Palladium-Catalyzed Self-Coupling Reaction of Terminal Alkynes in the Presence of *p*-Chloranil: A Practical Method for the Synthesis of Triethynylethenes

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Abstract: Pd-catalyzed reaction of aliphatic-1-alkynes in the presence of *p*-chloranil afforded triethynylethenes as exclusive self-coupling products in good yields. On the other hand, diynes were obtained when aromatic alkynes were used.

Key words: coupling reaction, alkyne, quinone, triethynylethene, palladium catalyst

Interest in conjugated organic materials has grown because of their potential applications in molecular wires, switches, and other components for molecular electronics, nonlinear optics (NLO), organic conductors, and light-emitting diodes.[1–4] With regard to acetylenic scaffolding,[5] derivatives of 1,2-diethynylethene (**1**, DEE, hex-3-ene-1,5-diyne) and tetraethynylethene (**2**, TEE, 3,4-diethynylhex-3-ene-1,5-diyne) have provided a unique class of π-conjugated building blocks (Figure 1).[6] The interesting properties of these compounds have resulted in an array of modifications specially directed to oligomerization/polymerization.[4c] It is surprising, however, that synthetic reports and structural studies of the other module, triethynylethene (**3**, 3-ethynylhexa-3-en-1,5-diyne), is rarely reported.[7]

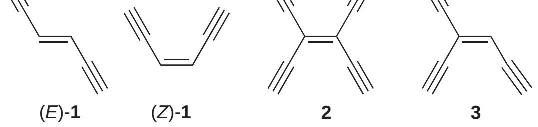
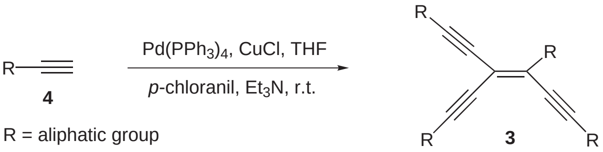


Figure 1

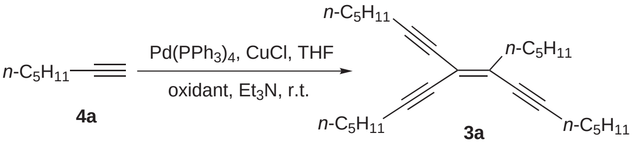
The palladium-catalyzed coupling reaction has proved to be an extremely powerful tool to construct carbon−carbon bonds.[8] In a typical Pd-catalyzed process, oxidative coupling of terminal alkynes occurred in the presence of oxidants, such as chloroacetone,[7a] bromoacetate,[9] iodine,[10] allyl bromide[11] and O_2.[12] These reactions resulted in the corresponding symmetrical 1,3-diynes in good yields. It had been reported earlier that reaction of terminal alkynes in the presence of chloroacetone (as oxidant) afforded 1,3-diynes together with triethynylethenes.[7a] As a part of our continuing program on the application of quinones as oxidants in organic synthesis,[13] herein we report a Pd(0)−Cu(I)-catalyzed reaction of aliphatic-1-alkynes **4** in the presence of *p*-chloranil, to afford triethynylethenes **3** as the exclusive self-coupling product (Scheme 1).



Scheme 1

Our method has similarities to a related process reported by Rossi and coworkers.[7a] The reaction of aliphatic 1-alkynes with tetrakis(triphenylphosphan)palladium $[Pd(PPh_3)_4]$, copper iodide, and triethylamine in benzene in the presence of chloroacetone afforded mixtures of 1,4-dialkyl-l,3-butadiynes (30–50%) and 3-ethynylhexa-3-en-1,5-diyne (28–50%). However, our procedure gave 3-ethynylhexa-3-en-1,5-diyne in excellent yields when aliphatic 1-alkynes were used. Only trace amount of 1,4-dialkyl-1,3-butadiynes was observed by GC−MS. During the course of our study, we examined other oxidants such as 1,4-benzoquinione, 2,3-dichloronaphthalene-1,4-dione, and 4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile (DDQ) and *p*-chloranil worked as a good oxidant. The results are listed in Table 1. For example, the reaction of alkynes **4a** with $Pd(PPh_3)_4$, copper chloride,

Table 1 Pd(0)-Catalyzed Self-Coupling Reaction of Hept-1-yne with Oxidants



Entry	Oxidant	Yield (%)
1	–	trace
2	1,4-benzoquinione,	32
3	2,3-dichloronaphthalene-1,4-dione	trace
4	DDQ	trace
5	*p*-chloranil	90

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and triethylamine in tetrahydrofuran in the presence of *p*-chloranil afforded **3a** in 90% yield.[14]

Under the optimized conditions, the self-coupling reaction of various terminal alkynes **4** was next examined and the results[14] are shown in Table 2.

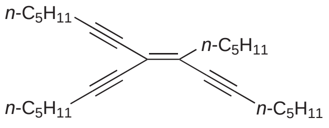
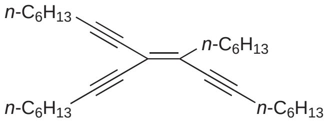
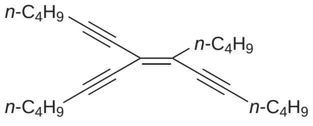
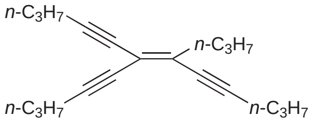
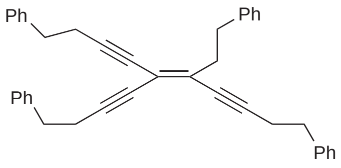
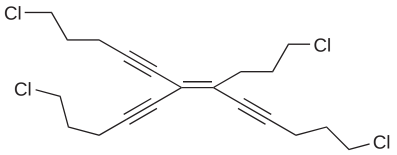
To extend the scope of the reaction, we next investigated the aromatic 1-alkynes. However, under the optimized conditions, aromatic 1-alkynes afforded good to excellent yields of diaryldiynes **5**[15] (Table 3, entries 1–3). No formation of any triethynylethenes **3** was observed. In the reaction of 1-ethynylcyclohex-1-ene, **5d**[15d] was also provided in 72% yield (Table 3, entry 4).

To investigate the reaction mechanism, we conducted a similar reaction of tetradeca-6,8-diyne (**6**) together with hept-1-yne (**4a**) under the optimized conditions (Scheme 2). Product **3a** was observed by GC−MS. No formation of cross-coupling product was observed. That means the diyne was not an intermediate.

Furthermore, we conducted the reaction using hept-1-yne (**4a**) and hex-1-yne (**4c**) in one pot under the optimized conditions as shown in Scheme 3. Several compounds, including homocoupling products (peaks A and E) and cross-coupling products (peaks B−D) were observed by GC−MS, and the results shown in Figure 2. The structures of the peaks are illustrated in Table 4.

Based on the above results, we proposed the reaction mechanism as follows. Pd(0) species reacted with oxidant to generate Pd(II). The alkynylcopper intermediate **7** is formed from the reaction of a terminal alkyne and copper chloride in the presence of triethylamine and it undergoes double transmetallation with Pd(II). The transmetallation yields the dialkynylpalladium intermediate **8**. One of the triple bonds in intermediate **8** inserts into another C−Pd bond to form intermediate **9**, which then undergoes double reductive elimination to form *sp*^{2}–*sp* coupling product **3** and Pd(0) (Scheme 4).

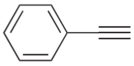
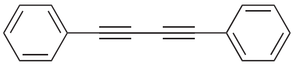
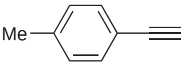
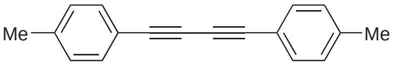
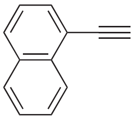
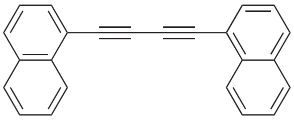
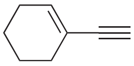
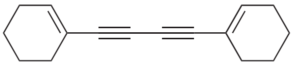
Table 2 Pd(0)-Catalyzed Self-Coupling Reaction of 1-Alkynes

Entry	R—≡	Product	Yield (%)[a]
1	n-C_5H_{11}—≡ **4a**	 **3a**	90
2	n-C_6H_{13}—≡ **4b**	 **3b**	81
3	n-C_4H_9—≡ **4c**	 **3c**	65
4	n-C_3H_7—≡ **4d**	 **3d**	52
5	$PhCH_2CH_2$—≡ **4e**	 **3e**	68
6	$Cl(CH_2)_3$—≡ **4f**	 **3f**	79[b]

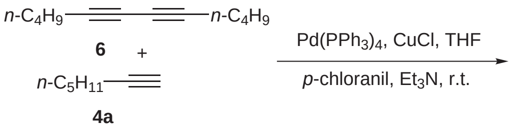
[a] Isolated yield.

[b] $Pd(PPh_3)_2Cl_2$ was used as catalyst.

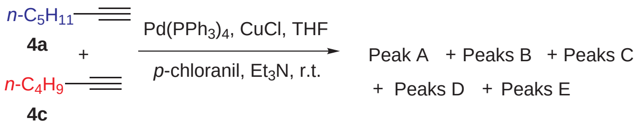
Table 3 Pd(0)-Catalyzed Homocoupling Reaction of 1-Alkynes

Entry	R—≡	Product	Yield (%)[a]
1		 **5a**	84
2		 **5b**	79
3		 **5c**	82
4		 **5d**	72

[a] Isolated yield.



Scheme 2



Scheme 3

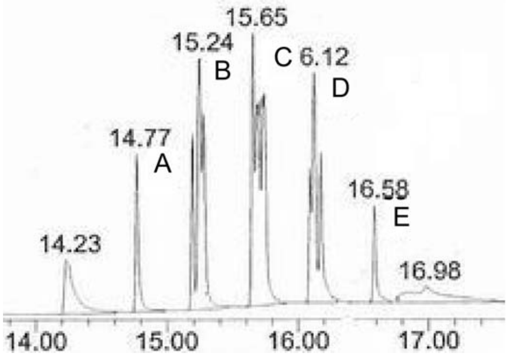


Figure 2 GC−MS chart of the cross-coupling reaction

Table 4 Cross-Coupling Reaction of Hept-1-yne (**4a**) and Hex-1-yne (**4c**)

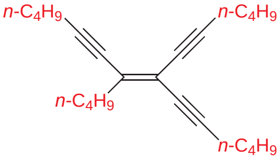
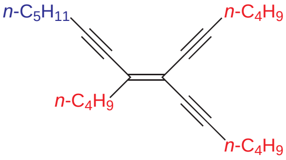
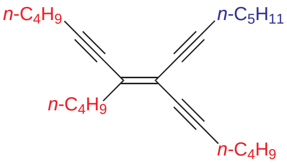
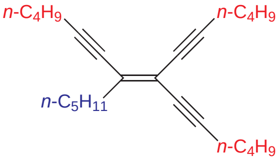
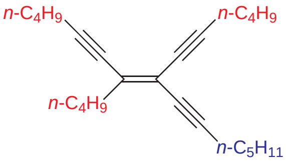
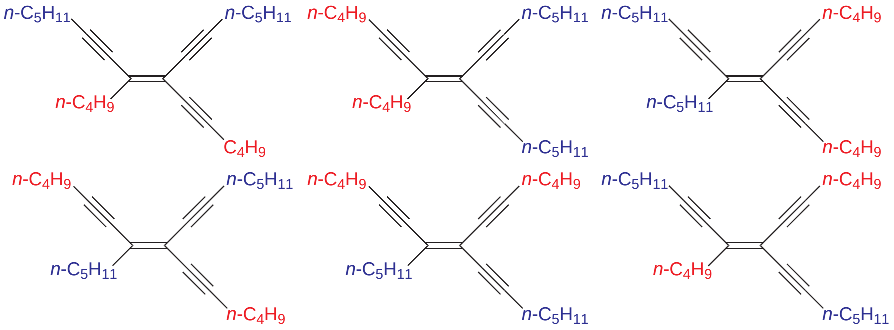
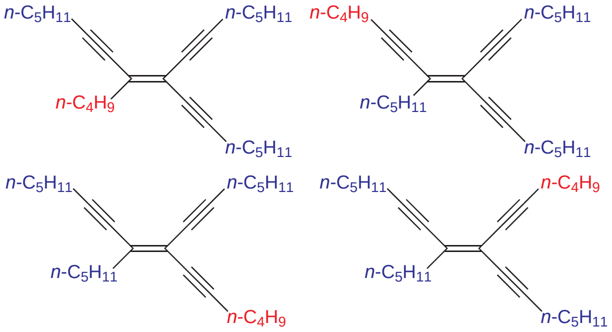
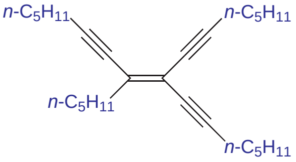
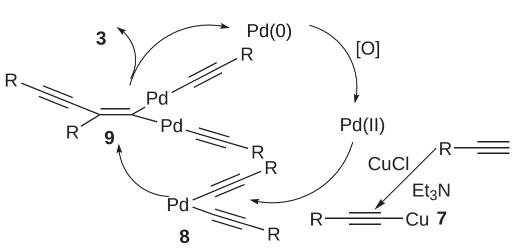
Peak	Time (min)	MW	Product
A	14.77	324	
B	15.24	338	   

Table 4 Cross-Coupling Reaction of Hept-1-yne (**4a**) and Hex-1-yne (**4c**) (continued)

Peak	Time (min)	MW	Product
C	15.65	352	
D	16.12	366	
E	16.58	380	



Scheme 4

In summary, we have developed a Pd(0)−Cu(I)-catalyzed self-coupling reaction of terminal alkynes in the presence of *p*-chloranil, to afford triethynylethenes. This simple and efficient process may be useful in the synthesis of new organic materials with interesting electronic and optical applications. Studies are in progress in order to clarify the detailed mechanism and the scope.

Acknowledgment

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(14) **Typical Reaction Procedure and Spectroscopic Data:** To a solution of $Pd(PPh_3)_4$ (40 mg, 3.5 mmol%), CuCl (2 mg, 0.5 mmol%), 1-heptyne (525 μL, 4.0 mmol) in THF (6 mL), *p*-chloranil (1.0 mmol) and Et_3N (2.6 mmol, 0.4 mL) were added under a N_2 atmosphere. The mixture was allowed to stir at r.t. for 12 h, and quenched with 3 N HCl. The resulting solution was extracted with Et_2O and washed with a sat. NaCl solution. The combined Et_2O fractions were dried over Na_2SO_4 and concentrated under vacuum to yield the crude product. The crude product was purified by flash chromatography on silica gel using PE as the eluent. Removal of the solvent yielded **3a** (342 mg) as a colorless liquid (90% isolated yield).

8-(Hept-1-ynyl)-9-pentylhexadeca-8-en-6,10-diyne (3a)
^{1}H NMR ($CDCl_3$/TMS, 300 MHz): δ = 0.88–0.93 (m, 12 H), 1.28–1.47 (m, 16 H), 1.51–1.62 (m, 8 H), 2.34–2.44 (m, 8 H). ^{13}C NMR ($CDCl_3$/TMS, 75 MHz): δ = 14.0, 19.7, 19.7, 20.0, 22.3, 22.5, 27.9, 28.4, 28.5, 28.6, 31.1, 31.4, 34.6, 77.8, 79.3, 81.0, 92.5, 96.9, 100.9, 109.3, 138.1. GC−MS: *m/z* = 380. HRMS: *m/z* calcd for $C_{28}H_{44}$: 380.3443; found: 380.3441.

9-Hexyl-10-(oct-1-ynyl)octadeca-9-en-7,11-diyne (3b)
^{1}H NMR ($CDCl_3$/TMS, 300 MHz): δ = 0.85–0.89 (m, 12 H), 1.28 (d, *J* = 2.7 Hz, 16 H), 1.34–1.59 (m, 16 H), 2.33–2.42 (m, 8 H). ^{13}C NMR ($CDCl_3$/TMS, 75 MHz): δ = 14.0, 19.7, 20.0, 22.5, 28.1, 28.5, 28.7, 28.7, 28. 8, 31.3, 31.4, 31.7, 34.6, 77.6, 79.1, 80.8, 92.5, 96.9, 100.9, 109.1, 138.1. GC−MS: *m/z* = 436. HRMS: *m/z* calcd for $C_{32}H_{52}$: 436.4069; found: 436.4071.

7-Butyl-8-(hex-1-ynyl)tetradeca-7-en-5,9-diyne (3c)
^{1}H NMR ($CDCl_3$/TMS, 300 MHz): δ = 0.86–0.93 (m, 12 H), 1.24–1.59 (m, 16 H), 2.34–2.43 (m, 8 H). ^{13}C NMR ($CDCl_3$/TMS, 75 MHz): δ = 13.5, 13.5, 13.6, 13.8, 19.30, 19.4, 21.9, 22.2, 30.3, 30.6, 30.7, 30.8, 34.3, 77.7, 79.2, 80.9, 92.3, 96.8, 100.8, 109.1, 138.0. GC−MS: *m/z* = 324. HRMS: *m/z* calcd for $C_{24}H_{36}$: 324.2817; found: 324.2815.

6-(Pent-1-ynyl)-7-propyldodeca-6-en-4,8-diyne (3d)
^{1}H NMR ($CDCl_3$/TMS, 300 MHz): δ = 0.91 (t, *J* = 7.2 Hz, 3 H), 1.00 (q, *J* = 7.2 Hz, 9 H), 1.49–1.63 (m, 8 H), 2.31–2.41 (m, 8 H). ^{13}C NMR ($CDCl_3$/TMS, 75 MHz): δ = 13.4, 13.6, 21.5, 21.6, 21.7, 22.0, 36.6, 77.8, 79.3, 81.0, 92.3, 96.8, 100.7, 109.2, 137.9. GC−MS: *m/z* = 268. HRMS: *m/z* calcd for $C_{20}H_{28}$: 268.2191; found: 268.2194.

5-Phenethyl-1,10-diphenyl-6-(4-phenylbut-1-ynyl)deca-5-en-3,7-diyne (3e)
^{1}H NMR ($CDCl_3$/TMS, 300 MHz): δ = 7.08–7.28 (m, 20 H), 2.57–2.90 (m, 16 H). ^{13}C NMR ($CDCl_3$/TMS, 75 MHz): δ = 22.0, 22.0, 22.3, 34.4, 35.0, 35.2, 35.2, 36.5, 78.1, 79.6, 81.4, 92.4, 96.8, 100.9, 109.7, 126.0, 126.3, 126.4, 128.3, 128.4, 128.5, 128.5, 137.2, 140.5, 140.6, 140.7, 141.5. HRMS: *m/z* calcd for $C_{40}H_{36}$: 516.2817; found: 516.2820.

1,12-Dichloro-6-(5-chloropent-1-ynyl)-7-(3-chloropropyl)dodeca-6-en-4,8-diyne (3f)
^{1}H NMR ($CDCl_3$/TMS, 300 MHz): δ = 1.95–2.08 (m, 8 H), 2.52–2.68 (m, 8 H), 3.52–3.75 (m, 8 H). ^{13}C NMR ($CDCl_3$/TMS, 75 MHz): δ = 17.0, 17.2, 17.4, 31.2, 31.3, 31.8, 43.6, 43.6, 43.7, 44.3, 77.9, 79.7, 81.2, 91.2, 96.1, 99.7, 110.2, 136.5. GC−MS: *m/z* = 408. HRMS: *m/z* calcd for $C_{20}H_{24}Cl_4$: 404.0632; found: 404.0636.

(15) NMR data for **5a**−**d** were in accordance with literature values: (a) Organ, M. G.; Ghasemi, H.; Valente, C. *Tetrahedron* **2004**, *60*, 9453. (b) Damle, S. V.; Seomoon, D.; Lee, P. H. *J. Org. Chem.* **2003**, *68*, 7085. (c) Rodríguez, J. G.; Tejedor, J. L. *Tetrahedron* **2005**, *61*, 3033. (d) Loupy, A.; Meyer, G.; Tchoubar, B. *Tetrahedron* **1978**, *34*, 1323.