Palladium-Catalyzed Reductive Dimerizations of Highly Functionalized Allenes

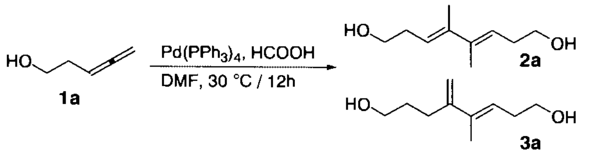
Chang Ho Oh,* Hee Sang Yoo, and Seung Hyun Jung
Department of Chemistry, Hanyang University, Sungdong-Gu, Seoul 133-791, Korea

(Received August 20, 2001; CL-010816)

A palladium compound in the presence of an equivalent of formic acid catalyzed reductive dimerizations of various allenes to the corresponding dienes.

Allenes are three-carbon functional groups possessing a 1,2-diene moiety and serve as valuable synthons in synthetic organic chemistry, and with proper substitution, they possess axial chirality.[1] The interesting reactivity of allenes originates mainly from their unique strained structure spreading over three contiguous carbons and thus a variety of preparation methods are available to construct the 1,2-diene moieties. In the past three decades allenes have attracted considerable attention in synthetic organic chemistry.[2] Among them, palladium-catalyzed reactions of allenes have been most extensively investigated to exhibit numerous transformations with a high level of selectivity.[3] Palladium catalyzed reactions of allenes are known generally to proceed via π-allylpalladium intermediates, which react with a wide variety of carbon and heteroatom nucleophiles.

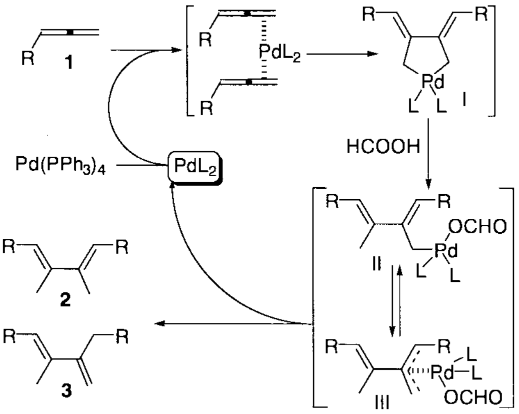
Allenes are known to be dimerized catalytically to give the cross-conjugated trienes.[4] Recently, Yamaguchi described an efficient synthesis of cross-conjugated trienes by the reaction of allenes with a catalyst combination of $Pd_2(dba)_3$ (dba = dibenzylideneacetone), *p*-nitrophenol as a promoter and $P(p\text{-tol})_3$.[5] During our study on palladium-catalyzed cyclizations of allenynes, we found that a palladium compound in the presence of an equivalent of formic acid catalyzed reductive dimerizations of allenes to the corresponding dienes and now we wish to report our preliminary results. We prepared several structurally diverse allenes according to the known procedures.[6] When the allene **1a** was treated with 1 mol% $Pd(PPh_3)_4$ in the presence of 1.2 equivalents of formic acid in DMF, the reaction occurred within 12 h at 30 °C to give a 1:1 mixture of products **2a** and **3a** after HPLC separation as shown in eq 1. This is the first successful example for reductive dimerizations of allenes.



(1)

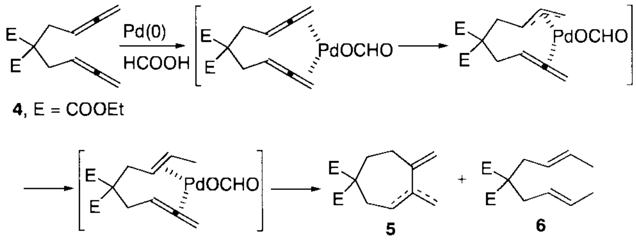
Formic acid could play an important role in reductive cleavage of the alkylpalladium intermediates.[7] It should be noted that the products were formed from center-to-center bond formation. The reductive dimerizations of various allenes under the above conditions proceeded well to give the corresponding dienes as shown in Table 1.

All reactions smoothly underwent C–C coupling between central carbons of allene groups at moderate temperature within 20 h in good yields (39–83% yields).[8] Functional groups in the substrates were tolerable varying from ether, hydroxy, and double or triple bonds.



Scheme 1.

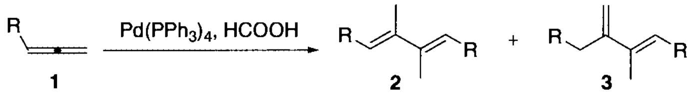
Mechanistic explanation was inferred from similar palladium-catalyzed reactions as shown in Scheme 1.[5] The possible catalytic species, PdL_2, might be coordinated with two molecules of the allene **1**, and then form palladacyclopentane intermediate I. The intermediate I could then react with HCOOH to give the allylpalladium intermediate II which could form the π–allylpalladium formate III.

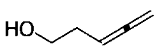
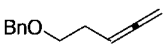
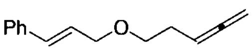
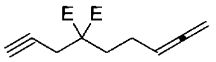
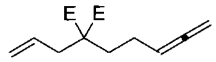
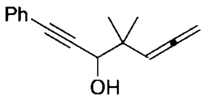
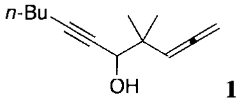


Scheme 2.

Finally, reductive cleavage of the π-allylpalladium formate III occurred at 1- and 3-positions to give the dienes **2** and **3**, respectively. For the allenes possessing sterically bulky R-group, reductive cleavage of π-allylpalladium intermediates occurred at the more hindered site to afford the dienes **3** exclusively.[3a] The intramolecular version was not successful. Treatment of bis(allene) **4** with the same conditions was expected to give the product **5**, but only the product **6** was isolated in low yield as shown in Scheme 2. Because of its steric demand in the intramolecular reaction, the bisallene **4** might not be simultaneously coordinated with the palladium catalyst; hence the reaction might proceed via π–allylpalladium intermediate followed by the rapid reductive elimination prior to carbon–carbon bond formation.

Table 1. Palladium-catalyzed dimerization/reductions of allenes



Entry	Substrates	Reagents (equivalent)	Solvent, Temp/°C, Time/h	Products	Yield/%
1	 **1a**	$Pd(PPh_3)_4$ (0.01), HCOOH (1.2)	DMF, 30, 12	**2a**, **3a** (1:1)	42
2	 **1b**	$Pd(PPh_3)_4$ (0.03), HCOOH (2.0)	DMF, 50, 3	**2b**, **3b** (1:1)	48
3	 **1c**	$Pd(PPh_3)_4$ (0.03), HCOOH (1.2)	DMF, rt, 6	**2c**, **3c** (1:1)	57
4	 **1d**	$Pd(PPh_3)_4$ (0.03), HCOOH (1.2)	DMF, rt, 7	**2d**, **3d** (1:1)	39
5	 **1e**	$Pd(PPh_3)_4$ (0.03), HCOOH (1.2)	DMF, rt, 5	**2e**, **3e** (1:1)	83
6	 **1f**	$Pd(PPh_3)_4$ (0.03), HCOOH (2.0)	Toluene, 35, 6	**3f**	75
7	 **1g**	$Pd(PPh_3)_4$ (0.03), HCOOH (2.0)	Toluene, 35, 20	**3g**	60

In summary, we have shown for the first time that a sequential dimerization/reduction of various allenes to the corresponding dienes was achieved in good to excellent yields.

This work was supported by Hanyang University, Korea, made in the program year of 2001. C. H. Oh thanks refrees for helpful suggestions in preparing this manuscript.

References and Notes

1 a) G. M. Coppola and H. F. Schuster, "Allenes in Organic Synthesis," Wiley, New York (1984). b) D. J. Pasto, *Tetrahedron*, **40**, 2805 (1984). c) R. Zimmer, C. U. Dinesh, E. Nandanan, and F. A. Khan, *Chem. Rev.*, **100**, 3067 (2000).

2 a) R. Zimmer, *Synthesis*, **1993**, 165. b) R. Grigg and V. Sridharan, *Pure Appl. Chem.*, **70**, 1047 (1998). c) M. Lautens, T. Rovis, N. D. Smith, and D. Ostrovsky, *Pure Appl. Chem.*, **70**, 1059 (1998).

3 a) J. Tsuji, "Palladium Reagents and Catalysis: Innovation in Organic Synthesis," Wiley, New York (1995). b) T. E. Müller and M. Beller, *Chem. Rev.*, **98**, 675 (1998). c) A. de Meijere and F. E. Meyer, *Angew. Chem., Int. Ed. Engl.*, **33**, 2379 (1994).

4 a) M. Englert, P. W. Jolly, and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **11**, 136(1972). b) D. J. Pasto, N. -Z. Huang, and C. W. Eigenbrot, *J. Am. Chem. Soc.*, **107**, 3160 (1985). c) D. R. Coulson, *J. Org. Chem.*, **38**, 1483 (1973).

5 M. Arisawa, T. Sugihara, and M. Yamaguchi, *Chem. Commun.*, **1998**, 2615.

6 a) W. G. Dauben and G. Shapiro, *J. Org. Chem.*, **49**, 4252 (1984). b) M. A. Henderson and C. H. Heathcock, *J. Org. Chem.*, **53**, 4736 (1988). c) C. Jonasson, A. Horvath, and J. Backvall, *J. Am. Chem. Soc.*, **122**, 9600 (2000). d) For Crabbe reaction, see, F. Crabbe, B. Nassim, and M-T. Robert-Lopes, *Org. Synth. Coll.*, **1990**, 276.

7 a) C. H. Oh, C. Y. Rhim, J. H. Kang, A. Kim, B. S. Park, and Y. Seo, *Tetrahedron Lett.*, **37**, 8875 (1996). b) C. H. Oh and H. H. Jung, *Tetrahedron Lett.*, **40**, 1535 (1999). c) C. H. Oh, H. H. Jung, J. S. Kim, and S. W. Cho, *Angew. Chem. Int. Ed.*, **39**, 752 (2000).

8 General procedure for dimerization/reduction of **1a**: In a 5-mL round-bottomed flask were placed allene **1** (70.2 mg, 0.821 mmol) and tetrakis(triphenylphosphine)palladium(0) (10.3 mg, 0.0088 mmol). Dry DMF (1.5 mL) was added to the above mixture by a syringe under argon atmosphere. And then formic acid (39 μL, 0.992 mmol) was added to the reaction mixture by a microsyringe at 0 °C. The reaction mixture was stirred for 12 h in a preheated 30 °C oil bath. Then extractive work-up and solvent evaporation under reduced pressure gave the crude products which were purified on flash column chromatography (eluent: hexane/ethyl acetate (1:1)) to give a 1: 1 mixture of **2a** and **3a** (overall 33.4 mg, 48%) as colorless oil.