

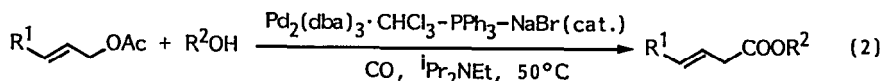
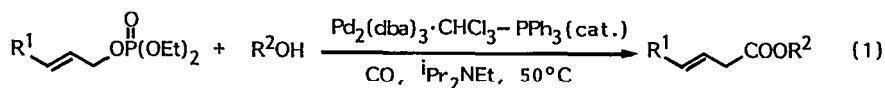
PALLADIUM(0)-CATALYZED CARBONYLATION OF ALLYL PHOSPHATES  
 AND ALLYL ACETATES. SELECTIVE SYNTHESIS OF  $\beta,\gamma$ -UNSATURATED ESTERS

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**Summary:** Palladium catalyzed carbonylations of allyl phosphates and allyl acetates give  $\beta,\gamma$ -unsaturated esters efficiently. The latter reaction requires bromide ion as a co-catalyst.

Carbonylation of allylic compounds is the fundamental and useful reaction for organic synthesis, and hence extensive study has been devoted. Carbonylation of allylic halides can be performed readily by using nickel<sup>1</sup> and palladium<sup>2,3</sup> catalysts; however, carbonylation of synthetically more important allylic alcohols, ethers, and acetates are difficult, and severe reaction conditions are required.<sup>3a,4-6</sup> Carbonylation of derivatives of allyl alcohols under mild conditions has been reported only on that of carbonates.<sup>7</sup> In the palladium catalyzed reactions of allyl acetates, allylpalladium complexes seem to be formed readily, however under CO atmosphere the back reaction of the complexes to the allyl acetates seems to proceed faster<sup>2,8</sup> than the insertion of CO into the complexes to give carbonylation products.

We have found that palladium catalyzed carbonylation of allyl phosphates gives  $\beta,\gamma$ -unsaturated esters efficiently (Eq. 1). Furthermore, carbonylation of allyl acetates can be performed under mild conditions by using bromide ion as a co-catalyst (Eq. 2).



Alkoxy carbonylation of allyl diethyl phosphates<sup>9</sup> in the presence of  $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3/\text{PPh}_3$  catalyst and base in ethanol under CO atmosphere (30 kg/cm<sup>2</sup>) at 50 °C gives (E)- $\beta,\gamma$ -unsaturated esters efficiently. Diethyl phosphate is an excellent leaving group as well as carbonate,<sup>7</sup> and the insertion of CO to the corresponding allylpalladium complexes seems to proceed fast in comparison with the back reaction. The representative results are summarized in Table 1. The present carbonylation proceeds stereoselectively. (E)- $\beta,\gamma$ -Unsaturated esters were obtained generally. The carbonylation of phosphate 1 gave diester 2<sup>10</sup> stereoselectively, indicating that the reaction proceeds with net inversion of configuration.<sup>11</sup>

Table 1. The Palladium Catalyzed Carbonylation of Allyl Phosphates<sup>a</sup>

entry	phosphate	product <sup>b</sup>	isolated yield(%)
1			90
2			76 <sup>c</sup>
3			84
4			76

<sup>a</sup>Reaction conditions:  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  (1.0 mol%),  $\text{PPh}_3$  (4.0 mol%),  $i\text{Pr}_2\text{NEt}$  (1.0 eq.), and anhydrous ROH (1.0 mL). 50 °C, 30 kg/cm<sup>2</sup>(CO), 5 h. <sup>b</sup>The product gives satisfactory IR, NMR, Mass spectral data, and elemental analysis. <sup>c</sup>60 kg/cm<sup>2</sup>(CO).

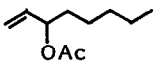
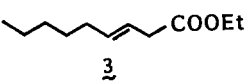
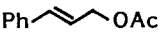

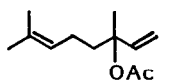
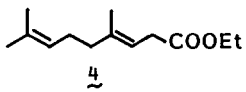
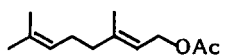
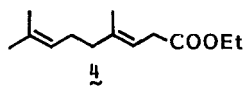
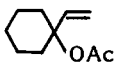
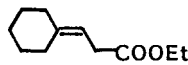
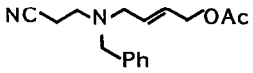
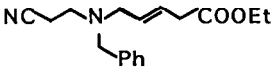
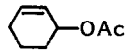
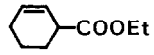
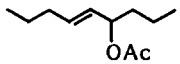
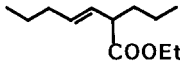
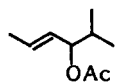
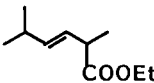
The palladium(0)-catalyzed carbonylation of allyl acetates is performed under mild conditions in the presence of base and a catalytic amount of bromide ion. A variety of allyl acetates can be converted into the corresponding  $\beta,\gamma$ -unsaturated esters. The representative results are summarized in Table 2.

The preparation of (E)-ethyl 3-nonenolate (**3**) is a typical example: A solution of 1-octen-3-yl acetate (0.850 g, 5.00 mmol),  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  (0.103 g, 0.10 mmol),  $\text{PPh}_3$  (0.105 g, 0.40 mmol), NaBr (0.103 g, 1.00 mmol), and  $i\text{Pr}_2\text{NEt}$  (0.87 mL, 5.00 mmol) in ethanol (5.0 mL) was stirred at 50 °C for 20 h under CO atmosphere (30 kg/cm<sup>2</sup>) in a 30 mL stainless-steel autoclave. Usual work-up followed by column chromatography ( $\text{SiO}_2$ ) gave (E)-ethyl 3-nonenolate (**3**) (0.786 g, 85%), which is homogeneous by TLC and GLC analyses.

Pd(0) catalysts such as  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ - $\text{PPh}_3$ ,  $\text{Pd}(\text{PPh}_3)_4$ , and  $\text{Pd}(\text{CO})(\text{PPh}_3)_3$  are effective catalysts, and Pd(II) catalysts such as  $\text{Pd}(\text{OAc})_2$  and  $\text{PdCl}_2(\text{MeCN})_2$  gave poor results. In order to trap liberating acetic acid, the addition of less nucleophilic bases such as  $i\text{Pr}_2\text{NEt}$ ,  $t\text{BuNMe}_2$ , and 2,2,6,6-tetramethylpiperidine is required. Simple nucleophilic amines such as  $\text{NEt}_3$  and pyridine gave poor results, because they may attack the allyl-palladium intermediates to give quarternary ammonium salts.<sup>12</sup> The addition of a co-catalyst such as NaBr,  $n\text{Bu}_4\text{NBr}$ , and LiI enhances the alkoxycarbonylation dramatically, although the addition of LiCl is not effective.

The carbonylation of linalyl acetate under conditions A (30 kg/cm<sup>2</sup> CO, 50 °C, 20 h, 4 mol% Pd(0) catalyst, 8 mol%  $\text{PPh}_3$ , and 20 mol% NaBr) gave ester **4** in >99% yield. However the carbonylation of geranyl acetate under the same conditions gave **4** only in 6% yield. Under severe conditions B (60 kg/cm<sup>2</sup> CO,

Table 2. The Palladium Catalyzed Carbonylation of Allyl Acetates

entry	acetate	product <sup>a</sup>	conditions <sup>b</sup>	isolated yield(%) <sup>c</sup>
1			A	85 (89)
2			A	84 (85)
3			A	90 (100)
4			B	(82)
5			A	80
6			A	57
7			B	(69)
8			B	51
9			B	59

<sup>a</sup>The product gives satisfactory IR, NMR, Mass spectral data, and elemental analysis.

<sup>b</sup>The reaction condition is same to the procedure described in the text. <sup>c</sup>The yield in parenthesis was determined by GLC.

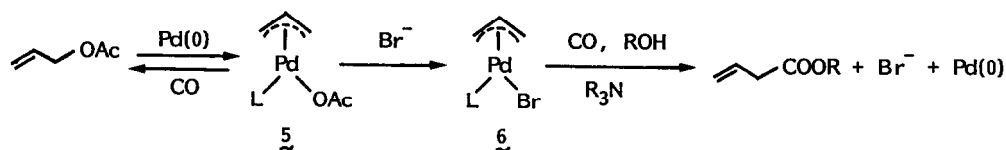
80 °C, 20 h, 4 mol% Pd(0), 8 mol% PPh<sub>3</sub>, 50 mol% NaBr) **4** was obtained in 82% yield (Entries 3 and 4). These results indicate that the oxidative addition of palladium(0) complex to allyl acetates occurs in a S<sub>N</sub>2'-fashion at the γ-position.<sup>13</sup>

The carbonylation of the acetates of secondary allyl alcohols (Entries 7-9) requires the conditions B because cis migration of carbonyl ligand on palladium metal is depressed by steric factor on the allylic carbon.

The enhancement of the carbonylation by means of the addition of a

co-catalyst may be due to the ligand exchange reaction of allylpalladium acetate (5) with bromide ion to form allylpalladium bromide (6), which undergoes facile carbonylation. Control experiments show that the carbonylation of allyl bromides proceeds fast.

Scheme-1



Further mechanistic study and synthetic application of  $\beta,\gamma$ -unsaturated esters are under investigation.

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- (E)-2: The E:Z ratio of 2 was determined to be 96:4 on the basis of GLC analysis (PEG 20M, 25 m x 0.25 mm).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.88 (ddd,  $J = 13.52, 10.77$ , and  $6.19$  Hz, 1 H,  $\text{H}^{2\alpha}$ ), 2.21-2.35 (m, 3 H,  $\text{H}^{2\beta}$  and  $\text{H}^6$ ), 2.82 (dddd,  $J = 10.77, 8.93, 5.73$ , and  $3.21$  Hz, 1 H,  $\text{H}^{1\beta}$ ), 3.21 (m, 1 H,  $\text{H}^{3\alpha}$ ), 3.69 (s, 3 H, COOMe), 3.70 (s, 3 H, COOMe), 5.75-5.87 (m, 2 H,  $\text{CH}=\text{CH}$ ).
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