Tetrahedron Letters, Vol. 34, No. 47, pp. 7615-7618, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

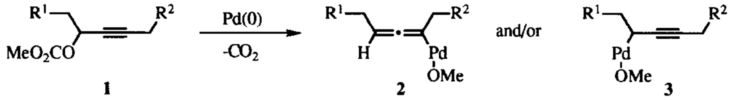
Preparation of Conjugated Enynes by the Palladium-catalyzed Elimination Reaction of Propargylic Carbonates

Tadakatsu Mandai*, Yoshikazu Tsujiguchi, Shin Matsuoka, Jiro Tsuji
Department of Applied Chemistry, Okayama University of Science,
Ridai-cho, Okayama 700, Japan

Key words
Conjugated enynes, Propargylic carbonates, Palladium catalysts

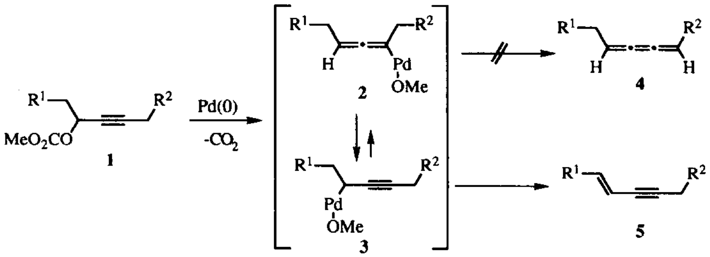
Abstract: Propargylic carbonates are cleanly converted to conjugated enynes by palladium-catalyzed elimination reaction under mild and neutral conditions.

We have demonstrated that propargylic carbonates undergo a number of palladium-catalyzed synthetically useful transformations such as hydrogenolysis with formic acid,[1] carbonylation,[2] nucleophilic substitution,[3] coupling with acetylenes,[4] and olefins.[5] Elsevier and coworkers reported that derivatives of propargyl chloride react with Pd(0) to form σ-allenylpalladium complexes and σ-propargylpalladium complexes [or (σ-prop-2-ynyl)palladium] depending on substituents. The latter is formed when there is a bulky substituent at the C-3 carbon.[6] Formation of similar complexes **2** and **3** as intermediates is expected in the palladium-catalyzed reactions of propargylic carbonates. All palladium-catalyzed reactions of propargylic carbonates we found so far can be explained by the formation of the allenylpalladium methoxide **2** as the common intermediates.

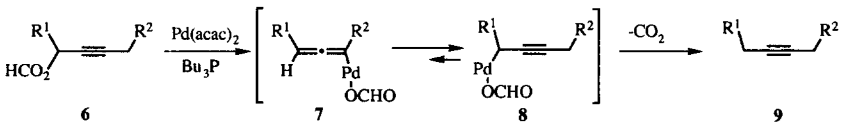


We examined the palladium-catalyzed elimination reaction of propargylic carbonates, expecting that conjugated enynes **5** would be formed through β-elimination of Pd-H from the intermediate **3,** rather than cumulative trienes **4** from **2.**[7] In the event, we have observed that the conjugated enynes **5** are provided selectively in good yields without contamination of the cumulenes **4,** as shown in Scheme I.

Scheme I



As the first exceptional reaction which can be explained to proceed via the propargylpalladium complex **8** instead of the allenylpalladium complex **7**, we found that propargylic formates undergo smooth hydrogenolysis to give disubstituted acetylenes **9** by using the active palladium catalyst [$Pd(acac)_2/Bu_3P=1/1$].[8]



The elimination reaction proceeded with a variety of propargylic carbonates under mild and neutral conditions, the results being listed in Table I. The reaction with tertiary propargylic carbonates derived from cyclic ketones proceeded smoothly to give conjugated enynes in good yields (entries 1-5).[9] On the other hand, the reactions of the tertiary carbonates derived from 2-octanone, which should provide two regioisomeric olefins, were significantly affected by the palladium catalysts used (entries 6 and 7). That is, 1,1-disubstituted olefins were formed by $Pd(OAc)_2/PPh_3$ in a highly regioselective manner. In sharp contrast to this, trisubstituted olefins were afforded selectively by the action of $Pd_2(dba)_3$/dppf. Bidentate phosphines are suitable for selective formation of trisubstituted olefins, dppf being much superior to dppe, dppp, and dppb.[10] Interestingly, the adjacent oxygen functionality has much influence on the regioselectivity, 1,1-disubstituted olefin being afforded with high regioselectivity (entry 8). Particularly, the reaction with $Pd(OAc)_2/PPh_3$ showed perfect regioselectivity.

Next, secondary propargylic carbonates were subjected to this elimination reaction, giving rise to conjugated enynes as well by the action of $Pd(OAc)_2/PPh_3$ (entries 9-11), but in poor stereoselectivity (entries 10 and 11). However, the reaction with $Pd_2(dba)_3$/dppf was sluggish. By this reaction, labile 2-(alkynyl)-butadienes, not easily available by the conventional methods,[11] were also obtained in satisfactory yields (entries 12 and 13).

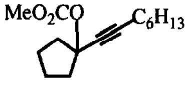
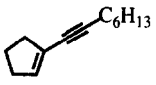
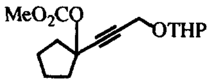
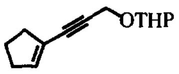
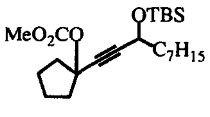
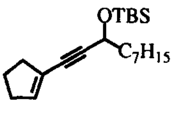
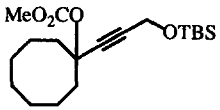
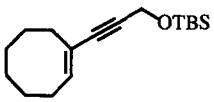
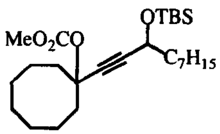
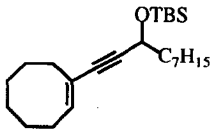
It is known that enynes can be prepared by the palladium-catalyzed coupling of terminal alkynes with vinyl halides.[12] However, vinyl halides with functional groups can not be prepared easily. Thus, a new, efficient synthetic method for conjugated enynes we have developed would be useful for organic synthesis.

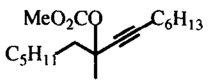
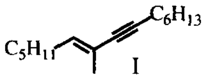
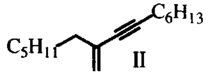
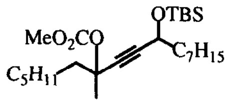
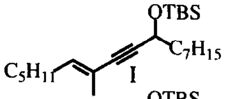
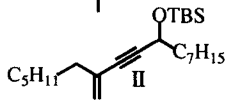
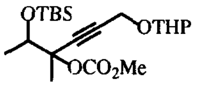
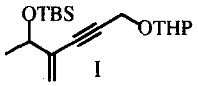
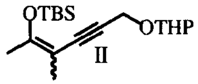
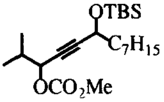
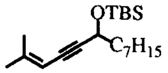
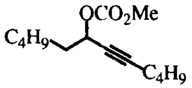
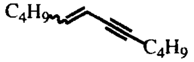
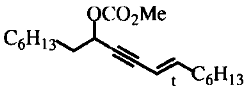
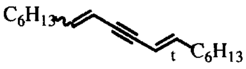
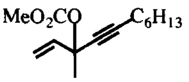
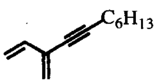
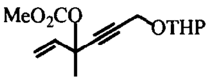
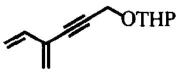
References and notes

1. Tsuji, J.; Sugiura, T.; Yuhara, M.; Minami, I. *Chem. Commun.*, **1986,** 922
2. Tsuji, J.; Sugiura, T.; Minami, I. *Tetrahedron Lett.*, **1986,** *27*, 731, Mandai, T.; Suzuki, S.; Ikawa, A.; Murakami, T.; Kawada, M.; Tsuji, J. *Tetrahedron Lett.*, **1991**, *32*, 7687, Mandai, T.; Ryoden, K.;Kawada, M.; Tsuji, J. *Tetrahedron Lett.*, **1991**, *32*, 7683. Mandai, T.; Kunitomi, H.; Higashi, K.; Kawada, M.; Tsuji, J. *Synlett*, **1991**, 697. Mandai, T.; Tsujiguchi, Y.; Tsuji, J.; Saito, S. *J. Am. Chem. Soc.*, **1993**, *115*, 5865.
3. Tsuji, J.; Watanabe, H.; Minami, I.; Shimizu, I. *J. Am. Chem. Soc.*, **1985**, *107*, 2196, Minami, I.; Yuhara, Y.; Watanabe, H.; Tsuji, J. *J. Organometal. Chem.*, **1987**, *334*, 225.
4. Mandai, T.; Nakata, T.; Murayama, H.; Yamaoki, H.; Ogawa, M.; Kawada, M.; Tsuji, J. *Tetrahedron Lett.*, **1990**, *31*, 7179, *J. Organometal. Chem.*, **1991**, *417*, 305.

5. Mandai, T.; Ogawa, M.; Yamaoki, H.; Nakata, T.; Murayama, H.; Kawada, M.; Tsuji, J. *Tetrahedron Lett.*, **1991**, *32*, 3397.
6. Elsevier, C. J.; Kleijn, H.; Boersma, J.; Vermeer, P. *Organometallics*, **1986**, *5*, 716, *Chem. Commun.*, **1983**, 1529
7. Our working hypothesis is based on the fact that formation of allenes via β-elimination of Pd-H from vinylic palladium complexes has not been reported so far.
8. Mandai, T.; Matsumoto,T.; Kawada, M.; Tsuji, J. *Tetrahedron Lett.*, **1993**, *34*, 2161.
9. As an exception, only poor results were obtained from the reaction of the propargylic carbonates derived from cyclohexanones. It may be difficult for palladium catalyst to take a smooth eclipsed form required for β-elimination in the transition state.
10. Following abbreviations are used; dppf [1,1'-bis(diphenylphosphino)ferrocene], dppe [1,2-bis(diphenylphosphino)ethane], dppp [1,3-bis(diphenylphosphino)propane], dppb[1,4-bis(diphenylphosphino)butane]
11. For example, $POCl_3$/Py: Bernstein, S.; Littell, R.; Williams, J. H. *J. Am. Chem. Soc.*, **1953**,*75*, 4830.
12. Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.*, **1975**, 4467. For synthetic application: Nicolaou, K. C.; Dai, W. M. *Angew. Chem. Int. Ed. Engl.*, **1991**, *30*, 1387.

Table I Palladium-catalyzed elimination reaction of propargylic carbonates

Entry	Propargyl carbonates	Palladium catalyst	Time (h)	Enynes	Yield[a] (%)	I/II[b]
1		A B	1 1		93 96	
2		A	2		85	
3		A B	2 2		88 85	
4		A	2		98	
5		A	2		76	

6		A	3		98	84/16
		B	1		95	28/72
7		A	2		83	81/19
		B	2		85	22/78
8		A	3		76	72/28
		B	4		70	100/0
9		B	8		83	
10		B	1.5		99 (E/Z=52/48)[c]	
11		B	1.5		96 (E/Z=57/43)[c]	
12		A	0.5		79	
13		A	0.5		68	

a) Isolated yields by flash column chromatography on SiO$_2$. b) Determined by ^{1}H NMR(400 MHz) and GLC (capillary column: 25m x 0.3 mm). Geometry of trisubstituted olefins is tentatively assigned as E.

c) Determined by ^{1}H NMR(400 MHz).

(A): Pd$_2$(dba)$_3$/dppf (5 mol%/10 mol%) (B) Pd(OAc)$_2$/PPh$_3$ (10 mol%/30 mol%) THF, reflux

(Received in Japan 3 July 1993; accepted 16 August 1993)