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Original article

Synthesis of symmetrical 1,3-diynes *via* tandem reaction of (*Z*)-arylvinyl bromides in the presence of DBU and CuI

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ABSTRACT

Microwave-assisted tandem reaction of (*Z*)-arylvinyl bromides involving an elimination and homocoupling in the presence of DBU and CuI in DMF affords a variety of symmetrical 1,3-diynes in good to excellent yields. This tandem process, eliminating the need of volatile and savory terminal alkynes, provides an alternative to the conventional homocoupling methods for the synthesis of symmetrical 1,3-diynes.

1. Introduction

Conjugated diynes are recurring building blocks for the synthesis of natural products, pharmaceuticals and bioactive compounds with anti-inflammatory, antifungal, anti-HIV, antibacterial, anticancer activities, *etc.* [1]. In addition, conjugated diynes have found wide applications in the construction of industrial intermediates and materials, particularly macrocyclic annulenes, organic conductors, supramolecular switches and carbon-rich materials [2–4]. Therefore, much attention [5] has been devoted to the development of new and efficient methods for the synthesis of diynes. A classical and effective route for preparing symmetrical 1,3-diynes was the homocoupling of volatile and savory terminal alkynes [6].

(*Z*)-Arylvinyl bromides, readily available from inexpensive cinnamic acid derivatives [7], are also versatile precursors in many useful organic transformations including the well-known Stille [8], Suzuki [9], and Sonogashira [10] couplings, as well as the Buchwald [11] methodology for stereospecific synthesis of substituted alkenes. Using the CuI-ethylenediamine catalytic system in toluene or 1,4-dioxane, they can be coupled with azoles to afford stereocontrolled *N*-vinylazoles, a key unit for the synthesis of poly(*N*-vinylazoles) serving as semiconductors and photosensitive materials [12]. Additionally, the versatility of (*Z*)-arylvinyl bromides has been exploited, notably, as alkyne equivalents [13].

In this article, we report a CuI-catalyzed tandem reaction of (*Z*)-arylvinyl bromides, which affords symmetrical diynes conveniently and efficiently. Our proposed synthetic route, which includes a cascade elimination and Glaser reaction, is shown in Scheme 1. We hypothesized that, in this reaction process, an elimination of (*Z*)-arylvinyl bromides **1** would occur in the presence of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) to produce the aryne **A**. Subsequently, a Glaser oxidative homocoupling of **A** through intermediate **B** catalyzed by CuI and DBU affords the desired product **2**.

2. Experimental

Melting points were recorded using a WRS-1B digital melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded using a Bruker DPX-400 spectrometer in $CDCl_3$ with $SiMe_4$ as an internal standard. MS data were measured with a Varian-310 mass spectrometer. A Xinyi MAS-II microwave synthesizer was used for all the microwave reactions. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with HuanghaiGF254 silica gel coated plates. Column chromatography was carried out using 300–400 mesh silica gel at medium pressure. The synthesis

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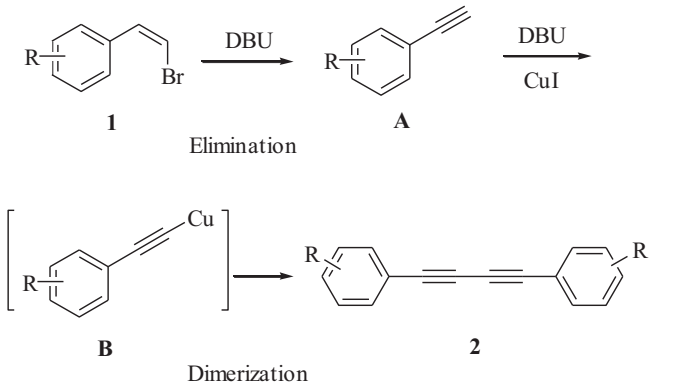


Scheme 1. Route for the synthesis of symmetrical diynes from (*Z*)-arylvinyl bromides.

of (*Z*)-arylvinyl bromides was achieved according to the reported methods [7a].

2.1. General procedure for 1,3-diynes (**2**)

(*Z*)-Arylvinyl bromides **1** (1 mmol) and DBU (2.2 mmol) were dissolved in DMF (2 mL) and the reaction system was irradiated using a microwave synthesizer (120 W) for 2 min. The reaction mixture was then removed from the microwave synthesizer and cooled to room temperature. To the reaction mixtures was added CuI (0.2 mmol). The mixture was stirred at room temperature for 8 h. After the completion of the reaction screened by TLC, the mixture was diluted with Et_2O (20 mL) and filtered. The filtrate was washed with brine (2× 10 mL) and H_2O (10 mL). The Et_2O layer was dried over Na_2SO_4, concentrated under reduced pressure. Purification of the residue by column chromatography on silica gel (EtOAc/petroleum ether = 1/20) afforded products **2**. The structure of 1,3-diynes **2b**–**2i** were fully consistent with their ^{1}H NMR data [14].

2.2. Selected data of compound **2**

1,4-Diphenylbuta-1,3-diyne (**2a**) [14,1a]: Yield: 182 mg (90%); white solid; mp 86–86.5 °C (lit. [5s] 86–87 °C); R_f = 0.9 (EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.37 (m, 6H, ArH), 7.52–7.54 (m, 4H, ArH). MS (ESI): *m*/*z* 202 [M^+].

1,4-Bis(4-methylpheny1)buta-1,3-diyne (**2b**) [14,1a]: Yield: 212 mg (92%); white solid; mp 182.1–182.5 °C (lit. [5t] 182–183 °C, lit. [5u] 137–138 °C); R_f = 0.85 (EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 6H, CH_3), 7.14 (d, 4H, *J* = 8.0 Hz, ArH), 7.42 (d, 4H, *J* = 8.0 Hz, ArH). MS (ESI): *m*/*z* 230 [M^+].

1,4-Bis(4-methoxypheny1)buta-1,3-diyne (**2c**) [14,1a]: Yield: 228 mg (87%); white solid; mp 139–140.5 °C (lit. [5t] 140–141 °C); R_f = 0.8 (EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82 (s, 6H, CH_3), 6.85 (d, 4H, *J* = 8.8 Hz, ArH), 7.46 (d, 4H, *J* = 8.8 Hz, ArH).

1,4-Bis(4-fluorophenyl)buta-1,3-diyne (**2d**) [1a]: Yield: 138 mg (56%); white solid; mp 187.3–188 °C (lit. [5t] 194–195 °C, lit. [5u] 187–189 °C); R_f = 0.8 (EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (t, 4H, *J* = 8.5 Hz, ArH),7.49–7.53 (m, 4H, ArH).

1,4-Bis(3-methylphenyl)buta-1,3-diyne (**2e**) [1a]: Yield: 205 mg (89%); white solid; mp 68–68.5 °C (lit. [5t] 68–70 °C, lit. [5v] 74–75 °C); R_f = 0.85 (EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 6H, CH_3), 7.17–7.35 (m, 8H, ArH).

1,4-Bis(3-methoxypheny1)buta-1,3-diyne (**2f**) [14]: Yield: 233 mg (89%); yellow solid; mp 91.8–92.9 °C (lit. [5t,5u] 92–93 °C); R_f = 0.8 (EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81 (s, 6H, CH_3), 6.93–7.24 (m, 8H, ArH).

1,4-Bis(2-chlorophenyl)buta-1,3-diyne (**2g**) [14]: Yield: 230 mg (85%); yellow solid; mp 139–140.5 °C (lit. [5u] 138–140 °C); R_f = 0.75 (EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.33 (m, 4H, ArH), 7.42 (d, 2H, *J* = 9.2 Hz, ArH), 7.58 (d, 2H, *J* = 6.0 Hz, ArH).

1,4-Bis(2-bromophenyl)buta-1,3-diyne (**2h**) [14]: Yield: 300 mg (83%); yellow solid; mp 132.5–133.8 °C; R_f = 0.8 (EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21–7.31 (m, 4H, ArH), 7.57–7.62 (m, 4H, ArH).

1,4-Bis(2-methoxypheny1)buta-1,3-diyne (**2i**) [14]: Yield: 223 mg (85%); white solid; mp 137.8–149.5 °C (lit. [5s] 138–140 °C); R_f = 0.8 (EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.88 (s, 6H, CH_3), 6.86–6.91 (m, 4H, ArH), 7.29–7.42 (m, 4H, ArH).

3. Results and discussion

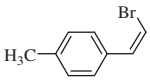
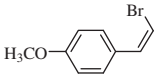
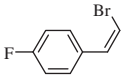
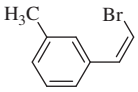
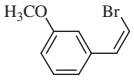
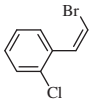
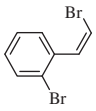
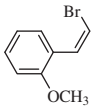
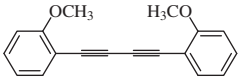
To screen suitable reaction conditions, (*Z*)-1-(2-bromovinyl)-benzene **1a** has been used as a model substrate. The initial attempt was carried out with **1a** (1 mmol) and DBU (2.2 mmol) using DMF (2 mL) as a solvent. The reaction mixture was stirred at 80 °C for 12 h and cooled to room temperature. CuI (2.5 mol%) was then added and the system was stirred for 8 h at room temperature. The expected product **2a** was afforded in 45% yield (Table 1, entry 1). The structure of compound **2a** was confirmed by ^{1}H NMR and was consistent with those in the literature [15]. Almost no improvement was observed when the reaction was prolonged to 24 h (Table 1, entry 2). Lower yield was obtained when the reaction was conducted at 120 °C (Table 1, entry 3). Fortunately, the reaction worked efficiently under microwave conditions (Table 1, entries 4–6). For instance, 85% yield of product **2a** was observed when the starting material **1a** and DBU in DMF was irradiated under microwave (120 W) for 1 min (Table 1, entry 4). The yield of **2a** reached 90% by increasing the irradiation time to 2 min (Table 1, entry 5). Further increase of the irradiation time to 5 min, however, decreased the yield to 80% (Table 1, entry 6). Other bases such as Et_3N, Cs_2CO_3 and EtONa were tested but failed to afford the desired product **2a** (Table 2, entries 7–9). When the amount of base was reduced to 1.5 mmol, the yield dropped significantly to 50% (entry 10). Inferior results were observed when other solvents were examined. When the solvent was changed to MeCN, DMSO, and THF, the yields decreased to 70%, 77% and 68%, respectively (Table 1, entries 11–13).

Table 1
Optimization of the reaction conditions based on **1a**.

Entry	Solvent	Base[a]	"△" or "MW"	Time[c]	Yield (%)[d] of **1a**
1	DMF	DBU	≥/80 °C	12 h	45
2	DMF	DBU	≥/80 °C	24 h	47
3	DMF	DBU	≥/120 °C	12 h	39
4	DMF	DBU	MW	1 min	85
5	DMF	DBU	MW	2 min	90
6	DMF	DBU	MW	5 min	80
7	DMF	Et_3N	MW	2 min	Trace
8	DMF	Cs_2CO_3	MW	2 min	Trace
9	DMF	EtONa	MW	2 min	Trace
10	DMF	DBU[b]	MW	2 min	50
11	MeCN	DBU	MW	2 min	70
12	DMSO	DBU	MW	2 min	77
13	THF	DBU	MW	2 min	68

[a] 2.2 mmol amount of bases were used except for entry 10.
[b] 1.5 mmol amount of bases was used.
[c] Heated or MV time for the elimination process in Scheme 1.
[d] Isolated yield.

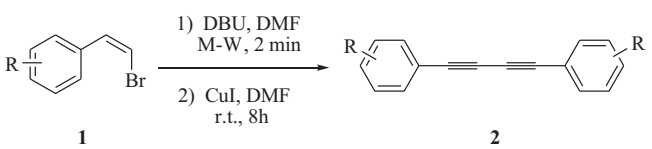
Table 2
Synthesis of 1,3-diynes **2** from (*Z*)-arylvinyl bromides **1** in the presence of DBU and CuI[a].

Entry	Substrate **1**		Product **2**		Yield of **2** (%)[b]
1		**1a**		**2a**	90
2		**1b**		**2b**	92
3		**1c**		**2c**	87
4		**1d**		**2d**	56
5		**1e**		**2e**	89
6		**1f**		**2f**	89
7		**1g**		**2g**	85
8		**1h**		**2h**	83
9		**1i**		**2i**	85

[a] Reaction conditions: (1) Reactions were conducted with (*Z*)-arylvinyl bromides **1** (1 mmol) and DBU (2.2 mmol) in DMF (2 mL) under MW (120 W) for 2 min; (2) CuI (20 mol%) was added to the cooled reaction system of (**1**), the mixture was stirred at rt for 8 h.
[b] Isolated yield based on substrate 1.

On the basis of these results, the optimal conditions involved the following parameters: DMF as solvent, 2.2 equiv. of DBU as base, microwave irradiation (120 W) for 2 min. and 20 mol% of CuI as catalyst.

Under the above optimized conditions, we have examined the substrate scope of this reaction. Our experiments indicate that a range of (*Z*)-arylvinyl bromides underwent the elimination-homocoupling process to produce the corresponding 1,3-diynes in good to excellent yields (Scheme 2 and Table 2). An electron-donating group and a weak electron-withdrawing group in the (*Z*)-arylvinyl bromide derivatives did not alter the efficiency of the reaction. For example, a variety of substituents like Me, OMe, Cl and Br on the aromatic ring are compatible with this reaction condition. The results are listed in Table 2 (Table 2, entries 2–3 and 5–9). The reaction was sluggish, however, in the case of (*Z*)-arylvinyl bromide bearing a strong electron-withdrawing group. For instance, (*Z*)-1-(2-bromovinyl)-4-fluorobenzene **1d** gave a relatively low yield of the product **2d** (56%, Table 2, entry 4). When (*Z*)-1-(2-bromovinyl)-4-nitrobenzene was employed under the optimized conditions, the reaction failed to furnish the expected product. In addition, the effect of steric hindrance was also screened. (*Z*)-arylvinyl bromide bearing Cl, Br and OMe functional groups on the *ortho*-position of the aromatic ring readily reacted under the established conditions, affording products **2g**, **2h** and **2i** in a yield of 85%, 83% and 85%, respectively (Table 2, entries 7–9).



Scheme 2. Synthesis of symmetrical 1,3-diynes.

4. Conclusion

In conclusion, we have developed a new method for the synthesis of symmetrical diynes from (*Z*)-arylvinyl bromides by CuI-catalyzed tandem reaction, avoiding the direct use of volatile terminal alkynes.

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