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Communications

Efficient One-Pot Synthesis of the Unsymmetrical Diarylalkynes from Two Different Aryl Bromides and Propiolic Acid by Using Pd(PPh₃)₄ Catalyst

Kyungho Park,¹ Wonyoung Kim, and Sunwoo Lee²

Department of Chemistry, Chonnam National University, Gwangju 500-757, Korea

*E-mail: scimaker@ejnu.net (K. Park); sunwoo@chonnam.ac.kr (S. Lee)

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Unsymmetrical diarylalkynes have attracted much attention, as the molecule structure, having an internal alkyne of two different aromatics, is a core in materials encountered π-conjugated systems.¹ Palladium catalyzed Sonogashira reaction is the most commonly used method for the arylation of terminal alkynes.² Instead of the terminal alkynes, the decarboxylative Sonogashira reaction is used from the alkyne carboxylic acids has several advantages, including a depreciable process for the treatment of the carbon dioxide as a reaction waste released after the complete conversion, and is stable for handling and storage.³ We reported a method for unsymmetrical coupling products from the site selective reaction of propiolic acid with aryl iodides and aryl bromides combinations.⁴ Unlike trimethylsilylacetylene and 2-methylbut-3-yn-ol, Propiolic acid as an alkyne source is very stable for handling and storage.⁵ Goossen reported the method for the synthesis of unsymmetrical diarylalkynes with the combination of two different aryl bromides in the presence of SPhos.⁶ Recently, we reported that the Pd(PPh₃)₄ catalyzed a selective Sonogashira reaction with aryl bromides at low temperature.⁷ Instead of the previous reports of the one pot reaction procedures for the synthesis of unsymmetrical diarylalkynes, we carried out an additional experiment due to the simplicity of the non-sequential addition of aryl bromides and non-column purification.

To investigate the method for the synthesis of unsymmetrical diarylalkynes, we screened ratios of 1a, 2a, propiolic acid, and reaction temperature, as summarized in Table 1. When all reactants had reached equal amounts, 3ab showed 26% yield (entry 1). However, in the case of adding more amounts of 1a or 2a than the others showed no yields (entry 2 and entry 3). The case of adding lower amounts of 1a or 2a than the others showed 23% and 33%, respectively (entry 4 and entry 5). When adding more propiolic acid than either 1a or 2a, the product showed 57% yield (entry 6). When the temperature for the second reaction was 60 °C, 3ab showed 68% yield (entry 7). However, when the temperature for the second reaction was 120 °C, 3ab showed no yield (entry 8).

Finally, unsymmetrical coupling of propiolic acid with two different of aryl bromides was carried out with the optimized condition. The results are summarized in Table 2. As expected, 1a with 2a afforded a corresponding product 60% yield (entry 1). The products coupled with propiolic acid, 1a and m- or o-methoxy bromobenzene showed 62% and 51% yield, respectively (entry 2 and entry 3). The combination of 1a with 2d, 2e, 2f or 2g showed 68%, 53%, 56%, and 58% yields, respectively (entry 4-7). The combination of 2a with 1b, 1c, 1d or 1e showed 66%, 48%, 45%, and 40% yields, respectively (entry 8-11). 1b with 2h afforded the desired product of 61% yield (entry 12).

In conclusion, an efficient method for the synthesis of...
unsymmetrical diarylalkynes from the Pd-catalyzed Sonogashira reaction with propiolic acid and two different aryl bromides has been developed. The various combinations of two different aryl bromides showed good yields. In addition, the column chromatography purification process is not needed in this method.

**Experimental Section**

**Experimental Procedure.** Aryl bromide A (3.0 mmol), aryl bromide B (3.0 mmol), propiolic acid (252.2 mg, 3.6 mmol), Pd(PPh₃)₄ (173.2 mg, 0.15 mmol) and DBU (1.09 g, 7.2 mmol) was mixed with DMSO (6 mL). The mixture was stirred at 35 °C for 24 h and 60 °C for 12 h. The resulting solution was poured into H₂O and extracted with Et₂O. The organic layer was dried over MgSO₄ and filtered. The solvent was removed under reduced pressure, and the resulting crude product was purified by recrystallization with warm hexane.

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**References**