# Palladium(0)-catalyzed phenoxycarbonylation of allylic carbonates

Catherine Goux [a], Paul Lhoste [a], Denis Sinou [a,*], Anna Masdeu [b]

[a] *Laboratoire de Synthèse Asymétrique, URA 463 du CNRS, CPE Lyon, Université Claude Bernard Lyon 1, 69622 Villeurbanne Cedex, France*
[b] *Departament de Quimica, Universitat Rovira i Virgili, Pza. Imperial Tarraco 1, 3005 Tarragona, Spain*

## Abstract

Phenoxycarbonylation of various allylic carbonates under various conditions in tetrahydrofuran is described. The nature and ratio of the products formed are dependent on the presence of water, carbon monoxide pressure and addition of various inorganic halides. The formation of a product arising from dimerization of the allylic carbonate is discussed.

## 1. Introduction

$\beta,\gamma$-Unsaturated esters are versatile building blocks in organic synthesis. They may be obtained by carbonylation of allylic compounds, for example allylic halides undergo easy carbonylation in the presence of nickel [1], cobalt [2] or palladium [3] complexes. The carbonylation of allylic acetates, phosphates or carbonates using palladium(0) complexes has been studied less [4]. Recently it was shown that such carbonylation could occur under very mild conditions in the presence of alcohol via an inter- and/or intramolecular path, leading to the corresponding esters or lactones in quite good yields.

We have recently shown that the reaction of phenols with allylic carbonates is catalyzed by palladium(0) complexes to afford the corresponding aryl allyl ethers [5]. We expected that performing this reaction under carbon monoxide would lead to the formation of various unsaturated aryl esters.

## 2. Results and discussion

The first experiment was carried out with ethyl cinnamyl carbonate 1 and phenol in methanol as the solvent at 50°C, giving (E)-methyl 4-phenyl-3-butenoate 2

as the major product (66%) together with a small amount of phenyl cinnamyl ether 3 (10%) whatever the pressure of carbon monoxide (Scheme 1). The use of other solvents such as tetrahydrofuran or dichloromethane gave mainly phenyl cinnamyl ether 3 as the major product, even under a high pressure of carbon monoxide, with a small amount of (E)-phenyl-3-butenoate 4 (entries 1–3) (Scheme 2). The formation of the cinnamyl phenyl ether instead of the unsaturated ester shows that the attack of the phenolate on the $\pi$-allyl complex is faster than the insertion of CO. We noticed previously that the rate of the reaction of phenols with allylic carbonates decreases drastically in the presence of a small amount of water [5e]. The addition of water to the reaction medium allowed the formation of the desired ester 4 in a larger amount and reduced the formation of the undesired phenyl cinnamyl ether 3. We also noticed the formation of quite large amounts of a third compound, 1,4-diphenyl-1,5-hexadiene 5, resulting formally from a reductive dimerisation of the cinnamyl
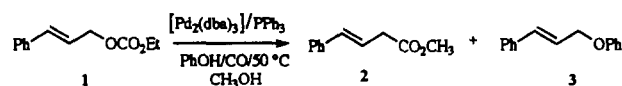


Scheme 1.
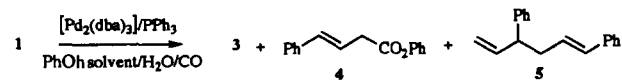


Scheme 2.

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* Corresponding author.

Table 1
Carbonylation of ethyl cinnamyl carbonate 1 [a]

| Entry | solvent (ml) | $T$ (°C) | $P_{CO}$ (atm) | Reaction time (h) | Products (%) [b] | | |
|---|---|---|---|---|---|---|---|
| | | | | | 3 | 4 | 5 |
| 1 | THF (10) | 50 | 5 | 4 | 92 | 2 | — |
| 2 | THF (10) | 50 | 30 | 6 | 99 | — | — |
| 3 | $CH_2Cl_2$ (10) | 50 | 30 | 24 | 97 | 3 | — |
| 4 | $THF/H_2O$ (9/0.5) | 50 | 5 | 7 | 42 | 27 | 19 |
| 5 | $THF/H_2O$ (9/1) | 50 | 5 | 20 | 38 | 25 | 37 |
| 6 | $THF/H_2O$ (9/1.5) | 50 | 5 | 24 | 41 | 12 | 47 |
| 7 | $THF/H_2O$ (9/1) | 50 | 50 | 10 | 34 | 33 | 33 |
| 8 | $CH_3CN/H_2O$ (5/5) | 50 | 30 | 24 | 8 | 27 | 29 |
| 9 | $THF/H_2O$ (9/1) | 30 | 30 | 20 | 43 | 41 | 16 |
| 10 | $THF/H_2O$ (9/2) | 30 | 50 | 20 | 6 | 27 | 67 |
| 11 | $THF/H_2O$ (9/3) | 30 | 50 | 20 | 14 | 19 | 67 |
| 12 | $THF/H_2O$ (9/3) | 30 | 60 | 20 | 5 | 14 | 56 |
| 13 | $THF/H_2O/CH_2Cl_2$ (9/1/4) | 30 | 50 | 10 [c] | 94 | — | — |
| 14 | $THF/H_2O$ (9/2) | 60 | 30 | 24 | 29 | 14 | 48 |
| 15 | $THF/H_2O$ (9/2) | 70 | 30 | 24 | 23 | 25 | 28 |

[a] General conditions: 0.66 mmol of ethyl cinnamyl carbonate 1, 0.8 mmol of phenol, 2 mol.% of $[Pd_2(dba)_3]$ and 16 mol.% of $PPh_3$ in the mentioned amount of solvent; quantitative transformation. [b] Determined by GC. [c] 57% transformation.

Table 2
Effect of halides on the phenoxycarbonylation of ethyl cinnamyl carbonate 1 [a]

| Entry | $P_{CO}$ (atm) | Halide [b] | [Phenol]/[1] | Reaction time (h) | Products (%) [c] | | |
|---|---|---|---|---|---|---|---|
| | | | | | 3 | 4 | 5 |
| 1 | 5 | NaBr | 30/25 | 45 | 21 | 44 | 8 |
| 2 | 50 | NaBr | 30/25 | 24 | 33 | 37 | 6 |
| 3 | 5 | LiBr | 30/25 | 14 [d] | 32 | 48 | 10 |
| 4 | 5 | LiBr | 25/25 | 24 [e] | 37 | 59 | 4 |
| 5 | 5 | LiBr | 17/25 | 24 [f] | 14 | 79 | 7 |
| 6 | 5 | KI | 50/25 | 24 | 87 | 2 | 11 |
| 7 | 5 | KI | 150/25 | 24 | 81 | 2 | 17 |
| 8 | 30 | KI | 50/25 | 63 | — | 79 | — |

[a] General conditions: 0.66 mmol of ethyl cinnamyl carbonate 1, the phenol, 2 mol.% of $[Pd_2(dba)_3]$ and 16 mol.% of $PPh_3$ in 9 ml of tetrahydrofuran and 1 ml of water; 50°C; quantitative transformation unless otherwise indicated. [b] 10 mol.% of halide. [c] Determined by GC. [d] 10% transformation. [e] 14% transformation. [f] 30% transformation.

carbonate 1. This compound was contaminated by a small amount of 3,4-diphenyl-1,5-hexadiene as shown by $^1H$ and $^{13}C$ NMR spectroscopies. The formation of

these compounds was also noted by Okano et al. [3g] during the carbonylation of cinnamyl chloride in a two-phase system in the presence of $[PdCl_2L_2]$ [$L = m$-$(Ph_2P)C_6H_4SO_3Na$] and also by other workers using various catalytic conditions [6].
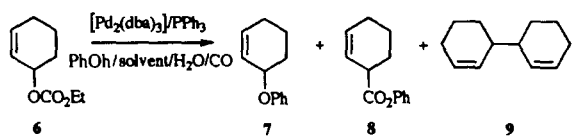
As shown in Table 1, the relative ratio of the three compounds depends strongly on the amount of water in the medium, the temperature of the reaction and the CO pressure. Increasing the amount of water at 50°C and under 5 atm CO decreased the amount of the ether 3, but favored the dimerization product 5 (entries 4–6). The addition of dichloromethane to the medium gave exclusively the ether 3 (entry 13). Under the conditions used for the carbonylation, cinnamyl phenyl ether 3 remained unchanged, showing that this compound is not a precursor of the unsaturated ester 4 [4c].

Using the methodology of Murahashi et al. [4c] for the carbonylation of various allylic acetates in the presence of various inorganic halides, we performed some experiments in the presence of NaBr, LiBr or KI, using a mixture of tetrahydrofuran and water as the solvent.
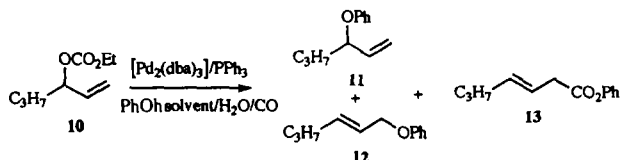
Table 3
Carbonylation of ethyl cyclohexenyl carbonate 6 [a]

| Entry | Solvent (ml) | $P_{CO}$ (atm) | Reaction time (h) | Conversion (%) | Products (%) [b] | | |
|---|---|---|---|---|---|---|---|
| | | | | | 7 | 8 | 9 |
| 1 | THF (10) | 30 | 26 | 70 | 38 | 31 | 31 |
| 2 | $THF/H_2O$ (9/1) | 30 | 26 | 70 | 30 | 37 | 21 |
| 3 | $THF/H_2O$ (9/1) | 5 | 26 | 86 | 22 | 46 | 27 |
| 4 | $THF/H_2O$ (9/1) [c] | 5 | 18 | 32 | 41 | 23 | 24 |
| 5 | $THF/H_2O$ (9/3) | 5 | 17 | 98 | 46 | 15 | 1 |
| 6 | $THF/H_2O$ (9/5) | 5 | 26 | 55 | 85 | — | 12 |

[a] General conditions: 0.67 mmol of ethyl cyclohexenyl carbonate 6, 0.8 mmol of phenol, 2 mol.% of $[Pd_2(dba)_3]$ and 16 mol.% of $PPh_3$ in the mentioned amount of solvent at 25°C. [b] Determined by GC. [c] LiBr (10 equiv.) added; 57% transformation.
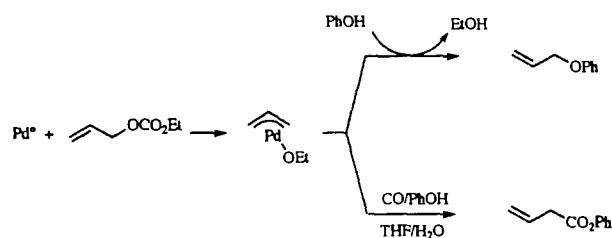
Scheme 3.



Scheme 4.



Scheme 5.

The results, summarized in Table 2, show that generally the presence of an inorganic salt favors the formation of the desired ester 4 and decreases the amount of the dimer 5. However, the presence of LiBr gives a less active catalyst (entries 3–5). The salt KI seems to be the inorganic halide which gives the highest activity. Carrying out the reaction under 5 atm CO gave the cinnamyl phenyl ether 3 as the major compound (entries 6 and 7), although increasing the CO pressure to 30 atm changed completely the selectivity (entry 8). The ester 4 was then obtained as the major compound, with some by-products whose structures were not determined. Under these conditions phenyl cinnamyl ether 3 gave no reaction, as already shown by Murahashi et al. [4b].

The results of the phenoxycarbonylation of cyclohexenyl ethyl carbonate 6 in the presence of phenol (Scheme 3), summarized in Table 3, show the formation of three products: the cyclohexenyl phenyl ether 7, the phenyl 2-cyclohexenecarboxylate 8 and the product 9 resulting from palladium-mediated reductive coupling of the carbonate, whatever the conditions used. However, it seems that increasing the amount of water hindered the formation of the ester, and that the presence of LiBr gave a less active catalyst. In the case of this compound, it was difficult to find the conditions leading predominantly to the formation of the unsaturated ester 8.

Finally, we studied the phenoxycarbonylation of 1-hexen-3-yl ethyl carbonate 10 under similar conditions (Scheme 4). The results, summarized in Table 4, show that phenoxycarbonylation occurred even in the absence of water. However, we observed the ethers 11 and 12 and the linear ester 13 formed from a competition between the attack of the phenolate anion on the $\pi$-allyl intermediate and from the insertion of CO in the $\pi$-allyl system intermediate. However, carrying out the reaction under higher pressure of carbon monoxide seemed to favor the formation of the ester 12 (compare entries 3 and 5 and entries 7 and 8). The presence of a halide such as LiBr gave a catalyst with lower activity. Products resulting from dimerization coupling ($m/z$ at 166 and 83) but in very low amounts were detected by GC-MS.

The formation of the allyl ether and the allylic ester may be rationalized by Scheme 5. Oxidative addition of allyl ethyl carbonate to the palladium(0) complex results in a $\pi$-allylpalladium ethoxy complex. This $\pi$-allyl complex could be attacked directly by the phenolate generated by an exchange reaction between ethoxy anion and phenol, to give the allyl phenyl ether. Another possibility is the insertion of carbon monoxide leading to an acyl palladium complex which forms the ester by reaction with phenol. As demonstrated by Murahashi et al. [4c], there is probably a ligand exchange between the ethoxide or the phenolate and the halide ion, which is the key step in this reaction. However, in the case of iodide, insertion of CO needed a higher CO pressure,

Table 4
Carbonylation of hex-1-en-3-yl ethyl carbonate 10 [a]

| Entry | Solvent (ml) | $P_{CO}$ (atm) | Reaction time (h) | Conversion (%) | Products (%) [b] | |
|---|---|---|---|---|---|---|
| | | | | | 11 + 12 | 13 |
| 1 | THF (10) | 5 | 24 | 95 | 67 | 30 |
| 2 | THF (10) | 30 | 6 | 45 | 52 | 48 |
| 3 | THF/H$_2$O (9/1) | 5 | 24 | 96 | 69 | 15 |
| 4 | THF/H$_2$O (9/1) [c] | 5 | 24 | 17 | 34 | 41 |
| 5 | THF/H$_2$O (9/1) | 30 | 24 | 89 | 29 | 38 |
| 6 | THF/H$_2$O (9/2) | 30 | 24 | 84 | 25 | 26 |
| 7 | THF/H$_2$O (9/3) | 5 | 6 | 87 | 32 | 12 |
| 8 | THF/H$_2$O (9/3) | 30 | 24 | 90 | 14 | 60 |

[a] General conditions: 0.66 mmol of hex-1-en-3-yl ethyl carbonate 10, 0.8 mmol of phenol, 2 mol.% of [Pd$_2$(dba)$_3$] and 16 mol.% of PPh$_3$ in the mentioned amount of solvent. [b] Determined by GC. [c] LiBr (10 equiv.) added.
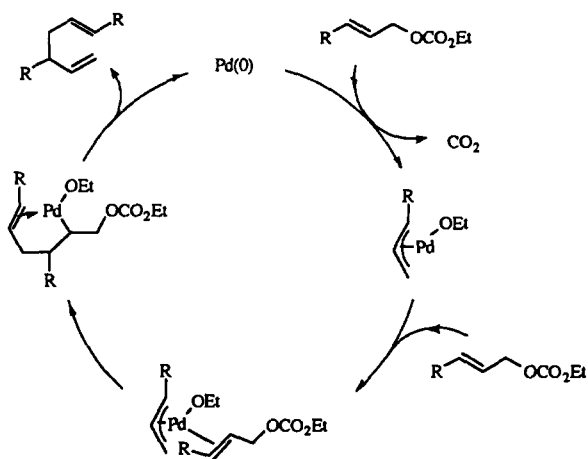
Scheme 6.

probably due to the bulkiness ot the anion. The presence of water favors the formation of the ester, probably by decreasing the nucleophilicity of the phenolate.

The formation of the dimerization product is more speculative. One possible mechanism is described in Scheme 6. Oxidative addition of the palladium(0) complex gives the $\pi$-allyl intermediate. Association of another molecule of allylic carbonate followed by insertion gives a $\sigma$-palladium complex. The dimer could be obtained by $\beta$-elimination of $OCO_2Et$, although such a $\beta$-elimination is not usual.

## 3. Conclusion

The phenoxycarbonylation of allylic carbonates occurs in the presence of carbon monoxide in THF. However, this reaction seems more difficult than the alkoxycarbonylation of these allylic carbonates. Allyl phenyl ether was always obtained in this reaction, as well as a product arising from dimerization of the allylic carbonate.

## 4. Experimental part

All reactions that involved palladium complexes were carried out under dinitrogen in Schlenk tubes. Tetrahydrofuran, acetonitrile or dichloromethane were freshly distilled before use. Column chromatography was performed using silica gel, Merck, grade 60 (230–400 mesh, 60 Å). GC analyses were carried out on a capillary column with Ultra-2 (5% diphenylsilicone, 95% dimethylsilicone) (25 m × 0.2 mm). All compounds were characterized through their $^1$H and $^{13}$C NMR spectra, using $CDCl_3$ as the solvent and $Me_4Si$ or chloroform-$d$ as internal standard; carbon multiplicities were obtained from DEPT experiments. The following chemicals were bought from Aldrich and used as re-

ceived: ($E$)-cinnamyl alcohol, cyclohex-2-en-1-ol, hex-1-en-3-ol, [$Pd_2(dba)_3$], $PPh_3$. The alcohols were converted to the corresponding ethyl carbonates in good yields using standard procedures. The ethers 3 [7], 7 [8] and 11–12 [5e] have already been described.

### 4.1. Palladium-catalyzed phenoxycarbonylation of allylic carbonates

A solution of the catalyst obtained from [$Pd_2(dba)_3$] (0.013 mmol) and $PPh_3$ (0.10 mmol) in 5 ml of solvent (THF or $THF/H_2O$) was transferred to a Schlenk tube containing the phenol and halide. This solution was introduced into a 100 ml stainless evacuated autoclave containing the carbonate (0.66 mmol) in 5 ml of THF. The CO was introduced at the desired pressure and the mixture was stirred at the indicated temperature. The conversion of the carbonate and the ratios of the products obtained were calculated from GC data. After evaporation of the solvent, the products were separated by column chromatography on silica using hexane/ethyl acetate or hexane/dichloromethane as the eluent, and characterized.

### 4.1.1. (E)-Phenyl 4-phenyl-3-butenoate 4

$R_f$ 0.62 (hexane/$CH_2Cl_2$ 7/3); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 3.50 (dd, $J$ = 7.0 and 1.3 Hz, 2 H, $CH_2$), 6.40 (dt, $J$ = 16.0 and 7.0 Hz, 1 H, –CH=), 6.61 (bd, $J$ = 16.0 Hz, 1 H, –CH=), 7.2–7.5 (m, 10 H, $C_6H_5$).

### 4.1.2. 1,4-Diphenyl-1,5-hexadiene 5

$R_f$ 0.61 (hexane/$CH_2Cl_2$ 7/3); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 2.65 (t, $J$ = 7.3 Hz, 2 H, –$CH_2$–), 3.42 (dm, $J$ = 7.3 Hz, 1 H, –CH <), 5.06 (dd, $J$ = 16.8 and 1.3 Hz, 1 H, =$CH_2$), 5.08 (dd, $J$ = 10.2 and 1.3 Hz, 1 H, =$CH_2$), 5.95–6.08 (m, 1 H, –CH=), 6.15 (m, 1 H, –CH=;), 6.4 (d, $J$ = 15.8 Hz, 1 H, –CH=), 7.1–7.4 (m, 10 H, $C_6H_5$); $^{13}$C (75 MHz, $CDCl_3$) $\delta$ 39.0 ($CH_2$), 50.0 (–CH <), 114.6 (=$CH_2$), 115.8 (–CH=), 131.4 (–CH=), 141.5 (–CH=), 126.0, 126.3, 126.9, 127.7, 128.5 and 138.0 ($C_6H_5$); MS (EI) $m/z$ (%) 117 ($M/2^+$, 100) consistent with the literature [6a].

### 4.1.3. Phenyl 2-cyclohexenecarboxylate 8

$R_f$ 0.70 (hexane/ethyl acetate 8/1); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.40–2.25 (m, 6 H, –$CH_2$–), 3.07–3.12 (m, 1 H, –CH <), 5.55–6.02 (m, 2 H, –CH=), 6.8–7.8 (m, 5 H, $C_6H_5$); MS (EI) $m/z$ (%) 202 ($M^+$, 2), 109 (13), 108 (65), 94 (13), 81 (100), 80 (78), 79 (41).

### 4.1.4. 2,2′-Bicyclohexenyl 9

$^1$H (300 MHz, $CDCl_3$) $\delta$ 1.10–2.33 (m, 14 H, –$CH_2$– and –CH <), 5.4–5.9 (m, 4 H, –CH=); MS (EI) $m/z$ (%) 162 ($M^+$, 2), 81 (100), 80 (15), 79 (22) consistent with the literature [6a].

#### 4.1.5. (E)-Phenyl 3-heptenoate 13

$R_f$ 0.70 (hexane/ethyl acetate 8/1); $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 0.99 (t, 3 H, -CH$_3$), 1.39–1.46 (m, 2 H, -CH$_2$-), 2.02–2.09 (m, 2 H, -CH$_2$-), 3.28 (dd, $J$ = 5.6 and 0.9 Hz, 2 H, -CH$_2$CO$_2$-), 5.62–5.68 (m, 2 H, -CH=), 7.07–7.40 (m, 5 H, C$_6$H$_5$); $^{13}$C (75 MHz, CDCl$_3$) $\delta$ 13.6 (CH$_3$), 22.3 (CH$_2$), 34.6 (CH$_2$-CH=), 38.2 (CH$_2$-CO$_2$), 121.0, 121.5, 125.8, 129.4 and 131.0 (-CH= and C$_6$H$_5$); MS (EI) $m/z$ (%) 204 (M$^+$, 2), 110 (100), 94 (44), 83 (21), 82 (41), 81 (50).

#### Acknowledgements

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