

Palladium-catalyzed alkoxy carbonylation of allylic natural terpenic functionalized olefins

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Abstract

The palladium-catalyzed alkoxy carbonylation of allyl carbonates and allyl chlorides derivatives from terpenic olefins was carried out under atmospheric pressure of carbon monoxide and at moderate temperature. The reaction offers a very good method for the preparation of new β , γ -unsaturated esters and thus to provide a useful entry to new functionalized terpenic olefin products. The retention of optical activity of the synthesized products when the reaction is carried out from optically active substrates, has also been checked and discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Palladium; Alkoxy carbonylation; Allylic functionalized terpenic olefin

1. Introduction

Recently, we reported that the oxidative functionalization of monoterpenes occurs with high activity and selectivity to give oxygenated derivatives of considerable interest for perfumery, flavor and pharmaceutical industry [1–3]. In order to extend the potential use of these cheap natural alkenes, we have focused our attention on the carbonylation of their allylic derivatives under atmospheric pressure of CO to improve the synthetic interest of the reaction.

The carbonylation of allylic compounds catalyzed by transition metal complexes is one of the most attractive tools to synthesize the β , γ -unsaturated carbonyl compounds, which are versatile building blocks. Indeed carbonylation of allyl ethers [4–5], acetates [6–8], formates [9], phosphates [8,10], carbonates [6,11] and chlorides [12–15] was reported. It

is nevertheless noteworthy that the carbonylation of synthetically more important allylic alcohol derivatives, such as allylic acetates and ethers is difficult and usually requires severe conditions. Recently, it was found that this reaction takes place under very mild conditions using allyl halides and carbonates. However, although the alkoxy carbonylation and hydroxy carbonylation of allylic functionalized simple alkenes have been extensively studied few works have been devoted to the corresponding reactions using natural terpenic alkenes derivatives [6,16] and more particularly cyclic terpenic derivatives.

The aim of the present study was to investigate on the one hand, the decarboxylation–carbonylation of allylic carbonates having limonene, pinene or myrcene skeletons obtained from the corresponding allylic alcohol and, on the other hand, the carbonylation of allylic chloride synthesized from α or β -pinene. It was found that the alkoxy carbonylation of these allylic terpenic olefins derivatives using various palla-

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dium complexes generally proceeds highly selectively under mild conditions to afford β , γ -unsaturated esters. Moreover, when the reaction was carried out from optically active allylic functionalized monoterpenes as substrates, attention was paid on the optical purity of the reaction products and the mechanistic implications of the results are discussed.

2. Results and discussion

2.1. Carbonylation of allyl carbonate

To examine the possibility to achieve efficiently the catalytic decarboxylation–carbonylation of allylic terpenic carbonates, perillyl carbonate **1** synthesized from the corresponding allylic alcohol according to the literature method was chosen as model substrate of this class of compounds. Systematic investigations of its reactivity in the presence of various palladium based catalytic systems were undertaken to define the best reaction conditions. The results are summarized in Table 1. Thus treatment of **1** in ethanol using Pd(OAc)₂-PPh₃ catalytic system (substrate/Pd = 50, P/Pd = 2) gave the corresponding allylic ethyl ester **6** in 73% yield after 16 h at 50°C under atmospheric pressure of CO (entry 1). At room temperature the reaction proceeds smoothly and the yield reached only 16% after 24 h (entry 5). Starting from Pd₂(dba)₃ as catalyst instead of Pd(OAc)₂ gave similar results (74% yield) (entry 4). On the other hand, in the absence of ligand practically no reaction took place

Table 1
Effect of catalyst and ligand on the carbonylation of perillyl carbonate **1**^a

Entry	Catalyst	Ligand	Reaction time (h)	Yield ^b (%)
1	Pd(OAc) ₂	PPh ₃	16	73
2	Pd(OAc) ₂	P(<i>o</i> -tolyl) ₃	16	26
3	Pd(OAc) ₂	None	26	2
4	Pd ₂ (dba) ₃	PPh ₃	16	74
5	Pd(OAc) ₂ ^c	PPh ₃	24	16
6	Pd/C	PPh ₃	24	12
7	Pd(OAc) ₂	2,2'-dipyridyl	24	Trace

^a Conditions: Pd(OAc)₂ 0.044 mmol; PPh₃ 0.088 mmol; substrate 2.23 mmol; PCO 1 atm; ethanol 5 ml; temperature 50°C.

^b Determined by GC.

^c At room temperature.

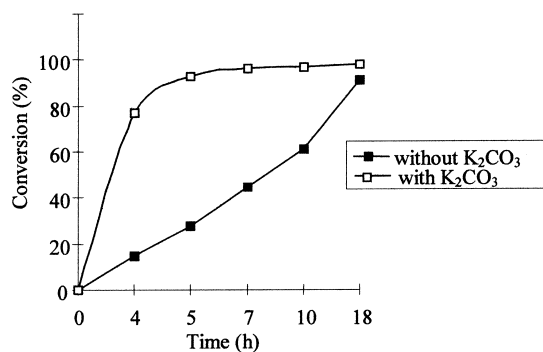


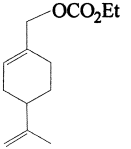
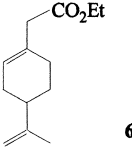
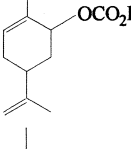
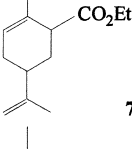
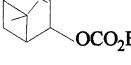
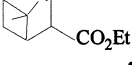
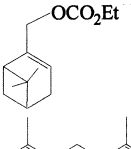
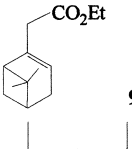
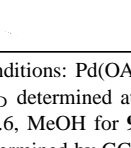
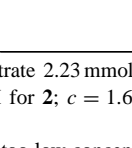
Fig. 1. Effect of K₂CO₃ on the activity of the allylic carbonylation of **1**.

(entry 3). In the same ways, other ligands than PPh₃ such as P(*o*-tolyl)₃ or 2,2'-dipyridyl lead to worse result. Finally, Pd/C system exhibited a low activity even in the presence of PPh₃.

Fig. 1 shows also that the allylic carbonylation rate of allylic carbonates is improved by the addition of base such as K₂CO₃. Indeed a 92% conversion (74% yield) was obtained after only 5 h of reaction at 50°C, whereas in the absence of base 16 h were needed to reach almost the same result.

The Pd(OAc)₂-PPh₃ system which give the best results with **1** was then used under previous conditions to catalyse the carbonylation of carbonates **2–5** derived from limonene, pinene and prepared as **1** from their corresponding allylic alcohols. The results obtained are collected in Table 2. Carvyl and myrtenyl carbonates **2** and **4** reacted similarly to **1** and carbonate **5** was even slightly more reactive (80% yield after 16 h). In contrast, verbenyl carbonate **3** exhibited a very poor activity as only 4% yield of ester was attained after 24 h under typical reaction conditions (Table 2 entry 3). It is also noteworthy that the carbonates **1–4** which were synthesized as indicated from the corresponding optically active natural allylic alcohols exhibited also an optical activity as indicated in Table 2. Therefore, in order to gain better insight on the mechanism of the reaction, we have checked the specific rotation of the esters obtained. It appeared that if ester **6** and to some extent **9** have preserved an optical activity, in contrast ester **7** derived from carvyl carbonate was found optically inactive. This indicates that the formation of this last ester occurs via a symmetrical palladium intermediate.

Table 2
Carbonylation of terpenic allylic carbonates^a

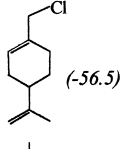
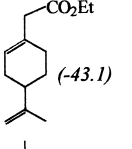
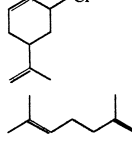
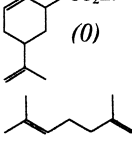
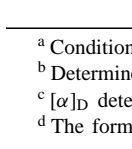
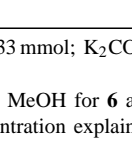
Entry	Allylic carbonate	$[\alpha]_D$	Time (h)	Product	$[\alpha]_D^b$	Yield ^c (%)	Conversion ^c (%)
1	 1	-38.5	16	 6	-51.2	73	91
2	 2	-81.5	16	 7	0	74	95
3	 3	-	24	 8	-	4	20
4	 4	-45.5	16	 9	+3.4	67	96
5	 5	-	16	 10	-	80	97

^a Conditions: Pd(OAc)₂ 0.044 mmol; PPh₃ 0.088 mmol; substrate 2.23 mmol; PCO 1 atm; ethanol 5 ml; temperature 50°C.

^b $[\alpha]_D$ determined at: *c* = 1.6, MeOH for **1**; *c* = 1.3, MeOH for **2**; *c* = 1.6, MeOH for **4**; *c* = 2.1, MeOH for **6**; *c* = 1.6, MeOH for **7**; *c* = 1.6, MeOH for **9**.

^c Determined by GC. The formation of various compounds in too low concentration (<1%) to be easily identified explains the difference between yield and conversion.

Table 3
Atmospheric pressure carbonylation of allylic chlorides^a

Allylic chloride $[\alpha]_D^c$	Time (h)	Product $[\alpha]_D^c$	Yield ^{b,d} (%)	Conversion ^{b,d} (%)
 11 (-56.5)	1.5	 6 (-43.1)	96	100
 12	5	 7 (0)	46	60
 13	1.5	 10	86	94

^a Conditions: allyl chloride 3.3 mmol; Pd(OAc)₂ 0.033 mmol; K₂CO₃ 9.7 mmol; ethanol 5 ml; PCO:1 atm; temperature 25°C.

^b Determined by GC.

^c $[\alpha]_D$ determined at: *c* = 2, MeOH for **11**; *c* = 1.3, MeOH for **6** and *c* = 1.6, MeOH for **7**.

^d The formation of various compounds in low concentration explains the difference between yield and conversion.

2.2. Carbonylation of allylic terpenic halides

In the second part of our work, we have studied the palladium-catalyzed alkoxycarbonylation of allylic chlorides **11**–**13** obtained from α , β -pinene and geraniol, respectively, as indicated in the experimental part. The carbonylation of perillyl chloride **11** dissolved in ethanol was achieved in high yield (96%) after only 1.5 h in the presence of catalytic amounts of Pd(OAc)₂ and anhydrous potassium carbonate as a base (stoichiometric) to give the allylated carbonyl product **6** under atmospheric pressure of carbon monoxide and at room temperature (Table 3). Practically similar results were obtained with geranyl chloride **13** under the same reaction conditions (86% yield after 1.5 h). On the other hand, carvyl chloride appeared less reactive as its conversion reached only 60% after 5 h. Moreover, the ester **6** obtained from perillyl chloride exhibited an optical activity¹ (as in the case of **6** resulting from perillyl carbonate) whereas the ester **7** is inactive.

Finally, in order to determine the scope and limitation of the reaction, systematic investigations were undertaken with **11** in the presence of different palla-

¹ One of the referee's has commented on the fact that the observed optical activity of the carbonylation compound **6** arising from the allylic chloride **11** was lower than that coming from the carbonate **1**, which would not be consistent with a complete retention of configuration. As a matter of fact, the synthesis of perillyl chloride from β -pinene has given in our hand a product whose specific rotation ($[\alpha]_{\text{D}}^{20} = -56^\circ$) does not necessarily correspond to a homochiral compound, due to: (i) the nature of the starting β -pinene (ee = 93%) and (ii) to the stereochemistry of the opening into the perillyl chloride, for which there is no information about the retention of configuration in the original paper [17]. The only reference related to the specific rotation of perillyl chloride gives a specific rotation $[\alpha]_{\text{D}} = -60^\circ$ [18]. However, we feel that we cannot take this value into consideration to evaluate the purity of our chloride. In any case, if there were a racemization during the carbonylation of perillyl chloride, this process would imply necessarily the formation of an internal symmetrical π -allylic group and a subsequent isomerization into the external one and carbonylation (that correspond formally in Scheme 3 to the migration of the double bond from position 2–3 to 2–7). As it has been shown that the carbonylation of **12** occurs under the same conditions giving **7** and that this compound **7** has not been detected in the perillyl chloride carbonylation, this racemization process is to our opinion unlikely. Further studies will be made in due course to analyze the optical purity of **11** and generally speaking to the other related compounds, due to the lack of information in the literature.

Table 4

Carbonylation of **11** with various catalytic systems^a

Entry	Catalyst	Temperature (°C)	Reaction time (h)	Yield ^b (%)
1	Pd(OAc) ₂	25	1.5	96
2	Li ₂ PdCl ₄	25	1.5	92
3	Pd(OAc) ₂ ^c	25	3	55
4	Pd/C	25	1.5	88
5	Pd ₂ (dba) ₃	25	1.5	94
6	PdCl ₂ (PPh ₃) ₂	25	2	90
7	Pd(OAc) ₂ ^d	25	3	76

^a Conditions: the reaction was carried out under atmospheric pressure of CO; allylic chloride **11** (3.3 mmol); K₂CO₃ (9.9 mmol); 1 mol% of catalyst in 5 ml of EtOH.

^b Determined by GC.

^c One milliliter of water was added to the reaction

^d In the presence of Na₂CO₃.

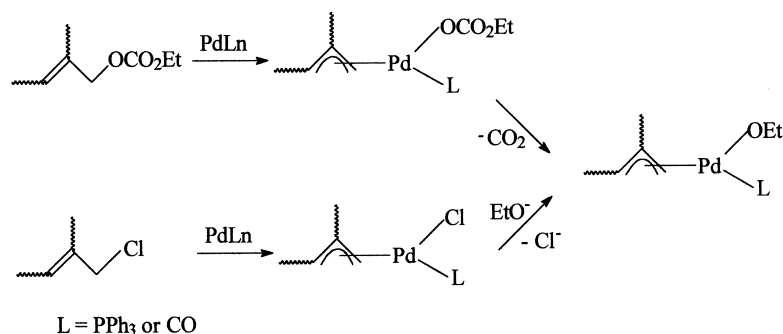
dium salts or complexes and under different reaction conditions. The results are summarized in Table 4.

The nature of the palladium catalyst precursor seems to have little effect on the results as the yield varies only between 90 and 96% according to the Pd precursor; the presence of phosphine is not needed and has rather a detrimental effect. More, the heterogeneous Pd/C system leads to 88% yield after 1.5 h. On the other hand, the use of sodium carbonate instead of K₂CO₃ at the same concentration with Pd(OAc)₂ resulted in some decrease of the ester yield (76% after 3 h), a lower solubility of Na₂CO₃ in organic solvents could explain this difference of results.² In the same way when methanol was used in place of ethanol as solvent only poor results were obtained.

2.3. Mechanistic aspects

It is well known that one of the most convenient and typical method to prepare a π -allyl-palladium complex is to bubble carbon monoxide into a solution of allyl chloride and Na₂PdCl₄ in methanol–water [19]. Moreover, it has been proposed that the carbonylation of allyl carbonate [6] (as well for example their cross coupling reaction with organosilicon compounds [20])

² Although the reaction is different, it has been frequently reported that in Suzuki cross coupling reaction of aryl halide with aryl boronic acids catalyzed by Pd, totally different results are obtained according the nature of the counteranion, when carbonate was used as base, however, no explanation has been given to rationalize this effect [22].

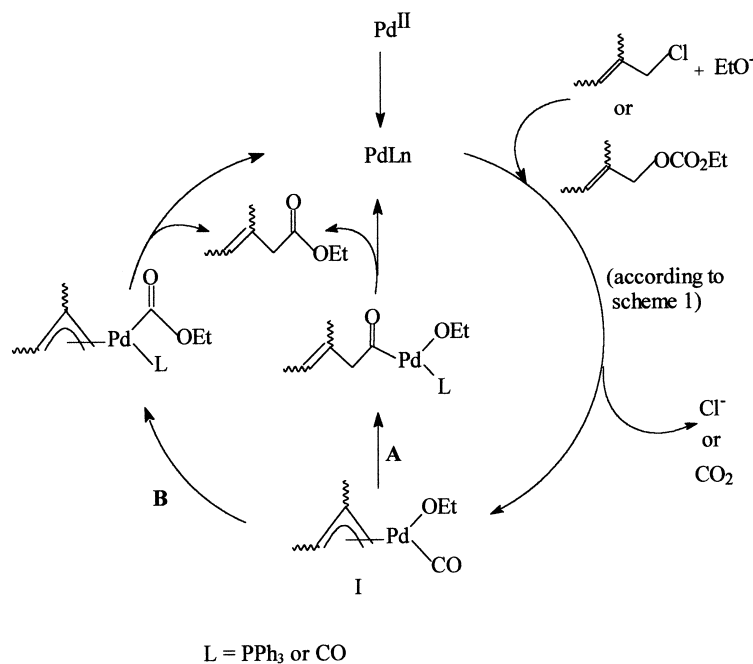


Scheme 1.

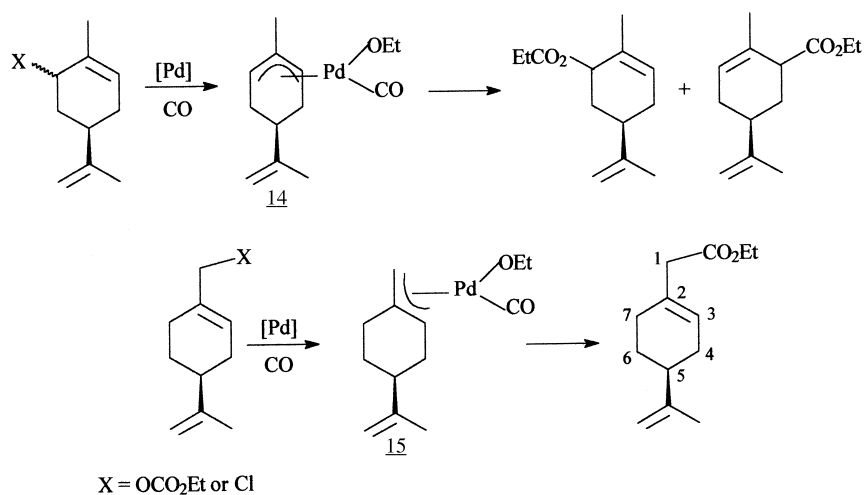
proceeds via the formation of a (π -allyl)(alkoxy) palladium intermediate generated by oxidative addition of the substrate to a Pd⁰ species followed by decarboxylation (Scheme 1).

Thus, we can assume that a π -allyl-palladium complex is probably involved in alkoxy-carbonylation of both allyl carbonates and allyl chlorides. From this species the reaction course can follow two main paths (Scheme 2). Migratory insertion of CO can occur in

the allyl-Pd bond to give an acyl-Pd (path A) or in the Pd-OR bond to afford an (allyl)(alkoxycarbonyl)-Pd intermediate (path B). The β , γ -unsaturated ester is finally obtained in each case by reductive elimination. Although it is difficult to delineate the exact mechanism of the reaction, it is noteworthy that it has been shown that insertion of carbon monoxide into the carbon-palladium bond of a (π -allyl)-palladium complex is generally difficult [21]. As a consequence,



Scheme 2.



Scheme 3.

path B has been proposed by Okano et al. due to the unusual activity observed in allylic halide carbonylation under mild conditions [13].

In our case, the formation of a π -allyl-palladium complex, whatever the following step, is in good agreement with the results obtained with the optically active substrate. Indeed the fact that carvyl carbonate **2** or carvyl chloride **12** leads to a symmetrical π -allyl palladium complex (**14**) as intermediate can explain that the resulting ester **7** does not exhibit any optical activity (see Scheme 3).

In contrast, complex **15** obtained from perillyl carbonate **1** or perillyl chloride **11** does not possess any symmetry as the alkoxy carbonylation occurs exclusively on the less substituted carbon (i.e. on the carbon bearing the reactive function OCO₂R or Cl on the substrate), the C5 carbon of the ester **6** must have the same configuration as in substrates **1** and **11** (see Scheme 3).

The low activity observed with allyl carbonates as compared with that of allyl chlorides is probably due to a greater difficulty to obtain the common (π -allyl)(alkoxy)Pd intermediate **I** (Scheme 2) as a result of a lower reactivity of these substrates toward Pd⁰ species and/or to the fact that the decarboxylation is difficult. It has also been mentioned that the carbonylation of allyl chloride occurs in the absence of phosphines and that the activity was even better without phosphine. In that case, chloride ions produced during the reaction course can stabilize the Pd⁰ intermediate

leading to a coordinatively unsaturated species which is particularly reactive toward the oxidative addition of the allyl chloride and subsequent π -allyl formation.

3. Conclusion

The palladium-catalyzed allylic carbonylation of allyl carbonates under mild reaction conditions gives β , γ -unsaturated ester selectively. Allyl chlorides are also carbonylated at ambient temperature. The carbonylation reaction is found to depend on the ligand and catalyst employed. The use of optically active monoterpenes as starting materials allowed to prepare new asymmetric functionalized compounds derived from natural products.

4. Experimental section

4.1. General remarks

Allyl carbonates and allyl halides were synthesized using procedures described below. Solvents were commercial grade. Catalysts and ligands were used without further purification. K₂CO₃ was dried under vacuum before using. Ethanol was dried over magnesium, distilled and stored under nitrogen atmosphere. The reaction mixtures were analyzed on a Varian 3400 CX series chromatograph equipped with

a FID, using silica capillary columns CP Sil 5 CB (20 m × 0.33 mm, Chrompack). The NMR spectra were recorded on a Bruker AM 400 in CDCl₃ solution by using TMS as an internal standard. The yields of esters were determined by GC.

4.2. Preparation of ethyl allyl carbonates [11]

To a cooled (0°C) and stirred solution of the allylic alcohol (100 mmol) and dry pyridine (200 mmol) in dry ether (100 ml) was added ethyl chloroformate (100 mmol) dropwise over 15 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 water and dried over MgSO₄. Following the evaporation of the solvent, the allyl carbonate was obtained in yields varying between 90 and 96%.

4.2.1. **1** [α]_D²⁰ = -38.5° (*c* = 1.6; *MeOH*)

¹³C NMR: δ 155.3 (C=O); 149.5 (=C); 132.2 (=C); 126.6 (=CH); 108.8 (=CH₂); 71.8 (-CH₂); 63.8 (OCH₂CH₃); 40.7 (-CH); 30.5 (-CH₂); 27.3 (-CH₂); 26.3 (-CH₂); 20.7 (OCH₂CH₃); 14.3 (-CH₃).

¹H NMR: δ 5.75 (1H, m, CH); 4.65 (2H, m, =CH₂); 4.45 (2H, s, CH₂-O); 4.1 (2H, q (*J* = 7.2 Hz), O-CH₂CH₃); 1.67 (3R, s, CH₃); 1.24 (3H, t (*J* = 7.2 Hz), OCH₂CH₃).

4.2.2. **2** [α]_D²⁰ = -81.5° (*c* = 1.3; *MeOH*)

¹³C NMR: δ 155.2 (C=O); 148.6–148.1 (=C); 132.5–130.3 (=C); 128.3–126.1 (=CH); 109.4–109.2 (=CH₂); 77.1–74.6 (-CHO); 63.8 (O-CH₂CH₃); 40.3–35.5 (-CH); 33.9–33.5 (-CH₂); 30.9–30.7 (-CH₂); 20.8–20.6 (CH₃); 20.4–18.6 (CH₃); 14.3 (CH₃).

¹H NMR: δ 5.61–5.54 (1H, m, =CH); 5.52–5.03 (1H, m, -CH-O); 4.67 (2H, m, =CH₂); 4.14 (2H, q (*J* = 7 Hz), OCH₂CH₃); 1.66 (6H, s, 2 CH₃); 1.25 (3H, t (*J* = 7 Hz), OCH₂CH₃).

4.2.3. **3**

¹³C NMR: δ 155.0 (C=O); 150.1 (=C); 115.2 (=CH); 78.9 (-CHO); 63.5 (O-CH₂CH₃); 47.5 (-CH); 45.4 (-CH); 39.6 (C-C); 35.6 (CH₂); 26.6 (CH₃); 22.6 (CH₃); 22.5 (CH₃); 14.3 (CH₃).

¹H NMR: δ 5.36 (1H, m, =CH); 5.34 (1H, m, -CH-O); 4.13 (2H, q (*J* = 6.6 Hz), OCH₂CH₃); 1.72

(3H, t (*J* = 1.4 Hz), -CH₃); 1.32 (3H, s, CH₃); 1.28 (3H, t (*J* = 6.6 Hz), -OCH₂CH₃); 1.0 (3H, s, -CH₃).

4.2.4. **4** [α]_D²⁰ = -45.5° (*c* = 1.6; *MeOH*)

¹³C NMR: δ 155.2 (C=O); 142.4 (=C); 122.2 (=CH); 103.3 (-C); 70.3 (CH₂-O); 63.7 (O-CH₂CH₃); 43.3 (-CH); 40.6 (-CH); 31.4 (-CH₂); 31.2 (-CH₂); 26.0 (-CH₃); 20.9 (-CH₃); 14.2 (-CH₃).

¹H NMR: δ 5.55 (1H, m, =CH); 4.42 (2H, dd (*J* = 3.2, 1.42 Hz), -CH₂-O); 4.12 (2H, q (*J* = 7.2 Hz), OCH₂CH₃); 1.24 (3H, t (*J* = 7.2 Hz), -OCH₂CH₃); 1.23 (3H, s, -CH₃); 0.76 (3H, s, -CH₃).

4.2.5. **5**

¹³C NMR: δ 155.0 (C=O); 142.6 (=C); 131.4 (=C); 123.4 (=CH); 117.6 (=CH); 64.1 (-CH₂); 63.4 (-CH₂); 39.3 (-CH₂); 25.9 (-CH₂); 25.3 (-CH₃); 17.3 (-CH₃); 16.2 (-CH₃); 13.9 (-CH₃).

¹H NMR: δ 5.33 (1H, t (*J* = 7.3 Hz), =CH); 5.02 (1H, t (*J* = 6.7 Hz), =CH); 4.6 (2H, d (*J* = 6.7 Hz), -CH₂-O); 4.15 (2H, q (*J* = 7.1 Hz), -OCH₂CH₃); 1.9 (3H, s, -CH₃); 1.62 (3H, s, -CH₃); 1.54 (3H, s, -CH₃); 1.25 (3H, t (*J* = 7.1 Hz), -OCH₂CH₃).

4.3. Preparation of allyl halides

4.3.1. Preparation of *trans*-carvyl chloride **12**

Trans-carvyl chloride **12** was prepared according to reference [21] by treatment of α -pinene (20 mmol) by dimethyl sulfoxide (80 mmol) and phosphorus oxychloride (20 mmol) in methylene chloride for 30 min over a temperature range of -20 to 20°C. At the end of the reaction, a solution of NaHCO₃ was added, and the mixture was extracted by CHCl₃. The organic phase was dried and the solvent removed leading to virtually pure *trans*-carvyl chloride in quantitative yield. The same procedure has been followed to prepare perillyl chloride **11** starting from β -pinene.

4.3.2. Preparation of geranyl chloride **13**

A dry 300 ml three-necked flask equipped with a magnetic stirring bar and reflux condenser was charged with 90 ml of carbon tetrachloride and 15.42 g of geraniol (0.10 mol). To this solution 34.09 g of triphenylphosphine (0.13 mol) was added, and the reaction mixture is stirred and heated to reflux for 1 h. This mixture is allowed to cool to room temperature, dry pentane is added (100 ml), and stirring is continued for an additional 5 min.

The precipitate of triphenylphosphine oxide is filtered and washed with 50 ml of pentane. The solvent is removed from the combined filtrate at the rotary evaporator under vacuum at room temperature. Distillation of the residue through a Vigreux column provides 13.0–14.0 g (75–81%) of geranyl chloride **13**, bp 47–49°C.

4.4. General procedure for the carbonylation

4.4.1. Carbonylation of allylic carbonates

In a flask fitted with a reflux condenser was placed, Pd(OAc)₂ (10 mg, 0.044 mmol), PPh₃ (23 mg, 0.088 mmol) and the atmosphere was replaced with carbon monoxide. Then the allylic carbonate (2.23 mmol) in 5 ml of dry EtOH was added under CO, and the mixture was stirred at 50°C or the indicated time. Aliquot samples were taken at regular intervals and analyzed by GC. At the end of the reaction, the mixture was filtered and concentrated in vacuum. The residue was purified by using silica gel chromatography column with hexane/AcOEt as eluent, and the resulting products are subjected to NMR analysis.

4.4.2. **6** [α]_D²⁰ = -51.2° (*c* = 2.1; *MeOH*)

¹³C NMR: δ 172 (C=O); 149.8 (=C); 130.9 (=C); 125.1 (=CH); 108.7 (=CH₂); 60.5 (OCH₂CH₃); 43.2 (-CH₂); 40.7 (-CH); 30.8 (-CH₂); 28.9 (-CH₂); 27.7 (-CH₂); 20.8 (OCH₂CH₃); 14.3 (CH₃).

¹H NMR: δ 5.52 (1H, m, =CH); 4.66 (2H, m, =CH₂); 4.1 (2H, q (*J* = 7.1 Hz), OCH₂CH₃); 2.9 (2H, s, -CH₂CO); 1.7 (3H, s, CH₃); 1.2 (3H, t (*J* = 7.1 Hz), OCH₂CH₃).

4.4.3. **7** [α]_D²⁰ = 0°

¹³C NMR: δ 173.8 (C=O); 130.7 (=C); 130.1 (=C); 124.5 (=CH); 109.2 (=CH₂); 60.5 (OCH₂CH₃); 45.5 (-CHCO₂Et); 40.3 (-CH); 32.0 (-CH₂); 30.6 (-CH₂); 22.3 (CH₃); 20.7 (-CH₃); 14.2 (OCH₂CH₃).

¹H NMR: δ 5.56 (1H, m, =CH); 4.70 (2H, m, =CH₂); 4.12 (2H, q (*J* = 7 Hz), OCH₂CH₃); 2.99 (1H, t (*J* = 5.1 Hz), -CHCO₂Et); 1.64 (3H, s, CH₃); 1.63 (3H, s, CH₃); 1.24 (3H, t (*J* = 7.1 Hz), OCH₂CH₃).

4.4.4. **9** [α]_D²⁰ = +3.4° (*c* = 1.6; *MeOH*)

¹³C NMR: δ 171.4 (C=O); 141.0 (=C); 120.6 (=CH); 60.3 (OCH₂CH₃); 45.7 (-CH); 42.6 (-CH₂-CO);

40.4 (-CH); 37.9 (-C); 31.6 (-CH₂); 31.3 (-CH₂); 26.2 (-CH₃); 20.9 (-CH₃); 14.2 (-CH₃).

¹H NMR: δ 5.39 (1H, m, =CH); 4.10 (2H, q (*J* = 7.2 Hz), OCH₂CH₃); 2.98 (2H, m; -CH₂-CO); 1.26 (3H, s, CH₃); 1.23 (3H, t (*J* = 7.3 Hz), OCH₂CH₃); 0.83 (3H, s, -CH₃).

4.4.5. **10**

¹³C NMR: δ 172.4 (C=O); 138.9 (=C); 131.5 (=C); 123.9 (=CH); 115.7 (=CH); 60.4 (OCH₂CH₃); 39.5 (-CH₂-CO); 33.7 (-CH₂); 26.4 (-CH₂); 25.6 (-CH₃); 17.6 (-CH₃); 16.3 (-CH₃); 14.2 (-CH₃).

¹H NMR: δ 5.30 (1H, m, =CH); 5.10 (1H, m, =CH); 4.10 (2H, q (*J* = 7.2 Hz) OCH₂CH₃); 3.0 (2H, dd (*J* = 7.2, 0.6 Hz); -CH₂-CO); 1.67 (3H, s, CH₃); 1.62 (3H, s, -CH₃); 1.59 (3H, s, -CH₃); 1.25 (3H, t (*J* = 7.2 Hz), OCH₂CH₃).

4.4.6. Carbonylation of allylic chlorides

By a similar procedure to that described for allylic carbonates, (7.5 mg, 0.033 mmol) of Pd(OAc)₂, (1.35 mg, 9.7 mmol) of anhydrous K₂CO₃ and a stirring bar were placed in a three necked flask. The atmosphere was replaced with carbon monoxide and allylic chloride (3.3 mmol) in 5 ml of ethanol was added under CO. The reaction mixture was stirred at 25°C for the reported time. The reaction was followed by GC. At the end of the reaction, the mixture was filtered and the solvent was removed under vacuum. The residue was chromatographed on silica gel with hexane/AcOEt as eluent to provide the carbonylated product.

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