Letters in Organic Chemistry, 2022, *19*, 28-33

RESEARCH ARTICLE

Microwave-assisted, Copper-free Sonogashira Coupling Between Aryl Halides and Terminal Alkynes Using Recyclable Ionic Liquid and Catalyst

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ARTICLE HISTORY

Received: October 18, 2020
Revised: December 20, 2020
Accepted: June 16, 2021

DOI:
10.2174/1570178618666210820101129

CrossMark

Abstract: An efficient method for the Sonogashira coupling reaction between aryl halides and terminal alkynes has been developed. The reaction was performed in ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) under microwave irradiation. High yields of products were obtained in a very short reaction time. Moreover, the medium and catalyst could be recovered and reused three times without considerable decrease in reaction yields.

Keywords: Coupling reaction, terminal alkynes, ionic liquid, microwave, trimethylsillylacetylene, iodide.

1. INTRODUCTION

The Sonogashira coupling reaction, which was established by Kenkichi Sonogashira *et al*., is one of the most powerful methods to prepare conjugated enynes or aryl alkynes [1]. The reaction has been widely applied in natural products chemistry, pharmaceuticals, and material science [2]. The original reaction employed palladium and copper co-catalyst for the coupling between terminal alkynes with various vinyl or aryl halides in amine solvent. The reaction has attracted intensive interest from chemists and numerous reaction modifications have been reported.

Besides $Pd(PPh_3)_2Cl_2$ and $Pd(PPh_3)_4$, a vast variety of Pd catalysts have been developed for this coupling reaction such as $PdCl_2$(dppe), $PdCl_2$(dppp), $PdCl_2$(dppf), $PdCl_2(MeCN)_2$, $Pd(OAc)_2$, $Pd_2(dba)_3$, $PdCl_2$, and PdI_2 [3a-e]. Solvents for this reaction have also been expanded [4a-c]. The effects of additives on this reaction have also been investigated [5a-c]. The reaction could be performed using phase transfer catalysts or biphasic system or solid supported Pd catalyst [6a-c]. The reaction could be especially achieved in the absence of Pd catalyst [7].

Recently, various approaches for the Sonogashira coupling reaction have been developed with the aim to avoid economic and environment costs. Diverse methods without using copper catalyst have well been documented [4a, 8a-f]. The use of ionic liquids as media for this reaction has drawn great attention of chemists [4a, 9a-d]. Furthermore, the application of microwave to this reaction has been widely investigated [10a-d]. However, combination of ionic liquid as medium and microwave as energy source for this reaction has not still been studied. Herein, we reported the Sonogashira coupling between aryl halide and terminal alkyne in ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) under microwave irradiation. High yields of arylalkynes were achieved in most cases and the ionic liquid along with the catalyst could be recycled three times with an insignificant decrease in reaction yield.

2. RESULTS AND DISCUSSION

We started our study by investigating the coupling reaction between iodobenzene **1a** with phenylacetylene **2a** in 1-butyl-3-methylimidazolium tetrafluoroborate with different Pd catalysts. Mixture of **1a** (1.5 mmol), **2a** (1.65 mmol; 1.1 equiv), Et_3N (6 mmol, 4 equiv), and Pd catalyst (5 mol%) in [Bmim][BF_4] (4 mL) was heated at 80 °C for 2h and the results are summarized in Table **1**. The use of $Pd(PPh_3)_4$, $PdCl_2$ and $PdCl_2(MeCN)_2$ as catalysts led to product **3a** in low yield (18%, 41%, 43%, entry 1, 4, 5, Table **1**, respectively). Moderate yields of coupling product were provided using $Pd(OAc)_2/PPh_3$, $Pd(OAc)_2$, $Pd_2(dba)_3$, $PdCl_2$(dppf) (entry 2, 3, 7, 8, Table **1**) catalysts. Among these four catalysts, $PdCl_2$(dppf) was the most efficient but not satisfactory. To our delight, under $PdCl_2(PPh_3)_2$ catalysis, product **3a** was furnished in very good yield (84%, entry 6, Table **1**).

We also used organic solvents for the coupling reaction to prove the efficiency of the ionic liquid. The reaction with the same conditions using $PdCl_2(PPh_3)_2$ as the catalyst was performed in two solvents, DMF and toluene. The yields of **3a** decreased greatly in these organic solvents (48% and 36%, respectively).

Concern about the environmental effect, we then carried out the reaction under microwave irradiation at 80 °C and the results are shown in Table **2**. Two minutes of microwave

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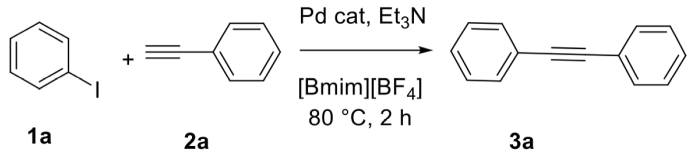
1875-6255/22 $65.00+.00

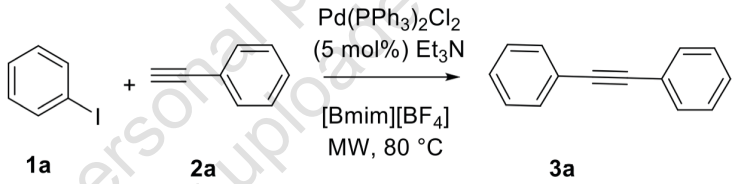
Table 1. Palladium-Catalyzed Coupling Reaction of iodobenzene and phenylacetylene in [BMIm][BF_4].



Entry	Pd Catalyst	Yield of 3a (%)[a]
1	$Pd(PPh_3)_4$	18
2	$Pd(OAc)_2/PPh_3$	63
3	$Pd(OAc)_2$	53
4	$PdCl_2$	41
5	$PdCl_2(MeCN)_2$	45
6	$PdCl_2(PPh_3)_2$	84
7	$Pd_2(dba)_3$	55
8	$PdCl_2$(dppf)	65

[a] Isolated yield based on iodobenzene.

Table 2. Sonogashira coupling between iodobenzene and phenylacetylene in [BMIm][BF_4] under microwave.



Entry	Time	Yield of 3a (%)[a]
1	2 minutes	83
2	5 minutes	91
3	10 minutes	91

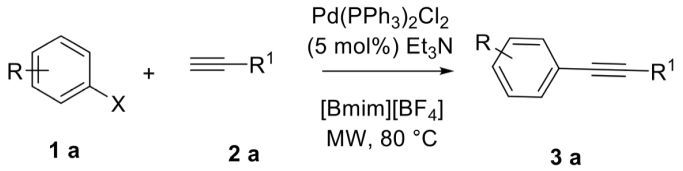
[a] Isolated yield based on iodobenzene.

irradiation provided **3a** in 83% yield (entry 1, Table **2**). In five minutes, reaction yield was considerably improved (91%, entry 2, Table **2**). However, reaction efficiency was not enhanced when the irradiation time was prolonged to 10 minutes (entry 3, Table **2**). Thus, we concluded that the optimized conditions for the reaction include: [Bmim][BF_4] solvent, $PdCl_2(PPh_3)_2$ catalyst and microwave irradiation at 80 °C in 5 minutes. Clearly, microwave irradiation not only reduced reaction time but also improved reaction efficiency.

With the optimized conditions in hand, we then expanded the Sonogashira coupling reaction for different alkynes and aryl halide, including chlorides, bromides and iodides and the results are displayed in Table **3**. In general, under these conditions, all iodide derivatives provided aryalkynes products in excellent yields. Compared to iodides, the corresponding triflate, bromides, and chlorides were much less reactive and products were afforded in lower yields (entry 2, 3, 4, 8, 9, Table **3**). The presence of NO_2 group at the aryl halide moiety slightly reduced the reaction efficiency (entry 7, 12, 16, 17, Table **3**), while other groups such as F, Et, OH, NH_2, OAc barely affected reaction yields.

Noticeably, the ionic liquid medium along with the Pd catalyst was easily recovered and reused without significant decrease in catalytic activity. After reaction completion, the product was removed from the ionic liquid by extracting with *n*-hexane. The ionic liquid medium along with the Pd catalyst was washed with water and used for the next run. The second and third runs for the reaction between **1a** and **2a**

Table 3. Synthesis of arylalkynes *via* Sonogashira coupling in ionic liquid under microwave irradiation.



Entry	R, X	R1	Products	Yields (%)a
1	H, I	Ph	**3a**	91 (87, 85, 76)b (84)c
2	H, Br			77
3	H, Cl			56
4	H, Tf			81
5	p-F, I	Ph	**3b**	87
6	*p*-COOMe, I	Ph	**3c**	88
7	*p*-NO2, I	Ph	**3d**	82
8	*p*-OH, I	TMS	**3e**	93
9	*p*-OH, Br			76
10	*p*-OH, Cl			58
11	*p*-F, I	TMS	**3f**	90
12	*m*-NO2, I	TMS	**3g**	83
13	*m*-NH2, I	TMS	**3h**	94
14	*o*-Et, I	TMS	**3i**	92
15	*p*-OAc, I	TMS	**3j**	92
16	*m*-NO2, I	*n*-C5H11	**3k**	83
17	*p*-NO2, I	*n*-C4H9	**3l**	83

[a] Isolated yield based on Aryl halides.
[b] Yields of 3a for the second, third, and forth runs under the same conditions for the first run, respectively
[c] Yields of 3a for the gram-scale synthesis (5 mmol, 1.02 gram of 1a)

resulted in product **3a** in 87% and 85%, respectively. However, the yield of **3a** decreased to 76% for the fourth run. The reaction could be performed on gram-scale without considerable decrease in product yield (84%).

3. EXPERIMENTAL SECTION (FOR RESEARCH ARTICLES ONLY)

3.1. Materials and Methods

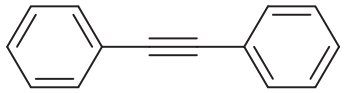
All chemicals were purchased from Sigma- Aldrich company. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova NMR Spectrometer (^{1}H NMR running at 500 MHz and ^{13}C NMR running at 125 MHz) instrument. $CDCl_3$ was used as the NMR solvent. ^{1}H NMR chemical shifts are quoted in δ values in ppm and are referenced relative to the chemical shift of $CDCl_3$ (7.26 ppm). For microwave synthesis, all reactions were performed in a CEM microwave reactor at 80 ºC, 60 W in a 10 mL capped vial.

3.2. General Procedure for the Sonogashira Coupling Reaction

Aryl halide (1.5 mmol), alkyne (1.8 mmol, 1.2 equiv), $Pd(PPh_3)_2Cl_2$ (53 mg, 0.075 mmol, 0.05 equiv) and Et_3N (666 mg, 6 mmol, 4 equiv) were added to 10 mL microwave vial containing 4 mL [BMIm][BF_4]. The mixture was irradiated in a microwave reactor at 80 °C for 5 minutes. Completion of the reaction was confirmed by TLC. Then the mixture was extracted with hexane (4 x 10 mL) and the organic layers were combined. The solvent was removed by an evaporator and the residue was purified by flash column chromatography to afford the corresponding product. The ionic liquid containing catalyst was washed with water (3 x 5mL) then was placed in a high vacuo system to remove water residue. The ionic liquid was used for the next cycle without further purification.

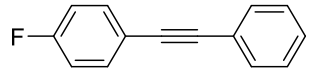
3.3. Physical and Spectral Data

3.3.1. Diphenylacetylene (3a)



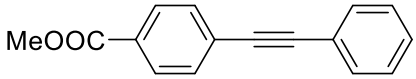
(246 mg, 91% yield from iodobenzene; 208 mg, 77% yield from bromobenzene; 151 mg, 56% yield from chlorobenzene). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.53 (m, 4H), 7.36 – 7.35 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.6, 128.3, 128.2, 123.2, 89.3. NMR spectroscopic data matched with the published data [11].

3.3.2. 1-fluoro-4-(phenylethynyl)benzene (3b)



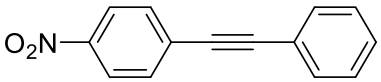
(256 mg, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 4H), 7.37 – 7.33 (m, 3H), 7.07 – 7.03 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7 (*J* = 254 Hz), 161.2, 133.5, 133.4, 131.5, 128.4, 128.3, 123.1, 119.3, 115.7, 115.5, 89.0, 88.3. NMR spectroscopic data matched with the published data [11].

3.3.3. methyl 4-(phenylethynyl)benzoate (3c)



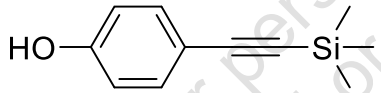
(315 mg, 88% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 – 8.01 (m, 2H), 7.60 – 7.58 (m, 2H), 7.56 – 7.54 (m, 2H), 7.37 – 7.36 (m, 3H), 3.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 131.7, 131.5, 129.5, 129.4, 128.7, 128.4, 128.0, 122.6, 92.3, 88.6, 52.2. NMR spectroscopic data matched with the published data [12].

3.3.4. 1-nitro-4-(phenylethynyl)benzene (3d)



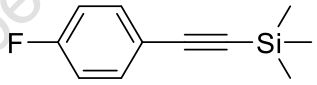
(376 mg, 82% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 – 8.20 (m, 2H), 7.68 – 7.65 (m, 2H), 7.58 – 7.55 (m, 2H), 7.41 – 7.38 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.91, 132.23, 131.80, 130.22, 129.25, 128.51, 123.60, 122.04, 94.67, 87.52. NMR spectroscopic data matched with the published data [11].

3.3.5. 4-((trimethylsilyl)ethynyl)phenol (3e)



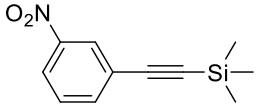
(265 mg, 93% yield from p-iodophenol; 217 mg, 76% yield from *p*-bromophenol; 165 mg, 58% yield from *p*-chlorophenol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 2H), 0.22 (d, *J* = 1.0 Hz, 9H). ^{13}C NMR (125 MHz, cdcl$_3$) δ 156.1, 156,0, 133.7, 115.4, 105.3, 92.5, 0.1. NMR spectroscopic data matched with the published data [13].

3.3.6. ((4-fluorophenyl)ethynyl)trimethylsilane (3f)



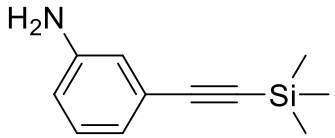
(259 mg, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.02 (t, *J* = 8.5 Hz, 2H), 0.28 (s, 9H). NMR spectroscopic data matched with the published data [14].

3.3.7. Trimethyl((3-nitrophenyl)ethynyl)silane (3g)



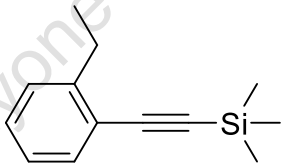
(273 mg, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 0.28 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 137.5, 129.2, 126.6, 124.9, 123.1, 102.1, 97.6, -0.30. NMR spectroscopic data matched with the published data [15].

3.3.8. 3-((trimethylsilyl)ethynyl)aniline (3h)



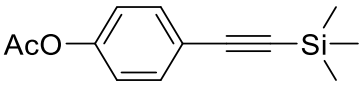
(266 mg, 94% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.73 – 6.68 (m, 2H), 4.27 (bs, 2H), 0.31 (s, 9H). ^{13}C NMR (125 MHz, CDC_3) δ 148.3, 132.3, 129.9, 117.8, 114.2, 107.8, 101.9, 99.8, 0.2. NMR spectroscopic data matched with the published data [16].

3.3.9. ((2-ethylphenyl)ethynyl)trimethylsilane (3i)



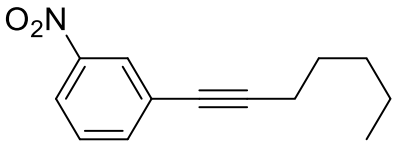
(279 mg, 92% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.0 Hz, 1H), 7.36 – 7.23 (m, 1H), 7.20 (d, *J* = 7.0 Hz, 1H), 7.13 (t, *J* = 7.0 Hz, 1H), 2.82 (t, *J* = 7.5, 1.8 Hz, 2H), 1.26 (q, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, CCl_3) δ 147.0, 132.6, 128.9, 128.1, 125.7, 122.5, 104.1, 978.0, 28.0, 14.8, 0.2. NMR spectroscopic data matched with the published data [17].

3.3.10. 4-((trimethylsilyl)ethynyl)phenyl acetate (3j)



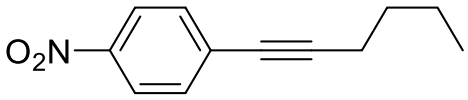
(282 mg, 92 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 8.5 Hz, 2H), 2.29 (s, 3H), 0.24 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm)**:** 169.1, 150.6, 133.2, 121.6, 120.9, 104.2, 94.4, 21.2, 0.0. NMR spectroscopic data matched with the published data [18].

3.3.11. 1-(hept-1-yn-1-yl)-3-nitrobenzene (3k)



(270 mg, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.10 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 2.42 (t, *J* = 7.0 Hz, 2H), 1.66 – 1.58 (m, 2H), 1.48 – 1.40 (m, 2H), 1.37 (dd, *J* = 14.6, 7.3 Hz, 2H), 0.93 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.1, 137.3, 129.1, 126.4, 126.0, 122.2, 93.7, 78.5, 31.1, 28.2, 22.2, 19.4, 14.0. NMR spectroscopic data matched with the published data [19].

3.3.12. 1-(hex-1-yn-1-yl)-4-nitrobenzene (3l)



(270 mg, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 2.45 (t, *J* = 7.0 Hz, 2H), 1.66 – 1.42 (m, 4H), 0.96 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 132.2, 131.2, 123.4, 96.7, 79.3, 30.4, 22.0, 19.2, 13.6. NMR spectroscopic data matched with the published data [3d].

CONCLUSION

In summary, we have demonstrated an efficient method for the Sonogashira coupling reaction between aryl halides and terminal alkyne. Advantages of the synthesis include short reaction time, good functional group tolerance, high yields of products, no copper catalyst and environmentally benign conditions. Moreover, the medium and catalyst could be recovered and reused three times without a considerable decrease in reaction yields

CONSENT FOR PUBLICATION

Not applicable

AVAILABILITY OF DATA AND MATERIALS

The authors confirm that the data supporting the findings of this research are available within the article

FUNDING

None.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

ACKNOWLEDGEMENTS

We thank to Vinh University for financial support.

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