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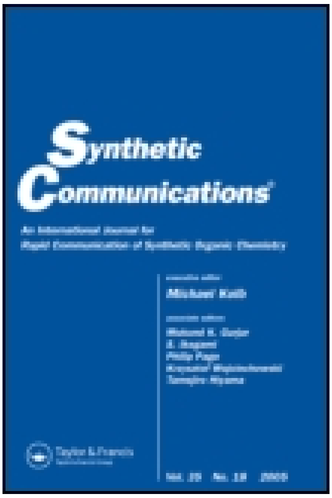

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Nickel-Catalyzed Alkynylation of Aryl Iodides (Sonogashira Reaction) in Water

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NICKEL-CATALYZED ALKYNYLATION OF ARYL IODIDES (SONOGASHIRA REACTION) IN WATER

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The Sonogashira coupling of terminal acetylenes with aryl iodides, catalyzed by Ni-Cu, in the presence of sodium lauryl sulfate as the surfactant and cesium carbonate as the base, in water, leads to the formation of aryl alkyne products.

Keywords: Alkynylation; aryl iodide; nickel catalyst; Sonogashira reaction

INTRODUCTION

The palladium-catalyzed coupling reaction of aryl and vinyl halides with terminal alkynes (Sonogashira reaction) is one of the most versatile tools in modern synthetic chemistry and has great potential for industrial applications.[1–4] The original Sonogashira reaction was generally performed in the presence of large amounts of palladium and copper(I) iodide as cocatalyst in organic solvents, which were economically and environmentally malignant.

Compared with the most frequently used, expensive palladium catalysts [e.g., $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$], the nickel methods have an economic advantage and hence remain attractive in large- or industrial-scale preparations.

In recent years, a variety of modifications have been developed for this reaction, including phase-transfer,[5] aqueous,[6] solventless,[7] and copper-free[8] versions and the use of a variety of promoters[9] and solvents.[10] Particularly interesting are the reactions catalyzed only by Cu complexes without palladium.[11] However, in most of the catalytic processes, organic solvents are usually employed as the reaction media, often creating a great deal of safety, health, and environmental issues as a result of their flammability, toxicity, and volatility. From economic and environmental standpoints, it is desirable to avoid any use of hazardous and expensive organic solvents. The use of water or aqueous solution represents one of the most economically and environmentally viable alternatives to organic solvents for metal-catalyzed reactions.[12]

Several examples of palladium-catalyzed Sonogashira reactions in aqueous media have been reported.[13] Herein, we report the Sonogashira reaction of aryl iodides with terminal alkynes catalyzed by $Ni(PPh_3)_2Cl_2$ in the presence of CuI, sodium lauryl sulfate, and cesium carbonate in water.

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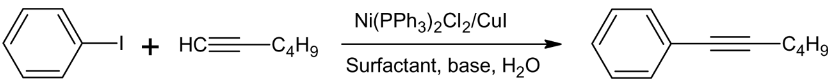
RESULTS AND DISCUSSION

As a starting point for the development of the methodology and optimization of the reaction conditions, we chose to study the coupling of iodobenzene with 1-hexyne as the model reaction, and the effects of the base, surfactant, and catalyst on the reaction were examined. First, several bases were screened for the reaction in the presence of a catalytic amount of $Ni(PPh_3)_2Cl_2$. As shown in Table 1, the reaction is significantly influenced by the base employed. The reaction works very well when inorganic bases such as K_2CO_3 and Cs_2CO_3 are used (entries 2 and 3 in Table 1), with the best result obtained in the case of cesium carbonate as the base (entry 3 in Table 1).

The influences of the amounts of surfactant and catalyst were investigated using the reaction of iodobenzene with 1-hexyne. The results are shown in Table 2. Increasing the amount of the nickel catalyst could shorten the reaction time but does not increase the yield (entry 1). Low nickel concentration often prolonged the reaction time and decreased the yield (entry 2). The use of surfactant is also critical for the success of the reaction: without a surfactant/phase-transfer reagent, the yield dropped from 85% to 20% (compare entries 3 and 7). We also found that despite an increase in the amount of the surfactant, the reaction yield did not increase (entry 6). Low surfactant concentration often decreased the yield (entry 5). No reaction was observed when Ni(II) alone was used as the catalyst (entry 4).

To examine the scope for this coupling reaction, a variety of terminal alkynes were coupled with various aryl iodides in water in the presence of catalytic amounts of $Ni(PPh_3)_2Cl_2$, CuI, and sodium lauryl sulfate at 60°C. The experimental results are summarized in Table 3. As shown in this table, the Sonogashira coupling reactions of aryl iodides with a variety of terminal alkynes proceeded smoothly under mild conditions, giving the corresponding coupling products in moderate to high yields.

Table 1. Effect of base on the Sonogashira reaction of iodobenzene with 1-hexyne in water[a]



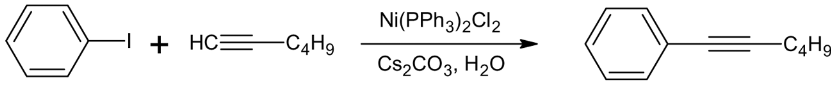
3a

Entry	Base	Yield[b] (%)
1	KOH	50
2	K_2CO_3	75
3	Cs_2CO_3	85
4	Et_3N	47
5	DIEA	60
6	Pyrrolidine	35
7	Piperidine	38

[a] Reaction conditions: iodobenzene (1.0 mmol), 1-hexyne (1.5 mmol), $Ni(PPh_3)_2Cl_2$ (0.01 mmol), CuI (0.02 mmol), sodium lauryl sulfate (0.07 mmol), base (2.0 mmol), and degassed water (5 mL) at 60°C for 4 h under Ar.

[b] GC yields.

Table 2. Effects of catalyst and surfactant on the Sonogashira reaction of iodobenzene with 1-hexyne in water[a]



3a

Entry	$Ni(PPh_3)_2Cl_2$ (mol %)	CuI (mol %)	Sodium lauryl sulfate (mol %)	Yield[b] (%)
1	2	4	7	82[c]
2	0.5	1	7	72[d]
3	1	2	7	85
4	1	—	7	NR
5	1	2	3	45
6	1	2	10	57
7	1	2	—	20

[a] Reaction conditions: iodobenzene (1.0 mmol), 1-hexyne (1.50 mmol), Cs_2CO_3 (2.0 mmol), and degassed water (5 mL) at 60°C for 4 h under Ar.

[b] GC yields.

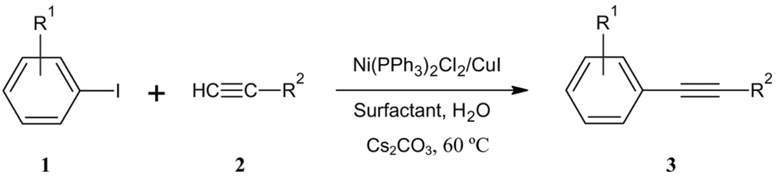
[c] Reaction time: 2 h.

[d] Reaction time: 7 h.

The optimized catalyst system was quite general and tolerant of a range of functional groups.

The aryl iodides with electron-withdrawing groups reacted with **2** to give the desired products in high yields under the reaction conditions in a short reaction

Table 3. Sonogashira reactions of terminal alkynes with aryl iodides[a]



1 **2** **3**

Entry	R^1	R^2	Time (h)	Product	Yield[b] (%)
1	H	n-C_4H_9	4	**3a**	85
2	4-NO_2	n-C_4H_9	2	**3b**	92
3	H	Ph	4.5	**3c**	80
4	4-NO_2	Ph	2.5	**3d**	85
5	3- NO_2	Ph	3.5	**3e**	82
6	4-$COCH_3$	Ph	3.5	**3f**	82
7	4-CH_3	Ph	5	**3g**	74
8	4-OCH_3	Ph	5	**3h**	72
9	H	Me_3Si	5	**3i**	81
10	4-OCH_3	Me_3Si	6	**3j**	70

[a] Reaction conditions: **1** (1.0 mmol), **2** (1.5 mmol), $Ni(PPh_3)_2Cl_2$ (0.01 mmol), CuI (0.02 mmol), sodium lauryl sulfate (0.07 mmol), Cs_2CO_3 (2.0 mmol), and degassed water (5 mL) at 60°C under Ar.

[b] GC yields.

time. In contrast, the methoxyl-substituted aryl iodide reacted with **2** to give the desired products in moderate yields in a longer period of reaction time.

In summary, we have developed an efficient method via the nickel-catalyzed Sonogashira coupling reaction of aryl iodides with terminal alkynes in water using sodium lauryl sulfate as the surfactant under argon. The reaction is an inexpensive alternative to the palladium-catalyzed process and results in good yields of the desired product.

EXPERIMENTAL

General Procedure for the Sonogashira Coupling Reaction

A round-bottom flask with a reflux condenser was charged with aryl iodide (1.0 mmol), terminal acetylene (1.5 mmol), $Ni(PPh_3)_2Cl_2$ (0.01 mmol), CuI (0.02 mmol), sodium lauryl sulfate (0.07 mmol), and cesium carbonate (2.0 mmol), and these ingredients were mixed under an argon atmosphere in 5 mL of water. The mixture was heated at 60°C for 2–8 h. After completion of the reaction, the resulting solution was concentrated in vacuo, and the crude product was subjected to silica-gel column chromatography using $CHCl_3$–CH_3OH (98:2) as eluent to afford the pure product (Table 3).

Data

1-Phenyl-1-hexyne (3a). Colorless liquid.[14] IR (neat): υ (cm^{-1}) 3050, 2960, 2875, 2232, 1598, 1499, 754, 690. ^1H NMR (400 MHz, $CDCl_3$): δ 7.41–7.38 (m, 2H), 7.32–7.26 (m, 3H), 2.40 (t, $J = 7.2$ Hz, 2H), 1.62–1.56 (m, 2H), 1.51–1.47 (m, 2H), 0.97 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.6, 126.2, 127.9, 124.2, 91.4, 80.6, 30.9, 21.0, 19.1, 13.8.

1-(4-Nitrophenyl)-1-hexyne (4b). Yellow liquid.[14] IR (neat): υ (cm^{-1}) 3080, 2936, 2873, 2234, 1594, 1520, 852. ^1H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, $J = 8.8$ Hz, 2H), 7.52 (d, $J = 8.8$ Hz, 2H), 2.42 (t, $J = 7.2$ Hz, 2H), 1.63–1.54 (m, 2H), 1.50–1.46 (m, 2H), 0.96 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 132.2, 130.9, 123.5, 96.6, 79.2, 30.5, 22.1, 19.2, 13.8.

Diphenyl acetylene (3c). Mp 59–60°C (lit.[15] 60–61°C). IR (KBr): υ (cm^{-1}) 3060, 1600, 1492, 756, 690. ^1H NMR (400 MHz, $CDCl_3$): δ 7.55–7.51 (m, 4H), 7.36–7.32 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.8, 128.2, 128.1, 123.3, 89.2.

1-(4-Nitrophenyl)phenylacetylene (3d). Mp 119–120°C (lit.[16] 120–121°C). IR (KBr): υ (cm^{-1}) 3084, 2221, 1592, 1515, 1495, 858, 767, 690. ^1H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, $J = 8.8$ Hz, 2H), 7.63 (d, $J = 8.8$ Hz, 2H), 7.59–7.56 (m, 2H), 7.40–7.36 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.8, 132.1, 131.9, 130.3, 129.5, 128.8, 124.1, 122.3, 94.7, 87.7.

1-(3-Nitrophenyl)phenylacetylene (3e). Mp 70–71°C (lit.[17] 69–70°C). IR (KBr): υ (cm^{-1}) 3078, 2210, 1600, 1530, 1521, 1347, 810, 764, 696. ^1H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H), 8.20–8.17 (m, 1H), 7.80 (d, $J = 7.6$ Hz, 1H), 7.56–7.50 (m, 3H), 7.42–7.38 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 137.1, 132.1, 129.6, 129.4, 128.2, 126.6, 124.9, 122.9, 122.3, 92.1, 87.0.

1-(4-Acetylphenyl)phenylacetylene (3f). Mp 94–95°C (lit.[16] 95–96°C). IR (KBr): υ (cm^{-1}) 3080, 2918, 2223, 1685, 1606, 1265, 835, 697. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, $J=8.0$ Hz, 2H), 7.63 (d, $J=8.0$ Hz, 2H), 7.52 (d, $J=2.4$ Hz, 2H), 7.40–7.37 (m, 3H), 2.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 136.4, 131.9, 131.6, 128.7, 128.5, 128.2, 128.1, 122.6, 92.9, 88.8, 26.5.

1-(4-Methylphenyl)phenylacetylene (3g). Mp 73–74°C (lit.[17] 73–74°C). IR (KBr): υ (cm^{-1}) 3030, 2918, 2860, 2215, 1596, 1510, 818, 697. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.52 (m, 2H), 7.42 (d, $J=8.0$ Hz, 2H), 7.36–7.29 (m, 3H), 7.16 (d, $J=8.0$ Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 131.6, 131.4, 129.2, 128.4, 128.1, 123.8, 120.1, 89.6, 88.7, 21.7.

1-(4-Methoxyphenyl)phenylacetylene (3h). Mp 59–60°C (lit.[17] 58–59°C). IR (KBr): υ (cm^{-1}) 3025, 2212, 1604, 1500, 1240, 835, 750, 695. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.43 (m, 4H), 7.31–7.28 (m, 3H), 6.86–6.83 (m, 2H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 133.0, 131.6, 128.3, 128.0, 123.4, 115.6, 113.9, 89.6, 88.1, 55.4.

1-Phenyl-2-(trimethylsilyl)acetylene (3i). Colorless liquid.[18] IR (neat): υ (cm^{-1}) 3080, 2160, 1598, 1490, 1250, 860, 755, 690. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47–7.44 (m, 2H), 7.31–7.29 (m, 3H), 0.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.1, 128.4, 128.2, 123.0, 105.1, 94.2, 0.01.

1-(4-Methoxyphenyl)-2-(trimethylsilyl)acetylene (3j). Colorless liquid.[18] IR (neat): υ (cm^{-1}) 2155, 1605, 1510, 1250, 835, 755, 700. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, $J=8.8$ Hz, 2H), 6.80 (d, $J=8.8$ Hz, 2H), 3.80 (s, 3H), 0.25 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 133.7, 115.1, 113.9, 105.4, 92.5, 55.2, 0.07.

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