

Direct Coupling of Benzene with Olefin Catalyzed by Pd(OAc)₂ Combined with Heteropolyoxometalate under Dioxygen

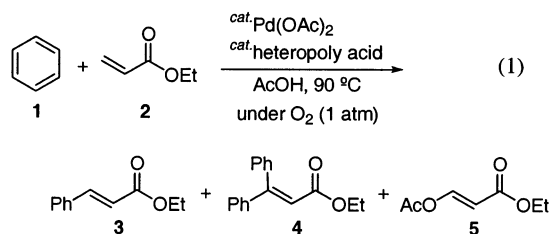
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The Heck–Mizoroki arylation of olefins with aryl halides and triflates is a highly versatile synthetic transformation, but the formation of undesired waste is unavoidable. In recent years, there has been a growing demand for the development of a catalytic method which can activate the C–H bond of arenes such as benzene instead of halobenzenes in organic synthesis.¹ Since the success of the activation of aryl C–H bonds through ortho-chelation by Ru complexes,² such C–H bond activations of substituted arenes have been made by Ru, Pd, and Rh complexes.¹ Although several transition metal compounds are reported to activate stoichiometrically the C–H bond of nonsubstituted aromatic compounds, it is still very difficult to carry out this catalytically.³ Fujiwara and co-workers have reported the stoichiometric and catalytic oxidative coupling of arenes with alkenes through the cleavage of aromatic C–H bonds assisted by Pd compounds.⁴ In 1978, Matveev et al. reported the Pd(II)-catalyzed arylation of ethylene in the presence of molybdovanadophosphoric acid.⁵ Several authors have reported catalysis by Pd compounds using peroxides and benzoquinones as oxidants in the coupling of benzene with olefins.^{4,6} Quite recently, a few important papers have appeared on the oxidative arylation of alkenes using dioxygen as a terminal oxidant. Matsumoto et al. showed that styrene was synthesized from the reaction of benzene with ethylene catalyzed by an Rh complex in acetic acid with elevated pressure of dioxygen.⁷ The Ru-catalyzed reaction of benzene with acrylates under O₂ (2 atm) and CO (6.1 atm) at 180 °C was reported by Milstein et al.⁸ However, these reactions call for severe reaction conditions, high reaction temperature, and high pressurized O₂ and CO. Therefore, it has been desired to develop a new catalytic system for the coupling reaction of olefins with arenes via the C–H bond activation which can operate under normal O₂ pressure and at up to 100 °C.

In the course of our study on the biphenyl synthesis from benzene by Pd(II) using molybdovanadophosphate and O₂ as a reoxidation system,⁹ we found that the oxidative coupling reaction of benzenes with acrylates is facilitated by the use of a catalytic amount of Pd(OAc)₂ combined with molybdovanadophosphoric acid (HPMoV) under dioxygen as a terminal oxidant (eq 1).



A typical reaction procedure is as follows: To an acetic acid solution (5 mL) of Pd(OAc)₂ (0.1 mmol), H₇PMo₈V₄O₄₀·*n*H₂O (43 mg), acetylacetone (0.1 mmol), and NaOAc (0.08 mmol) were added benzene (**1**, 15 mmol) and ethyl acrylate (**2**, 1.5 mmol). The flask was equipped with a balloon filled with O₂ (1 atm). The

Table 1. Oxidative Coupling Reaction of **1** with **2** Catalyzed by Pd(OAc)₂ Combined with HPMoV under Dioxygen Atmosphere^a

run	HPMoV	base	conv. (%)	yield (%)		
				3	4	5
1	H ₇ PMo ₈ V ₄ O ₄₀	NaOAc	91	63	5	12
2		NaOAc	11	7	0	2
3	H ₆ PMo ₉ V ₃ O ₄₀	NaOAc	98	66	11	11
4	H ₅ PMo ₁₀ V ₂ O ₄₀	NaOAc	93	63	10	11
5	H ₄ PMo ₁₁ V ₁ O ₄₀	NaOAc	99	63	15	10
6	H ₃ PMo ₁₂ O ₄₀	NaOAc	37	23	0	8
7 ^b	H ₇ PMo ₈ V ₄ O ₄₀	NaOAc	69	28	<1	23
8	H ₇ PMo ₈ V ₄ O ₄₀		34	12	0	8
9	H ₇ PMo ₈ V ₄ O ₄₀	LiOAc	76	46	1	14
10	H ₇ PMo ₈ V ₄ O ₄₀	CsOAc	90	54	3	13
11	H ₇ PMo ₈ V ₄ O ₄₀	KOAc	22	17	0	6
12	H ₇ PMo ₈ V ₄ O ₄₀	NH ₄ OAc	30	19	3	6
13	H ₇ PMo ₈ V ₄ O ₄₀	Na ₂ CO ₃	53	34	1	14
14 ^c	H ₇ PMo ₈ V ₄ O ₄₀	Na ₂ CO ₃	90	54	3	13
15 ^d	H ₇ PMo ₈ V ₄ O ₄₀	NaOAc	46	24	0	14
16 ^{d,e}	H ₇ PMo ₈ V ₄ O ₄₀	NaOAc	100	50	9	10
17 ^{f,g}	H ₇ PMo ₈ V ₄ O ₄₀	NaOAc		72	10	1
18 ^f	H ₇ PMo ₈ V ₄ O ₄₀	NaOAc		8	73	<1
19 ^{f,h}	H ₇ PMo ₈ V ₄ O ₄₀	NaOAc		72	10	1

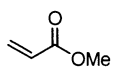
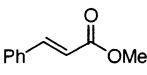
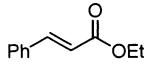
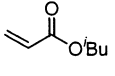
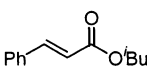
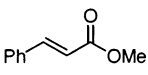
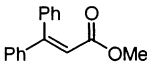
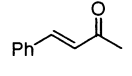
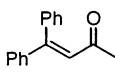

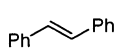
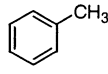
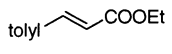

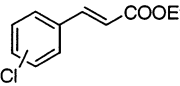

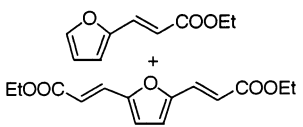
^a **1** (15 mmol) was allowed to react with **2** (1.5 mmol) in the presence of Pd(OAc)₂ (0.1 mmol), HPMoV (43–47 mg, ca. 0.02 mmol), acetylacetone (0.1 mmol), and base (0.08 mmol) in acetic acid (5 mL) at 90 °C for 6 h under O₂ (1 atm). Conversion and yields were based on **2** used. ^b **1** (7.5 mmol) was used. ^c Na₂CO₃ (0.04 mmol) was used. ^d In the absence of acetylacetone. ^e Pd(acac)₂ was used instead of Pd(OAc)₂. ^f The reaction was carried out using **1** (30 mmol) in propionic acid (5 mL). ^g The reaction was carried out for 3 h. ^h The reaction was carried out under air (1 atm).

mixture was stirred at 90 °C for 6 h. The products were isolated by column chromatography (230–400 mesh silica gel).

Table 1 summarizes the representative results for the reaction of **1** with **2**. The reaction of **1** with **2** catalyzed by the Pd(OAc)₂/H₇PMo₈V₄O₄₀/acetylacetone/NaOAc system afforded ethyl cinnamate (**3**) (63%) and ethyl β-phenylcinnamate (**4**) (5%) together with ethyl 3-acetoxyacrylate (**5**) (12%) derived from the reaction of **2** with acetic acid (run 1). The reaction had difficulty taking place in the absence of HPMoV (run 2). Several trends are apparent from the data in the Table 1. Product distributions were slightly influenced by the use of HPMoV differing in Mo and V content (runs 3–5). The combined catalytic system of Pd(OAc)₂ with 12-molybdophosphoric acid afforded a less satisfactory result than that with HPMoV (run 6). When the amount of **1** was halved, a considerable amount of **5** as a byproduct was obtained (run 7). The reaction without a base resulted in low yields of products (run 8). Among the bases examined, sodium acetate was found to give the best yield of **3** (66%). Lithium and cesium acetates led to **3** in 46 and 54% yields, respectively, but potassium and ammonium acetates were inert (runs 9–12). Sodium carbonate gave **3** in moderate yields (runs 13 and 14).

The reaction in the absence of acetylacetone resulted in the decrease of **3** (run 15). It is known that the oxidative arylation of

Table 2. Oxidative Coupling Reaction of Various Arenes with Alkenes Catalyzed by Pd(OAc)₂ Combined with H₇PMo₈V₄O₄₀ under Dioxygen Atmosphere^a

Run	Arene	Alkene	Product	Yield (%)
1	1			65
2	1	2		72
3	1			75
4	1			84
5	1			70
6 ^b	1			32
7 ^c		2		69 ^d
8 ^e		2		68 ^f
9 ^g		2		62 10

^a Arene (30 mmol) was allowed to react with alkene (1.5 mmol) in the presence of Pd(OAc)₂ (0.1 mmol), H₇PMo₈V₄O₄₀ (43 mg, ca. 0.02 mmol), acetylacetone (0.1 mmol), and NaOAc (0.08 mmol) in propionic acid (5 mL) at 90 °C for 3 h under O₂ (1 atm). Conversion and yields were based on alkene used. ^b For 10 h. ^c For 2 h. ^d The product was obtained as an isomeric mixture (*o:m:p* = 14:42:44). ^e For 6 h. ^f The product was obtained as an isomeric mixture (*o:m:p* = 27:40:33). ^g Furan (3 mmol) was reacted at 30 °C for 12 h in acetic acid (5 mL).

ethylene to styrene by Rh and Pd complexes is accelerated by adding a small amount of acetylacetone and that the formation of a byproduct like vinyl acetate is depressed.⁷ However, Pd(acac)₂ was employed in place of Pd(OAc)₂ to form **3** and **4** in relatively good yield even in the absence of acetylacetone (run 16).

When propionic acid was employed in place of acetic acid, the reaction was considerably enhanced, giving **3** in 72% yield within 3 h (run 17). The prolonged reaction time caused the formation of **4** (73%) as a major product (run 18). From the practical synthetic viewpoint, it is very important to note that the reaction in propionic acid took place even under air (1 atm) to give **3** in 72% yield (run 19).

On the basis of these results, the reaction of various arenes with alkenes was carried out under the same conditions as was run 17 in Table 1. Representative results are shown in Table 2. **1** smoothly reacted with several acrylate derivatives to form the corresponding cinnamates (65–84%) along with β -phenylcinnamates (5–20%) (runs 1–4). The arylation of 1-phenylbuten-3-one under these reaction conditions gave 1,1-diphenylbuten-3-one in 70% yield (run

5). Styrene, however, reacted with difficulty to give *trans*-styrene in 32% yield (run 6). The reaction of toluene with **2** afforded a regioisomeric mixture of coupling products in 69% yield (run 7). Chlorobenzene coupled with **2** in the same fashion as benzene **1** giving a mixture of coupling products (*o:m:p* = 27:40:33) in 68% yield (run 8). Furan gave the corresponding product in satisfactory yield even at 30 °C (run 9).

To obtain mechanistic information on the present reaction, a 1:1 mixture of benzene **1** and benzene-*d*₆ **1-d** was reacted with **2** under the same conditions as in Table 1, run 1. The ratio of the resulting **3** and **3-d** was found to be approximately **3/3-d** = 4. A kinetic isotope effect for the coupling of **1** with methyl acrylate is reported to be $k_H/k_D = 2$.⁸ Furthermore, no scrambling of deuterium was observed. These facts indicate that the cleavage of the C–H bond of **1** is the slowest step in a sequence of reactions. Because of the complexity of the present catalytic system, it seems difficult to make an accurate assessment about the reaction mechanism in the coupling reaction. However, we thought that the reaction proceeds via a reaction pathway similar to that proposed by Fujiwara et al.;^{4b} that is, σ -aryl-Pd(II) complex reacts with alkene **2** followed by β -hydride elimination to give aryl alkene **3** and Pd–H or Pd(0), which is reoxidized by HPMoV/O₂.¹⁰

In conclusion, we have documented a highly efficient Pd(II)-catalyzed direct coupling reaction of benzenes with acrylates using molecular oxygen as a terminal oxidant under mild conditions. Further mechanistic investigations as well as synthetic applications of the present catalytic system are in progress.

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- (10) σ -Aryl-Pd(II) complexes formed via electrophilic substitution of aromatic C–H bonds by cationic [Pd(OAc)]⁺ species have been reported to be the intermediates in the catalytic cycle.

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