JOC Note

Mild and Efficient Aryl–Alkenyl Coupling via Pd(II) Catalysis in the Presence of Oxygen or Cu(II) Oxidants

Jay P. Parrish, Young Chun Jung, Seung Il Shin, and Kyung Woon Jung*

Department of Chemistry, University of South Florida, 4202 East Fowler Avenue, Tampa, Florida 33620-5250

kjung@chuma.cas.usf.edu

Abstract: We report herein a mild and efficient method for carbon–carbon bond formation between aryl stannanes and olefins via Pd(II) catalysis in the presence of oxygen or Cu(II) oxidants as a reoxidant. The process allows reactions between various olefins and aryl stannanes of varying electron density. Coupling methods under these oxidation conditions are comparatively described, and the benefits and limitations are also discussed.

The Heck reaction has become a standard tool for carbon–carbon bond formation[1] and is frequently utilized to prepare valuable intermediates in organic syntheses.[2,3] Typical conditions require high temperatures and long reaction times as well as reactive substrates such as aryl iodides or triflates.[2,3] Due to recent advances addressing these issues, room-temperature reactions are feasible, even with unreactive aryl chlorides.[4] Different approaches employing organometallic variations have also been studied to avert the aforementioned shortcomings.[5] For instance, Heck successfully introduced mercurial or stannyl moieties as halide surrogates in carbon–carbon

TABLE 1. Transition Metal Oxidants Screened

$$\text{'BuO}_2\text{C} \diagup \xrightarrow[\substack{\textit{oxidant}, \text{NaOAc} \\ \text{THF, 23 °C, 1 h}}]{\text{PhSnBu}_3, \text{Pd(OAc)}_2} \text{'BuO}_2\text{C} \diagup\text{Ph}$$

1 → **2**

entry	oxidant (3.0 equiv)	yield (%)	entry	oxidant (3.0 equiv)	yield (%)
1	$CuCl_2$	96	6	$Cu(OH)_2$	15
2	$Cu(OAc)_2$	92	7	$CuCO_3$	14
3	$FeCl_3$	82	8	$AlCl_3$	14
4	CuF_2	63	9	MnO_2	10
5	$Cu(acac)_2$	21			

bond-forming reactions at ambient temperatures.[6] However, this modified procedure required a full equivalent of a Pd(II) reagent unless used in conjunction with Cu(II) salts as reoxidants. In addition, only limited examples were provided in regards to aryl stannanes and olefins, leaving this promising method far from general use.

To further develop the olefin/stannane coupling into an efficient catalytic protocol, we embarked on development of mild and versatile conditions by changing oxidants, bases, and solvents. While conducting our optimization studies, Mori reported a Pd(II)-catalyzed coupling of olefins and aryl stannanes using $Cu(OAc)_2$ as a catalyst reoxidant.[7] This methodology provided a catalytic alternative to Heck's conditions, allowing for the coupling of nonallylic olefins with aryl stannanes. However, the reaction conditions remained harsh (100 °C, 24 h, DMF) and provided limited examples. In an effort to mitigate these pitfalls, our studies have focused on specific Pd(II) reoxidants including transition metals, oxygen and air, and organic based oxidants.

Initially, we undertook reaction optimization using *tert*-butyl acrylate **1** and commercially available tributylphenyltin as the coupling partner in the presence of various transition metal reoxidants (Table 1). Of the oxidants screened, $CuCl_2$ and $Cu(OAc)_2$ were the most efficient (entries 1 and 2) while $FeCl_3$ and CuF_2 gave lower yields, still providing some reoxidation (entries 3 and 4). However, other examined transition metals proved ineffective for this transformation (entries 5–9). Although not shown in the table, other components were also varied in the presence of $CuCl_2$ as a default oxidant to seek optimal conditions. It was found that $Pd(OAc)_2$, $PdCl_2$, and $Pd(OCOCF_3)_2$ were all effective catalysts for this transformation, providing *tert*-butyl (*E*)-cinnamate **2** in greater than 90% yield. Palladium catalysts containing electron-donating ligands such as $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$ were ineffective. In addition to THF as the solvent of choice, polar solvents such as DMF and EtOH were equally adequate as reaction solvents, whereas in benzene, couplings remained incomplete after 24 h. More-

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TABLE 2. Effect of Base Choice on Coupling

entry	base (2.0 equiv)	time (h)	yield (%)
1	NaOAc	1	96
2	LiOAc	1	95
3	CsOAc	1	89
4	Et$_3$N	24	70
5	No base	5	67

TABLE 3. Effect of Oxidant Choice on Reaction of *tert*-Butyl Acrylate and PhSnBu$_3$

entry	oxidant	time (h)	yield (%)
1	none[a]	48	15
2	air	48	37
3	O$_2$	12	74

[a] Reaction was run under a N$_2$ atmosphere.

over, reaction conditions were tolerant to moisture, and an inert atmosphere was not necessary.

As shown in Table 2, base selection played an important role in the reaction. NaOAc and LiOAc were the bases of choice, giving *tert*-butyl (*E*)-cinnamate **2** in 96 and 95%, respectively (entries 1 and 2), and CsOAc was also effective (entry 3). Although tertiary amine bases are known to reduce Pd(II) catalysts in situ to Pd(0),[8] we observed a decrease in reaction efficiency when triethylamine was used, providing the coupled product in 70% yield after 24 h. Interestingly, a feature of this reaction was the ability to use base-free conditions in certain cases, therefore eliminating another undesirable reaction component. In the absence of a base, the reaction still proceeded in moderate yields, delivering *tert*-butyl (*E*)-cinnamate **2** in 67% after 5 h (entry 5). Despite these benefits, we found several limitations in the Cu(II)-promoted reaction. The use of CuCl$_2$ for allylic systems led to undesired chloroalkylation[9,10] although Cu(OAc)$_2$ avoided this side reaction.[11] This Cu(II)-promoted reaction was limited in substrates (vide infra), which was enough to invoke our attention to discover more efficient oxidants.

Since the discovery of the Wacker process as an industrially viable route to acetaldehyde,[12] molecular oxygen together with metal salts has been used to promote numerous palladium-catalyzed reactions.[13] As an environmentally benign source, oxygen drastically reduces cost and cleanup as well as avoids side reactions caused by metal salts and their byproducts.[14] Salient examples of oxygen-promoted metal-catalyzed carbon–carbon bond formations include aryl–aryl and aryl–alkenyl couplings.[15,16] Moreover, oxygen can be utilized as the sole source of catalyst reoxidant[17] presumably through coordination of oxygen to the metal.[18] Under similar conditions, carbon–carbon bond formation has been demonstrated between aryl stannanes and olefins, prompting us to adopt molecular oxygen as a reoxidizing agent in our Pd(II)-catalyzed coupling protocol.[19]

In comparison, the coupling reactions were run under nitrogen, air, or oxygen (Table 3). These gases were delivered either by bubbling or via oxygen balloon. Very low yields were found when the reaction was run under a nitrogen atmosphere, indicating the need for an oxygen source (entry 1). When air was used, only 37% yield of the desired product was obtained (entry 2). Likewise with oxygen, a 74% yield of **2** was acquired in a shorter reaction time (entry 3). From these results, we inferred that oxygen was the source of reoxidation and best applied in a pure form. We then established the optimal reaction conditions using NaOAc as the base. Other bases such as K$_2$CO$_3$ were also effective; however, organic bases including Et$_3$N were not. Solvent selection was crucial as only DMF or NMP worked well in all cases, while solvents such as THF or benzene did not. Using these optimized conditions, we investigated substrate limitations and compared their results with the Cu(II)-promoted reactions.

(8) Negishi, E.; Coperet, C.; Ma, S.; Liou, S.-Y.; Liu, F. *Chem. Rev.* **1996**, *96*, 365.

(9) Use of CuCl$_2$ effected chloroalkylation to produce **iii** in 73% yield.
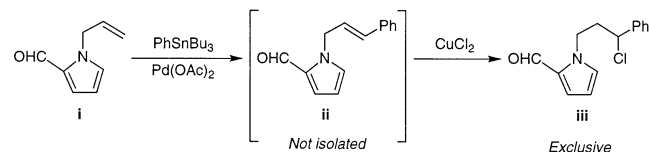
We think that the desired product **ii** does form, but reacts quickly by recoordinating with Pd(II). After metal–olefin coordination, chloride attacks the most activated, electron poor position, which is usually benzylic in our examples.

(10) For examples of chloroalkylation, see: (a) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5538. (b) Backvell, J.-E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 393. (c) Tamaru, Y.; Hojo, M.; Higashimura, H.; Yoshida, Z. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 735.

(11) The oxidation of Pd(0) is aided by the presence of chloride ions, which helps to stabilize Pd(II) and Cu(I). For a reference, see: Jira, R.; Freiesleben, W. *Organomet. React.* **1972**, *3*, 5.

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(13) For a review, see: Tsuji, J. *Palladium Reagents and Catalysis, Innovations in Organic Synthesis*; Wiley: New York, 1996; pp 19–124.

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(16) For recent examples, see: (a) Weissman, H.; Song, X.; Milstein, D. *J. Am. Chem. Soc.* **2001**, *123*, 337. (b) Matoba, K.; Motofusa, S.-I.; Cho, C. S.; Ohe, K.; Uemura, S. *J. Organomet. Chem.* **1999**, *574*, 3. (c) Miura, M.; Tsuda, T.; Satoh, T.; Pivsa-Art, S.; Nomura, M. *J. Org. Chem.* **1998**, *63*, 5211.

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TABLE 4. Comparison of Reoxidants

R—CH=CH2 $\xrightarrow[\text{Oxidant, NaOAc, Solvent}]{\text{PhSnBu}_3,\ \text{Pd(OAc)}_2}$ R—CH=CH—Ph
23 °C

entry	olefin	oxidant	
		Cu(II) [a]	oxygen [b]
1	(3)	0 %	82 %
2	Ph (4)	62 % (16 h)	72 % (24 h)
3	(5)	0 %	51 % (3 h) [c]
4	PhSO₂ (6)	0 %	73 % (20 h) [d]
5	BnO (7)	56 % (18 h) [e]	90 % (7 h)
6	(8)	60 % (8 h) [f]	81 % (18 h) [g]

[a] Cu(II) = CuCl$_2$; solvent = THF. [b] Solvent = DMF. [c] 55 °C. [d] E/Z = 2.3/1. [e] Cu(II) = Cu(OAc)$_2$. [f] E/Z = 1/11. [g] E/Z = 1/10.

As illustrated in Table 4, this newly developed oxygen protocol was generally more efficient than the Cu(II) method. In particular, some alkenes were not effected under Cu(II) conditions, however compatible with the oxygen conditions. Unactivated aliphatic alkenes such as 1-heptene (**3**) gave 82% yield of (*E*)-hept-1-enylbenzene in only 2 h whereas the Cu(II) protocol gave no desired product (entry 1). Aromatic nonallylic olefins including styrene (**4**) were comparable in both cases (entry 2). 4-Methyl-5-vinylthiazole (**5**), a heterocyclic nonallylic compound, gave 51% yield of the desired product under oxygen conditions, albeit in low yield and at 55 °C; however, Cu(II) conditions were not effective (entry 3). We attributed this moderate yield to the steric effects of the ortho methyl group. Allyl phenyl sulfone (**6**), which is an electron-poor allylic system, was converted smoothly to the (*E*)-(3-phenylsulfonylpropenyl)benzene in 73% yield with a 2.3/1 *E/Z* ratio after 20 h while resulting in no reaction under Cu(II) conditions (entry 4). Both allyl benzyl ether (**7**), an electron-rich allylic system, and 3-methylene-2-norbnanone (**8**), an activated vicinal disubstituted olefin, offered higher yields of the desired products in the presence of oxygen than Cu(II) oxidants (entries 5 and 6). These representative examples implied that both reoxidants were efficient and oxygen conditions were more versatile.

Next, we screened various nonallylic olefins to probe general applicability of both methodologies (Table 5). Electron- poor alkenes were sluggish in the presence of oxygen, and Cu(II) conditions were more reliable (entries 1 and 2). With 4-chloro- (**11**) and 4-bromostyrene (**12**), oxygen conditions gave no Stille products, producing only desired products in good yields (entries 3 and 4). Under the oxygen conditions, 5-bromo-1-pentene (**13**) gave 80% of the coupling product without any side products resulting from elimination or transmetalation, whereas the Cu(II) protocol failed to deliver the desired product (entry 5). Electron-rich 2,3,4-trimethoxystyrene (**14**) and gem-disubstituted olefins such as *tert*-butyl methacrylate (**15**)

TABLE 5. Coupling with Nonallylic Olefins

R—CH=CH2 $\xrightarrow[\text{Oxidant, NaOAc, Solvent}]{\text{PhSnBu}_3,\ \text{Pd(OAc)}_2}$ R—CH=CH—Ph
23 °C

entry	olefin	oxidant	
		Cu(II) [a]	oxygen [b]
1	(9)	65% (2 h)	55% (3 h) [c]
2	NC (10)	59% (5 h) [d]	-
3	Cl—(11)	-	72% (8 h)
4	Br—(12)	-	80% (8 h)
5	Br (13)	0%	80% (11 h)
6	MeO/OMe/OMe (14)	60% (6 h)	-
7	ᵗBuO₂C (15)	-	60% (8 h)

[a] Cu(II) = CuCl$_2$; solvent = THF. [b] Solvent = DMF. [c] 55 °C. [d] E/Z = 2.6/1.

TABLE 6. Coupling with Allylic Olefins

R—CH2—CH=CH2 $\xrightarrow[\text{Oxidant, NaOAc, Solvent}]{\text{PhSnBu}_3,\ \text{Pd(OAc)}_2}$ R—CH2—CH=CH—Ph
23 °C

entry	olefin	oxidant	
		Cu(II) [a]	oxygen [b]
1	Ph (16)	65 % (4 h)	82 % (2 h)
2	TBSO/MeO (17)	68 % (17 h) [c]	81 % (2 h) [d]
3	C₆F₅ (18)	0 %	65 % (12 h)
4	Ph—C(O)—O (19)	81 % (4 h)	67 % (12 h)
5	(20)	65 % (2 h)	70 % (36 h)
6	OHC-pyrrole (21)	60 % (18 h)	88 % (12 h)

[a] Cu(II) = Cu(OAC)$_2$; solvent = THF. [b] Solvent = DMF. [c] E/Z = 2.3/1. [d] E/Z = 1.6/1.

also furnished the corresponding coupling products without much difficulty (entries 6 and 7, respectively).

As shown in Table 6, these improved methods were effective in the formation of disubstituted olefins uniquely from allylic systems. Under both conditions, allylbenzene (**16**) was converted to (*E*)-1,3-diphenylpropene smoothly (entry 1), and electron-rich eugenol derivative (**17**) gave the coupled product in good yields (entry 2). However, electron-poor pentafluorobenzene (**18**) was successfully

reacted only under oxygen conditions (entry 3). From these examples, it was inferred that electron-rich substrates offered higher yields than electron-poor congeners as observed in the previous nonallylic systems. Subsequently, olefins with sensitive functional groups were subjected to both coupling reactions, delivering the desired olefins in moderate to good yields. Allyl phenylacetate (**19**) produced only 67% yield of the desired product along with 30% of ester hydrolysis product under the oxygen conditions; however, the Cu(II) method delivered 81% of desired olefin with no hydrolysis product (entry 4). Using both methods, allyl glycidyl ether (**20**) provided the coupled product in good yields (entry 5), and no epoxide ring-opening was detected. *N*-Allyl pyrrolecarboxaldehyde (**21**) was also compatible with both methodologies without any allylic migration (entry 6).

After screening various classes of olefins, we investigated the scope and limitation of aryl stannane coupling partners. In general, electron-rich aryl stannanes were effective as demonstrated with 3,4-dimethoxyphenyl stannane (**22**), giving almost quantitative yields under both reoxidant conditions (entry 1). On the other hand, aryl stannanes with electron-withdrawing groups including 4-trifluoromethylphenylstannane (**23**) and (4-tributylstannyl)benzaldehyde (**24**) were relatively sluggish under the oxygen conditions compared to the Cu(II) protocol (entries 2 and 3). Sterically congested 2-methoxyphenylstannane (**25**) was also compatible with both conditions (entry 4). These stannanes reacted with different olefins, exhibiting similar trends (entries 5–7). In conclusion, we applied oxygen and Cu(II) as catalyst reoxidants in the palladium-catalyzed coupling of olefins and aryl stannanes. Our methodologies allowed for the synthesis of disubstituted olefins from nonallylic and allylic systems in favor of *E*-isomers. The use of aryl stannanes with various electron densities and sterics was also feasible with this reaction. Oxygen conditions offered an improvement over transition metal promoted couplings due to elimination of metal salts and their byproducts that might cause side reactions. Thus, these oxygen conditions successfully facilitated aryl–alkenyl bond formation with several olefins incompatible with Cu(II) conditions. The synthetic applications of this method will be discussed in due course.

Experimental Section

Representative Experimental Procedure (Cu(II) condition): *tert*-Butyl acrylate (**1**; 64 mg, 0.5 mmol, 1 equiv) was dissolved in tetrahydrofuran (2.5 mL, 0.2 M solution) and stirred at room temperature. To this clear solution was added tributylphenyltin (184 mg, 0.5 mmol, 1 equiv) followed by a single addition of $CuCl_2$ (201 mg, 1.5 mmol, 3 equiv), NaOAc·$3H_2O$ (136 mg, 1.0 mmol, 2 equiv), and Pd(OAc)$_2$ (11 mg, 0.05 mmol, 0.1 equiv). The suspension was stirred at room temperature for 1 h, after which the mixture was diluted with diethyl ether (10 mL), filtered through a plug of neutral alumina, and washed with diethyl ether (3 × 10 mL). The filtrate was then concen-

TABLE 7. Various Aryl Stannanes Screened with Varying Electron Densities[a]

entry	olefin	R'SnBu$_3$	time (h)	yield (%)
1	*t*BuO$_2$C⌒ (**1**)	MeO / MeO—C$_6$H$_3$—SnBu$_3$ (**22**)	3 / 3	98 (A) / 96 (B)
2	**1**	F$_3$C—C$_6$H$_4$—SnBu$_3$ (**23**)	24 / 1	69 (A) / 85 (B)
3	**1**	OHC—C$_6$H$_4$—SnBu$_3$ (**24**)	16 / 2	60 (A) / 60 (B)
4	**1**	OMe / C$_6$H$_4$—SnBu$_3$ (**25**)	8 / 1	68 (A) / 75 (B)
5	BnO⌒ (**4**)	**22**	2	70 (A)
6	**4**	**24**	6	84 (A)
7	OHC—pyrrole-N-allyl (**21**)	**22**	12	60 (A)

[a] A: oxidant = O$_2$, solvent = DMF. B: oxidant = $CuCl_2$, solvent = THF.

trated in vacuo and purified by flash chromatography (30 g of SiO$_2$). Elution with petroleum ether (100 mL), then 9:1 hexanes/EtOAc afforded (*E*)-*tert*-butyl cinnamate (**2**; 98 mg, 96%) as a clear oil. Data for **2**: $R_f = 0.60$ (9:1 hexanes/EtOAc); ¹H NMR (250 MHz, CDCl$_3$) δ 1.56 (s, 9 H), 6.40 (d, $J = 16.0$ Hz, 1 H), 7.39 (m, 2 H), 7.53 (m, 3 H), 7.62 (d, $J = 16.0$ Hz, 1 H); ¹³C NMR (62.5 MHz, CDCl$_3$) δ 30.9, 55.4, 71.2, 114.4, 122.4, 128.4, 131.9, 140.3, 144.2, 158.7, 166.6.

Representative Experimental Procedure (Oxygen condition): *tert*-Butyl acrylate (**1**; 64 mg, 0.5 mmol, 1 equiv) was dissolved in DMF (2.5 mL, 0.2 M solution) and stirred at room temperature. To this clear solution was added tributylphenyltin (184 mg, 0.5 mmol, 1 equiv) followed by a single addition of NaOAc·$3H_2O$ (136 mg, 1.0 mmol, 2 equiv) and Pd(OAc)$_2$ (11 mg, 0.05 mmol, 0.1 equiv). The reaction flask was suspended over a balloon of oxygen, and the solution was stirred at room temperature for 12 h. The mixture was then diluted with diethyl ether (10 mL), filtered through a plug of neutral alumina, and washed with diethyl ether (3 × 10 mL). The filtrate was concentrated in vacuo, and subjected to flash chromatography (30 g of SiO$_2$). Elution with petroleum ether (100 mL), then 9:1 hexanes/EtOAc afforded (*E*)-*tert*-butyl cinnamate (75 mg, 74%).

Supporting Information Available: Spectral data for all the compounds in the schemes and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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