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PALLADIUM-CATALYZED CARBONYLATION OF PROPARGYLIC CARBONATES: PREPARATION OF 2,3- AND 2,4-DIENYL CARBOXYLATES

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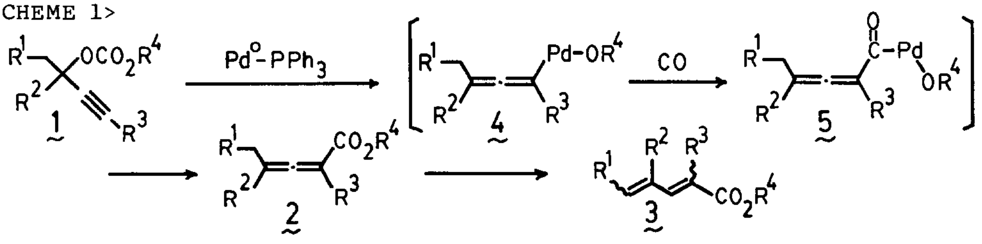
Summary: Propargylic carbonates are converted to 2,3-dienyl carboxylates by the palladium-catalyzed decarboxylation-carbonylation in alcohol under mild conditions. In ether, 2,4-dienyl carboxylates are obtained.

Palladium-catalyzed carbonylations of certain organic compounds are important synthetic methods for carbonyl compounds such as esters, amides, aldehydes, and ketones. Usually olefins, dienes, and aryl, vinyl, and allyl halides are carbonylated.[1] Also, palladium-catalyzed carbonylation of acetylenic compounds to give unsaturated esters[2] and lactones[3] are known. We reported that itaconate and aconitate were obtained by the palladium-catalyzed carbonylation of propargyl alcohol at 100°C under 100 atom in methanol containing hydrogen chloride.[4] Recently, we found that propargylic carbonates are reactive compounds and undergo smooth palladium-catalyzed reactions with soft nucleophiles.[5] These reactions can be explained by the formation of the (allenyl)palladium complex **4** as an intermediate by the displacement of the carbonate group with Pd(0) species. Then we speculated that the (allenyl)palladium complex **4** should react with carbon monoxide to give 2,3-dienyl carboxylate **2** and actually we observed a smooth decarboxylation-carbonylation reaction of propargylic carbonates. Here, we wish to report a new preparative method for 2,3-dienyl carboxylates **2** and 2,4-dienyl carboxylates **3** as expressed by the following scheme.

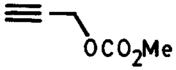
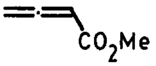
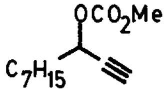
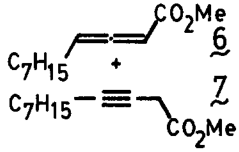
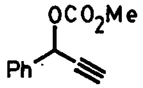
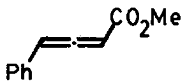
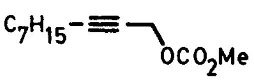
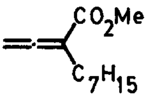
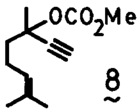
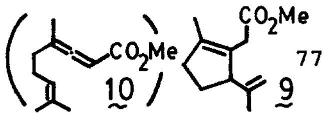
<SCHEME 1>

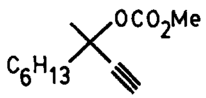
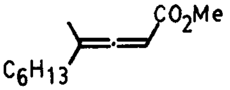
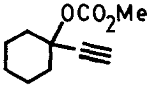
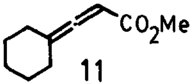
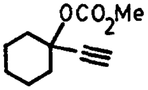
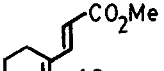
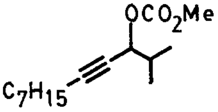
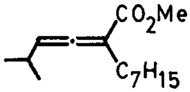


Results of the carbonylation of various propargylic carbonates are shown in <TABLE 1>. In all cases, carbon monoxide was introduced at the γ-position of the propargyl group. 2,3-Dienyl carboxylates were obtained in good yields by carrying out the reaction in methanol. The reaction proceeds even under atmospheric pressure of carbon monoxide, but is accelerated by increasing the pressure. The yield of methyl 2,3-butadienoate, the most simple 2,3-dienyl carboxylate, was somewhat low, mainly because it is a very reactive compound (run 1). In some cases, a mixture of allenyl and acetylenic carboxylates was obtained (run 2). The cyclopentene derivative **9** was obtained in 77% yield from dehydrolinalyl methyl carbonate (**8**). We considered that the first step must be the expected carbonylation to form **10** which undergoes intramolecular ene reaction to give **9**. To our surprise, the ene reaction proceeded even at room temperature and we could not isolate the 2,3-dienyl carboxylate **10**.

When the reaction was carried out in ether, instead of methanol, the 2,4-dienyl carboxylate **12** was formed (run 8). The 2,4-dienyl carboxylates **3** must be formed by the isomerization of the 2,3-dienyl carboxylates **2**. The palladium-phosphine complex seems to promote the isomerization. For example, **11** was converted to **12** quantitatively by the treatment with $Pd_2(dba)_3 \cdot CHCl_3$-dppe catalyst for 14 h at 50°C. The isomerization took place slowly in the absence of the catalyst.

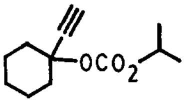
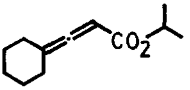
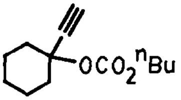
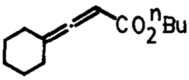
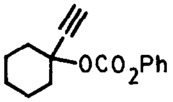
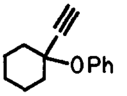
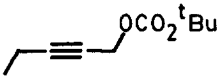
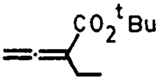
<Table 1>

RUN	PROPARGYL CARBONATE	TEMP.(°C)	P_{CO}(atom)	TIME(h)	PRODUCT	YIELD(%)
1		40	15	20		50$^{b)}$
2		50	10	12	 6 : 7 = 5 : 3$^{c)}$	76
3		40	30	5		71
4		40	10	12		82
5		20-30	1	1		77

6		40	5	15		99
7		50	15	14	 **11**	96
8[d)]		50	15	44	 **12**	92
9		50	12	24		85

a) General procedure; In a stainless steel axutoclave (50 mL), a solution of propargylic carbonate (3 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (0.03 mmol), and PPh_3 (0.24 mmol) in MeOH (6 mL) was placed and the autoclave was filled with CO (P_{CO} = 1-30 atom). Then the solution was stirred. After the reaction was complete, allenyl esters were isolated by column chromatography on silica gel or preparative GLC. b) Calculated by GLC analysis. c) Calculated by ^1H NMR analysis. d) Reaction was carried out using $Pd(OAc)_2$ (0.06 mmol) and dppe (0.12 mmol) in Et_2O (6 mL).

<TABLE 2>

RUN	PROPARGYL CARBONATE	SOLVENT	TEMP. (^oC)	P_{CO} (atom)	TIME (h)	PRODUCT	YIELD (%)
1		^iPrOH	20-30	10	5		76
2		^nBuOH	50	10	4		88
3		PhOH	50	10	6		60
4		^tBuOH	100	35	44		44

Procedure: See <TABLE 1>.

Various esters of 2,3-dienyl carboxylates can be prepared by using various carbonates. Some results are shown in <TABLE 2>. Propargyl carbonates of primary and secondary alcohols undergo the smooth decarboxylation-carbonylation to give corresponding esters. However, a yield of tertiary butyl ester was unsatisfactory (run 4). Only a small amount of phenyl ester was obtained under similar conditions (run 3). In this case, phenyl ether was major product.

Mechanism of the reaction is shown in <Scheme 1>. Oxidative addition of Pd(0) species to propargylic carbonate **1** followed by decarboxylation gives the (allenyl)palladium alkoxide complex **4**.[5)] Then carbon monoxide coordinates to the complex **4**, and inserts to the palladium-carbon bond to give **5**. Finally reductive elimination of **5** gives the 2,3-dienyl carboxylate **2** and regenerates the Pd(0) species. We found before that allylic carbonates are very reactive substrates in the palladium-catalyzed reactions.[6)] Especially they undergo smooth decarboxylation-carbonylation reaction.[7)] Similar to the reactions of allylic carbonates, carbonate as a leaving group is important in the present reaction.

Usually, 2,3-dienyl carboxylates **2** are prepared by the Wittig reaction of ketenes,[8)] or isomerization of 3-yne carboxylates under basic conditions.[9)] The present reaction offers efficient preparative method of **2**. As a related reaction, carbonylation of propargyl halides with $Ni(CO)_4$ to give 2,3-dienyl acids is known, but a stoichiometric amount of toxic $Ni(CO)_4$ is necessary and yields are low.[10)]

ACKNOWLEDGMENT: This research was financially supported by the Grant-in-Aids for Developmental Scientific Research, No. 60850153 and Encouragement of Young Scientist, No. 60790051 from the Ministry of Education, Science and Culture.

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