

Highly regioselective Heck-Mizoroki reaction catalyzed by Pd/phosphine ligand in DMSO/[bmim][BF₄] under microwave irradiation

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Abstract

This work established that highly regioselective Heck-Mizoroki arylation of olefins can be accomplished with aryl halides using Pd₂(dba)₃ (dba = dibenzylideneacetone) with phosphine ligand L [L = methyl 4,6-*O*-benzylidene-3-deoxy-3-(diphenylphosphino)- α -D-altropyranoside] as catalyst in DMSO/[bmim][BF₄] under microwave irradiation. In addition, the use of microwave irradiation greatly reduces the reaction time (from hours to minutes), allows low catalyst loading (0.01 mol%) and affords nearly quantitative product yields.

Keywords: Palladium catalyst, Heck reaction, regioselectivity, ionic liquid, microwave heating

Introduction

The past 40 years have witnessed remarkable discoveries that have greatly advanced the synthetic use of transition-metal-catalyzed reactions that involve the preparation of carbon-carbon bonds (C-C bonds).¹ The arylation of olefins was first reported by Heck,² and has received considerable attention since,³ also widely used, including polymers, pharmaceuticals and natural products.⁴ However, the reaction typically generates a mixture of both 1,1- and 1,2-products, hampering the reactions wider application in chemical synthesis.⁵

The first microwave-assisted Heck-Mizoroki reaction was reported by Hallberg and co-workers in 1996,⁶ the use of microwave to improve the synthetic methods has received extensive attention in the past few years, and the products were isolated in good to excellent yields since.⁷

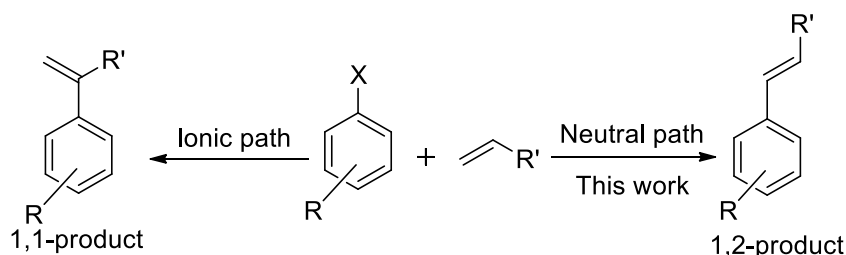
Leadbeater shown that Heck-Mizoroki reactions can be performed with Pd catalyst concentrations as low as 500 ppb in ionic liquid under microwave.⁸ However, aryl iodides and

chlorides coupled only in very low yields using this method. Recently, accelerated Heck-Mizoroki reactions using an *ortho*-palladated complex in ionic liquid with microwave irradiation were reported by Hajipour.⁹

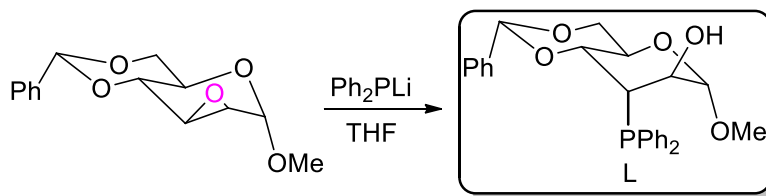
Xiao found that Pd-catalyzed regioselective Heck-Mizoroki reactions in a molecular solvent-ionic liquid afforded 1,1-products *via* an ionic pathway (Scheme 1), that regioselectivities were lower in the absence of an ionic liquid and that the choice of ligand was critical in achieving good selectivities.^{5a,10} Later, they found that hydrogen-bonding promoted oxidative addition and regioselective arylation of olefins with aryl halides.^{5b,11}

Methyl 4,6-*O*-benzylidene-3-deoxy-3-(diphenylphosphino)- α -D-allopyranoside (L) derived from D-glucose (Scheme 2) is more sterically demanding and electron-rich than triphenylphosphine.¹² Previously, we reported Pd(OAc)₂/L catalyzed aryl halides with styrene in DMA afforded good to excellent yields of products under conventional heating.¹³ However, our previous experiments usually gave rise to mixtures of 1,1- and 1,2-products (96:4-91:9), indicating that the ionic pathway co-existed in the coordination-insertion step, and the neutral pathway was favored by adding ionic liquid (TBAB). This observation was consistent with the lack of regioselectivity in normal intermolecular Pd/P catalyzed Heck-Mizoroki reactions.^{4a,10b,14}

With our previous data in hand, we now disclose that highly regioselective Heck reactions to afford 1,2-products can be carried out equally well by adding ionic liquid ([bmim][BF₄]) to reactions run in DMSO under microwave irradiation (Scheme 1).



Scheme 1. Two paths of the Heck-Mizoroki reactions.



Scheme 2. The synthesis of chiral phosphine ligand L.

Results and Discussion

As the initial research, we chose 4-bromotoluene and styrene as standard substrates to optimize suitable conditions for Heck-Mizoroki reaction (Table 1). Ionic liquid¹⁵ plays a critical role in many highly regioselective Heck reaction.^{5a,10} and we wanted to disclose its use in our system. So we examined the reaction in a molecular solvent-ionic liquid cocktail under microwave irradiation. We found that polar aprotic solvents *N,N*-dimethyl acetylamine (DMA), dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), 1-methyl-2-pyrrolidinone (NMP) were better solvents and DMSO was the best solvent (Table 1, entries 1-8). Although THF, MeCN, benzene and toluene are preferred in some cases.¹⁶ Herein, just moderate yields were found (Table 1, entries 5-8). Leadbeater found that the Heck-Mizoroki reaction in organic solvents such as DMF, NMP, and DMSO did not meet with success at low catalyst loadings (<0.05 mol%) and significant decomposition of the starting halide was observed in all of these solvents under conventional heating.⁸ Herein, ionic liquid has been used to prevent the decomposition of the starting substrates and stabilization of the palladium catalyst. For comparison, the reaction was also carried out in DMSO/[bmim][BF₄], DMSO/[bmim][Br] (Table 1, entries 9 and 10).

It is worthy of note that in the absence of the ionic liquid, more 1,1-disubstituted olefin was observed (92:8), showing that the ionic liquid plays an important role for the enhanced regioselectivity (Table 1, entry 25), this observation is consistent with our previously proposed mechanism for this reaction.¹³

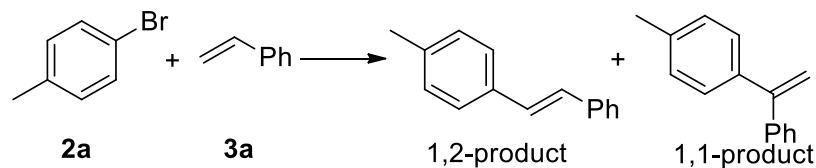


Table 1. Optimization of the typical reaction conditions^a

Entry	Pd source	Base	Solvent/Ionic liquid	Product ratio	Yield (%) ^b
1	Pd(OAc) ₂	K ₂ CO ₃	DMA/TBAB	95:5	97
2	Pd(OAc) ₂	K ₂ CO ₃	DMF/TBAB	94:6	90
3	Pd(OAc) ₂	K ₂ CO ₃	DMSO/TBAB	98:2	96
4	Pd(OAc) ₂	K ₂ CO ₃	NMP/TBAB	94:6	89
5	Pd(OAc) ₂	K ₂ CO ₃	Toluene/TBAB	91:9	80
6	Pd(OAc) ₂	K ₂ CO ₃	CH ₃ CN/TBAB	92:8	78
7	Pd(OAc) ₂	K ₂ CO ₃	THF/TBAB	94:6	81
8	Pd(OAc) ₂	K ₂ CO ₃	Benzene/TBAB	91:9	60
9	Pd(OAc) ₂	K ₂ CO ₃	DMSO/[bmim][BF ₄]	100:0	96

Table 1. Continued

Entry	Pd source	Base	Solvent/Ionic liquid	Product ratio	Yield (%) ^b
10	Pd(OAc) ₂	K ₂ CO ₃	DMSO/[bmim][Br]	99:1	95
11	PdCl ₂	K ₂ CO ₃	DMSO/[bmim][BF ₄]	100:0	90
12	Pd(O ₂ CCF ₃) ₂	K ₂ CO ₃	DMSO/[bmim][BF ₄]	100:0	95
13	Pd(COD)Cl ₂	K ₂ CO ₃	DMSO/[bmim][BF ₄]	100:0	94
14	Pd ₂ (dba) ₃	K ₂ CO ₃	DMSO/[bmim][BF ₄]	100:0	98
15	Pd ₂ (dba) ₃	KOH	DMSO/[bmim][BF ₄]	100:0	70
16	Pd ₂ (dba) ₃	K ₃ PO ₄	DMSO/[bmim][BF ₄]	100:0	>99
17	Pd ₂ (dba) ₃	NaOAc	DMSO/[bmim][BF ₄]	100:0	85
18	Pd ₂ (dba) ₃	Cs ₂ CO ₃	DMSO/[bmim][BF ₄]	100:0	95
19	Pd ₂ (dba) ₃	NaOBu ^f	DMSO/[bmim][BF ₄]	100:0	73
20	Pd ₂ (dba) ₃	K ₃ PO ₄	DMSO/[bmim][BF ₄]	100:0	>99 ^c
21	Pd ₂ (dba) ₃	K ₃ PO ₄	DMSO/[bmim][BF ₄]	100:0	98 ^d
22	None	K ₃ PO ₄	DMSO/[bmim][BF ₄]	-	<5
23	Pd ₂ (dba) ₃	K ₃ PO ₄	DMSO/[bmim][BF ₄]	-	<10 ^e
24	Pd ₂ (dba) ₃	K ₃ PO ₄	DMSO/[bmim][BF ₄]	97:3	96 ^f
25	Pd ₂ (dba) ₃	K ₃ PO ₄	DMSO	92:8	94
26	Pd ₂ (dba) ₃	K ₃ PO ₄	[bmim][BF ₄]	100:0	96

^a Reaction conditions: **2a** (1.0 mmol), **3a** (1.25 mmol), base (2.0 mmol), solvent (3.0 mL), catalyst 0.1 mol% (Pd:L = 1:2), ionic liquid 5.0 mol%, at 350 Watt for 20 min, ^b Determined by GC-MS with PhNO₂ as internal standard, average of two runs, ^c Catalyst 0.05 mol%, ^d Catalyst 0.01 mol%, ^e Without L, ^f Ionic liquid 1.0 mol%.

The best regioselectivity observed in the DMSO/[bmim][BF₄] solvent cocktail was in line with the arylation proceeding via the ionic liquid promoted neutral pathway. However, how the ionic liquids promote the neutral pathway remains unclear; tentatively, the oxygen atoms of L coordinate to the metal palladium center,^{11b} which enhances the rate of formation of the ionic palladium species.^{10b,17}

A variety of Pd(II) and Pd(0) complexes can serve as effective precatalysts.¹⁶ To identify the effect of different Pd source on this reaction, we investigated a series of Pd sources by taking the model reaction (Table 1, entries 9, 11-14). We observed that Pd₂(dba)₃ afforded optimum reaction rate, which is slightly higher than the other results (Table 1, entry 16).

The Pd:ligand mole ratio has a dramatic influence on Pd-catalyzed Heck-Mizoroki chemistry also,¹⁸ thus the amount of the phosphine added to the Heck-Mizoroki reaction must be carefully controlled. Amatore and Jutand have demonstrated that 2.0 equiv of phosphine ligand is required per equivalent of Pd when Pd(II) is used as a precatalyst, because 1.0 equiv of ligand is

consumed in the reduction of the Pd(II) precatalyst to the Pd(0) catalyst species.¹⁹ In all of the experiments, 1:2 mole ratio for Pd:phosphine was chosen. We confirmed that phosphine-free catalytic system almost did not work (*ca.* 10% GLC yield) (entry 24).

Of the bases studied in the model reaction with Pd₂(dba)₃/L in DMSO/[bmim][BF₄], K₂CO₃ and K₃PO₄ were more efficient, probably owed to their solubility in the reaction medium (Table 1, entries 15-20)²⁰ and we selected K₃PO₄ as the most suitable base. Next, the same experiment was repeated using 0.05 then 0.01 mol% of the catalyst loading under identical reaction conditions as above where complete consumption of the 4-bromotoluene was observed after 20 min of microwave with >99% and 98% GLC yields, respectively (Table 1, entries 21 and 22). The best loading of palladium was 0.01 mol%.

The result promoted us to investigate further the reactions of olefins with a series of aryl halides under our optimized conditions. The desired products were obtained in excellent yields both from a wide array of aryl iodides and bromides with olefin and also from aryl chlorides under microwave irradiation in 20 and 50 minutes, independently (Table 2).



Table 2. The scope of Pd₂(dba)₃/L catalyzed Heck-Mizoroki reactions ^a

Entry	X	R	Product	Yield (%) ^b
1	PhI 2b	Ph 3a	4a	98 ^c
2	4-MeOC ₆ H ₄ I 2c	Ph 3a	4b	99 ^c
3	4-MeOC ₆ H ₄ Br 2d	Ph 3a	4b	96
4	2-MeOC ₆ H ₄ Br 2e	Ph 3a	4c	94
5	4-TolBr 2a	Ph 3a	4d	98
6	PhBr 2f	Ph 3a	4a	97
7	4-AcC ₆ H ₄ Br 2g	Ph 3a	4e	95
8	2-AcC ₆ H ₄ Br 2h	Ph 3a	4f	94
9	4-NCC ₆ H ₄ Br 2i	Ph 3a	4g	95
10	4-FC ₆ H ₄ Br 2j	Ph 3a	4h	97
11	4-O ₂ NC ₆ H ₄ Br 2k	Ph 3a	4i	92
12	4-MeOC ₆ H ₄ Cl 2l	Ph 3a	4b	83
13	4-AcC ₆ H ₄ Cl 2m	Ph 3a	4e	85
14	4-FC ₆ H ₄ Cl 2n	Ph 3a	4h	88
15	PhCl 2o	Ph 3a	4a	87
16	4-TolCl 2p	Ph 3a	4d	78
17	4-MeOC ₆ H ₄ Cl 2l	CH ₂ OCH ₂ Ac 3b	4j	98

Table 2. Continued

Entry	X	R	Product	Yield (%) ^b
18	2-AcC ₆ H ₄ Br 2h	CH ₂ OCH ₂ Ac 3b	4k	95
19	PhBr 2f	CH ₂ OCH ₂ Ac 3b	4a	96
20	4-TolBr 2a	COCH ₂ O ⁿ Bu 3c	4l	97
21	4-MeOC ₆ H ₄ Br 2d	COCH ₂ O ⁿ Bu 3c	4m	98
22	4-TolBr 2a	COCH ₂ O ⁿ Bu 3c	4n	98
23	PhBr 2f	COCH ₂ O ⁿ Bu 3c	4o	98
24	4-TolBr 2a	Ph 3a	4d	96 ^d
25	4-TolCl 2p	Ph 3a	4d	10 ^d

^a Reaction conditions: Aryl halide (3.0 mmol), olefin (4.5 mmol), K₃PO₄ (6.0 mmol), catalyst 0.01 mol% [Pd₂(dba)₃:L = 1:2], [bmim][BF₄] 5.0 mol%, DMSO (9.0 mL), 350 Watt, 20 min for ArI and ArBr, 50 min for ArCl, ^b Isolated yield, average of two runs, ^c100 Watt, ^dCatalyst 0.1 mol%, oil bath, 140 °C, 3 h.

The order of reaction rate is dependent on the leaving group: Ar-I > Ar-OTf > Ar-Br >> Ar-Cl.²¹ Iodobenzene and 4-iodoanisole, for example, had been completely converted into the coupled products after 20 minutes (entries 1 and 2). Remarkably, the catalytic system was equally efficient with the aryl bromides: complete conversion had been achieved in the reactions of all aryl bromides tested in the experiments with olefin in 20 minutes (entries 3-11, 18-24). Electron neutral aryl chloride, chlorobenzene, gave the desired coupled product in 87% yield (entry 15). Aryl chlorides containing an electron donating group produced the corresponding coupled product in moderate yields (entries 12 and 16). We found aryl chlorides bearing electron-withdrawing fluoro and acetyl groups gave corresponding coupling products in slightly higher yields (entries 13 and 14). Among the aryl chlorides derivatives, 4-chlorotoluene exhibited the lowest yield (entry 16). So, with activated, and/or sterically hindered aryl chlorides, elongations of the reaction times were observed, along with the decrement of the product yields (entries 12–17). Compared to the conventional heating condition, the reaction time reduces from hours to minutes (entries 24 and 25).

Conclusions

In summary, Pd₂(dba)₃/L was an effective system for highly regioselective Heck-Mizoroki cross-coupling of various aryl iodides, bromides and chlorides with olefins in DMSO/[bmim][BF₄] under microwave irradiation. Compared to the conventional heating, it reduces the reaction time from hours to minutes with lower catalyst loading to afford the desired products in near quantitative yields. Further investigation of the mechanism of this procedure and asymmetric catalysis are currently underway in our laboratory.

Experimental Section

General. All chemicals employed in the syntheses were of analytical grade, obtained commercially, and used as received without further purification. Solvents were dried with standard methods and freshly distilled prior to use. Microwave irradiation was carried out using a NJL07-2 microwave oven (0–700 W). The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Perkin-Elmer FT-IR spectrometer. NMR spectra (^1H 400 MHz, ^{13}C 100 MHz, ^{31}P 161 MHz) were performed on a Bruker Avance III 400 MHz spectrometer. The NMR studies were carried out in high-quality 5 mm NMR tubes. Signals are quoted in parts per million as δ downfield from TMS or H_3PO_4 (85%) as an internal standard. Coupling constants (J values) are given in Hertz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet signal.

General procedure for the microwave-assisted Heck cross-coupling of styrene with aryl halides

In a two-necked round bottom flask, ligand and Pd precursor with appropriate amount and solvent (3.0 mL) were placed with a magnetic stir bar. After stirring for 5 min, a mixture of the aryl halide (1.0 mmol), styrene (1.5 mmol), and base (2.0 mmol) were added to the reaction flask. The reaction mixture was stirred under 350 W microwave irradiation. The whole course of reaction was monitored by GLC analysis with n-octane as an internal standard. The solvent was evaporated under reduced pressure after the reaction was completed. The resultant residual mixture was diluted with H_2O (5.0 mL), EtOAc (5.0 mL) and followed by extraction twice (2×5.0 mL) with EtOAc. The organic phase was dried over anhydrous MgSO_4 and the solvent was evaporated. The crude product was purified column chromatography (silica gel 100-200) with petroleum ether/EtOAc (10:1, v:v) and then characterized by NMR-spectroscopy, and were consistent with the literature data.

Typical experimental procedure

In our initial experiments, we chose the addition of styrene to 4-bromotoluene as a model reaction using $\text{Pd}(\text{OAc})_2$ as the palladium source, $\text{Pd}(\text{OAc})_2:\text{L} = 1:2$, K_2CO_3 as the base, and *N,N*-dimethylacetamide (DMA) as the solvent, TBAB was used as a co-catalyst, 120 °C and under MW (350 Watt).

GLC Analysis GLC spectra were carried out on an Agilent 6890, using an AT.SE-30 column of 50 m length, 0.32 mm diameter and 0.5 μm film thicknesses. GLC parameters for Suzuki reactions were as follows: injector temperature 280 °C; detector temperature 280 °C; initial temperature 60 °C; initial time 5 min; temperature ramp 1, 30 °C min^{-1} ; final temperature 200 °C; ramp 2, 20 °C min^{-1} ; final temperature 250 °C; run time 25 min; inject 1.0 μL ; helium as the GLC carrier gas; pressure of the system was 3.5 bar.

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