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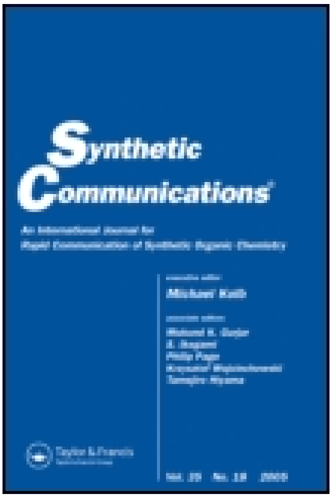

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Ultrasound-Promoted Ligand-Free Heck Reaction in Water

Guanghui An [a] , Xiaoyun Ji [a] , Jianlin Han [a] & Yi Pan [a]

[a] School of Chemistry and Chemical Engineering, Nanjing University, State Key Laboratory of Coordination , Nanjing , China

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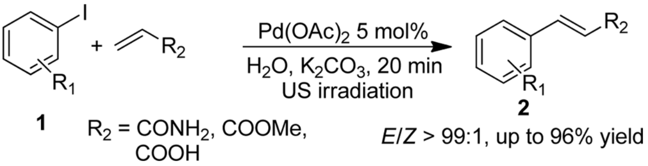
ULTRASOUND-PROMOTED LIGAND-FREE HECK REACTION IN WATER

Guanghui An, Xiaoyun Ji, Jianlin Han, and Yi Pan
School of Chemistry and Chemical Engineering, Nanjing University,
State Key Laboratory of Coordination, Nanjing, China

GRAPHICAL ABSTRACT



Abstract *An ultrasound irradiation–promoted Heck reaction catalyzed by ligand-free palladium acetate was described. The ultrasound-promoted Heck reaction was carried out under mild and environmentally friendly conditions, resulting in the corresponding products with good to excellent chemical yields (up to 96% yield) and high regioselectivities and stereoselectivities (E/Z > 99:1). Acrylamide and acrylic acid were used for the first time as substrates in the ultrasound-promoted Heck reaction. It was found that the reaction could be finished within 20 min.*

Keywords Aqueous media; Heck reaction; palladium acetate; ultrasound

INTRODUCTION

The palladium-catalyzed Heck reaction is one of the most powerful tools for carbon–carbon bond-formation processes in synthetic organic chemistry and organic methodology.[1] The Heck reaction has been thoroughly investigated in a variety of modifications,[2] and its extraordinary generality with a wide range of application for numerous commercially important products has been demonstrated.[3] However, the Heck reaction usually is performed under the protection of an inert atmosphere and needs long reaction times and high temperature.[4] Furthermore, some efficient catalysts developed for the Heck reaction require toxic solvents together with air-sensitive bulky phosphine ligands and the presence of hindered amines.[5] In recent years, the use of ionic liquids has been reported to try to improve the reaction

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Address correspondence to Jianlin Han or Yi Pan, School of Chemistry and Chemical Engineering, Nanjing University, State Key Laboratory of Coordination, Nanjing 210093, China. E-mail: molab@nju.edu.cn; yipan@nju.edu.cn

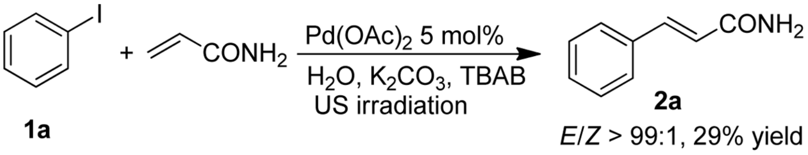
rate. However, even done in such media, the reactions still involved long reaction times (24–72 h) at temperatures ranging from 80 to 100 °C.[6]

Ultrasound has been reported to have an effect on the reaction rate of many organic reactions.[7] These reactions with the assistance of ultrasound radiation usually can be carried out under mild conditions and can be completed within a very short reaction time. Although in the past decade, some examples of Heck reactions under ultrasound radiation have been reported,[8,9] ultrasound-promoted Heck reactions have not been well documented and still remain a great challenge in the scope of substrates, reaction time, reaction temperature, and solvent. During our continuous research about the Heck reaction,[10] we found that the reaction between acrylamide and iodobenzene is completed within 20 min under ultrasound irradiation. Herein, we report a ligand-free Heck reaction in water under ultrasound irradiation. Acrylamide is studied for the first time in the Heck reaction under ultrasound irradiation, with the reaction being faster than those reported so far.[8,9,11]

RESULTS AND DISCUSSION

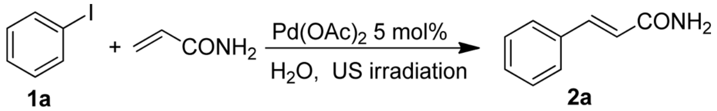
In this work, an ultrasound probe was used to improve the efficiency of the ultrasound radiation. The iodobenzene and acrylamide were chosen as substrates for initial study. The ultrasound-promoted reaction was carried out in water with K_2CO_3 as base catalyzed by $Pd(OAc)_2$ in the presence of tetrabutylammonium bromide (TBAB) at 80 °C (Scheme 1). After 30 min, the desired product, (*E*)-cinnamamide, was observed with 29% yield.

To improve the chemical yield of this ultrasound-promoted reaction, the reaction condition was systematically optimized (Table 1). First, the surfactants for the current reaction were investigated. Sodium dodecane-1-sulfonate was the most efficient one among all the surfactants examined, and the best yield was detected (86%, Table 1, entry 5). However, the previous reported efficient surfactant TBAB for Heck reaction[8f] seems not a suitable one for the current system, and only 29% yield was obtained (entry 1). Other surfactants, such as benzyltriethylammonium chloride and polyethylene glycol, did not improve the chemical yields (entries 2–4). The bases used in this reaction also have a great effect on the formation of products. Potassium carbonate was an efficient base for this reaction and gave the best chemical yield (entry 5). When strong inorganic bases such as sodium hydroxide and potassium hydroxide were used, almost no corresponding product was obtained (entries 6 and 7). The weak bases KOAc and $NaHCO_3$ also gave very poor yields of products (entries 8 and 10). The temperature plays an important role on the chemical yields. When the reaction was carried out at 60 °C, only 47% yield was observed (entries 11 and 12). A moderate yield was found when the temperature



Scheme 1. Heck reaction between iodobenzene and acrylamide under ultrasound.

Table 1. Optimization of reaction conditions[a]



Entry	Surfactant	Base	Temp. (°C)	Time (min)	*E*/*Z*[b]	Yield (%)[c]
1	Tetrabutylammonium bromide (TBAB)	K_2CO_3	80	20	>99:1	29
2	Benzyltriethylammonium chloride	K_2CO_3	80	20	>99:1	21
3	PEG-200	K_2CO_3	80	20	>99:1	75
4	PEG-1000	K_2CO_3	80	20	>99:1	59
5	Sodium dodecane-1-sulfonate	K_2CO_3	80	20	>99:1	86
6	Sodium dodecane-1-sulfonate	KOH	80	20	>99:1	<10
7	Sodium dodecane-1-sulfonate	NaOH	80	20	>99:1	14
8	Sodium dodecane-1-sulfonate	KOAc	80	20	>99:1	16
9	Sodium dodecane-1-sulfonate	Na_2CO_3	80	20	>99:1	27
10	Sodium dodecane-1-sulfonate	$NaHCO_3$	80	20	>99:1	45
11	Sodium dodecane-1-sulfonate	K_2CO_3	40	20	>99:1	35
12	Sodium dodecane-1-sulfonate	K_2CO_3	60	20	>99:1	47
13	Sodium dodecane-1-sulfonate	K_2CO_3	70	20	>99:1	71
14	Sodium dodecane-1-sulfonate	K_2CO_3	90	20	>99:1	96
15	Sodium dodecane-1-sulfonate	K_2CO_3	100	20	>99:1	82
16	Sodium dodecane-1-sulfonate	K_2CO_3	90	5	>99:1	20
17	Sodium dodecane-1-sulfonate	K_2CO_3	90	10	>99:1	85
18	Sodium dodecane-1-sulfonate	K_2CO_3	90	15	>99:1	91
19	Sodium dodecane-1-sulfonate	K_2CO_3	90	25	>99:1	92
20	Sodium dodecane-1-sulfonate	K_2CO_3	90	30	>99:1	86

[a] Iodobenzene (5 mmol), acrylamide (6 mmol), base (7.5 mmol), $Pd(OAc)_2$ (0.05 mmol), surfactant (0.5 mmol), and water (20 mL).

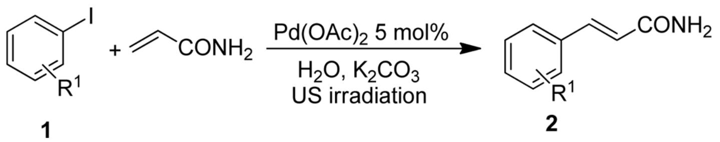
[b] Determined by ^1H NMR. Only *E*-isomer was detected.

[c] Isolated yield.

was increased to 70 °C (entry 13). The greatest yield was observed when the reaction was performed at 90 °C (96% yield, entry 14). However, the chemical yield decreased to 82% when the temperature was increased to 100 °C (entry 15). The ultrasound-promoted Heck reaction can be completed within 20 min. Although extending the reaction time gave no improvement on chemical yields (entries 19 and 20), the yield decreased to 85% when the reaction was stopped at 10 min (entry 17), and even lower yield was obtained when the reaction was stopped at 5 min (entry 16).

After getting the optimized reaction conditions, a series of aryl iodides were used as substrates and the corresponding products were observed in all cases (Table 2). As shown in Table 2, this reaction has a broad substrate range, including iodobenzene (Table 2, entry 1), and aryl iodides with electron-donating groups (entries 2 and 3) or electron-withdrawing groups on aromatic rings (entries 4 and 5). All reactions of the aryl iodides could give corresponding cinnamamide products with modest to excellent chemical yields (42–96%). These substrates also showed excellent stereoselectivities, and only *E*-isomers were observed for all the cases. However, in the case of the substrate containing bromine as a substituent on the aromatic ring (entry 6), only a trace amount of cinnamamide product was observed.

Table 2. Heck reaction between aryl iodides and acrylamide under ultrasound[a]



Entry	Aryl iodide	R^1	Products	E/Z^b	Yield (%)[c]
1	**1a**	H	**2a**	>99:1	96
2	**1b**	*o*-CH_3	**2b**	>99:1	42
3	**1c**	*m*-CH_3	**2c**	>99:1	62
4	**1d**	*p*-Cl	**2d**	>99:1	71
5	**1e**	*p*-$COCH_3$	**2e**	>99:1	66
6	**1f**	*p*-Br	**2f**	—	<10

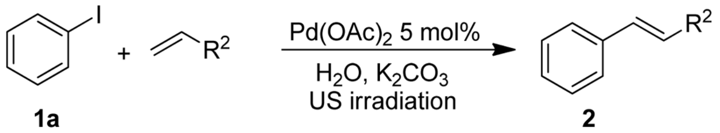
[a] Aryl iodide (5 mmol), acrylamide (6 mmol), K_2CO_3 (7.5 mmol), $Pd(OAc)_2$ (0.05 mmol), sodium dodecane-1-sulfonate (0.5 mmol), and water (20 mL) at 90 °C for 20 min.

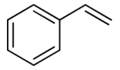
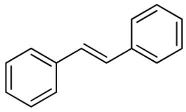
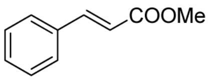
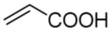
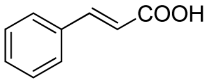
[b] Determined by ^1H NMR. Only *E*-isomer was detected.

[c] Isolated yields.

Besides acrylamide, three other active olefins (styrene, methyl acrylate, and acrylic acid) were also found to be suitable for the reaction (Table 3). The corresponding adducts were obtained in good yields of 54–82% and excellent stereoselectivities of > 99:1. A good yield was especially obtained for acrylic acid (82%,

Table 3. Heck reaction between iodobenzene and olefins under ultrasound[a]



Entry	Olefin	Products	E/Z[b]	Yield (%)[c]
1		 **2g**	>99:1	54
2		 **2h**	>99:1	76
3		 **2i**	>99:1	82

[a] Iodobenzene (5 mmol), olefin (6 mmol), K_2CO_3 (7.5 mmol), $Pd(OAc)_2$ (0.05 mmol), sodium dodecane-1-sulfonate (0.5 mmol), and water (20 mL), at 90 °C for 20 min.

[b] Determined by ^1H NMR. Only *E*-isomer was found.

[c] Isolated yields.

Table 3, entry 3). To our knowledge, this is also the first report about the acrylic acid used as olefin substrate in the ultrasound-promoted Heck reaction.

In conclusion, the Heck reaction of aryl iodides and active olefins in water catalyzed by $Pd(OAc)_2$ is considerably accelerated by ultrasound radiation. Acrylamide and acrylic acid were used for the first time in the ultrasound-promoted Heck reaction and gave good yields and excellent stereoselectivities. The ultrasound promoted Heck reaction could be completed within 20 min, which is faster than those reported until now.

EXPERIMENTAL

Reagents and solvents were purchased as reagent grade and used without further purification unless otherwise stated. All reactions were performed in standard oven-dried glassware under a nitrogen atmosphere unless otherwise stated. Melting points were determined using a Gallenkamp (Griffin) melting-point apparatus. Temperatures are expressed in degrees Celsius (°C) and are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz on a Bruker AM 300-MHz spectrometer. Chemical shifts (δ) are reported in parts per million relative to tetramethylsilane(TMS) ($\delta = 0$ ppm) as internal standards. Coupling constants (*J*) are reported in hertz (Hz). Multiplicities are reported as singlet (s), broad singlet (bs), doublet of doublets (dd) or multiplet (m).

General Procedures for Ultrasound-Assisted Heck Reaction

A three-necked flask was charge with an ultrasound probe, and then 5 mmol of iodobenzene, 6 mmol of acrylamide, 0.05 mmol of $Pd(OAc)_2$, 7.5 mmol of K_2CO_3 as base, 0.5 mmol of sodium dodecane-1-sulfonate, and 20 mL water were added in the flask. The reaction mixture was stirring strongly to make a good dispersion. After stirring, the mixture was directly placed in oil bath at 90 °C, and ultrasound radiation was started at the same time. After 20 min, the reaction mixture was filtered, evaporated, and directly purified by preparative thin-layer chromatographic (TLC) plate.

Characterized Data for Products 2a–2i

Compounds **2a–2i** are all known compounds.[11,12]

(*E*)-Cinnamamide (2a). White needle crystal. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.67 (d, $J = 15.6$ Hz, 1H), 7.52–7.55 (m, 2H), 7.38–7.40 (m, 3H), 6.49 (d, $J = 15.6$ Hz, 1H), 5.86 (br, 2H).

(*E*)-3-o-Tolylacrylamide (2b). White needle crystal. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.50–7.52 (d, $J = 15.4$ Hz, 1H), 7.08–7.14 (m, 2H), 7.01 (m, 1H), 6.91 (d, $J = 15.6$ Hz, 1H), 5.57 (br, 2 H), 2.34 (s, 3H).

(*E*)-3-m-Tolylacrylamide (2c). White needle crystal. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.56–7.59 (d, $J = 15.4$ Hz, 1H), 7.13–7.18 (m, 2H), 7.01 (m, 1H), 6.86 (d, $J = 15.6$ Hz, 1H), 5.57 (br, 2H), 2.34 (s, 3H).

(*E*)-3-(4-Chlorophenyl)acrylamide (2d). White needle crystal. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.63 (d, $J = 15.8$ Hz, 1H), 7.45 (d, $J = 8.4$ Hz, 2H), 7.36 (d, $J = 8.4$ Hz, 2H), 6.44 (d, $J = 15.8$ Hz, 1H), 5.54 (br, 2H).

(*E*)-3-(4-Acetylphenyl)acrylamide (2e). White needle crystal. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.87–7.89 (m, 2H), 7.59–7.64 (d, $J = 15.7$ Hz, 1 H), 7.50–7.53 (m, 2H), 6.44–6.49 (d, $J = 15.7$ Hz, 1H), 2.53 (s, 3H), 5.57 (br, 2H).

(*E*)-1,2-Diphenylethene (2g). White needle crystal. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.51 (d, $J = 4.75$ Hz, 4H), 7.35 (t, $J = 5.0$ Hz, 4H), 7.24 (m, 2H), 7.10 (s, 2H).

(*E*)-Methyl cinnamate (2h). White needle crystal. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.59 (d, $J = 15.7$ Hz, 1H), 7.29–7.64 (m, 5H), 6.45 (d, $J = 15.7$ Hz, 1H), 3.81 (s, 3H).

(*E*)-Cinnamic acid (2i). White needle crystal. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.82 (d, $J = 15.5$ Hz, 1H), 7.57–7.60 (m, 2H), 7.42–7.44 (m, 3H), 6.44 (d, $J = 15.5$ Hz, 1H).

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