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Preparation of Triesters by Palladium-Catalyzed Vicinal Carbonylation of 1-Substituted-3-methoxycarbonyl-2-propynyl Methyl Carbonates

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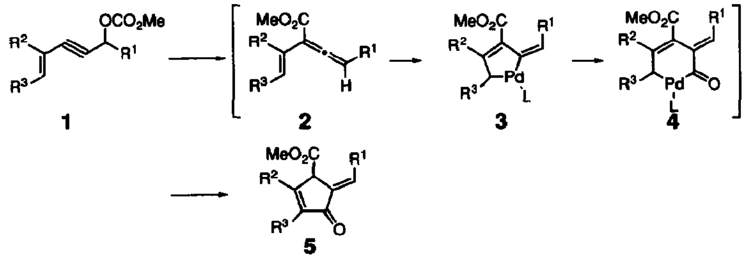
Summary: The palladium-catalyzed vicinal carbonylation of the 1-substituted-3-methoxycarbonyl-2-propynyl methyl carbonates 6 proceeds at room temperature under atmospheric pressure of CO to give the triesters 7 in good yields.

Palladium-catalyzed carbonylation is one of the most powerful synthetic tools in organic synthesis.[1] We have so far focused on the palladium-catalyzed carbonylations of 2-alkynyl methyl carbonates, demonstrating their diverse applicability to organic synthesis.[2,3] The carbonylation of 2-alkynyl methyl carbonates introduces only *one mole of CO* to form allenyl esters.[4] In contrast, the carbonylation of 4-en-2-ynyl methyl carbonates **1** undergoes *vicinal carbonylation*[5] to incorporate *two moles of CO* leading to a one-step construction of cross-conjugated cyclopentenones **5** as shown in Scheme I.

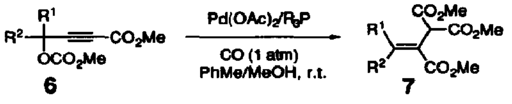
Scheme I



Intermediary allenyl esters **2** would be reactive enough to allow the formation of the palladacycles **3** and the cyclic acylpalladium complexes **4** by the insertion of the second CO. The ketones **5** are released by reductive elimination of Pd(0) species and ensuing olefin isomerization to a cross-conjugated system. This observation suggests that the geminal functional groups (i.e. ester carbonyl and alkenyl groups) of **2** play an important role in increasing the reactivity of the allenyl sp carbon to result in smooth reactions as shown in Scheme I.

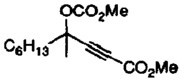
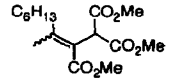
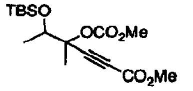
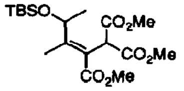
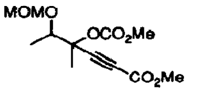
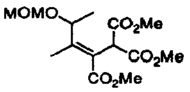
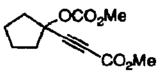
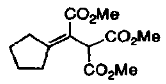
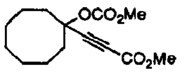
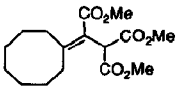
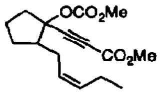
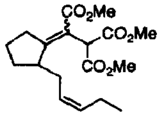
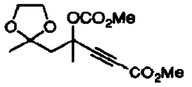
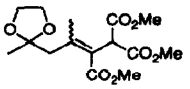
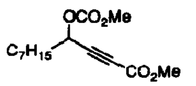
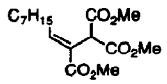
In our studies to gain more insight into the reactive intermediates **2**, we have found that the vicinal carbonylation of the 1-substituted-3-methoxycarbonyl-2-propynyl methyl carbonates **6** takes place very smoothly to give the triesters **7** in good yields as shown in Scheme II.

Scheme II

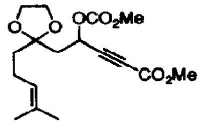
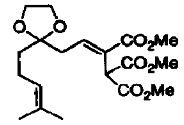
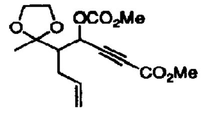
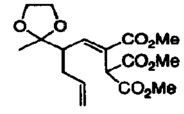
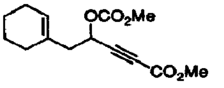
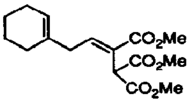


This vicinal carbonylation is applicable to the synthesis of a wide variety of **7**, the results being summarized in Table I. Bidentate phosphine ligands such as [1,3-bis(diphenylphosphino)propane] (dppp) and [1,1'-bis(diphenylphosphino)ferrocene] (dppf) are most effective for the reaction, while the reaction using a combination of $Pd(OAc)_2/PPh_3$ is too slow to be practical. In this reaction, the secondary carbonates are less reactive than tertiary ones, whereas the reaction is much accelerated by increasing pressure of CO (5 atm) (entries 8-11).

Table 1. The palladium-catalyzed vicinal carbonylation of 1-substituted-3-methoxycarbonyl-2-propynyl methyl carbonates **6**[a]

Entry	2-Propynyl carbonates **6a—k**[d]	R_3P	Time/h	Triester[b] **7a—k**[e]		Yield/%[c]
1		dppf	1.5		*E/Z=3/1*	81
2		dppp	9		*E*	76
3		dppf	18		*E*	93
4		dppf	1.5			79
5		dppf	1.5			86
6		dppf	2		*E/Z=7/1*	73
7		dppp	18		*E/Z=3/2*	88
8[f]		dppp	24		*E*	68

(continued)

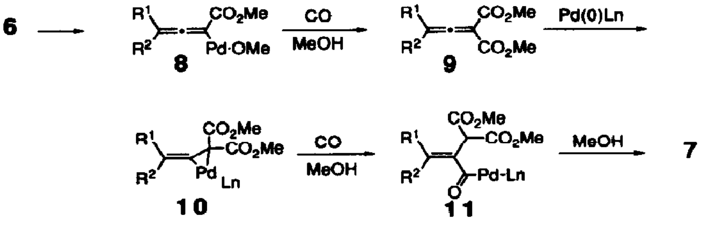
9^f		dppf	24		*E*	72
10^f		dppf	24		*E*	67
11^f		dppf	24		*E*	63

(a) Carried out using Pd(OAc)$_2$/dppp (5 mol% for each) or Pd(OAc)$_2$/dppf (5 mol% for each) under 1 atm of CO at room temperature. (b) The E/Z ratio of the triester was determined by ^{1}HNMR (400 MHz) and the stereochemistry was tentatively assigned. (c) Isolated by column chromatography (SiO$_2$). (d) Numbered as **6a**—**6k** from entries 1 to 11. (e) Numbered as **7a**—**7k** from entries 1 to 11. (f) Performed under 5 atm of CO.

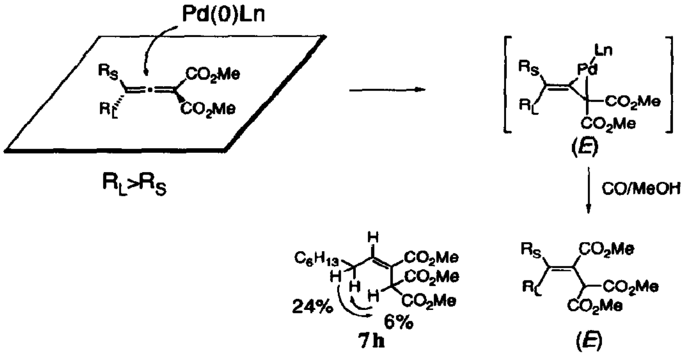
A typical procedure is exemplified as follows (entry 4). A mixture of the carbonate[6] (**6d**: 113.0 mg, 0.5 mmol), Pd(OAc)$_2$ (5.6 mg, 0.025 mmol), and dppf (13.9 mg, 0.025 mmol) in toluene/MeOH (1.5 ml/0.3 ml for each) was stirred under 1 atm of CO at room temperature for 1.5 h. The reaction mixture was diluted with ether (30 ml) and passed through a Florisil pad. Removal of the solvent and flash column chromatography (SiO$_2$) of a crude oil gave the triester (**7d**: 107 mg, 79 %). ^{1}H NMR (400 MHz) δ 1.65–1.70 (m, 4H, CH$_2$), 2.15–2.21 (m, 2H, CH$_2$), 2.37–2.44 (m, 2H, CH$_2$), 3.65 (s, 3H, OCH$_3$), 3.77 (s, 6H, OCH$_3$), 4.34 (s, 1H, CH). ^{13}C NMR (100 MHz) δ 26.3, 26.5, 29.2, 29.6, 52.5, 55.3, 59.3, 131.5, 140.0, 167.8. HRMS: (M$^+$- C$_2$H$_2$O$_2$) Calcd C$_{11}$H$_{16}$O$_4$: 212.1049. Found: 212.1031.

One possible reaction mechanism can be proposed as follows. The allenyl geminal esters **9**, *not isolable*, would be formed via the allenylpalladium complexes **8**. The compounds **9** would be susceptible to Michael type addition of Pd(0)Ln species to their allenyl sp carbons, resulting in the formation of the palladacycles **10**. Finally, **7** are released by the second CO insertion into **10** followed by methanolysis as outlined in Scheme III.

Scheme III



The formation of **9**, no proof for which is available at present, would be supported by the observation that E geometry was accomplished with high stereoselectivity as shown in entries 2, 3, and 8—11, respectively. Namely, such high stereoselectivity can be rationalized by nucleophilic attack of Pd(0)Ln species to the allenyl sp carbon from the less hindered side of an alkyl substituent (R_S). The stereochemistry of the triester **7h** in entry 8, for example, can be assigned as E by NOE experiments as shown below.



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1) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: Berlin, Heidelberg, **1980**; p 159-162.

2) (a) Mandai, T.; Ryoden, K.; Kawada, M.; Tsuji, J. *Tetrahedron Lett.* **1991**, *32*, 7683. (b) Mandai, T.; Suzuki, S.; Ikawa, A.; Murakami, T.; Kawada, M.; Tsuji, J. *Tetrahedron Lett.* **1991**, *32*, 7687. (c) Mandai, T.; Kunitomi, H.; Higashi, K.; Kawada, M.; Tsuji, J. *Synlett* **1991**, 697.

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4) Tsuji, J.; Sugiura, T.; Minami, I. *Tetrahedron Lett.* **1986**, *27*, 731.

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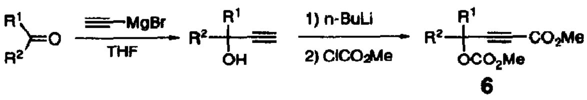
6) 1-Substituted-3-carbomethoxy-2-propynyl methyl carbonates **6** were prepared as follows. Aldehydes or ketones were treated with a commercially available THF solution of ethynylmagnesium bromide (1.2 eq) at 0 °C for 0.5 h. The corresponding propargylic alcohols were deprotonated in THF with n-BuLi (2.2 eq) at -80 °C for 1 h. After addition of methyl chloroformate (2.5 eq) at –80 °C, the reaction mixture was gradually warmed to room temperature during several hours. The carbonates **6** thus obtained were purified by flash column chromatography (SiO_2).



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