

PALLADIUM-CATALYZED DECARBOXYLATION-CARBONYLATION OF ALLYLIC CARBONATES  
 TO GIVE  $\beta,\gamma$ -UNSATURATED ESTERS UNDER MILD CONDITIONS

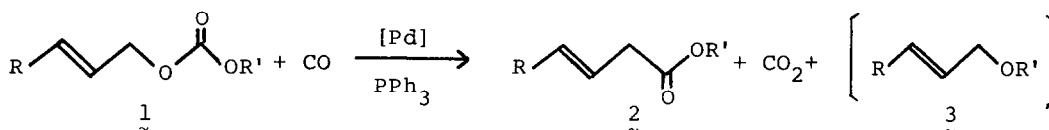
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**Summary:** Allylic carbonates undergo facile palladium-catalyzed decarboxylation-carbonylation under mild conditions to give  $\beta,\gamma$ -unsaturated esters in high yields using palladium-phosphine complex as a catalyst.

We have reported the stoichiometric carbonylation reaction of  $\pi$ -allylpalladium chloride in alcohol to give 3-butenolate.<sup>1)</sup> Also allyl chloride was carbonylated using  $\text{PdCl}_2$  or  $\pi$ -allylpalladium chloride as the catalyst to give the same ester.<sup>2,3,4)</sup> But high CO pressure was necessary (90 ~ 100 atm<sup>2,4)</sup> and 500 atm<sup>3)</sup>). The reaction is very slow under low pressure.

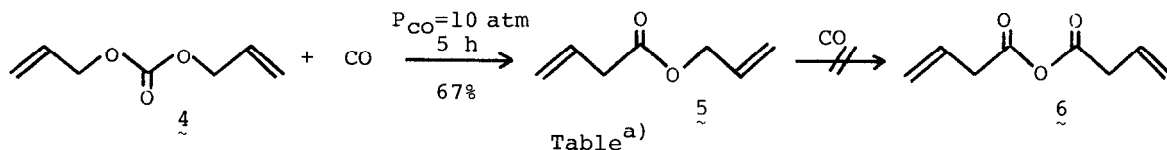
On the other hand, the reaction of allylic esters with nucleophiles catalyzed by a palladium-phosphine complex is a well-established reaction, which proceeds via the formation of  $\pi$ -allylpalladium complexes as intermediates.<sup>5,6)</sup> We were interested in the reaction of allylic esters with CO under mild conditions, but the attempted palladium-catalyzed carbonylation of allyl acetate and allyl phenyl ether in alcohol in the presence or absence of bases under low CO pressure gave disappointing results. Now we found that allylic carbonates **1** react with CO under mild conditions. Decarboxylation-carbonylation takes place to give  $\beta,\gamma$ -unsaturated esters **2** in high yields.



In a typical example, ethyl methallyl carbonate (3.6 g, 25 mmol),  $\text{Pd}(\text{OAc})_2$  (112 mg, 0.5 mmol), and  $\text{PPh}_3$  (262 mg, 1.0 mmol) were placed in a small pressure bottle and the reaction was carried out at 50°C under 10 atm of CO for 8 h. After the reaction, ethyl 3-methyl-3-butenolate was isolated by distillation (2.43 g, 76%) at 45°C/20 mm: NMR ( $\text{CCl}_4$ )  $\delta$  1.23 (3 H, t,  $\text{CH}_3$ ), 1.80 (3 H, s,  $\text{CH}_3$ ), 2.91 (2 H, s,  $-\text{CH}_2-$ ), 4.05 (2 H, q,  $-\text{OCH}_2-$ ), 4.80 (2 H, br s,  $=\text{CH}_2$ ). Results of the carbonylation with several carbonates are shown in the Table.

The reaction proceeds even under atmospheric pressure using a rubber balloon filled with CO. It was somewhat accelerated by increasing the pressure up to 10 atm. Reaction temperature showed a significant effect. At room temperature,

almost no reaction took place. At high temperature (above 80°C), simple decarboxylation to give the allyl alkyl ethers **3** was the main reaction path.<sup>7)</sup> The optimum temperature for the decarboxylation-carbonylation was found to be 50°C. As the catalyst, palladium combined with phosphine ligands was used. Several phosphine and phosphite ligands were tested, but PPh<sub>3</sub> showed the best results. Thus Pd(OAc)<sub>2</sub> and PPh<sub>3</sub> were used most conveniently. The following chemoselective carbonylation was observed with diallyl carbonate (**4**). Only allyl 3-butenolate (**5**) was obtained. No further carbonylation of the allyl ester **5** was observed, showing that allyl carbonate is much more reactive than allyl ester.



Substrate	P <sub>CO</sub> (atm)	Time (h)	Product	Yield (%) <sup>b)</sup>
	10	8		76
	1	5		67 <sup>c)</sup>
	1	4		71
	5	5		94
	5	5		74
	5	5		80

a) Carried out with Pd(OAc)<sub>2</sub>-2PPh<sub>3</sub> (1:2,2 mol%) at 50°C.

b) Isolated yields unless otherwise noted.

c) Determined by G.L.C..

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