were combined, dried over anhydrous $MgSO_4$, and filtered; the solvent was evaporated to give 212 mg (8.1%) of a pale yellow oil, which was further purified by GC. ^1H NMR δ 1.34 (s, 9 H), 1.42 (s, 9 H), 1.48 (t, J = 8 Hz, 3 H), 4.43 (q, J = 8 Hz, 2 H), 7.48 (d, J = 1.5 Hz, 1 H), 7.89 (d, J = 1.5 Hz, 1 H); ^{13}C NMR δ 14.6, 30.5, 30.9, 35.2, 38.1, 61.5, 169.7; IR (neat) 1710 cm^{-1}; UV λ_{max} 271 nm (ϵ 3540), 228 nm (ϵ 8600); MS, m/z 263 (M^+). Anal. Calcd for $C_{16}H_{25}NO_2$: C, 72.96; H, 9.57; N, 5.32. Found: C, 72.91; H, 9.36; N, 5.53.

Ethyl 4,5-Di-*tert*-butyl-2-picolinate. The previous experiment is repeated with the following changes. The addition of the *tert*-butylacetylene is completed in $^1/_2$ h, the subsequent stirring in 15 min, the addition of ethyl cyanoformate in 10 min, and the final stirring in 15 min. This yields 627 mg (23.8%) of crude product that was further purified by dissolution in 150 mL hexanes and extraction with 1 N HCl (3 × 100 mL). The combined acidic water layers were then made alkaline with concentrated NaOH and extracted with CH_2Cl_2 (2 × 100 mL), the combined orgnaic layers were dried over $MgSO_4$ and filtered, and the solvent was removed. The resulting pale yellow oil was crystallized from pentane to afford a cream-colored solid, mp 61–62 °C lit.[1] mp 62.5–63.5 °C: ^1H NMR δ 1.45 (t, J = 7.5 Hz, 3 H), 1.57 (s, 9 H), 1.60 (s, 9 H), 4.47 (q, J = 7.5 Hz, 2 H), 8.29 (s, 1 H), 8.90 (s, 1 H); ^{13}C NMR δ 14.4, 33.8, 34.2, 36.9, 37.9, 61.5, 165.8; IR ($CHCl_3$) 1710 cm^{-1}; UV λ_{max} 265 nm (ϵ 6890), 233 nm (ϵ 14640); MS, m/z 263 (M^+).

4,5-Di-*tert*-butyl-2-picolinic Acid. To a mixture of 52.6 mg (0.2 mmol) of the ethyl ester and 5.08 mg (0.02 mmol) of I_2 in a 10-mL round-bottomed flask was added 0.4 g (2 mmol) of trimethylsilyl iodide under a nitrogen atmosphere. The solution was stirred and refluxed in an oil bath at 125 °C for 24 h, allowed to cool, evaporated at low pressure to small volume, quenched with 10 mL of water followed by 10 mL of a saturated $Na_2S_2O_3$ solution, and extracted with $CHCl_3$ (3 × 10 mL). The organic layers are combined and dried over anhydrous $MgSO_4$, filtered, and evaporated to give a cream-colored solid. Recrystallization from $CHCl_3$ gave 34.3 mg (73%) of white needles: mp 209 °C; ^1H NMR δ 1.59 (s, 9 H), 1.63 (s, 9 H), 8.52 (s, 1 H), 9.26 (s, 1 H), 15.10 (s, 1 H); ^{13}C NMR δ 33.6, 34.0, 37.4, 38.7, 164.2; IR ($CHCl_3$) 1750, 2400, 3650 cm^{-1}; UV λ_{max} 274 nm (ϵ 7960), 228 nm (ϵ 13760); MS, m/z 235 (M^+). Anal. Calcd for $C_{14}H_{21}NO_2$: C, 71.49; H, 8.94; N, 5.96. Found: C, 71.30; H, 8.93; N, 5.82.

4,6-Di-*tert*-butyl-2-picolinic acid was obtained similarly from the ethyl ester in 42% yield as a light brown solid. Recrystllization from pentane gives a white solid; mp 138 °C; ^1H NMR δ 1.36 (s, 9 H), 1.41 (s, 9 H), 7.61 (d, J = 2.5 Hz, 1 H), 8.08 (d, J = 2.5 Hz, 1 H); ^{13}C NMR δ 30.5, 31.0, 35.8, 37.8, 168.7; IR ($CHCl_3$) 1750, 2400, 3650 cm^{-1}; UV λ_{max} 269 nm (ϵ 2350), 227 nm (ϵ 1990); MS, m/z 235 (M^+). Anal. Calcd. for $C_{14}H_{21}NO_2$: C, 71.49; H, 8.94; N, 5.96. Found: C, 71.3; H, 8.90; N, 5.80.

3,4-Di-*tert*-butylpyridine. A sample of 100 mg (0.42 mmol) of 4,5-di-*tert*-butyl-2-picolinic acid is placed in a small glass tube (4 × $^1/_4$ in.), which is closed with a serum cap and purged with nitrogen. While the tube remains connected to the bubbler, it is lowered into an oil bath at 210–220 °C. After the solid melts, bubbling is observed to become more vigorous. After the reaction a viscous yellow liquid remains; it is purified by GC to yield a clear colorless liquid: ^1H NMR δ 1.52 (s, 9 H), 1.56 (s, 9 H), 7.39 (d, J = 5.5 Hz, 1 H), 8.29 (d, J = 5.5 Hz, 1 H), 8.75 (s, 1 H); ^{13}C NMR δ 33.9, 34.4, 36.6, 37.7; UV λ_{max} 266 nm (ϵ 2620), 225 nm (ϵ 1265); MS, m/z 191 (M^+). Anal. Calcd for $C_{13}H_{21}N$: C, 81.67; H, 11.0; N, 7.33. Found: C, 80.97; H, 11.17; N, 7.17.

2,4-Di-*tert*-butylpyridine. 4,6-Di-*tert*-butyl-2-picolinic acid is placed in a micro distillation apparatus and heated in an oil bath at 220 °C. It melts at 138 °C but the evolution of gas does not commence until about 200 °C. As the acid decarboxylates, the product distils over as a light yellow oil, bp 210 °C: ^1H NMR δ 1.30 (s, 9 H), 1.37 (s, 9 H), 7.07 (dd, J = 2 Hz, 5 Hz, 1 H), 7.31 (dd, J = 0.7 Hz, 2 Hz 1 H), 8.45 (dd, J = 0.7 Hz, 5 H, 1 H); ^{13}C NMR[7] δ 30.8, 31.1, 35.2, 37.9; UV λ_{max} 266 nm (ϵ 2260), 259 nm (ϵ 3922); MS, m/z 191 (M^+).

3-*tert*-Butylpyridine. This was prepared on a 10-g scale from 3-picoline as described by Howie and Brown:[12] ^1H NMR δ 1.40 (s, 9 H), 7.20 (ddd, $J_{2,5}$ = 0.86 Hz, $J_{5,6}$ = 4.7 Hz, $J_{4,5}$ = 8.2 Hz, 1 H), 7.65 (ddd, $J_{4,6}$ = 1.7 Hz, $J_{2,4}$ = 2.6 Hz, 1 H), 8.4 (dd, 1 H), 8.65 (dd, 1 H); ^{1C} NMR δ 30.6, 33.2.

Acknowledgment. We are indbted to J. Muench for preparing 3-*tert*-butylpyridine, to M. Cohen and B. Eberle for running seveal of the cyclocongregation reactions, to Professor H. C. Brown for a copy of Dr. Howie's thesis, and to the NSF for financial support for this work and partial support to purchase the NMR spectrometer.

Registry No. *tert*-Butylacetylene, 917-92-0; ethyl cyanoformate, 623-49-4; aluminum bromide, 7727-15-3; ethyl 4,5-di-*tert*-butyl-2-picolinate, 89032-16-6; ethyl 4,6-di-*tert*-butyl-2-picolinate, 89032-17-7; 4,5-di-*tert*-butyl-2-picolinic acid, 89032-18-8; 4,6-di-*tert*-butyl-2-picolinic acid, 89032-19-9; 3,4-di-*tert*-butylpyridine, 89032-20-2; 2,4-di-*tert*-butylpyridine, 29939-31-9; 3-*tert*-butylpyridine, 38031-78-6.

(12) Howie, M. S. Thesis, Purdue University, 1957.

Palladium-Catalyzed Decarboxylation–Carbonylation of Allylic Carbonates To Form β,γ-Unsaturated Esters

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Allyl alkyl carbonates undergo a smooth decarboxylation–carbonylation reaction to afford β,γ-unsaturated esters at 50 °C under atmospheric or low pressure of carbon monoxide and neutral conditions in the presence of palladium–phosphine complexes as catalysts. The reaction offers a very good method for the preparation of β,γ-unsaturated esters from allylic alcohols.

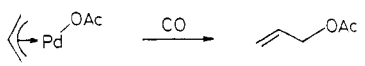
Various allylic compounds such as allylic halides, esters, ethers, and amines undergo several types of transformations in the presence of palladium–phosphine complexes as catalysts, and extensive studies have been carried out on these reactions.[1] However, one reaction of allylic compounds which receives much less attention is the carbonylation. We have shown that π-allylpalladium chloride can be converted to 3-butenoate under carbon monoxide pressure in alcohol.[2] Recently, Milstein carried out the carbonylation of π-allylpalladium complexes under mild conditions (25 °C, 50 psi) with added sodium car-

(1) Reviews: (a) Tsuji, J. "Organic Syntheses with Palladium Compounds"; Springer Verlag: Heidelberg, 1980; p 125. (b) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615.

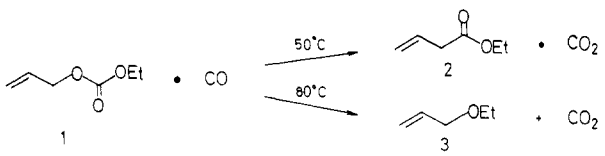
(2) Tsuji, J.; Morikawa, M.; Kiji, J. *Tetrahedron Lett.* **1963**, 1811.

0022-3263/84/1949-1341$01.50/0

Scheme I



Scheme II



boxylates as the base.[3] These carbonylation reactions, however, are stoichiometric.

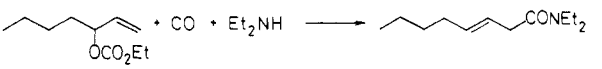
Palladium-catalyzed carbonylation of alkenyl and aryl halides proceeds smoothly under atmospheric or low pressure of carbon monoxide to afford α,β-unsaturated esters and aromatic esters, respectively, in high yields.[4] On the other hand, the palladium-catalyzed carbonylation of allylic halides has been reported by us[5] and two groups,[6,7] but it was carried out under somewhat drastic conditions. Particularly pressures above 100 atm seemed to be necessary. Also some side reactions were observed due to accumulation of hydrogen halide in reaction media. When a base is added to suppress the acid, it reacts directly with allylic halides. Thus there is no truly good catalytic process for allylic carbonylation under mild conditions.

We were interested in the carbonylation of allylic compounds, because it could offer a good synthetic method for β,γ-unsaturated esters. Particularly we intended to carry out the palladium-catalyzed carbonylation reaction of allylic compounds under mild conditions, so that it can be carried out easily in a laboratory. We found that β,γ-unsaturated esters can be obtained easily by the reaction of allyl alkyl carbonates under mild conditions. In other words, the decarboxylation–carbonylation or exchange reaction of carbon dioxide with carbon monoxide proceeds smoothly under mild conditions. A preliminary report has been given,[8] and details of the reaction are presented in this paper.

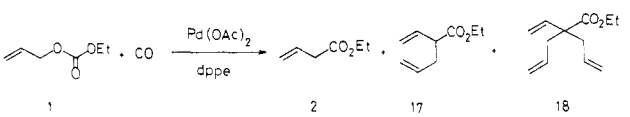
Results and Discussion

Allylic acetates are commonly used for the various types of palladium-catalyzed reactions. At first we attempted the carbonylation of allyl acetate, but only poor results were obtained. This result may be reasoned from the fact that π-allylpalladium acetate is converted to allyl acetate by reductive elimination when the complex is treated with carbon monoxide as reported by Takahashi[9] and Yamamoto[10] (Scheme I). Hegedus carried out the carbonylation of cinnamyl acetate catalyzed by palladium complexes in the presence of a stoichiometric amount of $NaCo(CO)_4$ in methanol to afford methyl 4-phenyl-3-butenoate. Attempted carbonylation of cinnamyl acetate by using a catalytic amount of (1-phenyl-π-allyl)palladium chloride without the cobalt complex gave the ester in 210% yield based on palladium.[11]

Scheme III



Scheme IV



Recently, we found that allylic carbonates are very reactive allylating agents and have carried out the palladium-catalyzed allylation of various nucleophiles at room temperature under neutral conditions.[12] When the reaction of allyl ethyl carbonate (1) with carbon monoxide under mild conditions was tried, a smooth reaction was observed to afford ethyl 3-butenoate (2) in high yield (Scheme II). Allyl ethyl ether (3) is a byproduct.[13] The reaction can be extended to various allyl carbonates which can be prepared easily by the reaction of allylic alcohols with alkyl chloroformates. Thus, this facile carbonylation reaction offers a good synthetic method for β,γ-unsaturated esters from allylic alcohols. The carbonylation reaction was carried out under various conditions with several allylic carbonates in order to define the scope of the reaction, and the results are shown in the Table I. In general, the carbonylation reaction could be effected under atmospheric pressure of carbon monoxide. Thus a laboratory scale experiment can be carried out easily in a flask equipped with a rubber balloon filled with carbon monoxide. Almost no effect of carbon monoxide pressure was observed in the reaction of allyl ethyl carbonate (1) (expt 1, 2, and 3). But higher yields of the esters were obtained with allyl carbonates having higher molecular weights (compare expt 12 and 13, 14 and 15, 18 and 19, and 20 and 21). The higher carbon monoxide pressure seems to suppress the formation of allyl alkyl ethers (expt 20 and 21). The most crucial reaction variable is temperature. At room temperature, almost no reaction took place (expt 11). The highest yield was obtained at about 50 °C. At temperatures higher than 50 °C, allyl alkyl ether formation as a competitive reaction occurred,[13] and, at 80 °C, exclusive ether formation took place without carbonylation (expt 10). Thus the optimal reaction conditions are 50 °C and 1–10 atm of carbon monoxide.

The reaction was carried out in various solvents. Common solvents such as benzene, THF, and acetonitrile gave rather negative effects. When alcohols were used as the solvent, the relative amounts of allyl alkyl ethers increased and the yield of the desired ester decreased (expt 4). Thus it was concluded that perhaps the best results could be obtained without the use of a solvent. When the reaction of ethyl 1-*n*-butyl-2-propenyl carbonate (4) was carried out in diethylamine at 50 °C under 8 atm for 10 h, *N,N*-diethylamide was obtained in 96% yield. Formation of the ester was not detected (Scheme III). Also we confirmed that the treatment of ethyl 3-octenoate (10) with diethylamine at 50 °C for 10 h did not afford the amide.

Palladium alone has no catalytic activity in this reaction, and phosphine as a ligand must be added (expt 9). Most

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(6) Dent, W. T.; Long, R.; Whitfield, G. H. *J. Chem. Soc.* **1964**, 1588.
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(8) Tsuji, J.; Sato, K.; Okumoto, H. *Tetrahedron Lett.* **1982**, *23*, 5189.
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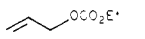
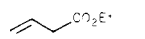
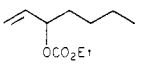
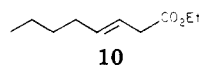
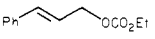
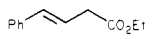
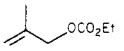
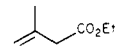
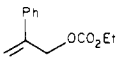
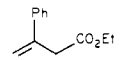
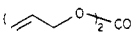
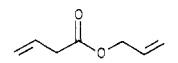
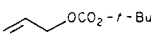
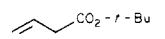
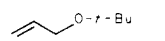
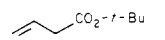
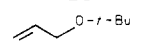
(11) Hegedus, L. S.; Tamura, R. *Organometallics* **1982**, *1*, 1188.
(12) Tsuji, J.; Shimizu, I.; Minami, I.; Ohashi, Y. *Tetrahedron Lett.* **1982**, *23*, 4809.
(13) Guibe, F.; M'Leux, Y. S. *Tetrahedron Lett.* **1981**, *22*, 3591.

Table I. Carbonylation of Allylic Carbonates under Different Conditions[a]

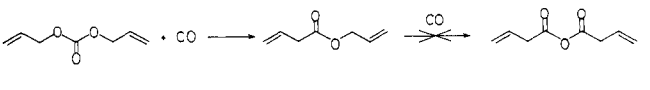
expt	substrates	ligand	pressure	temp	rxn time, h	product	yields[b]
1	 1	PPh_3	1	50	5	 2	75
2	1	PPh_3	10	50	5	2	65
3	1	PPh_3	20	50	5	2	72
4	1	PPh_3	1	50	5	2	48[c]
5	1	P-(*o*-Tol)$_3$	1	50	5	2	79
6	1	P-(*n*-Bu)$_3$	1	50	5	2	41
7	1	$P(OPh)_3$	1	50	5	2	14
8	1	$P(OEt)_3$	1	50	5	2	9
9	1	none	1	50	5	2	4
10	1	PPh_3	1	80	2	2	trace
11	1	PPh_3	1	20	22	2	trace
12	 4	PPh_3	1	50	6	 10	26
13	4	PPh_3	5	50	5	10	74
14	 5	PPh_3	1	50	4	 11	71
15	5	PPh_3	5	50	5	11	94
16	 6	PPh_3	10	50	8	 12	76
17	 7	PPh_3	5	50	5	 13	80
18	 8	PPh_3	5	50	5	 14	56
19	8	PPh_3	10	50	5	14	67
20	 9	PPh_3	1	50	20	 15	21
						 16	43
21	9	PPh_3	10	50	6	 15	54
						 16	5

[a] All reactions were carried out with 2 mol% of $Pd(OAc)_2$ and 4 mol% of ligand. [b] Yields of **2**, **15**, and **16** were determined by gas chromatography, and those of **10–14** are isolated yields. [c] EtOH was used as the solvent.

conveniently palladium acetate is used with ligands. As the ligand, triphenylphosphine and tri-(*o*-tolyl)phosphine gave the best results. Phosphites are not good ligands (expt 7 and 8). Bis(diphenylphosphino)ethane (dppe) seems to be very active. But when dppe was used for the carbonylation of allyl ethyl carbonate (**1**), allylation of ethyl 3-butenoate (**2**) occurred as a consecutive reaction, and 2-vinyl-4-pentenoate (**17**) and 2-allyl-2-vinyl-4-pentenoate (**18**) were obtained in addition to ethyl 3-butenoate. After 15 h of reaction time, the ratio of **3**, **17**, and **18** was 4:5:1. This observation shows that while dppe is a good ligand for the carbonylation reaction, this catalyst is also active for the allylation of β,γ-unsaturated esters (Scheme IV). Thus, palladium acetate and triphenylphosphine, both readily available materials, are the best choices. About 2 mol% of palladium and 4 mol% of the phosphine are sufficient to achieve a satisfactory reaction.

All reactions with various allylic carbonates proceed to give β,γ-unsaturated esters in satisfactory yields in 5–8 h by using 2 mol% of the palladium catalyst. When ethyl 1-*n*-butyl-2-propenyl carbonate (**4**) was subjected to the

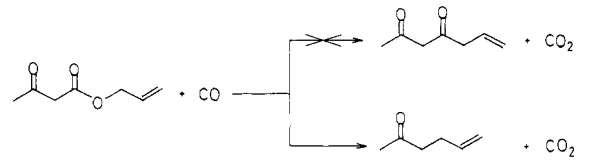
Scheme V



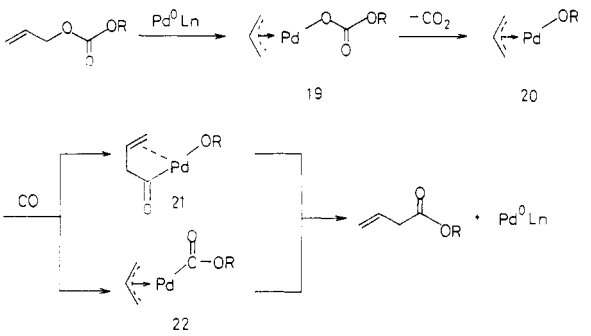
8 14

carbonylation, allylic rearrangement took place to give ethyl 3-octenoate (**10**) exclusively (expt 12 and 13). *tert*-Butyl esters may also be prepared by this carbonylation. Thus the reaction of allyl *tert*-butyl carbonate (**9**) at 50 °C under 10 atm of carbon monoxide afforded *tert*-butyl 3-butenoate (**15**) in 54% yield (expt 20). However the reaction of allyl ethyl carbonate (**1**) in a large excess of *tert*-butyl alcohol afforded only ethyl 3-butenoate (**2**) (Scheme V). The carbonylation of diallyl carbonate (**8**) afforded allyl 3-butenoate (**14**), and no further carbonylation took place (expt 18 and 19). This result clearly shows that the carbonylation under present conditions is possible only with allyl carbonate, and no reaction is possible with allyl carboxylate. We have shown that allyl acetoacetate undergoes facile palladium-catalyzed decar-

Scheme VI



Scheme VII



boxylation–allylation to give allylacetone under mild conditions.[14] We attempted the reaction of allyl acetoacetate with carbon monoxide expecting the formation of 6-heptene-2,4-dione, but no carbonylation took place and only decarboxylation–allylation took place to give allylacetone (Scheme VI)

The decarboxylation–carbonylation reaction can be explained by the following mechanism. The first step is the oxidative addition of allyl carbonate to give π-allylpalladium akloxide **20**. There are two possible reaction paths for carbon monoxide insertion. One possibility is the insertion of carbon monoxide to the π-allylpalladium bond to give 3-butenoylpalladium complex **21**. Another one is the insertion into the palladium–alkoxide bond to given (carboalkoxy)(π-allyl)palladium complex **22**. There is no evidence yet which will discriminate between these two possibilities. The final step is the reductive elimination to give the β,γ-unsatured ester. At the same time the Pd^0 species is regenerated (Scheme VII).

Experimental Section

General Procedure. ^1H NMR spectra were determined on a Hitachi Model R-24A spectrometer in CCl_4 solution at 60 MHz, and/or a Hitachi Model R-40 spectrometer in $CDCl_3$ solution at 90 MHz using tetramethylsilane as an internal standard. Data are reported in the form: δ value of signal (peak multiplicity, number of protons, coupling constant). Infrared spectra were obtained on a JASCO Model IRA-2 spectrometer as a neat liquid. Data are given in cm^{-1} with only the important diagnostic bands being reported. Boiling points are uncorrected.

Preparation of Ethyl Allyl Carbonate. To a cooled (0 °C) and stirred solution of allyl alcohol (100 mmol) and dry pyridine (200 mmol) in dry ether (100 mL) was added ethyl chloroformate (100 mmol) dropwise over 10 min. The mixture was stirred at room temperature for 3 h and then dilute hydrochloric acid was added. After extraction with ether, the organic layer was washed with brine and dried over $MgSO_4$. Following evaporation of the solvent, the allyl carbonate was isolated either by distillation or column chromatography.

Preparation of Allyl *tert*-Butyl Carbonate. To a suspension of sodium *tert*-butoxide (4.8 g, 50 mmol) in dry THF (50 mL), allyl chloroformate (6 g, 50 mmol) was added dropwise over 5 min at 65 °C with stirring under nitrogen. The mixture was stirred for 1 h at 65 °C, washed with brine, and extracted with ether. Fractional distillation gave a pure product in 42% yield: bp 100 °C (15 Torr); NMR (CCl_4) δ 1.45 (s, 9 H), 4.45 (d, J = 6 Hz, 2 H), 5.00–5.50 (m, 2 H), 5.50–6.20 (m, 1 H).

Preparation of Diallyl Carbonate. A solution of allyl alcohol (14 g, 0.5 mol) and pyridine (40 g, 0.5 mol) in dry ether (500 mL) was cooled to 0 °C under nitrogen. To this solution, trichloromethyl chloroformate (20 g, 0.1 mol) was added dropwise over 1 h at 0 °C. The mixture was stirred at 25 °C for 5 h and then filtered through Celite. The filtrate was washed with saturated aqueous $CuSO_4$ and brine. Fractional distillation gave diallyl carbonate in 67% yield bp 74 °C (24 Torr).

General Procedure for the Carbonylation. 1. Under Atmospheric Pressure. In a flask fitted with a reflux condenser was placed allylic carbonate (5 mmol). Then $Pd(OAc)_2$ (22.4 mg, 0.1 mmol) and PPh_3 (52.4 mg, 0.2 mmol) were added, and the atmosphere was replaced with CO. A rubber balloon filled with CO was attached to the top of the condenser. The mixture was stirred magnetically at 50 °C. Efficient stirring is important. After confirming the consumption of the carbonate by GLC, the ether was added to the mixture, which was filtered. After removal of the solvent, the residue was purified by distillation or column chromatography.

2. Under Pressure. The above shown reagents were placed in a small autoclave (50 mL) and CO was introduced up to 10 atm. Then the mixture was stirred at 50 °C. After the usual workup, the ester was isolated.

Identification of the Compounds. Most of the carbonates and β,γ-unsaturated esters are known compounds, except **4**, **7**, and **13**. The known compounds were identified by comparing their spectral data with those of authentic samples or reported data. The spectral and analytical data of the unknown compounds are shown below.

Ethyl 2-Phenyl-2-propenyl Carbonate (7). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 69.70; H, 6.82. NMR (CCl_4) δ 1.25 (t, 3 H, J = 7 Hz, CH_3), 4.1 (q, 2 H, J = 7 Hz, OCH_2CH_3), 4.9 (s, 2 H, allylic), 5.32, 5.45 (s, 1 H, 1 H, olefinic), 7.1–7.5 (m, 5 H, phenyl); IR (neat) 2970, 1745, 910 cm^{-1}.

Ethyl 1-*n*-butyl-2-propenyl carbonate (4): bp 52 °C (2 Torr). Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.55; H, 9.69. NMR (CCl_4) δ 0.8–1.05 (m, 3 H, CH_3), 1.25 (t, 3 H, J = 7 Hz, OCH_2CH_3), 1.1–1.9 (m, 6 H, $-(CH_2)_3-$), 4.05 (q, 2 H, J = 7 Hz, CH_2CH_3), 4.77–6.02 (m, 4 H, CHO, olefinic); IR (neat) 2950, 1750, 1465 cm^{-1}.

Ethyl 3-Phenyl-3-butenoate (13). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.58; H, 7.37. NMR (CCl_4) δ 1.1 (t, 3 H, J = 7 Hz, CH_3), 3.35 (s, 2 H, CH_2CO_2Et), 4.0 (q, 2 H, J = 7 Hz, OCH_2CH_3), 5.15, 5.43 (s, 1 H, 1 H, olefinic), 7.1–7.5 (m, 5 H, phenyl); IR (neat) 2970, 1770, 1630, 905 cm^{-1}.

Registry No. **1**, 1469-70-1; **2**, 1617-18-1; **4**, 86537-62-4; **5**, 86537-61-3; **6**, 70122-91-7; **7**, 86537-63-5; **8**, 15022-08-9; **9**, 70122-89-3; **10**, 1117-65-3; **11**, 5629-57-2; **12**, 1617-19-2; **13**, 5633-64-7; **14**, 1745-31-9; **15**, 14036-55-6; **16**, 1471-04-1; **17**, 42998-16-3; **18**, 42998-21-0; $Pd(OAc)_2$, 3375-31-3; PPh_3, 603-35-0; $P(o\text{-}Tol)_3$, 6163-58-2; $P(n\text{-}Bu)_3$, 998-40-3; $P(OPh)_3$, 101-02-0; $P(OEt)_3$, 122-52-1; allylic alcohol, 107-18-6; ethyl chloroformate, 541-41-3; allyl chloroformate, 2937-50-0; sodium *tert*-butoxide, 865-48-5; trichloromethyl chloroformate, 503-38-8.

(14) Shimizu, I.; Yamada, T.; Tsuji, J. *Tetrahedron Lett.* **1980**, *21*, 3199.