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Arylation Reactions

Palladium-Catalyzed γ-Arylation of α,β-Unsaturated Esters from Silyl Ketene Acetals**

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The palladium-catalyzed coupling of enolates with aryl and vinyl electrophiles has become a useful method for the construction of carbon–carbon bonds.[1] Although many palladium complexes have been identified that catalyze the coupling of enolates of ketones, esters, amides, and aldehydes with haloarenes, the vinylogous coupling of dienolates of α,β-unsaturated carbonyl compounds with haloarenes (γ-arylation) has been less studied. γ-Aryl α,β-unsaturated carbonyl compounds are useful building blocks because they can be further functionalized at the carbonyl or olefinic positions.[2]

To develop a catalyst for the γ-arylation of α,β-unsaturated carbonyl compounds, one must address several issues, including the regioselectivity for forming products from α-, β-, or γ-arylation, the selectivity for monoarylation versus diarylation, and the potential condensation of the reactive products. The selectivity for formation of products from α- or γ-arylation versus β-arylation depends on whether an enolate complex forms by transmetalation with the arylpalladium halide intermediate, as occurs during the α-arylation of carbonyl compounds, or whether it forms by insertion of the α,β-unsaturated carbonyl compound into the metal–aryl bond, as occurs during a Heck reaction. The selectivity for products from α- versus γ-arylation likely depends on the stability and reactivity of the series of isomeric arylpalladium dienolate intermediates that result from transmetalation.

Despite these obstacles, a few γ-arylation reactions of α,β-unsaturated ketones and aldehydes have been reported. Terao et al. reported the palladium-catalyzed γ-arylation of unfuntionalized α,β-unsaturated aldehydes and ketones.[3] Martin and Buchwald reported the γ-arylation of similar α-substituted α,β-unsaturated aldehydes.[4] Varseev and Maier later reported a sequential γ-arylation and dehydrogenation for the synthesis of substituted tetralones.[5] Finally, Hyde and Buchwald reported the γ-arylation of γ-substituted α,β- or β,γ-unsaturated ketones[6] and lactones[7] with aryl chlorides and bromides in moderate to good yield.

Despite these advances, the coupling of enolates of α,β-unsaturated esters is underdeveloped. The γ-arylation of acyclic esters has been limited to reactions of tin enolates in low to moderate yields.[8] Moreover, the previous couplings of α,β-unsaturated ketones and aldehydes have required elevated temperatures and substrates that contain substituents at either the α or γ position of the carbonyl compound for high yield.

Herein, we report the γ-arylation and γ-vinylation of α,β-unsaturated esters in high yield with broad scope by coupling aryl, heteroaryl, and vinyl halides with the corresponding silicon dienolates. These reactions occur in high yield with a variety of esters, including those lacking substituents at the α and γ positions, and with aromatic and vinylic electrophiles that contain potentially reactive functional groups. Moreover, these reactions occur without typical fluoride additives to activate silicon enolates.

Our studies of the coupling of haloarenes with the dienolates of α,β-unsaturated esters began with alkali metal dienolates of α,β-unsaturated esters. However, the reaction of bromobenzene with the alkali metal dienolate of methyl *trans*-2-hexenoate did not form the γ-aryl α,β-unsaturated esters in significant yield. Thus, we investigated reactions of silicon enolates of α,β-unsaturated esters. These studies were based on our prior work on the coupling of aryl halides with silyl enol ethers and silyl ketene acetals.[9–11]

Our initial studies on the coupling of silyl ketene acetals derived from α,β-unsaturated esters focused on the model palladium-catalyzed coupling of bromobenzene with the trimethylsilyl ketene acetal of methyl-2-hexenoate (**1a**). Most previous α-arylations of silyl ketene acetals or silyl enol ethers were conducted with fluoride additives, such as ZnF_2, CsF, MgF_2, Bu_3SnF, or CuF_2. In contrast to these previous studies, the coupling of silyl ketene acetal **1a** occurred without a fluoride additive. Instead, the reaction formed the γ-aryl *E*-product **2** in high yield in the presence of inexpensive zinc chloride. Previously reported coupling reactions of aryl halides with silicon enolates without a fluoride additive have been limited to the α-arylation and vinylation of silicon enolates in the presence of thallium acetate[11] or to intramolecular α-vinylations.[9]

A summary of the effect of the silyl group and additive on the coupling of bromobenzene with the silyl ketene acetals of methyl hexenoate is shown in Table 1. The γ-arylation product was formed in the highest yields with the triethylsilyl (TES) ketene acetal (**1b**; Table 1, entry 3). The coupling between **1b** and bromobenzene in the presence of ZnF_2 occurred in low yield (Table 1, entry 4), perhaps owing to the poor solubility of ZnF_2 in tetrahydrofuran. Reactions of **1b** with bromobenzene in the presence of $ZnBr_2$ and ZnI_2 (Table 1, entries 5 and 6) formed the γ-arylation product **2** in lower yield than the same reaction in the presence of $ZnCl_2$. The coupling between **1b** and bromobenzene with catalytic

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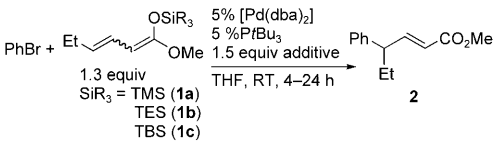
Table 1: Effects of the silyl group and zinc halides on the γ-arylation of silyl ketene acetals with bromobenzene.[a]



Entry	Acetal	Additive	*t* [h]	Yield [%][b]
1	**1b**	none	24	< 5
2	**1a**	$ZnCl_2$	2	82
3	**1b**	$ZnCl_2$	4	87
4	**1b**	ZnF_2	24	11
5	**1b**	$ZnBr_2$	4	81
6	**1b**	ZnI_2	25	< 5
7[c]	**1b**	$ZnCl_2$	12	83
8	**1c**	$ZnCl_2$	12	64

[a] Reaction conditions: acetal (0.26 mmol), PhBr (0.20 mmol), additive (0.30 mmol), $[Pd(dba)_2]$ (0.010 mmol), $PtBu_3$ (0.01 mmol), THF (0.8 mL). [b] Yields were determined by GC analysis with dodecane as an internal standard (average of two runs). [c] 0.2 equiv $ZnCl_2$

amounts of $ZnCl_2$ occurred in yields similar to those of reactions with stoichiometric $ZnCl_2$, although the reaction was slower (Table 1, entry 7). Ester **2** was not formed from the reaction of **1b** with bromobenzene in the absence of $ZnCl_2$ (Table 1, entry 1).

Several palladium catalyst systems for the coupling of silyl ketone acetal **1b** with bromobenzene were also explored; ester **2** did not form in a detectable amounts from the coupling of **1b** with bromobenzene in the presence of catalyst systems containing X-phos, dppe, dppf, Xantphos, *rac*-BINAP, PCy_3, or PPh_3 ligands. Ester **2** formed in the presence of $[Pd(dba)_2]$ and Qphos, but the yield was lower than that from the reaction conducted with a catalyst containing $PtBu_3$.

The coupling of silyl ketene acetal **1b** with chlorobenzene and iodobenzene was also attempted. The coupling product **2** was not detected from the reaction with chlorobenzene, and the γ-aryl α,β-unsaturated ester **2** was formed in only 29% yield from the coupling of **1b** with iodobenzene after 24 hours.

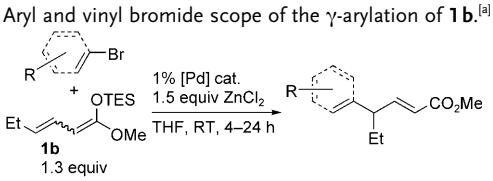
The scope of the γ-arylation with a variety of aryl bromides is shown in Table 2. γ-Aryl α,β-unsaturated esters were obtained in high yields from reactions with both electron-rich and electron-poor aryl bromides. The reaction proceeded in high yield with aryl bromides containing a single *ortho* substituent (Table 2, entries 6 and 7); higher catalyst loadings were required for more sterically hindered aryl bromides (Table 2, entry 8), but the reaction of 2,6-dimethylbromobenzene occurred in high yield. The reaction tolerated a variety of functional groups that could be used for further elaboration, such as a chloro, nitro, cyano, acyl, and a phenacyl group (Table 2, entries 21–25). The coupling also proceeded with aryl bromides that contained acidic N–H groups (Table 2, entries 16, 17, and 30).

A variety of heteroaryl bromides also successfully coupled with silyl ketene acetal **1b**, including the coupling of **1b** with bromothiophene, bromopyridine, and bromoquinoline (Table 2, entries 27–29), and the coupling of **1b** with 5-bromo indole containing an unprotected N–H bond (Table 2, entry 30). The coupling of **1b** with the BEt_3 adduct of 3-bromopyridine occurred faster and in comparable yields to the reactions of the free pyridine. The use of a borane to inhibit coordination of a pyridine to the catalyst and to promote carbon–halogen bond cleavage and subsequent reductive elimination has been previously reported for the amidation of aryl halides.[12]

The coupling also occurred with vinyl bromides; γ-vinyl-α,β-unsaturated esters were isolated in moderate yields from the reactions of 2-bromoindene and 1-bromo-2-methyl-1-propene (Table 2, entries 31 and 32).

The isolated complexes $[Pd(PtBu_3)_2]$ and $[\{(PtBu_3)Pd(\mu\text{-}Br)\}_2]$ were particularly active for the coupling of silyl ketene acetal **1b** with aryl bromides. For example, the coupling of **1b**

Table 2: Aryl and vinyl bromide scope of the γ-arylation of **1b**.[a]



Entry	R–Br	[Pd] cat.[b]	Yield [%][c]
1	PhBr	A	82
2[d]	PhBr	B	77
3[e]	PhBr	C	77
4	4-*t*Bu-C_6H_4Br	A	82
5	3,5-Me_2-C_6H_3Br	A	78
6	2-MeC_6H_4Br	A	83
7	2-PhC_6H_4Br	A	78
8[f]	2,6-$Me_2C_6H_3Br$	A	96
9[g]	2,6-$Me_2C_6H_3Br$	B	83
10	2,6-$Me_2C_6H_3Br$	C	95
11	1-bromonaphthalene	A	82
12	2-bromonaphthalene	A	90
13	2-OMe-C_6H_4Br	A	83
14	3-OMe-C_6H_4Br	A	81
15	4-OMe-C_6H_4Br	A	83
16[f,h]	4-NH_2-C_6H_4Br	A	74
17[h]	4-MeN(H)-C_6H_4Br	A	80
18	4-NMe_2-C_6H_4Br	A	83
19	4-CF_3-C_6H_4Br	A	77
20	4-F-C_6H_4Br	A	91
21	4-Cl-C_6H_4Br	A	91
22	4-CN-C_6H_4Br	A	81
23	4-NO_2-C6H4Br	A	82
24	4-C(O)Me-C_6H_4Br	A	58
25	4-C(O)Et-C_6H_4Br	A	84
26	4-CO_2Me-C_6H_4Br	A	89
27	3-bromothiophene	A	76
28	3-bromopyridine·BEt_3	A	58[i]
29	6-bromoquinoline	A	69[j]
30	5-bromoindole	A	64
31	2-bromoindene	A	51
32	1-Br-2-Me-1-propene	A	34

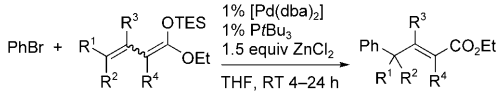
[a] Reaction conditions: **1b** (1.3 mmol), aryl or vinyl halide (1.0 mmol), $ZnCl_2$ (1.5 mmol), [Pd] cat. (0.010 mmol), THF (2 mL). [b] [Pd] cat.: A: $[Pd(dba)_2]$, $PtBu_3$ (1:1); B: $[Pd(PtBu_3)_2]$; C: $[\{P(tBu_3)Pd(\mu\text{-}Br)\}_2]$. [c] Yield of isolated product (average of two runs). [d] 0.4% [Pd] cat. [e] 0.1% [Pd] cat. [f] 5% [Pd] cat. [g] 2% [Pd] cat. [h] 2.6 equiv **1b**, 3.0 equiv $ZnCl_2$. [i] Isolated as uncoordinated pyridine. [j] Product was isolated in 85% purity.

with bromobenzene proceeded in high yield in the presence of just 0.4% $[Pd(PtBu_3)_2]$ (Table 2, entry 2) or 0.2% $[\{(PtBu_3)Pd(\mu\text{-}Br)\}_2]$ (Table 2, entry 3). The coupling between silyl ketene acetal **1b** and a larger 10 mmol scale of bromobenzene in the presence of 0.2% $[\{(PtBu_3)Pd(\mu\text{-}Br)\}_2]$ gave the coupled product ester **2** in 69% yield.

The coupling of the more sterically demanding substrates also proceeded with lower catalyst loadings of $[Pd(PtBu_3)_2]$ or $[\{(PtBu_3)Pd(\mu\text{-}Br)\}_2]$ than of the combination of $[Pd(dba)_2]$ and $PtBu_3$ (Table 2, entries 9 and 10). Thus, $[Pd(PtBu_3)_2]$ or $[\{(PtBu_3)Pd(\mu\text{-}Br)\}_2]$ could used in place of $[Pd(dba)_2]$ and $PtBu_3$ in most cases when a single-component catalyst is preferred.

The scope of the process with different silyl ketene acetals is shown in Table 3. The reaction tolerates substitution at the α, β, γ, or δ positions of the acetal. Products from reactions of silyl ketene acetals containing substituents at the α or β positions were isolated as a mixture of olefin geometries (Table 3, entries 1 and 2). The coupling of a silyl ketene acetal containing two substituents at the γ position required increased catalyst loading, but occurred in 75% yield (Table 3, entry 3). Finally a substrate substituted in the δ position reacted in similar yields. Under our reaction conditions, no product was observed from the γ-arylation of the silyl ketene acetals derived from α,β-unsaturated lactones.

Table 3: γ-Arylation of substituted silyl ketene acetals.[a]

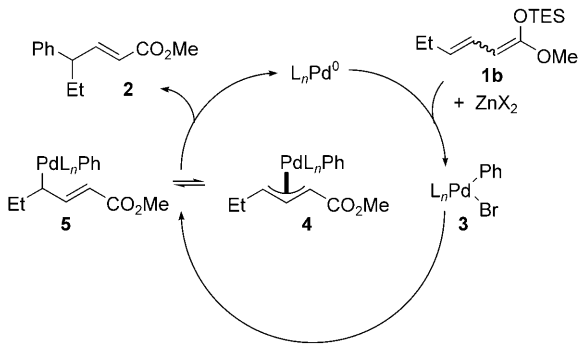


Entry	R^1	R^2	R^3	R^4	Yield [%][b]
1[c,d]	Me	H	H	Me	62 (*E*) 10 (*Z*)
2	Me	H	Me	H	57 (*E*) 5 (*Z*)
3[d]	Me	Me	H	H	75
4	*i*Pr	H	H	H	68

[a] Reaction conditions: acetal (1.5 mmol), PhBr (1.0 mmol), $ZnCl_2$ (1.5 mmol), $[Pd(dba)_2]$ (0.010 mmol), $PtBu_3$ (0.01 mmol), THF (2 mL). [b] Yield of isolated product (average of two runs). [c] 2.2 equiv silyl ketene acetal, 3.0 equiv $ZnCl_2$. [d] 2% $[Pd(dba)_2]$, 2% $PtBu_3$.

A potential mechanism for the palladium-catalyzed coupling of **1b** with aryl bromides is shown in Scheme 1. This catalytic cycle is analogous to that proposed for the palladium-catalyzed α-arylation of carbonyl compounds. In this cycle, the zinc chloride would facilitate the formation of the palladium dienolate complex (**4** and **5**), and reductive elimination from a palladium dienolate complex would generate the desired product. Reductive elimination from an η^3-palladium dienolate complex (**4**) has been reported by Kurosawa and co-workers,[13] but the zinc chloride induced transmetalation of a silyl ketene acetal or silyl enol ether with the palladium aryl halide complex has not been studied.

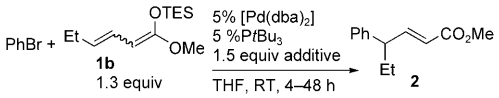
To understand the promoting effect of zinc chloride, we studied reactions containing additives that possess Lewis acidic properties or chloride ions. To determine if the Lewis



Scheme 1. Potential mechanism for the coupling of **1b** with PhBr. TES = triethylsilyl.

acidity of the zinc halide facilitates transmetalation of the enolate from silicon to palladium, we conducted the coupling of enolate **1b** with bromobenzene in the presence of BF_3·THF. The reaction with BF_3·THF in place of $ZnCl_2$ proceeded to full conversion, albeit over a longer reaction time and in diminished yield (Table 4, entry 3). To assess whether the zinc chloride served as a source of halide,[14] the coupling of enolate **1b** with bromobenzene was performed in the presence of zinc triflate. This reaction occurred in a yield that was comparable to that from the reaction in the presence of zinc chloride (Table 4. entry 2). Because the yield and reaction times for the coupling in the presence of zinc triflate were comparable to those of reactions in the presence of zinc chloride, we conclude that the $ZnCl_2$ is not simply a source of halide; instead the Lewis acidic property likely helps labilize the halide on palladium.[15]

Table 4: Effect of different additives on the coupling of **1b** with bromobenzene.[a]



Entry	Additive	*t* [h]	Yield [%][b]
1	$ZnCl_2$	4	87
2	$Zn(OTf)_2$	4	95
3	BF_3·THF	48	39
4	$N(octyl)_3MeCl$	8	83
5[c]	$N(octyl)_3MeCl$	24	45

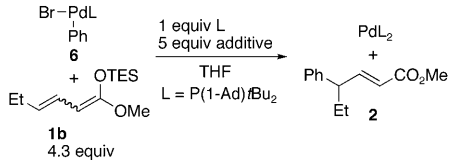
[a] Reaction conditions: **11** (0.030 mmol), **1b** (0.13 mmol), additive (0.15 mmol), THF (0.8 mL). [b] Yields were determined by GC analysis with dodecane as an internal standard (average of two runs). [c] Reaction performed in the presence of 4 equiv 4-ClC_6H_4Br.

At the same time, a genuine source of halide without Lewis acid did promote the coupling process. The reaction of **1b** with bromobenzene catalyzed by $[Pd(dba)_2]$ and $PtBu_3$ in the presence of methyltrioctylammonium chloride occurred in high yield (Table 4, entry 4), although the rate was slower than that for reactions conducted with zinc chloride. Because ammonium halides are not Lewis acidic, it appears that the γ-arylation process with the silyl enolates can be accelerated by

either a Lewis acid or a Lewis base. The palladium-catalyzed coupling of **1b** with bromobenzene in the presence of methyltrioctylammonium chloride and zinc chloride together required long times and did not occur in high yield (Table 4, entry 5); thus, we conclude that the ammonium chloride and zinc chloride promote the coupling of silyl ketene acetal and bromobenzene through different mechanisms.

To determine which portion of the catalytic cycle is affected by the zinc and ammonium additives, reactions of enolate **1b** were performed with an arylpalladium bromide complex that is closely related to the complexes that would be intermediates in the coupling process. Arylpalladium halide complexes of P(1-Ad)*t*Bu$_2$ (1-Ad = 1-adamantyl) are more easily isolated than those containing P*t*Bu$_3$, and the combination of [Pd(dba)$_2$] and P(1-Ad)*t*Bu$_2$ catalyzed the formation of **2** in 86% yield. Thus, we studied complex **6** containing P(1-Ad)*t*Bu$_2$. The reaction of silyl ketene acetal **1b** with complex **6** was faster in the presence of zinc chloride than in the absence of any additive (Table 5 entries 1 and 2). When the reaction between **6** and **1b** was performed in the presence of an excess

Table 5: Stoichiometric reactions between arylpalladium halide specides with **1b**.[a]



Entry	Additive	*t*	Yield **2** [%][b]
1	none	30 h	27
2	$ZnCl_2$	10 min	65
3[c]	$ZnCl_2$	10 min	82
4	$N(octyl)_4Cl$	30 min	69

[a] Reaction conditions: **6** (0.030 mmol), **1b** (0.13 mmol), additive (0.15 mmol), THF (0.8 mL). [b] Yields were determined by GC analysis with dodecane as an internal standard (average of two runs). [c] Reaction performed in the presence of 4 equiv 4-ClC_6H_4Br.

of an aryl halide (with an aryl moiety that is different from that bound to palladium) to trap the palladium(0) product, the γ-arylation product **2** was formed in yields that were comparable to those of the catalytic reaction (Table 5, entry 3). Thus, the zinc halide accelerates the transmetalation between silicon and palladium. Chloride sources also triggered the stoichiometric reaction of **6** with **1b**, but we have not yet identified the role of tetraalkylammonium halides in the catalytic process.

In summary, we have developed the first palladium-catalyzed coupling of aryl halides with acyclic α,β-unsaturated esters to form products from coupling at the γ position. These reactions are conducted via silyl ketene acetals, and, unlike many couplings of silicon enolates, does not require a fluoride additive. These reactions occur at room temperature with low catalyst loadings, in high yield with aryl bromides that contain a wide array of functional groups and with silyl ketene acetals that contain substitution at the α, β, γ, and δ positions. The product is formed by reductive elimination from a palladium dienolate complex. Further studies are required to determine the precise mechanism for activation of silyl ketene acetal, but the formation of this dienolate complex is promoted by the mildly acidic zinc chloride. Further studies on reactions of dienolates and efforts to develop stereoselective transformations of these species are in progress.

Experimental Section

General procedure for the γ-arylation of silyl ketene acetals catalyzed by P*t*Bu$_3$ and [Pd(dba)$_2$] (Table 2)**:** P*t*Bu$_3$ (2.0 mg, 0.010 mmol; in a 1 dram vial) was placed inside a drybox under either an argon or nitrogen atmosphere. Bromobenzene (157 mg, 1.00 mmol) was added, followed by triethyl(1-methoxyhexa-1,3-dienyloxy)silane (346 mg, 1.30 mmol). Zinc chloride (204 mg, 1.50 mmol) was then added, followed by [Pd(dba)$_2$] (5.8 mg, 0.010 mmol). A Teflon-coated stirrer bar was then added, followed by 2 mL of THF. The vial was closed with a cap that was lined with a PTFE/silicone septum and removed from the drybox. The reaction mixture was stirred at room temperature until GC analysis showed that full consumption of the aryl bromide had occurred. Upon completion, the reaction mixture was diluted with 30 mL of ethyl acetate (EtOAc) and washed three times with saturated $NaHCO_3$. An additional 10 mL of EtOAc was added to the combined aqueous washes for back-extraction. The combined organic solutions were washed once with brine and dried with anhydrous $MgSO_4$. The suspension was filtered through a plug of Celite. Volatile materials were removed by rotary evaporation. The crude mixture was then purified by column chromatography on silica gel (acetone/pentane) to give the γ-aryl α,β-unsaturated ester.

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