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Palladium/Copper-Catalyzed Oxidative Arylation of Terminal Alkenes with Aroyl Hydrazides

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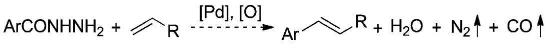
Abstract: An unprecedented oxidative arylation reaction of terminal alkenes with simple aroyl hydrazides has been developed under aerobic conditions for the stereoselective synthesis of 1,2-disubstituted alkenes. A range of aroyl hydrazides underwent palladium/copper-catalyzed oxidative Mizoroki–Heck reaction with terminal alkenes open to air in a 1:1 mixture of dimethyl sulfoxide and acetonitrile to give structurally diverse 1,2-disubstituted alkenes in moderate to excellent yields with excellent regio- and *E*-selectivity. The reaction tolerated a wide variety of functional groups, such as alkoxy, hydroxy, amino, fluoro, chloro, bromo, cyano, nitro, ester, amide, imide, phosphine oxide, and sulfone groups, and, moreover, molecular oxygen and dimethyl sulfoxide were demonstrated to serve as terminal oxidants. This study provides a useful method for the stereoselective synthesis of 1,2-disubstituted alkenes through direct transformation of the vinylic C–H bonds in terminal alkenes.

Direct transformation of the vinylic C–H bonds in terminal alkenes constitutes one of the most ideal methods for the stereoselective synthesis of 1,2-disubstituted alkenes. In this regard, terminal alkenes have been widely employed in the palladium-catalyzed Mizoroki–Heck reaction to couple with aryl sources, such as aryl halides and sulfonates.[1] Moreover, the scope of aryl sources has been significantly expanded by performing the Mizoroki–Heck-type reaction under oxidative conditions.[2] In 2002, Myers and co-workers disclosed an interesting palladium-catalyzed Mizoroki–Heck-type reaction using arenecarboxylic acids as aryl sources and Ag_2CO_3 as an oxidant at 120 °C.[3,4] Later on this decarboxylative Mizoroki–Heck reaction was subjected to a few modifications on reaction conditions, but it still required *ortho*-substituents on benzoic acids and suffers from the use of excess terminal alkenes ($\geq$1.5 equiv).[5] Although *ortho*-substituents are unnecessary for benzoic acid derivatives in the decarbonylative Mizoroki–Heck reaction of acid chlorides,[6] anhydrides,[7] and active esters,[8] most of these carboxylic acid derivatives are sensitive to moisture and the reaction frequently requires an elevated temperature up to 160 °C.

In contrast to many other types of carboxylic acid derivatives, simple aroyl hydrazides ($ArCONHNH_2$) are in general readily accessible solids that are compatible with moisture. Prompted by our recent studies on the oxidative removal of the $NHNH_2$ group from sulfonyl hydrazides[9] and carbazates,[10] together with our interest in alkene synthesis,[11] we envisioned that simple aroyl hydrazides could lose the $NHNH_2$ group in the presence of a palladium catalyst under oxidative conditions to generate certain aroylpalladium intermediates, extrusion of carbon monoxide from which followed by coupling with terminal alkenes would yield 1,2-disubstituted alkenes.[12] Moreover, we planned to use molecular oxygen as a terminal oxidant for the proposed arylation of terminal alkenes with simple aroyl hydrazides, and consequently, water, molecular nitrogen, and carbon monoxide were speculated to be generated as byproducts [Eq. (1)]. Hopefully, the reaction would proceed at lower temperature and exhibit broader substrate scope relative to that for the reaction with arenecarboxylic acids and their derivatives.[3–5,7,8]



(1)

To test the aforementioned hypothesis, we treated benzoyl hydrazide (**1a**) (1.1 equiv) with styrene (**2a**) and 5 mol% $PdCl_2$ in dimethyl sulfoxide open to air at 100 °C (oil bath) and found that alkene **3a** was formed in 10% yield with exclusive *E* selectivity (Table 1, entry 1). Subsequently, a range of solvents were examined and a slightly better yield was achieved from the reaction performed in a 1:1 mixture of dimethyl sulfoxide and acetonitrile (entry 7). Replacing $PdCl_2$ with $Pd(OAc)_2$ or $[Pd(PPh_3)_4]$ failed to promote the desired oxidative Mizoroki–Heck reaction (entries 8 and 9). To accelerate the possible switch between Pd^{II} and Pd^0 species that might be involved in the reaction (see below), we examined a few copper sources and found that the use of 1 mol% CuI improved the yield to 17% (entry 12). To our delight, the catalytic ability of $PdCl_2$/CuI (5:1) was dramatically enhanced by Brønsted acids and the ad-

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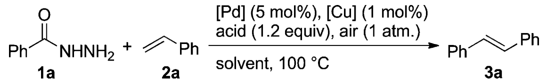
Table 1. Optimization of reaction conditions.[a,b]



Entry	[Pd]	[Cu]	Acid	Solvent	Yield [%][c]
1	$PdCl_2$	none	none	DMSO	10
2	$PdCl_2$	none	none	DMF	trace
3	$PdCl_2$	none	none	MeCN	trace
4	$PdCl_2$	none	none	dioxane	0
5	$PdCl_2$	none	none	toluene	0
6	$PdCl_2$	none	none	propanol	0
7	$PdCl_2$	none	none	DMSO/MeCN (1:1)	11
8	$Pd(OAc)_2$	none	none	DMSO/MeCN (1:1)	0
9	$[Pd(PPh_3)_4]$	none	none	DMSO/MeCN (1:1)	0
10	$PdCl_2$	CuCl	none	DMSO/MeCN (1:1)	9
11	$PdCl_2$	CuBr	none	DMSO/MeCN (1:1)	11
12	$PdCl_2$	CuI	none	DMSO/MeCN (1:1)	17
13[d]	$PdCl_2$	CuI	TsOH	DMSO/MeCN (1:1)	19
14	$PdCl_2$	CuI	TsOH	DMSO/MeCN (1:1)	86
15	$PdCl_2$	CuI	H_2SO_4	DMSO/MeCN (1:1)	43
16[e]	$PdCl_2$	CuI	TsOH	DMSO/MeCN (1:1)	77

[a] Reaction conditions: hydrazide **1a** (0.44 mmol), alkene **2a** (0.40 mmol), [Pd] (5 mol%), [Cu] (if any, 1 mol%), acid (if any, 1.2 equiv), air (1 atm.), solvent (1.0 mL), 100 °C (oil bath), 3 h. [b] In all cases alkene **3a** was obtained as a single regioisomer with >99:1 *E/Z* selectivity. [c] Isolated yield. [d] 20 mol% TsOH was used. [e] The reaction was run at 80 °C (oil bath). Ac = acetyl, Ts = *p*-toluenesulfonyl.

dition of 1.2 equivalents of *p*-toluenesulfonic acid improved the yield to 86% (entry 14). Whereas the reaction did take place at a lower temperature, the desired product was obtained in a lower yield (entry 16).

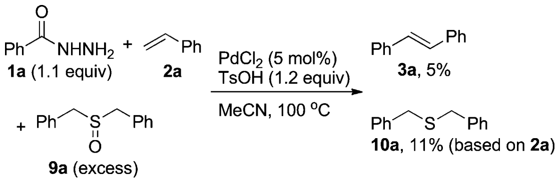
In the presence of 5 mol% $PdCl_2$, 1 mol% CuI, and 1.2 equivalents of *p*-toluenesulfonic acid and open to air, a range of aroyl hydrazides smoothly underwent oxidative Mizoroki–Heck reaction with arylethenes at 100 °C (oil bath) to give structurally diverse 1,2-diaryl alkenes in moderate to good yields with excellent regio- and *E*-selectivity (Table 2, entries 1–25).[13] It is noteworthy that both electron-withdrawing and -donating groups were successfully introduced into the aromatic rings of the products by employing the aroyl hydrazides or the arylethenes bearing such groups and that the oxidative conditions were mild enough to be compatible with very electron-rich aryl groups, such as hydroxyphenyl, aminophenyl, and thienyl groups (entries 3, 4, 14, and 17). This chemistry was successfully extended to a variety of terminal alkenes, such as acrylates, acrylamides, N-protected allylamines, allylphosphine oxides, and allyl sulfones, and a range of functionalized 1,2-disubstituted alkenes were obtained in moderate to excellent yields with extremely high regio- and *E*-selectivity (entries 26–31). When compared to previously reported Mizoroki–Heck-type reactions of arenecarboxylic acids and their derivatives,[3–8] the reaction exhibited broader scope with regard to terminal alkenes through oxidative arylation of the vinylic C–H bonds in the *N*-allyl, *S*-allyl, and *P*-allyl groups. In addition, as demonstrated by the results summarized in Table 2, the reaction tolerated a wide variety of functional groups, such as alkoxy, hydroxy, amino, fluoro, chloro, bromo, cyano, nitro, ester, amide, imide, phosphine oxide, and sulfone groups.

In sharp contrast to benzoyl hydrazide (**1a**), an N′-substituted aroyl hydrazide, such as PhCONHNHBn (**5a**) failed to undergo oxidative Mizoroki–Heck reaction with styrene (**2a**) to give alkene **3a** under the standard conditions. This result indicates that the $NHNH_2$ group is essential for the oxidative Mizoroki–Heck reaction of terminal alkenes with aroyl hydrazides.

Control experiments indicated that the desired reaction did not occur in the absence of $PdCl_2$ and a much lower yield was obtained from the reaction without CuI (Table 3, entries 1 and 2). Furthermore, we examined the catalytic ability of $[Pd(OTs)_2(MeCN)_2]$, which might be generated from $PdCl_2$ and *p*-toluenesulfonic acid, and found that the corresponding reaction gave only 16% yield (entry 3). These results suggest that $PdCl_2$ serves as the major active Pd^{II} catalyst, which can be regenerated through copper-mediated aerobic oxidation after being reduced to Pd^0 during the reaction (see below). The $PdCl_2$/CuI (5:1) catalyst system was also responsible for a minor side reaction, the Wacker oxidation of styrene (**2a**),[14] wherein a trace amount of acetophenone was generated and condensed with benzoyl hydrazide (**1a**) to give Ph(Me)C=NHNHCOPh (**6a**) that was tentatively assigned by electrospray ionization (ESI) mass spectrometric analysis of the reaction mixture.[15] Moreover, the ESI mass spectrometric analysis allowed tentative assignment of two other byproducts, PhCONHNHCOPh (**7a**) and PhCOCH=CHPh (**8a**),[16] which lend substantial support to the formation of the proposed key aroylpalladium intermediate during the reaction (see below).

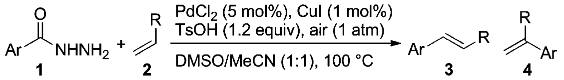
For comparison, the reaction of benzoyl hydrazide (**1a**) with styrene (**2a**) was performed under an oxygen atmosphere to give alkene **3a** in 65% yield (Table 3, entry 4). The higher concentration of molecular oxygen led to a lower yield probably by accelerating the decomposition of the hydrazide (see below). Much to our surprise, the reaction did take place in the absence of an oxygen atmosphere albeit that the desired product was obtained in a much lower yield (entry 5). Furthermore, CuI proved to be irrelevant to the reaction without oxygen (entry 6). These results allow us to conclude that the solvent, dimethyl sulfoxide, is capable of serving as an oxidant to convert Pd^0 to Pd^{II} (see below).[17] To our delight, this conclusion was unambiguously confirmed by the experiment shown in Equation (2). When dibenzyl sulfoxide (**9a**) rather than dimethyl sulfoxide was used as the cosolvent for the reaction of benzoyl hydrazide (**1a**) with styrene (**2a**) in the presence of 5 mol% $PdCl_2$ and 1.2 equivalents of *p*-toluenesulfonic acid under a nitrogen atmosphere, a significant amount of dibenzyl sulfoxide (**9a**) was found to be reduced to give dibenzyl sulfide (**10a**).

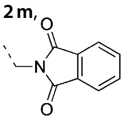
Aroyl hydrazides were subjected to decomposition either by $PdCl_2$ or by CuI under the standard reaction conditions. Treatment of benzoyl hydrazide (**1a**) with 1.1 equivalents of *p*-tolu-



(2)

Table 2. Oxidative arylation of terminal alkenes with aroyl hydrazides.[a]



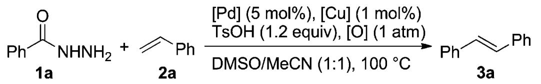
Entry	**1**, Ar	**2**, R	**3**	Yield [%][b]	**3**/**4**[c]	E/Z[c]
1	**1a**, Ph	**2a**, Ph	**3a**	86	>99:1	>99:1
2	**1b**, 4-MeO-Ph	**2a**, Ph	**3b**	60	96:4	>99:1
3	**1c**, 4-HO-Ph	**2a**, Ph	**3c**	51	>99:1	>99:1
4[d]	**1d**, 4-H$_2$N-Ph	**2a**, Ph	**3d**	59	97:3	>99:1
5	**1e**, 4-F-Ph	**2a**, Ph	**3e**	56	>99:1	>99:1
6	**1f**, 4-Cl-Ph	**2a**, Ph	**3f**	82	>99:1	>99:1
7	**1g**, 4-Br-Ph	**2a**, Ph	**3g**	72	>99:1	>99:1
8	**1h**, 4-F$_3$C-Ph	**2a**, Ph	**3h**	57	>99:1	>99:1
9[e]	**1i**, 4-NC-Ph	**2a**, Ph	**3i**	42	>99:1	>99:1
10[f]	**1j**, 4-O$_2$N-Ph	**2a**, Ph	**3j**	46	>99:1	>99:1
11	**1k**, 3-Cl-Ph	**2a**, Ph	**3k**	88	>99:1	>99:1
12[f]	**1l**, 3-O$_2$N-Ph	**2a**, Ph	**3l**	64	>99:1	>99:1
13	**1m**, 2-Me-Ph	**2a**, Ph	**3m**	80	>99:1	>99:1
14[g]	**1n**, 2-HO-Ph	**2a**, Ph	**3n**	45	>99:1	>99:1
15	**1o**, 2-naphthyl	**2a**, Ph	**3o**	77	>99:1	>99:1
16	**1p**, 1-naphthyl	**2a**, Ph	**3p**	73	96:4	>99:1
17	**1q**, 3-thienyl	**2a**, Ph	**3q**	44	>99:1	>99:1
18	**1a**, Ph	**2b**, 4-MeO-Ph	**3b**	74	>99:1	>99:1
19	**1a**, Ph	**2c**, 4-Cl-Ph	**3f**	69	>99:1	>99:1
20	**1a**, Ph	**2d**, 4-Br-Ph	**3g**	77	>99:1	>99:1
21	**1a**, Ph	**2e**, 3-Cl-Ph	**3k**	60	>99:1	>99:1
22	**1a**, Ph	**2f**, 2-MeO-Ph	**3r**	77	91:9	>99:1
23	**1a**, Ph	**2g**, 2-O$_2$N-Ph	**3s**	56	>99:1	97:3
24	**1a**, Ph	**2h**, 2-naphthyl	**3o**	73	>99:1	>99:1
25	**1a**, Ph	**2i**, 1-naphthyl	**3p**	74	93:7	>99:1
26	**1a**, Ph	**2j**, CO$_2n$Bu	**3t**	58	>99:1	>99:1
27	**1a**, Ph	**2k**, CONHBn	**3u**	69	>99:1	>99:1
28	**1a**, Ph	**2l**, CONHPh	**3v**	69	>99:1	>99:1
29	**1a**, Ph	**2m**, 	**3w**	91	>99:1	>99:1
30	**1a**, Ph	**2n**, CH$_2$POPh$_2$	**3x**	89	>99:1	>99:1
31	**1a**, Ph	**2o**, CH$_2$SO$_2$Ph	**3y**	70	>99:1	>99:1

[a] Reaction conditions: hydrazide **1** (0.44 mmol), alkene **2** (0.40 mmol), PdCl$_2$ (5 mol%), CuI (1 mol%), TsOH (0.48 mmol), air (1 atm), DMSO/MeCN (1:1, 1.0 mL), 100°C (oil bath), 3 h. [b] Isolated yield. [c] Determined by ^{1}H NMR spectroscopic analysis. [d] TsOH (0.96 mmol) was used. [e] Hydrazide (0.60 mmol) and TsOH (0.68 mmol) were used. [f] The reaction was run with 10 mol% PdCl$_2$ under oxygen (1 atm.). [g] The reaction was run at 120°C (oil bath) for 13 h. Bn = Benzyl.

enesulfonic acid, excess air, and 5 mol% PdCl$_2$ led to the formation of benzophenone (**11a**) and benzoic acid (**12a**) in 34 and 30% yields, respectively (Scheme 1). On the other hand, replacing 5 mol% PdCl$_2$ with 1 mol% CuI only gave benzoic acid (**12a**) in 45% yield.[18] However, neither benzophenone (**11a**) nor benzoic acid (**12a**) could react with styrene (**2a**) to give alkene **3a** under the standard conditions.

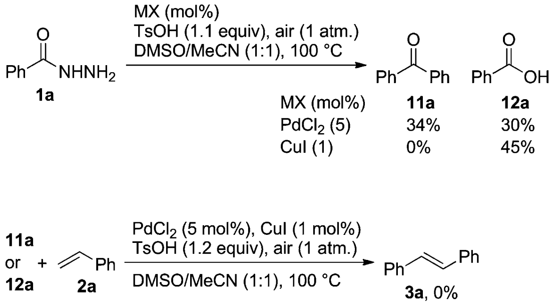
On the basis of the above experimental results, we propose the following reaction pathways for the palladium/copper-catalyzed oxidative arylation of terminal alkenes with aroyl hydrazides (Scheme 2). While hydrazide **1** can form a salt with *p*-toluenesulfonic acid, reversal of the salt-forming reaction allows hydrazide **1** to displace a Pd^{II} catalyst, PdXY (X, Y = Cl, OTs, I), to give hydrazide–Pd^{II} complex **13**, β-hydride elimination of which results in the formation of diazene **14** and HPdX.[9a,10] Displacement of PdXY with diazene **14** followed by successive extrusion of molecular nitrogen and carbon monoxide leads to the formation of arylpalladium **17**, which undergoes regioselective alkene insertion followed by stereoselective β-hydride elimination to give alkene **3** and release HPdX. Reductive elimination of HPdX regenerates Pd^0, which is converted to PdXY either by copper-mediated aerobic oxidation[14] or by oxidation with the solvent dimethyl sulfoxide.[17]

Table 3. Control experiments.[a,b]

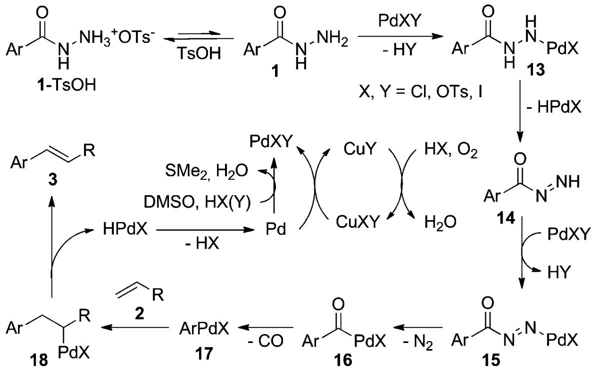


Entry	[Pd]	[Cu]	[O]	Yield [%][c]
1	none	CuI	air	0
2	PdCl$_2$	none	air	53
3	Pd(OTs)$_2$(MeCN)$_2$	CuI	air	16
4	PdCl$_2$	CuI	O$_2$	65
5[d]	PdCl$_2$	CuI	none	49
6[d]	PdCl$_2$	none	none	49

[a] Reaction conditions: hydrazide **1a** (0.44 mmol), alkene **2a** (0.40 mmol), [Pd] (if any, 5 mol%), CuI (if any, 1 mol%), TsOH (1.2 equiv), air or O$_2$ (if any, 1 atm.), DMSO/MeCN (1:1, 1.0 mL), 100°C (oil bath), 3 h. [b] In all cases alkene **3a** was obtained as a single regioisomer with >99:1 E/Z selectivity. [c] Isolated yield. [d] The reaction was run under nitrogen (1 atm.).

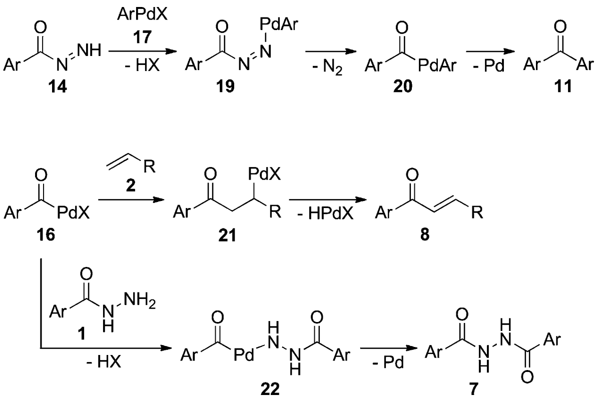


Scheme 1. Decomposition of benzoyl hydrazide (**1a**).



Scheme 2. Proposed reaction pathways.

Two of the intermediates proposed for the above reaction pathways, diazene **14** and aroylpalladium **16**, have been speculated to account for the side reaction pathways depicted in Scheme 3. Displacement of arylpalladium **17** with diazene **14** followed by extrusion of molecular nitrogen results in the formation of aroylpalladium **20**, reductive elimination of which gives ketone **11**. Aroylpalladium **16** undergoes alkene insertion followed by β-hydride elimination to give α,β-unsaturated ketone **8**. On the other hand, displacement of aroylpalladium **16** with hydrazide **1** followed by reductive elimination gives diacyl hydrazide **7**.



Scheme 3. Proposed side reaction pathways.

In summary, we have developed, for the first time, an oxidative arylation reaction of terminal alkenes with simple aroyl hydrazides under aerobic conditions for the stereoselective synthesis of 1,2-disubstituted alkenes. In the presence of 5 mol% $PdCl_2$, 1 mol% CuI, and 1.2 equivalents of *p*-toluenesulfonic acid and open to air, a range of aroyl hydrazides smoothly underwent oxidative Mizoroki–Heck reaction with terminal alkenes in a 1:1 mixture of dimethyl sulfoxide and acetonitrile to give structurally diverse 1,2-disubstituted alkenes in moderate to excellent yields with excellent region- and *E*-selectivity. Notably, the reaction tolerated a wide variety of functional groups, such as alkoxy, hydroxy, amino, fluoro, chloro, bromo, cyano, nitro, ester, amide, imide, phosphine oxide, and sulfone groups. Moreover, molecular oxygen and dimethyl sulfoxide were demonstrated to serve as terminal oxidants for the palladium/copper-catalyzed oxidative arylation of terminal alkenes with aroyl hydrazides.

Experimental Section

General procedure for the oxidative arylation of terminal alkenes with aroyl hydrazides

$PdCl_2$ (3.5 mg, 0.02 mmol), CuI (0.8 mg, 0.004 mmol), and $TsOH{\cdot}H_2O$ (91.3 mg, 0.48 mmol) were added to a solution of hydrazide **1** (0.44 mmol) in DMSO/MeCN (1:1, 1.0 mL) under an air atmosphere at room temperature. The mixture was stirred for 1 h, and alkene **2** (0.40 mmol) was added. The mixture was heated at 100 °C (oil bath) for 3 h, cooled to room temperature, and directly purified by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:100 ~ 1:1), to give alkenes **3** and **4** (if any).

Acknowledgements

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Keywords: alkenes · arylation · hydrazides · oxidation · palladium

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