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Catalysis and Regioselectivity of the Aqueous Heck Reaction by Pd(0) Nanoparticles under Ultrasonic Irradiation

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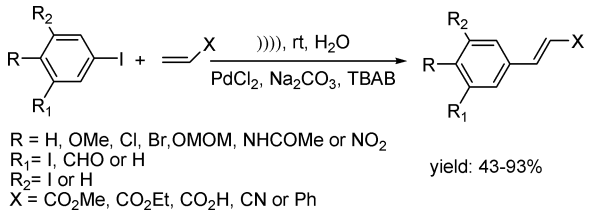

An aqueous Heck reaction carried out under ultrasonic irradiation at the ambient temperature (25 °C) has been shown in this study to afford high yields of corresponding products. It was found that as a catalyst for the reaction palladium forms nanoparticles in-situ, characterized by transmission electron microscopy (TEM) and X-ray powder diffraction (XRD) analyses, and can be recycled. Furthermore, the Heck reaction under such mild and environmentally friendly conditions offers excellent regioselectivity of *para*- over *ortho*-substitution in phenyl iodides especially with electron-donating groups.

The palladium-catalyzed Heck reaction[1] between aryl halides and alkenes is a versatile method for carbon−carbon bond formation in organic synthesis.[2]To minimize adverse impact of organic solvents on the environment, recent efforts have been directed toward using aqueous solvents for chemical reactions,[3] including the Heck reaction.[4] However, high temperatures were required in all of the latter cases.[5] Moreover, although regioselectivity is required for constructing complex molecules, to the best of our knowledge, there has been no report about the regioselectivity of aryl iodides in the Heck reaction, except for the regioselective coupling of α-position of olefin double bond.[6] In this study, we report a Heck reaction with excellent regioselectivity of *para*- over *ortho*-substitution in phenyl iodides that is catalytized in situ by palladium nanoparticles under aqueous and ultrasonic condition at ambient temperature (25 °C).

The Heck reaction of iodobenzene with methyl acrylate was initially studied in the presence of $PdCl_2$ in water. The reaction mixture of 1 mmol of iodobenzene, 2 mmol of methyl acrylate, 0.02 mmol of $PdCl_2$, Na_2CO_3 as base, and 1 mmol of tetrabutylammonium bromide (TBAB) was stirred in 3 mL of water at 25 °C for 4.5 h. (*E*)-Methyl cinnamate **1** was obtained with a yield of only 10%. Inspired by the report that ultrasonic irradiation may promote organic reactions,[7,8] we performed the same reaction under ultrasonic irradiation hoping to realize the Heck reaction in water without heating. Indeed, the reaction carried out under such conditions resulted in an enhancement of the yield from 10% to 86%. The reaction conditions were systematically optimized, and the results are presented in Table

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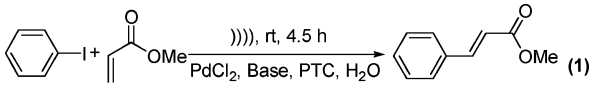
TABLE 1. Optimization of Base and PTC for Heck Reaction of Iodobenzene and Methyl Acrylate[a]



entry	base	PTC	yield(%)[b]
1	Na_2CO_3	TBAB	86
2	Na_2CO_3	—	0
3	Na_2CO_3	TEAB[c]	trace
4	Na_2CO_3	TMAI[d]	trace
5	Na_2CO_3	TEAI[e]	trace
6	NaOH	TBAB	53
7	Et_3N	TBAB	67
8	NaOAc	TBAB	40

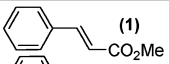
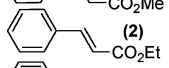
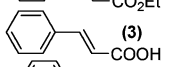
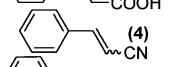
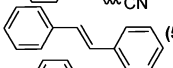
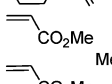
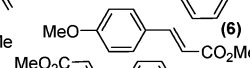
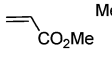
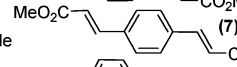
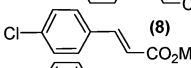
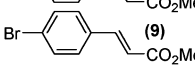
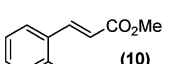
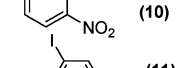
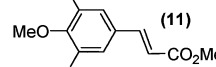
[a] Reaction conditions: iodobenzene (1 mmol), methyl acrylate (2 mmol), phase transfer catalyst (PTC) (1 mmol), base (3 mmol), and $PdCl_2$ (0.02 mmol) in 3 mL of water; the mixtures was sonicated at ambient temperature (25 °C) in running water bath for 4.5 h. [b] Isolated yield. [c] TEAB is tetraethylammonium bromide. [d] TMAI is tetramethylammonium iodide. [e] TEAI is tetraethylammonium iodide.

1. It was found that tetrabutylammonium bromide (TBAB) was the best phase transfer catalyst (PTC) among the quaternary ammonium salts tested (Table 1, entry 1) and no product was observed without PTC (Table 1, entry 2) while sodium carbonate was the best base for this reaction. Although the reaction could also proceed in organic solvents (such as DMF, CH_3CN, or EtOH), the yields are lower than that in water. It may be partly due to Na_2CO_3 having greater solubility and showing stronger basicity in water than in organic solvents.

To expand the scope of reaction substrates, different aryl iodides and olefins were employed in this Heck reaction under the same ultrasonic aqueous condition, as shown in Table 2. Heck reactions of iodobenzene with ethyl acrylate, acrylic acid, acrylonitrile, and styrene afforded good yields (entries 2−5, Table 2). All the products in these Heck reactions are *E* isomers except for cinnamonitrile, which was a mixture of *E*:*Z* isomers (4:1) (entry 4, Table 2). The iodobenzene with electron-donating substitution could also be the reaction substrate with a good reaction yield (entry 6, Table 2). The reaction of 1,4-diiodobenzene proceeded well in both two substitution positions and afforded dicoupling product **7** with modest yield (entry 7, Table 2). Chemoselectivity was observed when 1-chloro-4-iodobenzene or 1-bromo-4-iodobenzene was employed as the reaction substrate. The reactions occurred exclusively with aryl iodides, but not aryl bromide or chloride, and gave corresponding products **8** and **9** with excellent yields (entries 8 and 9, Table 2). For an ortho-substituted iodobenzene, however, could not react with alkenes smoothly under this condition. Even after 4 h sonication, no product was detected by TLC from the mixture of 1-iodo-2-methylbenzene and methyl acrylate (entry 10, Table 2), but moderate yield of the product was isolated from the coupling reaction between 1-iodo-2-nitrobenzene and methyl acrylate (entry 11, Table 2). These results indicated that this reaction was highly sensitive to both steric hindrance and electron efforts because methyl and nitro have similar size but methyl is a mild electron-donating group while nitro is a strong electron-withdrawing one.

To understand the regioselectivity of this Heck reaction, we studied several aromatic polyiodides. As expected, aryl iodides with electron-donating groups can be carried out in these coupling reactions in the *para*- but not *ortho*-substitution positions (entries 12−15, Table 2). Notably, in each of these reactions, even with an excess amount of methyl acrylate,

TABLE 2. Heck Reaction Promoted by Ultrasonic Aqueous Media[a]

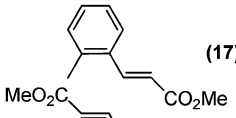
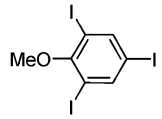
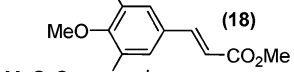
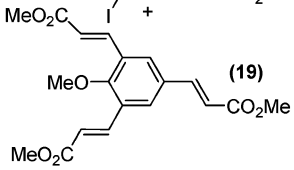
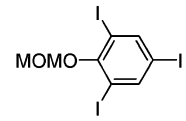
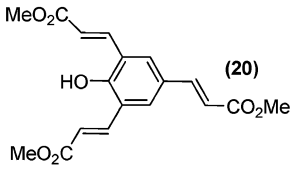
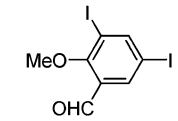
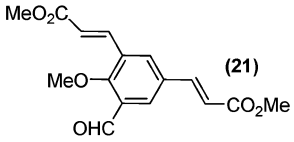
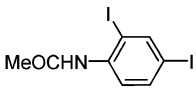
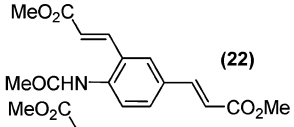
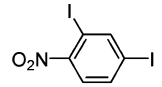
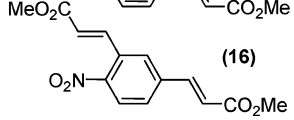
entry	ArX	alkene	product	time(h)	yield(%)[d]
1				4.5	86
2				4.5	82
3				5	83
4[b]				5	78
5				5	75
6				6	76
7[c]				12	43
8				4.5	93
9[c]				5.5	90
10			—	4	—
11[c]				4	55
12[c]				8	68
13[c]				8	76
14[c]				8	70
15[c]				5	75
16[c]				6	43
					20

[a] Reaction conditions: ArX (1 mmol), alkene (2 mmol), TBAB (1 mmol), Na_2CO_3 (3 mmol), and $PdCl_2$ (0.02 mmol) in 3 mL of water; the mixtures were sonicated at ambient temperature (25 °C) in running water bath for the corresponding time. [b] *E*:*Z* = 4:1 of the products was observed from ^1H NMR. [c] 1 mL of CH_2Cl_2 was added to dissolve the phenyl iodides. [d] Isolated yield.

i.e., as much as 6 times more than aryl iodides, and 6% $PdCl_2$, only monocoupling products of *para*-substitution, but not dicoupling products, were isolated with good yields (68−76%). As for phenyl iodides with an electron-withdrawing group (entry 16, Table 2), both mono- and dicoupling products were obtained. However, the former one is highly in excess compared to the other one. Also, because of the mild condition, this reaction is applicable to substituents, including aldehyde, methoxy, methoxy methoxy (−OMOM), and acetamide groups, which are sensitive to heat and acidic conditions (entries 12−15, Table 2).

To the best of our knowledge, this is the first example of regioselectivity of phenyl iodides in the Heck coupling reaction. These monocoupling products **8**−**15** (entries 8−9, 12−16) can be further carried out in the next coupling reactions (such as

TABLE 3. Heck Coupling Reactions of Aromatic Polyiodides with Methyl Acrylate in Water at 90 °C[a]

entry	ArX	product	time(h)	yield[e]
1		 **(17)**	5	62
2[b,c]		 **(18)** +  **(19)**	10	15 + 73
3[b,c]		 **(20)**	8	60
4[b,d]		 **(21)**	10	83
5[b,d]		 **(22)**	6	74
6[b,d]		 **(16)**	5	73

[a] Reaction conditions: ArX (1 mmol), methyl acrylate (6 mmol), TBAB (2 mmol), $NaHCO_3$ (3 mmol), and $PdCl_2$ (0.02 mmol) in 3 mL of water.[b] 1 mL of CH_2Cl_2 was added to dissolve the aryl iodides. [c] $PdCl_2$ (0.06 mmol) was used. [d] $PdCl_2$ (0.04 mmol) was used. [e] Isolated yield.

Heck, Suzuki, Stille, etc.) via a change of reaction conditions to afford various molecules. It was noted that temperature played a crucial role in controlling the regioselectivity of coupling. The similar regioselectivity could be acquired when these aromatic polyiodides reacted with methyl acrylate at 60 °C and by using $NaHCO_3$ instead of Na_2CO_3 as base. If the temperature was increased to 90 °C, the corresponding polycoupling products **18**−**22** and **16** were obtained with good yields (entries 2−6, Table 3). The −OMOM group decomposed to −OH under these reaction conditions (entry 3, Table 3) and was stable under ultrasonic irradiation (entry 13, Table 2).

To determine the catalyst for the reaction, we further investigated the reaction process. After 30 min reaction of iodobenzene with methyl acrylate, the reaction mixture was isolated and analyzed by "in situ" transmission electron microscopy (TEM) (Figure 1) and X-ray power diffraction (XRD) (Figure 2c). The TEM image showed the Pd nanoparticles were formed with a size of 6−16 nm (Figure 1).[9−11] It has been shown that colloidal palladium nanoparticles were generated via thermolysis of $[PdCl_2(C_6H_5CN)_2]$ in the presence

(9) Several reviews about nano catalysis were reported, see: (a) Roucoux, A.; Schulz, J.; Patin, H. *Chem. Rev.* **2002**, *102*, 3757. (b) Astruc, D.; Lu, F.; Aranzaes, J. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 7852. (c) Moreno-Mañas, M.; Pleixats, R. *Acc. Chem. Res.* **2003**, *36*, 638.

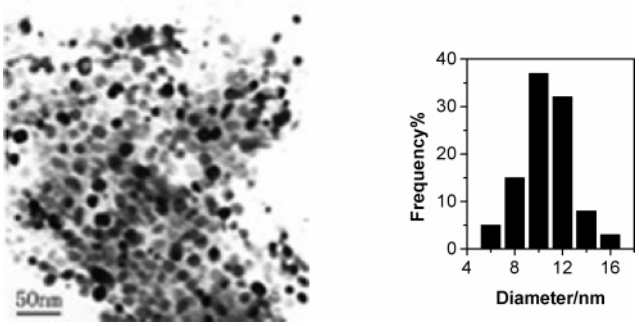


FIGURE 1. TEM image of Pd nanoparticles formed under ultrasound (left). Distribution of the size of the palladium nanoparticles (right).

of NaOAc at 130 °C or $Pd(NO_3)_2$ with an excess of tetraoctylammoniumacetate (n-$C_8H_{17})_4N^+(CH_3CO_2^-$) in THF at 60 °C, and it was proven that acetate serves as the reductant in these cases.[12] Sonochemical preparation of Pd nanoparticles from metal salt (K_2PdCl_4 or Na_2PdCl_4) in aqueous solution was also reported, and it was presumed that Pd^{2+} can be reduced to Pd^0 by radical produced by acoustic cavitation under ultrasound conditions.[13] To understand how the palladium particles were generated in our study, we first examined and found that the mixture of $PdCl_2$ (0.1 mmol), TBAB (1 mmol), and H_2O (3 mL) after ultrasonication for 30 min showed no palladium particles (Figure 2a). Palladium particles were formed in such a mixture upon addition of 2 mmol of methyl acrylate followed by sonication for 20 min. The formation of in situ palladium particles was confirmed by mixing $PdCl_2$ (0.1 mmol), methyl acrylate (2 mmol), TBAB (1 mmol), and H_2O (3 mL) followed by sonication for 30 min (Figure 2b). These results suggest that methyl acrylate, which was required for formation of the palladium particles, possibly acted as a reducing agent for $PdCl_2$ (Figure 2a,b).[4c] The XRD pattern of the in situ formed palladium particles in the Heck reaction seems consistent with that of metallic palladium (Figure 2c).[14] It was noted that ultrasonic irradiation was essential in the Pd nanoparticle formation; without it, generation of the nanoparticles was slow, and aggregation would likely occur. We postulated that insertion of Pd into a C−I bond benefits from synergistic action between the surface energy of Pd nanoparticles and the energy of ultrasonication stemming from cavitation.[15] Formation and

(10) For recent reports on nano-Pd catalyst organic reactions, see: (a) Chung M.-K.; Schlaf, M. *J. Am. Chem. Soc.* **2004**, *126*, 7386. (b) Jansat, S.; Gómez, M.; Philippot, K.; Muller, G.; Guiu, E.; Claver, C.; Castillón, S.; Chaudret, B. *J. Am. Chem. Soc.* **2004**, *126*, 1592. (c) Ooe, M.; Murata, M.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Nano Lett.* **2002**, *2*, 999. (d) Calò, V.; Nacci, A.; Monopoli, A.; Montingelli, F. *J. Org. Chem.* **2005**, *70*, 6040. (e) Schmidt, B. *Chem. Commun.* **2003**, 1654. (f) Luo, C. C.; Hiroyuki, O.; Wai, C. M.; Kim, H.; Kim, J.; Ohde, M. *J. Am. Chem. Soc.* **2002**, *124*, 4550.

(11) For recent reports on nano-Pd catalyst Heck reaction, see: (a) Cassol, C. C.; Umpierre, A. P.; Machado, G.; Wolke, S. I.; Dupont, J. *J. Am. Chem. Soc.* **2005**, *127*, 3298. (b) Zhang, Y. H.; Wang, Y. G. *J. Mol. Catal. A: Chem.* **2005**, *229*, 7. (c) Caló, V.; Nacci, A.; Monopoli, A.; Laera, S.; Cioffi, N. *J. Org. Chem.* **2003**, *68*, 2929. (d) Kim, S.-W.; Kim, M.; Lee, W. Y.; Hyeon, T. *J. Am. Chem. Soc.* **2002**, *124*, 7642. (e) Yeung, L. K.; Crooks, R. M. *Nano Lett.* **2001**, *1*, 14.

(12) (a) Reetz, M. T.; Westermann, E. *Angew. Chem., Int. Ed.* **2000**, *39*, 165. (b) Reetz, M. T.; Maase, M. *Adv. Mater.* **1999**, *11*, 773.

(13) (a) Fujimoto, T.; Terauchi, S.-Y.; Umehara, H.; Kojima, I.; Henderson, W. *Chem. Mater.* **2001**, *13*, 1057. (b) Okitsu, K.; Yue, A.; Tanabe, S.; Matsumoto, H. *Chem. Mater.* **2000**, *12*, 3006.

(14) The XRD patterns have three characteristic dihedrals: 40.119, 46.659, and 68.125, with the relative intensities of 100%, 60%, and 42%, respectively.

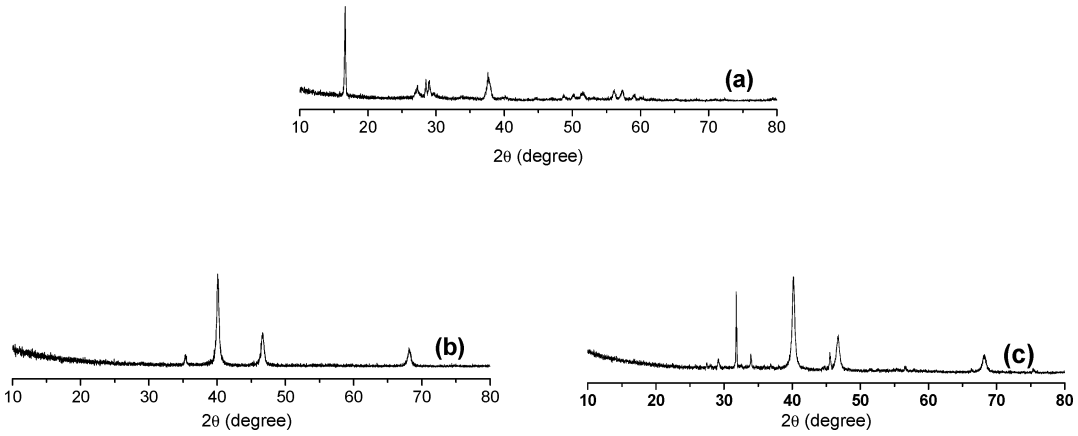


FIGURE 2. (a) XRD pattern of $PdCl_2$ (0.1 mmol), TBAB (1 mmol), and H_2O (3 mL) under ultrasonic irradiation for 30 min. (b) XRD pattern of $PdCl_2$ (0.1 mmol), TBAB (1 mmol), methyl acrylate (2 mmol), and H_2O (3 mL) under ultrasonic irradiation for 30 min. (c) XRD pattern of the reaction system (1 mmol iodobenzene, 2 mmol methyl acrylate, 0.02 mmol $PdCl_2$, 3 mmol Na_2CO_3, and 1 mmol TBAB in 3 mL of water) under ultrasonic irradiation for 30 min.

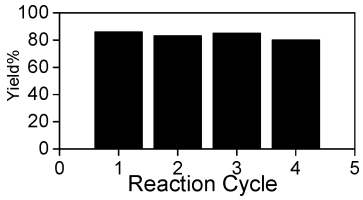


FIGURE 3. Recycling experiments for the Heck reaction.

collapse of bubbles in ultrasonic irradiation may liberate a considerable amount of energy in a short time. Moreover, the use of TBAB not only stablizes Pd nanoparticles and mediates dispersion of reactants in water, but also enhances the polarity of the C−I bond, and no product was observed without TBAB (Table 1, entry 2).[16] Therefore, both ultrasonication and TBAB favor C−I bond insertion by Pd, thereby promoting the Heck reaction.

In view of the economy of the reaction, recovery and recycling of the Pd catalyst is significant, which we investigated on a model reaction with iodobenzene and methyl acrylate. In the first cycle, the coupling product was obtained with a yield of 86% (Figure 3). After the product was separated,[17] new starting materials were added to the remnant water layer that contained the palladium particles from the first reaction. After sonication for another 4.5 h, the mixture produced the coupling product with a yield of 83% in the second cycle. Similarly, the third cycle afforded a yield of 85%, and the fourth afforded 80% yield. After the four cycles, it was found that palladium still was present in the nanosized form, suggesting that the reaction activity of the palladium can remain for many cycles.

In conclusion, we have developed an environmentally sound Heck reaction in this study. This palladium-catalyzed reaction can be carried out in aqueous solution at ambient temperature with good yields of corresponding products. This method can distinguish the C−I bonds with good regioselectivity in different chemical environments. In situ formation of palladium nanoparticles has been confirmed by TEM and XRD analyses, and the palladium nanoparticles can be reused for multiple reactions. Further study for the mechanism of the reaction and the scope of its application is in progress in our laboratory.

Experimental Section

Typical Procedure for Heck Reaction under Ultrasound. Iodobenzene (0.208 g, 1 mmol), methyl acrylate (0.172 g, 2 mmol), TBAB (0.322 g, 1 mmol), Na_2CO_3 (0.318 g, 3 mmol), and $PdCl_2$ (0.0035 g, 0.02 mmol) were placed in a 10 mL glass flask with 3 mL of water. After the mixture was sonicated at ambient temperature (25 °C) in running water bath for 4.5 h, it was extracted with ethyl acetate for three times. The combined organic extracts were dried using anhydrous Na_2SO_4 and evaporated under reduced pressure; the mixture was then purified by column chromatography over silica gel to afford product **1** with high purity. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): $\delta = 7.69$ (d, $J = 16.1$ Hz, 1H), 7.50−7.53 (m, 2H), 7.39−7.37 (m, 3H), 6.44 (d, $J = 16.1$ Hz, 1H), 3.80 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): $\delta = 167.1$, 114.7, 134.2, 130.2, 128.8, 128.0, 117.7, 51.5. IR (liquid film, cm^{-1}): $\nu = 3028$, 2951, 1719, 1638, 1450, 1434, 1276, 1203, 1172, 980, 768. HRMS calcd $C_{10}H_{10}O_2$ (M^+): 162.0681. Found: 162.0676.

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Supporting Information Available: Typical procedure for the Heck reaction and the catalyst recycling under ultrasound conditions; characterization data for products **1**−**22**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) The role of PTC in Heck reaction has been systematically studied by Jeffery, see: Jeffery, T. *Tetrahedron* **1996**, *52*, 10113.

(17) The catalysts can be recovered by extracting the mixture with petroleum ether (see Supporting Information).