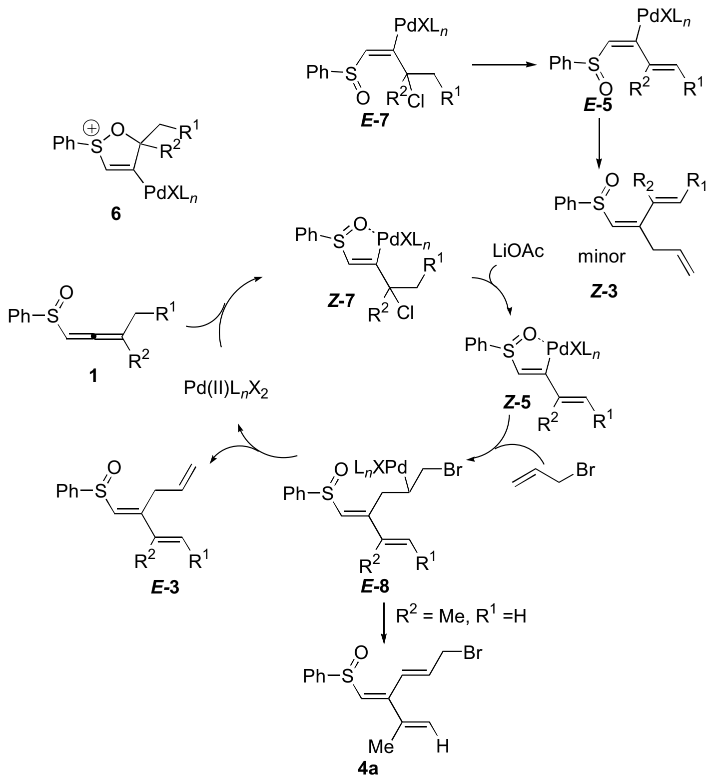


Entry	**1**		Time (h)	Yield of **3** (%)	*E*/*Z*[b]
	R^1	R^2			
1	CH_3	C_2H_5	8	73 (**3b**)	92:8
2	C_2H_5	n-C_3H_7	2	58 (**3c**)	97:3
3	n-C_3H_7	n-C_4H_9	2	78 (**3d**)	93:7
4	n-C_4H_9	n-C_5H_{11}	2	60 (**3e**)	93:7
5	$(CH_2)_3$		9	78 (**3f**)	93:7
6	$(CH_2)_4$		4.5	63 (**3g**)	92:8
7	H	Ph	39	35 (**3h**)	95:5

[a] The reaction was carried out using 0.5 mmol of sulfoxide, 2 equiv of LiOAc, and 5 mol% of $PdCl_2(CH_3CN)_2$, 1.0 mL of allyl bromide, and 1.0 mL of dry THF under N_2 and refluxed for the indicated time.
[b] *E*/*Z* Ratio referred to the 1,2-C=C bond and determined by the ^1H NMR analysis of the olefinic protons in the crude product.



Scheme 2.



Scheme 3.

carbopalladation and β-H elimination of *E*-**5** with allyl bromide.[12] The stereochemistry of the 1,2-C=C bond in the product **3** may be determined by the chelation between the sulfinyl oxygen and palladium in *Z*-**5** while the configuration of 3,4-C=C bond may be determined by the possible steric repulsion between Pd and R^1 in **5**. The formation of products from **6**-type intermediates was not the major pathway.

In conclusion, we have observed an interesting Pd-catalyzed coupling reaction of 1,2-allenylic sulfoxides and allyl bromide, which provides an efficient entry to the synthetically useful 2-allyl-1(*E*),3(*E*)-alkadienyl sulfoxides highly stereoselectively. Due to the coordination ability of the sulfinyl group with Pd, the halopalladation is not only regioselective but also highly stereoselective. This observation may open up a new area for the regio- and stereoselective intermolecular reactions of allenes. Further study in this area is being carried out in our laboratory.

Acknowledgements

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