



# Chemoselectivities in palladium- and rhodium-catalyzed allenyne cyclizations

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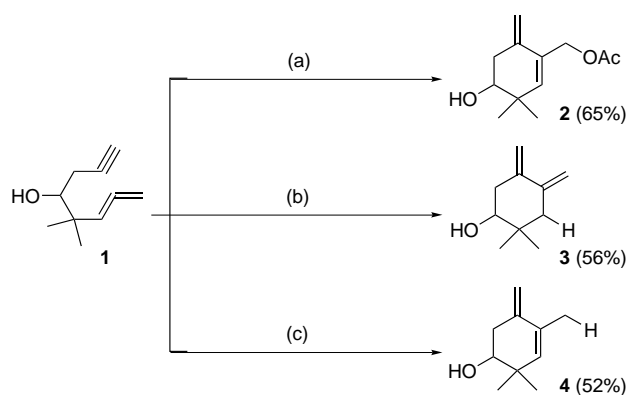
**Abstract**—Allenynes exhibited different modes of cyclizations depending on metallic catalysts. Palladium compounds would catalyze 1,7-allenynes to the corresponding six-membered carbocycles incorporating a hydrogen or an acetate group depending upon additives used. A rhodium compound catalyzed the cyclization of those allenynes to give the five membered rings chemoselectively. © 2001 Elsevier Science Ltd. All rights reserved.

Transition metal-catalyzed carbon–carbon bond-forming reactions based on allenes are of current interest in organic synthesis.<sup>1</sup> As only a few study of transition metal-mediated cyclizations involving allenes are found in the literature,<sup>2</sup> no systematic studies on the feasibility and selectivity of the cyclization have been executed.<sup>3</sup> Sato and co-workers studied allenyne cyclization mediated by Ti(II) to give the corresponding five-membered carbocycles.<sup>4</sup> We have long been interested in searching an efficient and selective methodology for enyne and enediyne cycloreductions using transition metal catalysts.<sup>5</sup> As a part of our continuing studies, we envisaged that transition metal-catalyzed cyclizations of allenynes could allow opportunities to develop novel transformations characteristic of these compounds. Allenynes, designed as synthetic homologues of enynes, have two functional groups of a triple bond and an allene.

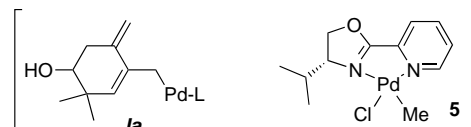
Here, we wish to report our preliminary results on the first examples of the transition metal-dependent cyclizations of 1,7-allenynes.<sup>6</sup> When allenyne **1** was heated with 3 mol% of Pd(PPh<sub>3</sub>)<sub>4</sub> and 1.2 equiv. of acetic acid in toluene for 3 h, the cyclization was completed to give the six-membered carbocycle **2** (65% yield) as a major product. (Scheme 1). When allenyne **1** was heated with 5 mol% of Pd(OAc)<sub>2</sub>, 10 mol% of PPh<sub>3</sub> and 1.2 equiv. of formic acid in toluene, the reaction was completed within 0.2 h but gave the cycloreduced product **3**.

Mechanistically, we assumed that hydropalladation at a triple bond followed by carbopalladation at the allene might give the allylpalladium intermediate **1a**. While the

allylpalladium acetate would undergo reductive elimination to afford the acetate product **2**, the allylpalladium formate yielded the cycloreduced product **3**. Incorporation of such groups (H- or AcO-) was also found when formic acid or acetic acid was replaced by triethylsilane. Thus, when the allenyne **1** and triethylsilane (2.0 equiv.) in chloroform was heated under a catalytic system of 1:1 mixture of palladium compound **5** (5 mol%) and NaBAR<sub>4</sub> (Ar=3,5-bis-(trifluoromethyl)phenyl, 5 mol%) for 23 h, the corresponding cycloreduced product **4** was isolated in 52% yield.<sup>7</sup>



- a) 3 mol% Pd(PPh<sub>3</sub>)<sub>4</sub>, 1.2 eq AcOH, toluene, 100 °C, 3h.  
b) 5 mol% Pd(OAc)<sub>2</sub>, 10 mol% PPh<sub>3</sub>, 1.2 eq HCOOH, toluene, 80 °C, 0.2h.  
c) 5 mol% **5**, 5 mol% NaBAR<sub>4</sub>, 2.0 eq Et<sub>3</sub>SiH, CHCl<sub>3</sub>, 50 °C, 23h.



Scheme 1.

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These additive-dependent reactions were interesting and thus further tested with a similar allenyne **6**. A benzene solution of the allenyne **6** and triethylsilane (3.0 equiv.) was stirred for 2 h at 50°C under the catalytic conditions prepared from Pd<sub>2</sub>(dba)<sub>3</sub> (3 mol%), P(*o*-tol)<sub>3</sub> (6 mol%), and acetic acid (3 mol%), the cyclo-reduced product **7** was isolated in 48% yield. The allenyne **6** with 3 mol% of Pd(PPh<sub>3</sub>)<sub>4</sub> and 1.2 equiv. of formic acid in toluene afforded the cyclo-reduced product **8** in 61% yield that exhibited the same trend as those of the allenyne **1** (Scheme 2).

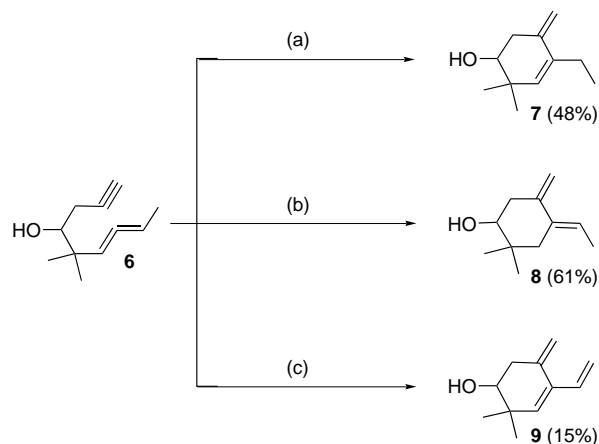
When allenyne **6** was heated with 3 mol% of Pd(PPh<sub>3</sub>)<sub>4</sub> and 1.2 equiv. of acetic acid in toluene for 3 h, the reaction was sluggish to give the six-membered triene **9** (15% yield) as an isolable product without acetate incorporation, presumably via β-elimination of alkyl-palladium intermediate like *Ia*.

The scope of allenyne cyclization reaction was then examined under rhodium catalytic conditions. A catalytic amount of tris(triphenylphosphine)rhodium chloride (5 mol%) in the presence of formic acid (1.2 equiv.) decomposed the allenyne **1**. Use of silver tetrafluoroborate (5 mol%) as an additive allowed isolation of two major products **10** and **11** as shown in Scheme 3.

Use of silver triflate instead of silver tetrafluoroborate dramatically increased the product ratio from 1:1 to 10:1 but in still low yield. Since the products **10** and **11** were expected to be highly acid sensitive, in situ hydrolysis of the products by *p*-TsOH in aqueous acetone was accomplished to give the corresponding α,β-unsaturated aldehydes **12** and **13** in 68 and 7% yields, respectively. Then, its *tert*-butyldimethylsilyl (TBS) protected allenyne **14** was tested. Cyclization of the allenyne **14** was conducted under the rhodium catalytic conditions to give the corresponding TBS-protected product **15a–b** as shown in Table 1.

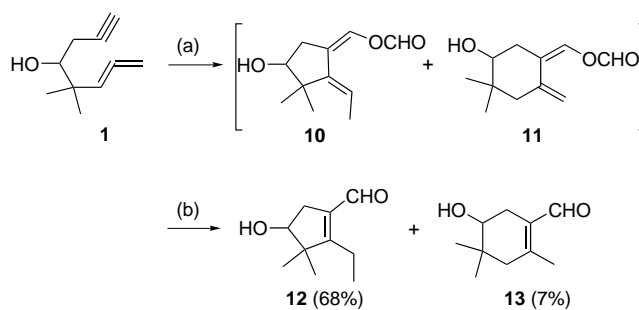
It should be worth noting that use of acetic acid as an additive afforded the acetate-incorporated product **15b** in 40% yield. Stereoselectivity in this cyclization was also excellent by analyzing <sup>1</sup>H NMR of the crude products.

In summary, allenynes **1**, **6**, and **14** exhibited different modes of cyclization reactions depending on metallic catalysts. Although we have only a few examples, the



- a) 3 mol% Pd<sub>2</sub>(dba)<sub>3</sub>, 6 mol% P(*o*-tol)<sub>3</sub>, 3 mol% CH<sub>3</sub>COOH, 3.0 eq Et<sub>3</sub>SiH, benzene, 50 °C, 2h.  
 b) 3 mol% Pd(PPh<sub>3</sub>)<sub>4</sub>, 1.2 eq HCOOH, toluene, 90 °C, 0.5h.  
 c) 3 mol% Pd(PPh<sub>3</sub>)<sub>4</sub>, 1.2 eq CH<sub>3</sub>COOH, toluene, 90 °C, 3h.

Scheme 2.

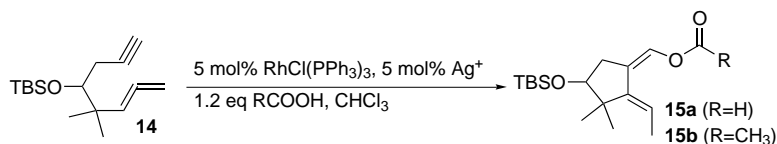


- (a) 5 mol% RhCl(PPh<sub>3</sub>)<sub>3</sub>, 5 mol% AgOTf, 1.2 eq HCOOH CHCl<sub>3</sub>, reflux, 12h; (b) *p*-TsOH (cat), acetone/H<sub>2</sub>O, 4h.

Scheme 3.

present cyclizations depending upon metallic catalyst afforded the important organic compounds with a good synthetic potential. Incorporation of a hydrogen or an acetate group in the palladium-catalyzed allenyne cyclization could be explained by reductive elimination of allylpalladium intermediate. The most important here comes from the rhodium-catalyzed cyclization that gives the five membered ring chemoselectively, although a mechanism is not clear yet. In the near future, we will

Table 1. Rhodium- and Ag<sup>+</sup>-catalyzed allenyne cyclization



RCOOH	Ag <sup>+</sup>	Temp (°C)/time (h)	Products	Yield (%)
HCOOH	AgBF <sub>4</sub>	55/8	<b>15a</b>	85
HCOOH	AgOTf	rt/4	<b>15a</b>	60
CH <sub>3</sub> COOH	AgOTf	rt/10	<b>15b</b>	40

present the mechanistic details and the full scope of the rhodium-catalyzed allenyne cyclizations.

### Acknowledgements

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- General procedure for cyclization of allenyne **1**: A 5 mL round-bottomed flask were charged with palladium compound **5** (2.9 mg, 0.0084 mmol), NaBAR<sub>4</sub> (Ar = 3,5-bis(trifluoromethyl)phenyl, 8.0 mg, 0.0090 mmol), and triethylsilane (64.3 mg, 0.547 mmol) and purged with a slow stream of dry argon gas. To this flask was added dry chloroform (0.5 mL) and then added a solution of allenyne **1** (41.2 mg, 0.274 mmol) in dry chloroform (1 mL) by cannula at 0°C under an argon atmosphere. The reaction mixture was stirred for 24 h in a preheated 50°C oil bath. Then the reaction mixture was concentrated under reduced pressure and separated on flash column chromatography (eluent: hexane/ethyl acetate (20:1)) to give the cyclized product **4** (21.5 mg, 52%) as colorless oil. All new compounds **2**, **3**, **4**, **7**, **8**, **9**, **12**, **13** and **15a–b** were fully characterized by <sup>1</sup>H, <sup>13</sup>C NMR, IR, and high-resolution mass spectra.