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Synthesis of (*E*)-1,2-Divinyl-1,2-diethynylethene (DVDEE) via the Palladium-Catalyzed Reaction of Conjugated Diynes. A New Building Block for Molecular Scaffolding

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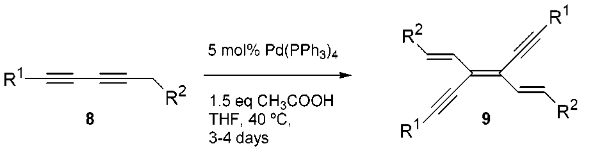
In the past decades, considerable attention has been devoted to the exploration of conjugated organic materials and polymers as sources of advanced materials for electronic and optical applications.[1] In acetylenic scaffolding,[2] derivatives of tetraethynylethene (**1**, TEE, 3,4-diethynylhex-3-ene-1,5-diyne) and (*E*)-1,2-diethynylethene (**2**, DEE, (*E*)-hex-3-ene-1,5-diyne) have provided a unique class of π-conjugated building blocks (Chart 1).[3] Owing to their planar, one- and two-dimensionally conjugated frameworks, interesting structural, redox, electronic properties, photochemical switching,[4] and nonlinear optical (NLO) observations[5] have been disclosed. The interesting properties of these compounds have resulted to an array of modifications especifically directed to oligomerization/polymerization and donor/acceptor substitution.[5c] The expansion of the central olefinic fragment of TEEs and DEEs leading to allenes **(±)-3** and **4**[6] and butatrienes **5** and **6**[7] (Chart 1) has also been explored. It is surprising, however, that synthetic reports and structural studies of a potentially viable module, containing trans divinyl-diethynyl around the central olefinic fragment, for acetylenic scaffolding, have not been made. Herein we report the direct and simple synthesis of compounds containing the core module (*E*)-1,2-divinyl-1,2-diethynylethene **7**, which we defined as DVDEE.

The palladium-catalyzed carbon−carbon bond formation in the intramolecular cyclization of *nonconjugated diynes* occurs in the presence of acetic acid.[8] The key in this process was the in situ formation of palladium−hydride species. In an attempt to form the Pd−H species in the regioselective addition of phenols to *conjugated diynes* by addition of acetic acid,[9] we observed that no addition of phenol occurred. Instead dimerization of the diyne took place with no incorporation of phenol.[10] The observation then led us to focus on optimizing this intriguing dimerization process. Thus in the presence of 5 mol % $Pd(PPh_3)_4$ and 1.5 equiv of acetic acid in THF at 40 °C for 3−4 days, the conjugated diyne **8** undergoes dimerization to give **9** in moderate to good yields (eq 1).



(1)

Chart 1. Carbon-Rich Building Blocks for Acetylenic Scaffolding

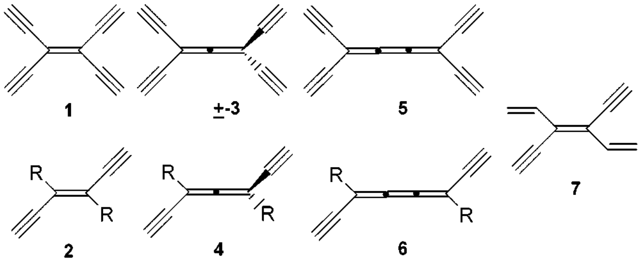
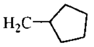


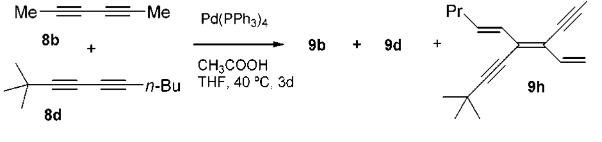
Table 1. Pd-Catalyzed Dimerization of Conjugated Diynes **8**[a]

Entry	Diyne **8**	Product **9**	Yield %[b]
1	**8a** (R^1= *n*-Butyl; R^2= *n*-Propyl)	**9a**	66
2	**8b** (R^1= Methyl; R^2= H)	**9b**	71
3	**8c** (R^1=  ;R^2= cyclopentyl)	**9c**	63
4	**8d** (R^1= *t*-Butyl; R^2= *n*-Propyl)	**9d**	60
5	**8e** (R^1= *t*-Butyl; R^2= CH_2Ph)	**9e**	82
6	**8f** (R^1= TMS; R^2= *n*-Propyl)	**9f**	40
7	**8g** (R^1= TMS; R^2= cyclopentyl)	**9g**	41

[a] The reaction of **8** (1.0 mmol) was carried out in the presence of 5 mol % $Pd(PPh_3)_4$ and 1.5 equiv of acetic acid in THF at 40 °C for 3−4 days. The reaction was monitored by GC. [b] Isolated yields through silica gel column chromatography.

The results are shown in Table 1. The symmetrical conjugated diyne **8a** underwent facile dimerization to give **9a** in 66% yield. In the absence of Pd catalysts, no reaction occurred. The use of benzoic, formic, and trifluoroacetic acids did not give the desired products. Employing catalytic amounts of acetic acid gave lower yields at longer time. At higher temperatures (70−100 °C), decomposition of the diyne occurred. THF was the best solvent although 1,4-dioxane and ethyl acetate gave comparable results. Other solvents such as toluene, benzene, dichloromethane, acetonitrile, and methanol gave lower yields. Similarly, symmetrical diynes **8b** and **8c** underwent dimerization to give **9b** and **9c**, respectively, in good yields. Likewise, the dimerization of unsymmetrical diynes **8d** and **8e** also proceeded smoothly to afford **9d** and **9e**, respectively. Moreover, trimethylsilyl protected diynes **8f** and **8g** also underwent dimerization to afford **9f** and **9g**, respectively, in moderate yields. Terminal diynes, however, gave a complex polymeric mixture and phenyl monosubstituted diynes did not give dimerized products.

Cross coupling reaction was also possible as shown in the coupling of **8b** and **8d** to give in combined 65% yield of homocoupling products **9b** and **9d** and the cross coupling product **9h** in 1:1:2 statistical distribution (eq 2).



(2)

The configuration of **9** at the tetrasubstituted central olefin was established to be *E* as evidenced by NOE investigations of **9h**. Moreover, the *E* configuration was unambiguously determined by X-ray analysis of **9e**, which is stable at room temperature (Figure 1).

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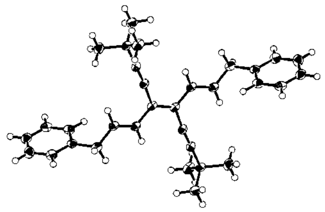
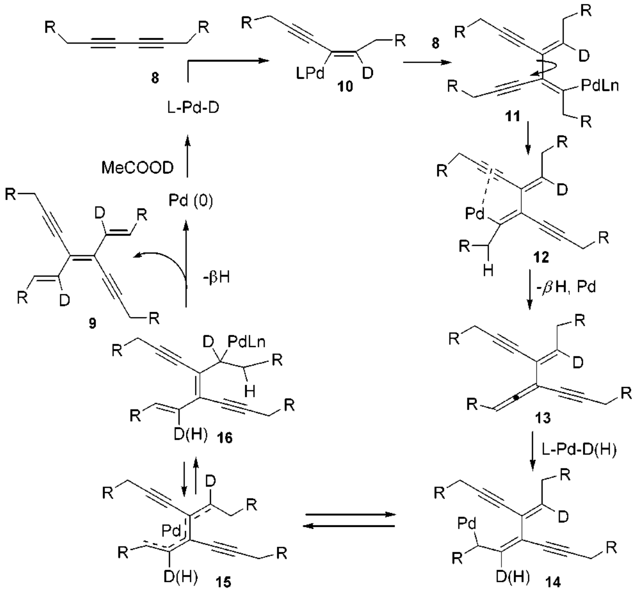


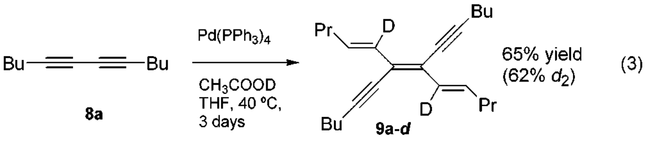
Figure 1. ORTEP representation of **9e**.

Scheme 1 *.* Plausible Mechanism



The dimerization of **8a** is representative. To an argon-flushed mixture of dry THF and $Pd(PPh_3)_4$ (0.025 mmol, 28.9 mg) was added the diyne **8a** (0.5 mmol, 0.098 mL) and acetic acid (1.5 equiv) and the mixture was stirred at 40 °C for 3−4 days. The reaction is not sensitive to air and opening the reaction vessel to allow air increases the reaction rate. The start of the reaction is indicated by a darkening of the reaction mixture from a previously clear yellow solution. After the completion of the reaction, which was monitored by GC, the mixture was then filtered through a short silica column with ethyl acetate as eluent. Separation by silica column chromatography (hexane as an eluent) afforded the dimerized product **9a** in 66% yield.

To shed light on the mechanism, a deuterium-labeling experiment was carried out. The homocoupling of **8a** in the presence of deuterated acetic acid gave the dimerized product **9a**-*d* in 65% yield with 62% d_2 incorporation as shown in eq 3. Deuterium incorporation on other carbons were not observed.



(3)

A plausible mechanism is shown in Scheme 1. Formation of palladium-deuteride species occurs followed by deuteriopalladation to give **10**. Insertion of the second diyne gives **12**,[11] which then undergoes β-hydride elimination to give **13**. Facile readdition of Pd-D species affords **14**, which then undergoes rearrangement to give **16**. β-Hydride elimination then gives **9** and Pd(0) is regenerated.

The proposed mechanism is consistent with the absence of reaction for terminal and phenyl-monosubstituted diynes. In fact, it seems that for the dimerization to occur, the starting conjugated diyne **8** should have no further aromatic conjugation. Thus the silyl-substituted DVDEEs such as **9f** and **9g** serve as the attractive module for further functionalization, such as oligomerization and donor/acceptor attachments, for electronic and optical investigations. As shown in the crystal structure, the DVDEE core module is flat, which satisfies the planarity criterion for efficient conjugation in NLO materials. Moreover, all compouds are stable in solution for several months and **9e** is stable even in neat solution.

The present Pd-catalyzed reaction is unprecedented and the synthesis of the DVDEE core module has not been known previously. This simple and efficient process may be useful in the synthesis of a new class of organic material with interesting electronic and optical applications.

Supporting Information Available: Experimental details, compound data, and X-ray data for **9e** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Due to the Pd−alkyne interaction, **12** may be more stable than **11**.

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