Palladium-Catalyzed Copper-Free Sonogashira Coupling Reaction in Water and Acetone

Shengyin Shi, Yuhong Zhang*

Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. of China Fax +86(571)87953244; E-mail: yhzhang@zjuem.zju.edu.cn *Received 11 April 2007*

Abstract: An efficient palladium-catalyzed copper-free Sonogashira reaction in water and acetone has been developed under mild conditions. The results showed that the aryl iodides could carry out the cross-coupling reaction with a variety of terminal alkynes in high yields in water–acetone in the absence of amine, copper(I) salts, or phosphine ligands at 60 °C for one hour, and good yields were obtained for aryl bromides at 60 °C for 12–24 hours in the presence of triphenylphosphine and piperidine. The method could be used to synthesize polyethynyl aromatic compounds in a one-pot reaction.

Key words: copper-free, palladium-catalyzed, Sonogashira coupling, aqueous

The Sonogashira reaction via the coupling of terminal alkynes with aryl or alkenyl halides has provided a powerful synthetic tool in organic chemistry and constitutes the key step in the preparation of many natural products and functionalized materials.^{1,2} Generally, the Sonogashira reaction is performed in the presence of palladium complex and copper salts using a variety of ligands in organic solvents.^{3,4} However, copper salts can induce the homocoupling of the terminal alkynes when the reaction is exposed to air or oxidants,⁵ and thus lead to low yields of desired products and separation problems. Recently, copper-free Sonogashira reaction has been developed and good results were achieved,^{6–11} which include the use of other metal co-catalysts,⁸ special reaction techniques,^{9,10} and special ligands.¹¹

The development of transition-metal-catalyzed reactions in aqueous solvent system has aroused much interest due to the economical and environmental reasons.¹² The palladium–copper-catalyzed Sonogashira reaction in aqueous media has been applied in the synthesis of biomolecules using aqueous soluble phosphine ligands.¹³ Very recently, Yang et al. reported an elegant copper-free Sonogashira reaction in water, but only examples of aryl iodides were given and the reaction time was relatively long (around 24 h).^{13h} In accordance with our research program on the catalytic reactions in aqueous phase, we have studied the effects of water on the palladium-catalyzed coupling reactions.¹⁴ In this paper, we report the results of Sonogashira coupling reactions in water and acetone without copper salts.

SYNLETT 2007, No. 12, pp 1843–1850 Advanced online publication: 27.06.2007 DOI: 10.1055/s-2007-984533; Art ID: W07307ST © Georg Thieme Verlag Stuttgart · New York Initially, we chose the coupling of 1-iodo-4-methoxybenzene (1 mmol) and 1-ethynylbenzene (1.5 mmol) as the model reaction to study the Sonogashira reaction in water in the absence of copper and phosphine ligands. The reaction was carried out under different conditions for one hour using 1 mol% $Pd(OAc)_2$ as the catalyst and the results were summarized in Table 1. It was found that the reaction was sluggish in pure acetone (Table 1, entry 1). However, the reaction rate was significantly promoted by the addition of water and an optimum yield was achieved when the amount of water to acetone was 3 g to 3 g (Table 1, entries 2-4). Phase-transfer agents and ionic liquids like PEG 2000, [bmim]BF₄, and [bmim]PF₆ gave poor yields when used in a mixture with water (Table 1, entries 5–7). Among the bases tested, Na₂CO₃, K₂CO₃, K₃PO₄, Et₃N, and piperidine gave poor yields (Table 1, entries 9–13), while high yields were obtained with strong bases such as NaOH and KOH (Table 1, entries 3 and 8). Raising or lowering the reaction temperature did not improve the yield (Table 1, entries 14 and 15).

We next explored the scope and limitation of this aqueous catalytic system for different substrates.¹⁵ A variety of the aryl iodides were subjected to the conditions and the results were summarized in Table 2. The yields were generally high after one hour for both electron-rich and electron-deficient aryl iodides and all of the products were easily separated by the extraction with diethyl ether (Table 2, entries 1–11). In the reaction of 1-bromo-4iodobenzene with phenylacetylene, 1,4-biphenyl-ethynylbenzene was isolated as a byproduct, and 1-bromo-4phenylethynyl benzene was obtained in a moderate yield (Table 2, entry 7), but excellent yield and selectivity was afforded when using 1-chloro-4-iodobenzene as the substrate (Table 2, entry 8). The hydrolysis of 4-iodobenzonitrile lowered the desired coupling yield (Table 2, entry 10) and no coupling product was obtained with ethyl 4iodobenzoate. Excellent yield was obtained for 1-iodonaphthalene (Table 2, entry 6). It is worth mentioning that the catalytic system could tolerate a broad range of functional groups, such as OMe, OH, NH₂, and COMe, NO₂. The coupling of various terminal alkynes delivered the products with high yields (Table 2, entries 12-20).

In the case of aryl bromides, the catalytic system presented low activity and only a 38% yield was obtained for the activated 1-bromo 4-nitrobenzene (Table 2, entry 21). Trace of the coupling product was observed with bromobenzene. In order to optimize the performance for aryl bromides in water–acetone, we examined the Sonogashira reaction of 1-(4-bromophenyl)ethanone and phenylacetylene in the presence of 10 mol% PPh₃ under various reaction conditions. It was found that a combination of 5 mol% PdCl₂ and 2 equivalents piperidine gave the best isolated yield of 84% at 60 °C for 12 hours (Table 3, entry 7). This optimized reaction conditions were applicable to a range of aryl bromides.¹⁶ As presented in Table 3, high yields were afforded for the electron-deficient aryl bromides (Table 3, entries 1–8), but longer reaction time was required for the electron-rich aryl bromides (Table 3, entries 10, 11). 1-Bromo-4-chlorobenzene reacted with phenylacetylene gave 1-chloro-4-(2-phenylethynyl)benzene as the only product, thus showing a good selectivity (Table 3, entry 8). The coupling reaction of 1-bromonaphthalene and bromoheteroaryl delivered moderate to good yields after the reaction time was prolonged to 24 hours (Table 3, entries 12–16). The hydrolysis of groups such as CN and CO_2Et was suppressed markedly in this catalytic system and good coupling yields were obtained (Table 3, entries 4–6, 19, 20). Unfortunately, the catalytic system was inactive for aryl chlorides (Table 3, entries 21 and 22).

 Table 1
 Effect of Solvent, Base, and Temperature on the Sonogashira Reaction^a

		1% Pd(OAc) ₂			
́ _/	b H ₂ (ase, 1 h / / / D-acetone			
Entry	Solvent (g:g)	Base	Temp (°C)	Conv. (%)	Yield (%) ^b
1	acetone-H ₂ O (6:0)	NaOH	60	10	10
2	acetone-H ₂ O (4:2)	NaOH	60	42	38
3	acetone-H ₂ O (3:3)	NaOH	60	100	87
4	acetone-H ₂ O (2:4)	NaOH	60	63	53
5	H ₂ O–PEG2000 (3:3)	NaOH	60	50	50
6	H ₂ O-[bmim]BF ₄ (3:3)	NaOH	60	0	0
7	$H_2O-[bmim]PF_6(3:3)$	NaOH	60	3	3
8	acetone– $H_2O(3:3)$	КОН	60	100	88
9	acetone-H ₂ O (3:3)	Na ₂ CO ₃	60	14	14
10	acetone-H ₂ O (3:3)	K ₂ CO ₃	60	32	32
11	acetone– $H_2O(3:3)$	K_3PO_4	60	83	74
12	acetone– $H_2O(3:3)$	Et ₃ N	60	27	27
13	acetone-H ₂ O (3:3)	piperidine	60	58	38
14	acetone– $H_2O(3:3)$	NaOH	50	94	83
15	acetone– $H_2O(3:3)$	NaOH	80	71	53

^a Reaction conditions: 1-iodo-4-methoxybenzene (1 mmol), phenylacetylene (1.5 mmol), base (2 mmol).

^b GC yield based on the amount of 1-iodo-4-methoxybenzene used.

Table 2	Sonogashira	Reaction of	Aryl Iodides	with Te	erminal Alkynes ^a
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Table 2	Sonogashira	Reaction	of Aryl Iodid	es with	Terminal	Alkynes ^a	(continued)
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	D ² —	1 mol% Pd(OAc) ₂	p2	
RI +	R	NaOH, 60 °C, 1 h H ₂ O–acetone	K	
Entry	\mathbb{R}^1	Alkyne	Product	Yield (%) ^b
3	4-NH ₂	а		88
4	4-Me	а		98
5	Н	а		90
6	1-Naph	а		99
7	4-Br	а	Br-	68
8	4-C1	а		91
9	4-COMe	а	$\sim \sim - \sim -$	90
10	4-CN	а		66
11	4-NO ₂	а	0 ₂ N-	93
12	4-OMe	 b	<i>⊳</i> - <u>⟨</u> _}-≡- <u></u>	92
13	4-OMe	\rightarrow =	,o-√>-=- ⟨-	85
14	4-OMe			50
15	Н	b		84
16	Н	c		83
17	Н	d		75
18	4-NO ₂	b	0 ₂ N-	85
19	4-NO ₂	c	0 ₂ N-	99
20	4-NO ₂	d		94

 Table 2
 Sonogashira Reaction of Aryl Iodides with Terminal Alkynes^a (continued)



^a Reaction conditions: aryl halide (1 mmol), terminal alkyne (1.2 mmol), 1 mol% $Pd(OAc)_2$, NaOH (2 mmol), H_2O -acetone = 3:3 g, 60 °C (bath temperature), 1 h.

^b Isolated yields.

° 6 h.

 Table 3
 The Coupling of Aryl Bromides with Terminal Alkynes^a

R ¹ ————————————————————————————————————	r + R^2 $\xrightarrow{PdCl_2, Pl}$ H_2O-ac	Ph ₃ , piperidine	- <u>-</u> R ²	
Entry	Bromide	Alkyne	Time (h)	Yield (%) ^b
1	O ₂ N-Br		12	85
2	D ₂ N Br	a	12	94
3	Br NO ₂	а	12	86
4	EtOOC-Br	a	12	95
5	NCBr	а	12	83
6	Br	а	12	90
7	O Br	а	12	84
8	ClBr	а	24	80
9	Br	а	24	52
10	—————Br	а	24	61°
11	O-Br	а	24	67°

R ¹ -	$-Br + R^2 - H_2O - acetor} - H_2O - acetor}$	piperidine ne, 60 °C	$-R^2$	
Entry	Bromide	Alkyne	Time (h)	Yield (%) ^b
12	Br	а	24	58°
13	Br Br	a	24	77
14	N=Br	a	12	66
15	Br	а	12	85
16	S Br	а	12	53
17	O ₂ N-Br		12	70
18	O ₂ N-Br		12	72
19	EtOOC-	a	1	91
20		а	1	87
21	O ₂ N-CI	а	48	42
22	СІ	а	48	Trace

Table 3	The Coupling of Aryl Bromides with Terminal Alkynes ^a ((continued)
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^a Reaction conditions: aryl halide (1 mmol), terminal alkyne (1.2 mmol), 5 mol% PdCl₂, 10 mol% PPh₃, piperidine (2 mmol), H₂Oacetone = 3:3 g, 60 °C (bath temperature), N_2 . ^b Isolated yield.

^c Terminal alkyne (1.5 mmol).

Table 4	Coupling of E	Dihaloaryls and	Polyhaloaryls with	Terminal Alkynes ^a
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Entry	Halide	Alkyne	Time (h)	Product	Yield (%) ^b
3	Br	a	24		64
4	BrBr	а	24		51
5	Br	a	24		47
6	Br Br	a	48		58°
7	Br Br	a	48		46 ^d
8	Br N Br	a	48		78
9	Br	e	48		68

 Table 4
 Coupling of Dihaloaryls and Polyhaloaryls with Terminal Alkynes^a (continued)

^a Reaction conditions: dihalide (1 mmol), terminal alkyne (2.4 mmol), 10 mol% $PdCl_2$, 20 mol% PPh_3 , piperidine (4 mmol), H_2O -acetone = 3:3 g, 60 °C (bath temperature), N_2 .

^b Isolated yield.

^c Reaction conditions: trihalide (1 mmol), terminal alkyne (3.6 mmol), 15 mol% PdCl₂, 30 mol% PPh₃, piperidine (6 mmol),

 H_2O -acetone = 3:3 g, 60 °C (bath temperature), N_2 .

^d Reaction conditions: tetrahalide (1 mmol), terminal alkyne (4.8 mmol), 20 mol% PdCl₂, 40 mol% PPh₃, piperidine (8 mmol), H₂O-acetone = 3:3 g, 60 °C (bath temperature), N₂.

The PdCl₂–PPh₃–H₂O–acetone catalytic system was also utilized to synthesize the polyethynyl aromatic compounds (Table 4), which have currently attracted much attention because of their potential applications in various optoelectronic devices.¹⁷ It can be seen that the use of 10 mol% PdCl₂ and 20 mol% PPh₃ at 60 °C delivered the biethynylaryls as the main products (Table 4, entries 1-5).¹⁶ More PdCl₂ and PPh₃ were required for tribromo- and tetrabromobenzene (Table 4, entries 6 and 7). In the reaction of 2,6-dibromopyridine, 2,6-biethynyl pyridine was afforded in 78% yield (Table 4, entry 8). Ethynylation of bromoiodobenzene with 2-ethynyl pyridine gave the desired product in 68% yield (Table 4, entry 9).

In summary, we have developed a copper-free Sonogashira reaction in aqueous media under mild reaction conditions. The catalytic system tolerates a range of groups, including the unprotected hydroxy and amino groups. The high efficiency and easy separation of the products make the method attractive and viable in aqueous media.

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- (15) General Procedure for the Sonogashira Reaction of Aryl Iodides

A mixture of NaOH (0.08 g, 2 mmol), Pd(OAc)₂ (2 mg, 1 mol%), distilled H₂O (3 g), and acetone (3 g, 3.8 mL) was stirred for 5 min. Then, aryl iodides (1 mmol) and terminal alkynes (1.2 mmol) were introduced and the mixture of the reaction was heated to 60 °C for 1 h. Afterward, the reaction solution was cooled to r.t. and extracted four times with Et₂O (4 × 10 mL). The combined organic phase was analyzed by GC and GC-MS. Further purification of the product was achieved by flash chromatography on a silica gel column. 1-(2-Phenylethynyl)naphthalene (Table 2, entry 6): ¹H NMR (500 MHz, CDCl₃, TMS): $\delta = 8.43-8.45$ (d, 1 H, J = 8.35 Hz), 7.72–7.80 (m, 3 H), 7.61–7.63 (m, 2 H), 7.55 (m, 1 H), 7.46–7.48 (m, 1 H), 7.33–7.38 (m, 1 H), 7.30–7.32 (m, 3 H). MS (EI): m/z (%) = 229 (20) [M⁺ + 1], 228 (100) [M⁺], 226 (43).

(16) General Procedure for the Sonogashira Reaction of Aryl Bromides and Polyhaloaryls

A mixture of piperidine (0.17 g, 2 mmol; for dihalides, 4 mmol; for trihalides, 6 mmol; for tetrahalides, 8 mmol), PdCl₂ (11 mg, 5 mol%; for dihalides, PdCl₂ = 10 mol%; for trihalides, PdCl₂ = 15 mol%; for tetrahalides, PdCl₂ = 20 mol%), PPh₃ (26 mg, 10 mol%; for dihalides, PPh₃ = 20 mol%; for trihalides, PPh₃ = 30 mol%; for tetrahalides, PPh₃ = 40 mol%), distilled H₂O (3 g), and acetone (3 g, 3.8 mL) was stirred for 5 min under nitrogen. Then, aryl bromides or polyhaloaryls (1 mmol) and terminal alkynes (1.2 mmol; for dihalides, alkynes = 2.4 mmol; for trihalides, alkynes = 3.6 mmol; for tetrahalides, alkynes = 4.8 mmol) were introduced and the mixture of the reaction was heated to 60 °C for the indicated time under nitrogen. Afterwards,

the reaction solution was cooled to r.t. and extracted with $Et_2O~(4\times10~mL)$. The combined organic phase was analyzed by GC and GC–MS. Further purification of the product was achieved by flash chromatography on a silica gel column.

1,4-Bis(2-phenylethynyl)benzene (Table 4, entry 1): ¹H NMR (500 MHz, CDCl₃, TMS): δ = 7.52–7.54 (m, 4 H), 7.50 (s, 4 H), 7.34–7.36 (m, 6 H). MS (EI): *m/z* (%) = 279 (25) [M⁺ + 1], 278 (100) [M⁺], 139 (10).

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