ORGANIC LETTERS

2008
Vol. 10, No. 3
433−436

Palladium(0)-Catalyzed Decarboxylation of Buta-2,3-dienyl 2′-Alkynoates: Approach to the Synthesis of 2-Alkynyl Buta-1,3-dienes

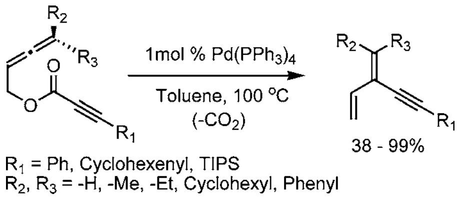
So Hee Sim, Hee-Jun Park, Sang Ick Lee, and Young Keun Chung*

Intelligent Textile System Research Center, and Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151-747, Korea

ykchung@plaza.snu.ac.kr

Received October 23, 2007

ABSTRACT



The Pd(PPh$_3$)$_4$-catalyzed decarboxylation of buta-2,3-dienyl 2′-alkynoates allows the rapid construction of 2-alkynyl buta-1,3-dienes. The carbon–carbon bond-forming reaction occurs at the central position of an allene moiety.

The development of catalytic versions of C−C bond-forming processes is a topic of great importance in modern organic chemistry.[1] In this context, transition-metal-catalyzed decarboxylative couplings[2] continue to attract a great deal of attention because they allow the use of readily available carboxylic acids or esters under neutral conditions to produce a C−C coupling product and CO_2 as the only byproduct. In particular, palladium-catalyzed decarboxylative couplings have been widely used in many useful reactions, such as a decarboxylative Heck coupling,[3] aldol addition,[4] decarboxylative alkylation,[5] decarboxylative aza-Michael addition−allylation,[6] decarboxylative cross-coupling,[7] and decarboxylative protonation.[8]

---

(1) (a) McFadden, R. M.; Stoltz, B. M. *J. Am. Chem. Soc.* **2006**, *128*, 7738−7739. (b) Trost, B. M.; Bream, R. N.; Xu, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 3109−3112. (c) Patil, N. T.; Huo, Z.; Yamamoto, Y. *J. Org. Chem.* **2006**, *71*, 6991−6995. (d) Wang, C.; Tunge, J. A. *Org. Lett.* **2006**, *8*, 3211−3214. (e) Ragoussis, V.; Giannikopoulos, A. *Tetrahedron Lett.* **2006**, *47*, 683−687. (f) Rayabarapu, D. K.; Tunge, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 13510−13511. (g) Mohr, J. T.; Behenna, D. C.; Harned, A. M.; Stoltz, B. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 6924−6927. (h) Magdziak, D.; Lalic, G.; Lee, H. M.; Fortner, K. C.; Aloise, A. D.; Shair, M. D. *J. Am. Chem. Soc.* **2005**, *127*, 7284−7285. (i) Kuwano, R.; Ishida, N.; Murakami, M. *Chem. Commun.* **2005**, 3951−3952. (j) Trost, B. M.; Xu, J. *J. Am. Chem. Soc.* **2005**, *127*, 2846−2847.

(2) (a) Waetzig, S. R.; Tunge, J. A. *J. Am. Chem. Soc.* **2007**, *129*, 4138−4139. (b) Goossen, L. J.; Deng, G.; Levy, L. M. *Science* **2006**, *313*, 662−664. (c) Waetzig, S. R.; Rayabarapu, D. K.; Weaver, J. D.; Tunge, J. A. *Angew. Chem., Int. Ed.* **2006**, *45*, 4977−4980. (d) Burger, E. C.; Tunge, J. A. *Org. Lett.* **2004**, *6*, 4113−4115. (e) Trost, B. M.; Xu, J. *J. Am. Chem. Soc.* **2005**, *127*, 17180−17181. (f) You, S.-L.; Dai, L.-X. *Angew. Chem., Int. Ed.* **2006**, *45*, 5246−5248. (g) Nakamura, M.; Hajra, A.; Endo, K.; Nakamura, E. *Angew. Chem., Int. Ed.* **2005**, *44*, 7248−7251.

(3) (a) Myers, A. G.; Tanaka, D.; Mannion, M. R. *J. Am. Chem. Soc.* **2002**, *124*, 11250−11251. (b) Tanaka, D.; Myers, A. G. *Org. Lett.* **2004**, *6*, 433−436. (c) Tanaka, D.; Romeril, S. P.; Myers, A. G. *J. Am. Chem. Soc.* **2005**, *127*, 10323−10333.

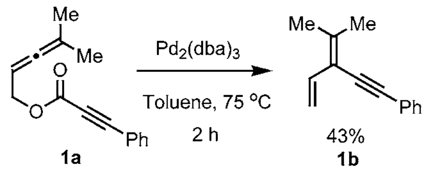
(4) (a) Lou, S.; Westbrook, J. A.; Schaus, S. E. *J. Am. Chem. Soc.* **2004**, *126*, 11440−11441. (b) Lalic, G.; Aloise, A. D.; Shair, M. D. *J. Am. Chem. Soc.* **2003**, *125*, 2852−2853. (c) Orlandi, S.; Benaglia, M.; Cozzi, F. *Tetrahedron Lett.* **2004**, *45*, 1747−1749.

(5) (a) Burger, E. C.; Tunge, J. A. *Org. Lett.* **2004**, *6*, 2603−2605. (b) Tunge, J. A.; Burger, E. C. *Eur. J. Org. Chem.* **2005**, 1715−1726. (c) Behenna, D. C.; Stoltz, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 15044−15045. (d) Waetzig, S. R.; Rayabarapu, D. K.; Weaver, J. D.; Tunge, J. A. *Angew. Chem., Int. Ed.* **2006**, *45*, 4977−4980. (e) Imao, D.; Itoi, A.; Yamazaki, A.; Shirakura, M.; Ohtoshi, R.; Ogata, K.; Ohmori, Y.; Ohta, T.; Ito, Y. *J. Org. Chem.* **2007**, *72*, 1652−1658. (f) You, S.-L.; Dai, L.-X. *Angew. Chem., Int. Ed.* **2006**, *45*, 5246−5248. (g) Nakamura, M.; Hajra, A.; Endo, K.; Nakamura, E. *Angew. Chem., Int. Ed.* **2005**, *44*, 7248−7251. (h) Burger, E. C.; Tunge, J. A. *J. Am. Chem. Soc.* **2006**, *128*, 10002−10003. (i) Knight, J. G.; Ainge, S. W.; Harm, A. M.; Harwood, S. J.; Maughan, H. I.; Armour, D. R.; Hollinshead, D. M.; Jaxa-Chamiec, A. A. *J. Am. Chem. Soc.* **2000**, *122*, 2944−2945. (j) Sabrina, R. S; Siegfried, B. *Angew. Chem., Int. Ed.* **2007**, *46*, 3966−3970. (k) Yeagley, A. A.; Chruma, J. J. *Org. Lett.* **2007**, *9*, 2879−2882.

10.1021/ol702577g CCC: $40.75

Allenynes are very interesting substrates because of their high degree of unsaturation.[9] Thus, they have been used as substrates in various catalytic reactions, including cycloisomerization,[10] [2 + 2] cycloaddition reaction,[11] ring-closing metathesis,[12] Pauson−Khand reactions,[13] and ene-type reactions.[14] Recently, we found that there has been no example of palladium-catalyzed decarboxylation that involves buta-2,3-dienyl 2′-alkynoates. Furthermore, if we control the decarboxylation reaction, 2-alkynyl buta-1,3-dienes instead of allenynes would be obtained. Recently, Shi reported[15] the synthesis of 2-alkynyl buta-1,3-dienes by the reaction of the corresponding diiodides from methylenecyclopropanes with substituted alkynes via Sonogashira coupling in the presence of $Pd(PPh_3)_4$/CuI catalysis. Formation of 2-alkynyl buta-1,3-dienes by the reaction of cross-metathesis of 1,3-diynes with an olefin was also reported by Lee.[16] 2-Ethynyl buta-1,3-diene has been used as the diene component in Diels−Alder addition reactions.[17] Recently, π-conjugated polymers have been widely explored as advanced materials for electronic and photonic applications.[18] Many chromophores have 2-phenylethynyl buta-1,3-diene as a substructure.[19] Herein we report a new approach to conjugated dienynes that relies upon the palladium-catalyzed decarboxylation of allenyl alkynoates.

Decarboxylation was studied using 4-methylpenta-2,3-dienyl 3-phenylpropiolate (**1a**) as a model substrate and $Pd_2(dba)_3$ as a catalyst in toluene at 75 °C (eq 1). After 2 h of reaction time, 2-phenylethynyl buta-1,3-diene (**1b**) was obtained in 43% yield.



1a **1b** (1)

Thus, we initially screened the reaction parameters, such as the palladium catalyst, the reaction solvent, the reaction temperature, and the reaction time, for the decarboxylation of **1a** (Table 1).

Table 1. Pd-Catalyzed Decarboxylation of **1a**[a]

entry	catalyst	solvent	T (°C) [t (h)]	yield (%)[b]
1	2.5 mol % of $Pd_2(dba)_3$	toluene	75 [2]	43
2	2.5 mol % of $Pd_2(dba)_3$/dppe(1:1)	toluene	75 [0.5]	>99
3	5 mol % of $Pd(PPh_3)_4$	toluene	75 [0.5]	>99
4	1 mol % of $Pd(PPh_3)_4$	toluene	75 [0.5]	99
5	1 mol % of $Pd(PPh_3)_4$	toluene	25 [24]	n.r.[c]
6	1 mol % of $Pd(PPh_3)_4$	toluene	45 [24]	34 (37)
7	1 mol % of $Pd(PPh_3)_4$	THF	75 [24]	12 (74)
8	1 mol % of $Pd(PPh_3)_4$	DCE	75 [24]	47 (50)
9	1 mol % of $Pd(OAc)_2/PPh_3$ (1:1)	toluene	75 [6]	67
10	1 mol % of $[C_3H_5]PdCl{-}NHC(Ipr)$	toluene	75 [24]	n.r.

[a] **1a** (0.12 g, 0.54 mmol) in 5 mL of solvent was used. [b] Isolated yield. [c] n.r. = no reaction.

An addition of dppe to $Pd_2(dba)_3$ slightly increased the catalytic activity (entry 2). However, as Table 1 shows, $Pd(PPh_3)_4$ was the best catalyst of those examined. The loading of the catalyst can be lowered to 1 mol % with a quantitative yield (entry 4). When the solvent and the reaction temperature were screened using $Pd(PPh_3)_4$ as a catalyst (entries 4−8), the best yield (>99%) was obtained in toluene at 75 °C for 0.5 h (entry 4). The $Pd(OAc)_2/PPh_3$ (1:1) system shows a slightly lower activity (entry 9). Complex (π-C_3H_5)-Pd(IPr)Cl (IPr = *N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-

---

(6) (a) Patil, N. T.; Huo, Z.; Yamamoto, Y. *J. Org. Chem.* **2006**, *71*, 6991−6995. (b) Bourgeois, D.; Craig, D.; Grellepois, F.; Mountford, D. M.; Stewart, A. J. W. *Tetrahedron* **2006**, *62*, 483−495. (c) Craig, D.; Grellepois, F. *Org. Lett.* **2005**, *7*, 463−465.

(7) (a) Goossen, L. J.; Rodriguez, N.; Melzer, B.; Linder, C.; Deng, G.; Levy, L. M. *J. Am. Chem. Soc.* **2007**, *129*, 4824−4833. (b) Olivier, B. *Angew. Chem., Int. Ed.* **2007**, *46*, 1373−1375. (c) Becht, J.-M.; Catala, C.; Le Drian, C.; Wagner, A. *Org. Lett.* **2007**, *9*, 1781−1783. (d) Goossen, L. J.; Melzer, B. *J. Org. Chem.* **2007**, *72*, 7473−7476.

(8) (a) Mohr, J. T.; Nishimata, T.; Behenna, D. C.; Stoltz, B. M. *J. Am. Chem. Soc.* **2006**, *128*, 11348−11349. (b) Matsubara, S.; Yokota, Y.; Oshima, K. *Org. Lett.* **2007**, *9*, 2071−2073. (c) Olivier, R.; Abdelkhalek, R.; Françoise, H.; Jacques, M. *Eur. J. Org. Chem.* **2002**, 3986−3994.

(9) (a) Hashmi, A. S. K. In *Modern Allene Chemistry*; Krause, N., Hashmi, A. S. K., Eds.; Wiley-VCH: Weinheim, Germany, 2004; pp 877−923. (b) Brummond, K. M.; Chen, H. In *Modern Allene*; Krause, N., Hashmi, A. S. K., Eds.; Wiley-VCH: Weinheim, Germany, 2004; pp 1041−1089. (c) Ma, S. *Chem. Rev.* **2005**, *105*, 2829−2872.

(10) (a) Lemiere, G.; Gandon, V.; Agenet, N.; Goddard, J.-P.; de Kozak, A.; Aubert, C.; Fensterbank, L.; Malacria, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 7596−7599. (b) Murakami, M.; Kadowaki, S.; Matsuda, T. *Org. Lett.* **2005**, *7*, 3953−3956. (c) Lee, S. I.; Sim, S. H.; Kim, S. M.; Kim, K.; Chung, Y. K. *J. Org. Chem.* **2006**, *71*, 7120−7123. (d) Matsuda, T.; Kadowaki, S.; Goya, T.; Murakami, M. *Synlett* **2006**, 575−578. (e) Cardran, N.; Cariou, K.; Herve, G.; Aubert, C.; Fensterbank, L.; Malacria, M.; Marco-Contelles, J. *J. Am. Chem. Soc.* **2004**, *126*, 3408−3409. (f) Jiang, X.; Ma, S. *J. Am. Chem. Soc.* **2006**, *129*, 11600−11607. (g) Jiang, X.; Ma, S. *J. Am. Chem. Soc.* **2007**, *129*, 11600−11607.

(11) (a) Mukai, C.; Hara, Y.; Miyashita, Y.; Inagaki, F. *J. Org. Chem.* **2007**, *72*, 4454−4461. (b) Ohno, H.; Mizutani, T.; Kadoh, Y.; Aso, A.; Miyamura, K.; Fujii, N.; Tanaka, T. *J. Org. Chem.* **2007**, *72*, 4378−4389. (c) Oh, C. H.; Gupta, A. K.; Park, D. I.; Kim, N. *Chem. Commun.* **2005**, 5670−5672. (d) Ohno, H.; Mizutani, T.; Kadoh, Y.; Miyamura, K.; Tanaka, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 5113−5115. (e) Alcaide, B.; Almendros, P.; Aragoncillo, C. *Org. Lett.* **2003**, *5*, 3795−3798. (f) Jiang, X.; Ma, S. *Tetrahedron* **2007**, *63*, 7589−7595.

(12) Mukai, C.; Inagaki, F.; Yoshida, T.; Kitagaki, S. *Tetrahedron Lett.* **2004**, *45*, 4117−4121.

(13) (a) Shibata, T.; Kadowaki, S.; Hirase, M.; Takagi, K. *Synlett* **2003**, 573−575. (b) Mukai, C.; Inagaki, F.; Yoshida, T.; Yoshitani, K.; Hara, Y.; Kitagaki, S. *J. Org. Chem.* **2005**, *70*, 7159−7171. (c) Mukai, C.; Hirose, T.; Teramoto, S.; Kitagaki, S. *Tetrahedron* **2005**, *61*, 10983−10994. (d) Park, J. H.; Kim, S. Y.; Kim, S. M.; Lee, S. I.; Chung, Y. K. *Synlett* **2007**, 453−459.

(14) Shibata, T.; Takesue, Y.; Kadowaki, S.; Takagi, K. *Synlett* **2003**, 268−270.

(15) Shao, L.-X.; Shi, M. *J. Org. Chem.* **2005**, *70*, 8635−8637.

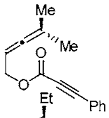
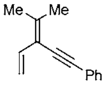
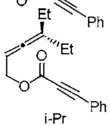
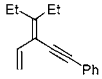
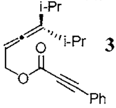
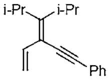
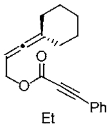
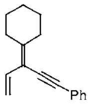
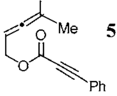
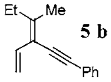
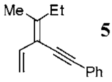
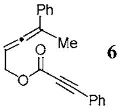
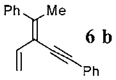
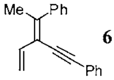
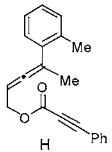
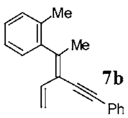
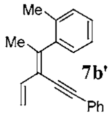
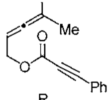
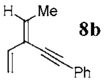
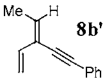
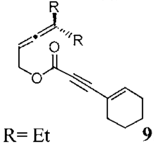
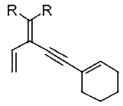
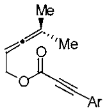
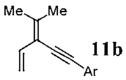
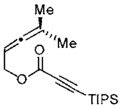
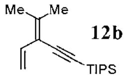
(16) Kim, M.; Miller, R. L.; Lee, D. *J. Am. Chem. Soc.* **2005**, *127*, 12818−12819.

(17) Hopf, H.; Jager, H.; Ernst, L. *Liebigs Ann.* **1996**, 815−824.

(18) (a) Kros, A.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. *Adv. Mater.* **2002**, *14*, 1779−1782. (b) Carroll, R. L.; Gorman, C. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 4378−4400. (c) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537−2574. (d) Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791−804. (e) Liphardt, M.; Goonesekera, A.; Jones, B. E.; Ducharme, S.; Takacs, J. M.; Zhang, L. *Science* **1994**, *263*, 367−369. (f) Miller, J. S. *Adv. Mater.* **1993**, *5*, 671−676. (g) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628−630. (h) Buckley, A. *Adv. Mater.* **1992**, *4*, 153−158. (i) Nalwa, H. S. *Adv. Mater.* **1993**, *5*, 341−358.

(19) (a) Michinobu, T.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Frank, B.; Moonen, N. N. P.; Gross, M.; Diederich, F. *Chem.−Eur. J.* **2006**, *12*, 1889−1905. (b) Pahadi, N. K.; Camacho, D. H.; Nakamura, I.; Yamamoto, Y. *J. Org. Chem.* **2006**, *71*, 1152−1155. (c) Michinobu, T.; May, J. C.; Lim, J. H.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Gross, M.; Biaggio, I.; Diederich, F. *Chem. Commun.* **2005**, 737−739.

Table 2. Pd(PPh$_3$)$_4$-Catalyzed Decarboxylation of Buta-2,3-dienyl 2′-alkynoates[a]

entry	reactant	product	T(°C)[t(h)]	yield (%)[b] (E/Z)[c]
1	 **1a**	 **1b**	75(0.5)	>99
2	 **2a**	 **2b**	100(1)	>99
3	 **3a**	 **3b**	100(1) 70(3)	38 68
4	 **4a**	 **4b**	100(4)	97
5	 **5a**	 **5 b**  **5b′**	100(1) 70(3)	77(1.2:1)[c] 61(1.3:1)[c]
6	 **6a**	 **6 b**  **6b′**	100(1) 70(3)	86(2:1)[c] 62(19:1)[c]
7	 **7a**	 **7b**  **7b′**	100(1) 70(3)	93(14:1)[c] 95(15:1)[c]
8	 **8a**	 **8b**  **8b′**	100(0.5)	>99 (1.8:1)[c]
9	 R= Et **9a**	 **9b** (R= Et)	100(0.25)	92
10	R= Me **10a**	**10b** (R= Me)	100(0.5)	80
11	 **11a** (Ar= p-Tolyl)	 **11b**	100(0.5)	87
12	 **12a**	 **12b**	100(0.25)	86

[a] Buta-2,3-dienyl 2′-alkynoate (0.54 mmol) in 5 mL of solvent was used. [b] Isolated yield. [c] The ratio was determined by ^{1}H NMR

2-ylidene) has no catalytic activity (entry 10). When the reaction was carried out in toluene at 100 °C, the reaction time could be shortened to 10 min. Thus, the optimized reaction conditions were established to be as follows: 1 mol % of Pd(PPh$_3$)$_4$, toluene, and 100 °C.

We next investigated the palladium-catalyzed decarboxylation of various buta-2,3-dienyl 2′-alkynoates under the optimized reaction conditions (Table 2). The reaction time was highly dependent upon the substrate and ranged from 15 min to 1 h. The catalytic amount of Pd(PPh$_3$)$_4$ induced the decarboxylation of buta-2,3-dienyl alkynoates to produce carbon−carbon bond-coupling products of 2-alkynyl buta-1,3-dienes. The yields of 2-alkynyl buta-1,3-dienes were satisfactory, except for the case of 4-*iso*-propyl-5-methylhexa-2,3-dienyl 3-phenylpropiolate in entry 3. However, lowering the reaction temperature to 70 °C and increasing the reaction time to 3 h dramatically increased the yield from 38 to 68%.

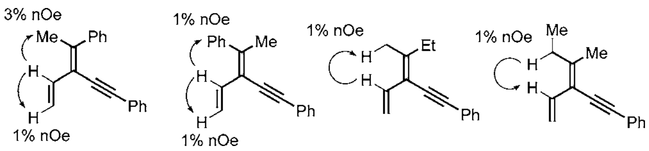


Figure 1. NOE studies of the products.

For buta-2,3-dienyl 2′-alkynoates bearing unsymmetric substituents on the allenic carbon (entries 5−8), the isomeric ratio of the two isomers (E/Z) was determined by the NOE study of the products (Figure 1). The overall yields were 77−99% with an E/Z ratio ranging from 1.2:1 to 14:1. To examine the temperature effect on the E/Z ratio of the product, the reaction temperature was lowered to 70 °C. For the substrates in entries 5 and 7, the E/Z ratio was insensitive to the reaction temperature. However, the effect of the reaction temperature on the E/Z ratio was quite dramatic for entry 6.

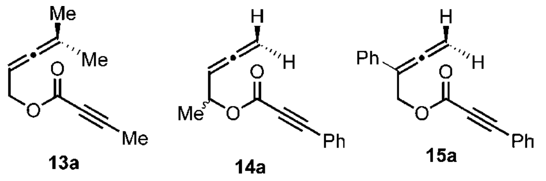


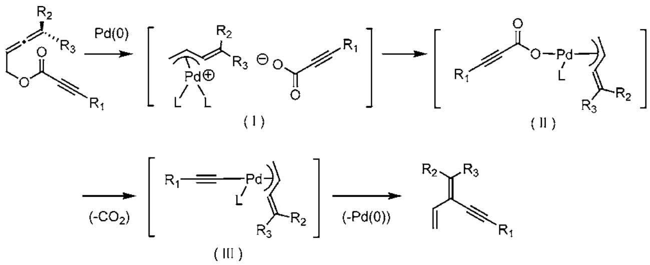
Figure 2. Other buta-2,3-dienyl 2′-alkynoates tested for Pd-catalyzed decarboxylation.

For entry 6, lowering the reaction temperature to 70 °C led to a dramatic change of the E/Z ratio from 2:1 to 19:1. The dominant existence in the E isomer compared to the Z isomer was presumably due to steric effects.

Unfortunately, our attempts to isolate major products for the substrates given in Figure 2 failed presumably due to decomposition under our reaction conditions.

The present novel palladium(0)-catalyzed carbon−carbon bond-coupling reaction is characterized by its rapidness and is unique among the reported palladium-catalyzed carbon–carbon bond-forming reactions that occur at the central position of an allene moiety. This observation suggests an intermediacy of a π-allylpalladium(II) complex. The presumed reaction pathway based on the proposition of Tunge[1f] is shown in Scheme 1. The reaction is initiated by the oxidative addition of buta-2,3-dienyl 2′-alkynoate to Pd(PPh$_3$)$_4$ to produce a π-allylpalladium(II) complex with a free or ion-paired carboxylate (**I**). Nucleophilic addition of carboxylate anion to the π-allylpalladium cation followed by decarboxylation generates a π-allylpalladium complex intermediate (**III**).

Scheme 1



A reductive elimination produces 2-alkynyl buta-1,3-diene and the palladium(0) catalyst. The result of the cross-coupling experiment shown in eq 2 is compatible with the presumed reaction pathway involving **I**.

When a crossover reaction using a mixture of **1a** and **10a** was carried out in the presence of Pd(PPh$_3$)$_4$, complete crossover was observed: a mixture of four possible crossover products was obtained in 93% yield with a ratio of 1.6:1.0:0.6:0.7 (eq 2).

$$\mathbf{2a} + \mathbf{10a} \xrightarrow[\substack{\text{Toluene} \\ 100\ ^\circ\text{C}}]{3\ \text{mol}\ \%\ \text{Pd(PPh}_3)_4} \begin{array}{ccccccc} \mathbf{2b} & + & \mathbf{10b} & + & \mathbf{1b} & + & \mathbf{9b} \\ 1.6 & & 1.0 & & 0.6 & & 0.7 \end{array} \quad \begin{array}{c} \mathbf{(2)} \\ (93\%) \end{array}$$

In conclusion, we have developed an efficient synthesis of 2-alkynyl buta-1,3-dienes from buta-2,3-dienyl 2′-alkynoates. Utilizing this and related methods for the synthesis of π-conjugated polymers will be the subject of future reports.

Acknowledgment. This work was supported by the Korea Research Foundation grant funded by the Korean Government (MOEHRD) (KRF-2005-070-C00072) and the SRC/ERC program of MOST/KOSEF (R11-2005-065). S.H.S. thanks the Brain Korea 21 fellowships and Seoul Science Fellowships.

Supporting Information Available: Experimental details and spectroscopic characterization of all isolated compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OL702577G