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Iridium complex-catalyzed carbonylation of allylic phosphates

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Abstract

$[Ir(cod)Cl]_2$ with a ligand such as $P(2\text{-furyl})_3$, $PPh_2C_6F_5$ or $AsPh_3$ showed high catalytic activity for the carbonylation of allylic phosphates in the presence of alcohols to give the corresponding β,γ-unsaturated esters. The carbonylation of diethyl (*E*)-3-phenyl-2-propenyl phosphate in the presence of EtOH under an initial carbon monoxide pressure of 40 kg cm^{-2} at 100 °C gave ethyl (*E*)-4-phenyl-3-butenoate in 90% yield. No (*Z*)-isomer was obtained. The reaction proceeded smoothly without using an amine as an additive. The carbonylation of 2-alkenyl diethyl phosphates in the presence of EtOH gave a mixture of ethyl (*E*)- and (*Z*)-3-alkenoate. The stereochemistry of the starting material was lost by *syn–anti* isomerization of the π-allyl iridium intermediate prior to the insertion of carbon monoxide into the iridium–carbon bond. Increasing the steric bulkiness of the substituent at the γ-position of the allyl system or increasing the initial carbon monoxide pressure increased the selectivity for a product with the same stereochemistry as the starting material.

Keywords: Iridium; Carbonylation; Allylic phosphates; *syn–anti* Isomerization; β,γ-Unsaturated esters; π-Allyl iridium

1. Introduction

Synthetic reactions that include π-allyl metal intermediates have been extensively studied and used to construct complex organic molecules. The reaction of a π-allyl metal intermediate with nucleophiles is recognized as one of the most useful synthetic reactions [1]. Another important version of this reaction is an insertion reaction into a metal–carbon bond of the π-allyl ligand [2]. The insertion of carbon monoxide into a transition metal–carbon bond is a fundamental step for introducing a carbonyl group into an organic molecule [3]. The reaction of a π-allyl metal intermediate with carbon monoxide has attracted much attention. Catalytic carbonylation of allylic esters and halides in the presence of alcohols is the most straightforward method for preparing β,γ-unsaturated esters. Several transition metal complexes such as with palladium [4], rhodium [5] and ruthenium [6] have been shown to be efficient catalysts for this carbonylation.

We were the first to show that an iridium complex could be an efficient catalyst for allylic substitution [7]. As the selectivity of iridium complex-catalyzed allylic substitution is quite different from that of a palladium complex-catalyzed reaction, an iridium complex catalyst is a useful complement to a palladium complex catalyst.

Recently, a few examples of iridium complex-catalyzed carbonylation have been reported [8]. An iridium complex is attractive as a new and efficient catalyst for carbonylation. These results prompted us to study the iridium complex-catalyzed carbonylation of allylic esters. In this paper, we report the first example of an iridium complex-catalyzed carbonylation of allylic esters in the presence of alcohols.

2. Results and discussion

2.1. Carbonylation of 3-aryl-2-propenyl diethyl phosphates

Various allylic compounds such as allylic esters [4a,e,g,h,k,l], allylic alcohols [4b–d], allylic amines [4f] and allylic ethers [4j,o] have been used as substrates for carbonylation. In this study, an allylic compound was carbonylated in the presence of five equivalents of EtOH and a catalytic amount of $[Ir(cod)Cl]_2$ and PPh_3 (P/Ir =

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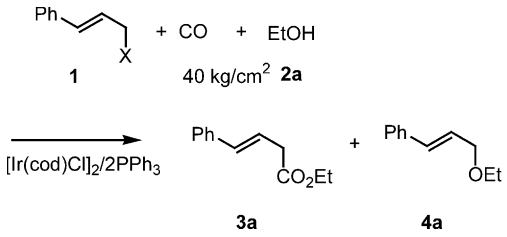
Table 1
Carbonylation of **1** [a]

Entry	Substrate	Conditions	Yield (%) [b]	
			3a	**4a**
1	**1a** X = $OPO(OEt)_2$	100 °C 24 h	80	2
2	**1b** X = OCO_2Et	160 °C 24 h	29	1
3	**1c** X = OAc	160 °C 24 h	3	2
4	**1d** X = OH	160 °C 24 h	34	6
5	**1e** X = Cl	100 °C 24 h	0	0

[a] A mixture of **1a** (3 mmol), EtOH (15 mmol), $[Ir(cod)Cl]_2$ (0.06 mmol), PPh_3 (0.12 mmol) and dioxane (10 ml) was stirred under an initial carbon monoxide pressure of 40 kg cm^{-2}.
[b] Isolated yield.

1) under an initial carbon monoxide pressure of 40 kg cm^{-2} (Eq. (1)). The results are summarized in Table 1. Phosphate **1a** was smoothly carbonylated. Carbonate **1b**, which was a good substrate for palladium complex- and ruthenium complex-catalyzed carbonylation, gave product in 29% yield (entry 2) [4l,6]. Acetate **1c**, alcohol **1d** and halide **1e** gave a product in low yields (entries 3–5). No (*Z*)-**3a** was obtained. Conversions of **1b**–**d** were low, but **1e** was completely consumed.



(1)

The effect of a ligand on the carbonylation of phosphate **1a** was examined. The results are summarized in Table 2. Reactions were carried out at 100 °C for 24 h under an initial carbon monoxide pressure of 40 kg cm^{-2}. The ratio of phosphorous atom to Ir atom was important. The reaction at a P/Ir ratio of 1 gave **3a** in 80% yield (entry 1). The reaction at a P/Ir ratio of 2 decreased the yield of **3a** slightly, but increased the yield of **4a** (entry 2). Based on this result, we examined the effects of various phosphorous ligands on carbonylation at a P/Ir ratio of 1. Phosphine, which is a more electron-donating ligand than PPh_3, decreased the yield of **3a** (entries 3 and 4). These donating ligands increased the yield of **4a**. Electron-withdrawing ligands such as $PPh_2C_6F_5$, P(2-furyl)$_3$ and $AsPh_3$ gave good results (entries 5–7). Although $P(OPh)_3$ was an efficient ligand for iridium complex-catalyzed allylic substitution [7], $P(OPh)_3$ gave **3a** in 47% yield (entry 8). $P(OEt)_3$ gave a result comparable to that with PPh_3 (entry 9). The catalytic activities of several Ir complexes with $AsPh_3$ (As/Ir = 1) were examined. $[Ir(cot)_2Cl]_2$ showed a catalytic activity comparable to that of $[Ir(cod)Cl]_2$ (entry 11), while Ir(cod)(acac) and $[Ir(cod)_2]BF_4$ were less efficient than $[Ir(cod)Cl]_2$ (entries 10 and 12). $Ir_4(CO)_{12}$ showed no catalytic activity (entry 13).

The effect of the solvent on the carbonylation of **1a** was examined. Five equivalents of EtOH to **1a** were used. The results are summarized in Table 3. Dioxane gave the best results (entry 1). Palladium complex-catalyzed carbonylation of allylic phosphates was carried out using EtOH as a solvent [4a,h,k], but this decreased the yield of **3a** (entry 5).

The effects of the initial carbon monoxide pressure and reaction temperature on the reaction of **1a** were examined. The results are summarized in Table 4. The reaction under carbon monoxide atmosphere did not

Table 2
Effect of catalyst on carbonylation of **1a** [a]

Entry	Catalyst	Ligand	P or As/Ir	Yield (%) [b]	
				3a	**4a**
1	$[Ir(cod)Cl]_2$	PPh_3	1	80	2
2	$[Ir(cod)Cl]_2$	PPh_3	2	76	8
3	$[Ir(cod)Cl]_2$	P(*n*-Bu)$_3$	1	35	22
4	$[Ir(cod)Cl]_2$	PPh_2Me	1	68	9
5	$[Ir(cod)Cl]_2$	$PPh_2C_6F_5$	1	86	3
6	$[Ir(cod)Cl]_2$	P(2-furyl)$_3$	1	88	0
7	$[Ir(cod)Cl]_2$	$AsPh_3$	1	90	0
8	$[Ir(cod)Cl]_2$	$P(OPh)_3$	1	47	10
9	$[Ir(cod)Cl]_2$	$P(OEt)_3$	1	80	1
10 [c]	$[Ir(cod)_2]BF_4$	$AsPh_3$	1	32	53
11	$[Ir(cot)_2Cl]_2$	$AsPh_3$	1	89	1
12 [c]	Ir(cod)(acac)	$AsPh_3$	1	77	2
13 [d]	$Ir_4(CO)_{12}$	$AsPh_3$	1	0	0

[a] A mixture of **1a** (3 mmol), EtOH (15 mmol), Ir complex (0.06 mmol), ligand and dioxane (10 ml) was stirred under an initial carbon monoxide pressure of 40 kg cm^{-2} at 100 °C for 24 h.
[b] Isolated yield.
[c] Ir complex (0.12 mmol).
[d] Ir complex (0.03 mmol).

Table 3
Effect of a solvent on carbonylation of **1a** [a]

Entry	Solvent	Yield (%) [b]	
		3a	**4a**
1	Dioxane	90	0
2	Benzene	86	3
3	1,2-Dichloropropane	85	1
4	MeCN	29	25
5	EtOH	53	22

[a] A mixture of **1a** (3 mmol), EtOH (15 mmol), $[Ir(cod)Cl]_2$ (0.06 mmol), $AsPh_3$ (0.12 mmol) and solvent (10 ml) was stirred under an initial carbon monoxide pressure of 40 kg cm^{-2} at 100 °C for 24 h.
[b] Isolated yield.

Table 4
Effect of carbon monoxide pressure and reaction temperature on carbonylation of **1a** [a]

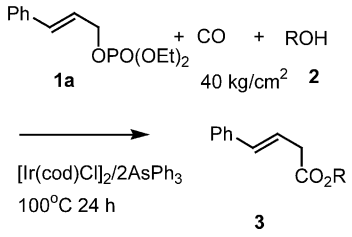
Entry	Initial CO pressure (kg cm^{-2})	Temperature (°C)	Yield (%) [b]	
			3a	**4a**
1	1	100	0	0
2	5	100	93	0
3	20	100	90	0
4	40	100	90	0
5	20	60	0	0

[a] A mixture of **1a** (3 mmol), EtOH (15 mmol), $[Ir(cod)Cl]_2$ (0.06 mmol), $AsPh_3$ (0.12 mmol) and dioxane (10 ml) was stirred under carbon monoxide pressure for 24 h.
[b] Isolated yield.

give **3a** (entry 1). Phosphate **1a** was recovered in quantitative yield. The carbon monoxide pressure is essential for obtaining **3a**. The reaction at 60 °C did not give **3a** (entry 5).

Phosphate is a leaving group in this carbonylation. As the reaction proceeds to give **3a**, diethyl phosphate is formed to make the reaction mixture acidic. The use of an amine can scavenge liberated diethyl phosphate to make the reaction mixture neutral. In palladium complex-catalyzed carbonylation of allylic phosphate, it is well known that the use of an amine is necessary to obtain a product in high yield [4h,k]. With this carbonylation, the use of an amine resulted in a decrease in the yield of **3a**. The reaction of **1a** in the presence of five equivalents of EtOH and 1.2 equivalents of Et_3N under an initial carbon monoxide pressure of 40 kg cm^{-2} at 100 °C for 24 h gave **3a** in 69% yield. When $(i\text{-}Pr)_2NEt$ or pyridine was used in place of Et_3N, the yield of **3a** was 21 and 5%, respectively. Carbonylation without an amine gave a better result than that with an amine. The coordination of an amine might saturate the metal center to reduce the catalytic activity.

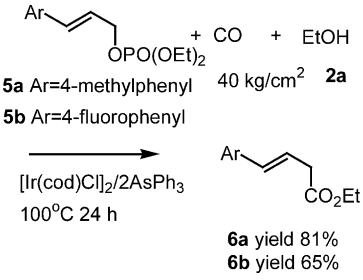
Various alcohols could be used for the carbonylation (Eq. (2)). The results are summarized in Table 5. Five equivalents of an alcohol to **1a** were used. Carbonylation of **1a** in the presence of *n*-hexanol (**2b**) or *i*-PrOH (**2c**) gave the product in a yield comparable to that in the presence of EtOH (**2a**) (entries 2 and 3). A functionalized alcohol such as methyl glycolate (**2d**) gave the corresponding product **3d** in 52% yield (entry 4). The electron-withdrawing property of an ester group should reduce the nucleophilicity of an alcohol, thereby decreasing the yield of **3**. Carbonylation of **1a** in the presence of *tert*-BuOH (**2e**) did not give the corresponding product **3e**. Steric bulkiness of tertiary alcohol would retard nucleophilic attack to an acyl group on the metal [9].



(2)

It is well known that carbonylation in the presence of water gives the corresponding carboxylic acid. Carbonylation of **1a** in the presence of five equivalents of water under an initial carbon monoxide pressure of 40 kg cm^{-2} at 100 °C for 24 h did not give the corresponding carboxylic acid, but phosphate **1a** was completely consumed.

Carbonylation of (*E*)-3-aryl-2-propenyl diethyl phosphate (**5**) was carried out under the same reaction conditions as with **1a** (Eq. (3)). Phosphate **5a** was smoothly carbonylated to give **6a** in 81% yield, whereas the carbonylation of phosphate **5b** gave **6b** in 65% yield. Introducing an electron-withdrawing group on an aromatic ring decreased the product yield.



(3)

2.2. Carbonylation of 3-substituted-2-propenyl diethyl phosphates

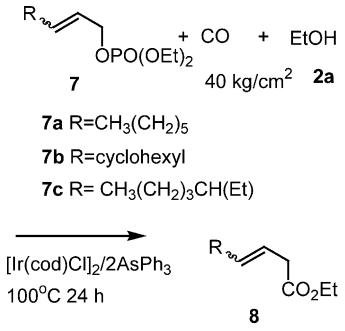
The carbonylation of diethyl (*E*)-2-nonenyl phosphate ((*E*)-**7a**) in the presence of EtOH under an initial carbon monoxide pressure of 40 kg cm^{-2} at 100 °C for 24 h gave an 88:12 mixture of (*E*)- and (*Z*)-ethyl 3-decenoate ((*E*)- and (*Z*)-**8a**) in 69% yield (Table 6; entry 1) (Eq. (4)). Carbonylation of (*Z*)-**7a** under the same

Table 5
Carbonylation of **1a** [a]

Entry	Alcohol	Product	Yield (%) [b]
1	**2a** R = Et	**3a**	90
2	**2b** R = $CH_3(CH_2)_5$	**3b**	85
3	**2c** R = $(CH_3)_2CH$	**3c**	82
4	**2d** R = $CH_3O_2CCH_2$	**3d**	52

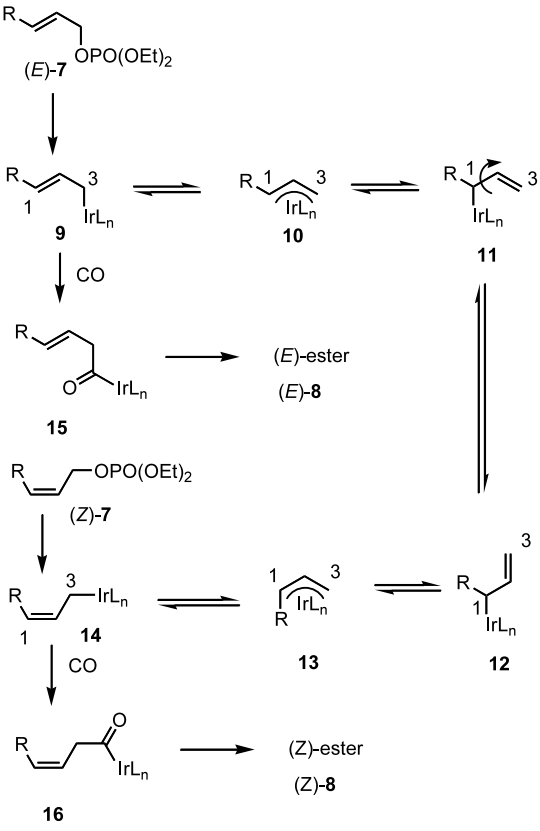
[a] A mixture of **1a** (3 mmol), alcohol (15 mmol), $[Ir(cod)Cl]_2$ (0.06 mmol), $AsPh_3$ (0.12 mmol) and dioxane (10 ml) was stirred under an initial carbon monoxide pressure of 40 kg cm^{-2} at 100 °C for 24 h.
[b] Isolated yield.

reaction conditions gave a similar result (entry 2). Both reactions gave the corresponding (*E*)-ester as a major product regardless of the stereochemistry of the starting material.



(4)

The loss of the stereochemistry of the starting material can be explained by *syn–anti* isomerization [10] of the π-allyl Ir intermediate (Scheme 1). Oxidative addition of (*E*)-**7a** gives σ-allyl intermediate **9** [11]. σ-π-σ Interconversion of **9** gives σ-allyl intermediate **11**. Rotation around the C1–C2 bond in **11** followed by σ-π-σ interconversion gives σ-allyl intermediate **14**. Insertion of CO into the C3–Ir bond in **14** followed by nucleophilic attack by the alcohol gives (*Z*)-**8**. It is well known that a *syn* π-allyl metal complex is thermodynamically more stable than the corresponding *anti* π-allyl metal complex [12]. The equilibrium between **10** and **13**



Scheme 1.

seems to be shifted toward **10**. Therefore, (*E*)-**8** is obtained as a major product.

Intermediates **11** and **12** are sterically more congested than **9** and **14**, since an iridium metal is attached to a secondary carbon. When the substituent at C-1 is sterically bulky, we can expect that *syn–anti* isomerization is decelerated. This would lead to the insertion of CO into the Ir–C3 bond in intermediate **9** or **14** prior to *syn–anti* isomerization. If this hypothesis is correct, the carbonylation of phosphate **7** bearing a sterically bulky substituent at the γ-position should increase the selectivity for a product with the same stereochemistry as the starting material.

We examined the carbonylation of phosphate bearing a secondary alkyl group at the γ-position in the allyl system. The results are summarized in Table 6. Carbonylation of (*E*)-**7b**, where a cyclohexyl group is substituted at the γ-position, in the presence of EtOH under an initial carbon monoxide pressure of 40 kg cm^{-2} at 100 °C for 24 h gave a 93:7 mixture of (*E*)- and (*Z*)-**8b** in 64% yield (entry 3). As expected, the selectivity for the (*E*)-ester increased. Similarly, carbonylation of (*E*)-**7c** in the presence of EtOH under the same reaction conditions gave a 95:5 mixture of (*E*)- and (*Z*)-**8c** in 55% yield (entry 5). Carbonylation of (*Z*)-phosphate bearing a secondary alkyl group at the γ-position in the allyl system is expected to increase the selectivity for (*Z*)-**8**.

Table 6
Carbonylation of **7** [a]

Entry	Substrate	Yield of **8** (%) [b]	Ratio *E*/*Z* [c]
1	(*E*)-**7a** R = *n*-Hex	69	88:12
2	(*Z*)-**7a** R = *n*-Hex	77	71:29
3	(*E*)-**7b** R = cyclohexyl	64	93:7
4	(*Z*)-**7b** R = cyclohexyl	68	62:38
5	(*E*)-**7c** R = $CH_3(CH_2)_3CH(Et)$	55	95:5
6	(*Z*)-**7c** R = $CH_3(CH_2)_3CH(Et)$	66	37:63

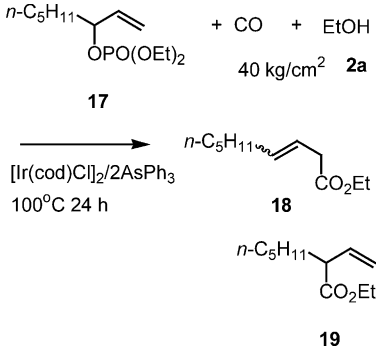
[a] A mixture of **7** (3 mmol), EtOH (15 mmol), $[Ir(cod)Cl]_2$ (0.06 mmol), $AsPh_3$ (0.12 mmol) and dioxane (10 ml) was stirred under an initial carbon monoxide pressure of 40 kg cm^{-2} at 100 °C for 24 h.
[b] Isolated yield.
[c] Determined by ^{1}H-NMR.

The carbonylation of (*Z*)-**7b** in the presence of EtOH under the same reaction conditions gave a 62:38 mixture of (*E*)- and (*Z*)-**8b** in 68% yield (entry 4). The selectivity for (*Z*)-ester was increased compared to that in the carbonylation of (*Z*)-**7a**. Changing the substituent at the γ-position from a cyclohexyl group to a 1-ethylpentyl group increased the selectivity for the (*Z*)-ester. Carbonylation of (*Z*)-**7c** in the presence of EtOH under an initial carbon monoxide pressure of 40 kg cm^{-2} at 100 °C for 24 h gave a 37:63 mixture of (*E*)- and (*Z*)-**8c** in 66% yield (entry 6). The selectivity for (*Z*)-**8c** was greater than that for (*E*)-**8c**. Notably, the (*Z*)-ester was obtained as a major product. The *Z* stereochemistry of the starting material was retained to some extent.

The initial pressure of carbon monoxide affected the stereoselectivity of the carbonylation of 2-alkenyl diethyl phosphate (**7a**–**c**). The results are summarized in Table 7. In the case of (*E*)- and (*Z*)-**7a**, the selectivity for a product with the same stereochemistry as the starting material increased as the initial pressure of carbon monoxide increased [13]. The selectivity for (*E*)-**8a** increased from 84 to 90% (entries 1–4). The selectivity for (*Z*)-**8a** also increased from 21 to 37% (entries 5–8). The carbonylation of **7b** and **7c** showed the same tendency.

The effect of the initial pressure of carbon monoxide on stereoselectivity can be explained as follows. Carbon monoxide at high pressure coordinates to the iridium center to saturate the coordination site. It shifts the equilibrium between the σ-allyl intermediate and π-allyl intermediate toward the σ-allyl intermediate. Carbon monoxide at high pressure might also promote the insertion of carbon monoxide prior to σ–π interconversion, leading to retention of stereochemistry.

Finally, we examined the reaction of regioisomeric phosphate **17** (Eq. (5)). Carbonylation of **17** in the presence of EtOH gave an 89:11 mixture of (*E*)- and (*Z*)-**18** in 55% yield. No **19** was obtained. Oxidative addition of **17** gives intermediate **11** or **12** (Scheme 1). Insertion of CO into the Ir–C1 bond seems to be more difficult than that into the Ir–C3 bond, since the C1 carbon is more sterically congested than the C3 carbon. Therefore, a product was obtained from **9** and **14**.



(5)

In conclusion, an iridium complex is an efficient catalyst for the carbonylation of allylic phosphates in

Table 7
Effect of carbon monoxide pressure on carbonylation of **7** [a]

Entry	Substrate	Initial CO pressure (kg cm^{-2})	Yield of **8** (%) [b]	Ratio *E*/*Z* [c]
1	(*E*)-**7a** R = *n*-Hex	5	70	84:16
2		20	70	87:13
3		40	69	88:12
4		90	68	90:10
5	(*Z*)-**7a** R = *n*-Hex	5	80	79:21
6		20	69	70:30
7		40	77	71:29
8		90	61	63:37
9	(*E*)-**7b** R = cyclohexyl	5	60	91:9
10		40	64	93:7
11		90	64	94:6
12	(*Z*)-**7b** R = cyclohexyl	5	73	82:18
13		40	68	62:38
14		90	69	55:45
15	(*E*)-**7c** R = $CH_3(CH_2)_3CH(Et)$	5	74	95:5
16		40	55	95:5
17		90	47	95:5
18	(*Z*)-**7c** R = $CH_3(CH_2)_3CH(Et)$	5	74	49:51
19		20	72	37:63
20		40	66	37:63
21		90	60	37:63

[a] A mixture of **7** (3 mmol), EtOH (15 mmol), $[Ir(cod)Cl]_2$ (0.06 mmol), $AsPh_3$ (0.12 mmol) and dioxane (10 ml) was stirred under carbon monoxide pressure at 100 °C for 24 h.
[b] Isolated yield.
[c] Determined by ^{1}H-NMR.

the presence of alcohols. Iridium complex-catalyzed carbonylation has rarely been studied. This success should offer a new approach to iridium complex-catalyzed organic synthesis.

3. Experimental

3.1. General

^{1}H-NMR and ^{13}C-NMR spectra were measured on Bruker AVANCE-400 spectrometer or JEOL EX-270 spectrometer using Me_4Si as an internal standard. Samples were dissolved in $CDCl_3$ or benzene-d_6 solutions. GC analyses were performed on a Shimadzu GC-14A by using a 3 mm × 2 m glass columns packed with either 5% PEG-HT on 60/80 mesh chromosorb w AW-DMCS or 5% OV-17 on 60/80 mesh chromosorb w AW-DMCS. Column chromatography was carried out on 70-230 mesh silica gel (Merck; silica gel 60). Elemental analyses were performed at the Microanalytical Center of Kyoto University.

3.2. Materials

All reagents and the solvents were dried and purified before use by the usual procedures. Allylic phosphates were prepared by the reaction of the corresponding alcohols with diethyl chlorophosphate. (*E*)-3-Phenyl-2-propen-1-ol, (*E*)-2-nonen-1-ol, (*Z*)-2-nonen-1-ol, 1-octen-3-ol, (*E*)-1-chloro-3-phenyl-2-propene and (*E*)-3-phenyl-2-propenyl acetate were purchased. Ethyl (*E*)-3-phenyl-2-propenyl carbonate was prepared by the reaction of (*E*)-3-phenyl-2-propen-1-ol with ethyl choloroformate. (*E*)-3-(4-Methylphenyl)-2-propen-1-ol, (*E*)-3-(4-fluorophenyl)-2-propen-1-ol and (*E*)-3-cyclohexyl-2-propen-1-ol were prepared by the published method [7a]. $[Ir(cod)Cl]_2$, $[Ir(cot)_2Cl]_2$ and $[Ir(cod)_2]BF_4$ were prepared by the published method [14–16]. Ir(cod)(acac) and $Ir_4(CO)_{12}$ were purchased.

3.2.1. (*E*)-4-Ethyl-2-octen-1-ol

To a solution of NaH (0.528 g, 22 mmol) in 1,2-dimethoxyethane (40 ml) was added ethyl (diethylphosphono)acetate (5.381 g, 24 mmol) dropwise at 0 °C. The mixture was gradually warmed to room temperature for 10 min. 2-Ethylhexanal (2.564 g, 20 mmol) was added, and the resulting mixture was stirred at room temperature for 2 h. Water was added and the mixture was extracted with ether. The ether solution was dried with $MgSO_4$ and evaporated in vacuo. Medium-pressure column chromatography (*n*-hexane–AcOEt = 95/5) of the residue gave pure ethyl (*E*)-4-ethyl-2-octenoate (yield 76%, 3.014 g). Reduction of ethyl (*E*)-4-ethyl-2-octenoate by DIBALH gave (*E*)-4-ethyl-2-octen-1-ol. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.84 (t, $J = 7.4$ Hz, 3H), 0.88 (t, $J = 7.2$ Hz, 3H), 1.16–1.46 (m, 8H), 1.83–1.88 (m, 2H), 4.10 (d, $J = 5.2$ Hz, 2H), 5.41 (dd, $J = 15.4$, 8.7 Hz, 1H), 5.58 (dt, $J = 15.4$, 5.2 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 11.6, 14.0, 22.8, 27.7, 29.4, 34.4, 44.0, 63.7, 128.8, 137.5.

3.2.2. (*Z*)-3-Cyclohexyl-2-propen-1-ol [17]

To a solution of NaH (0.696 g, 29 mmol) in THF (100 ml) was added ethyl (diphenylphosphono)acetate (6.406 g, 20 mmol) dropwise at 0 °C. The mixture was stirred at 0 °C for 20 min, and the mixture was then cooled to −78 °C for 10 min. Cyclohexanecarboxaldehyde (2.243 g, 20 mmol) was added, and the resulting mixture was gradually warmed to room temperature for 21 h. Water was added and the mixture was extracted with ether. The ether solution was dried with $MgSO_4$ and evaporated in vacuo. Medium-pressure column chromatography (*n*-hexane) of the residue gave pure ethyl (*Z*)-3-cyclohexyl-2-propenoate (yield 54%, 1.968 g). Reduction of ethyl (*Z*)-3-cyclohexyl-2-propenoate by DIBALH gave (*Z*)-3-cyclohexyl-2-propen-1-ol. ^{1}H-NMR ($CDCl_3$, 400MHz) δ 1.04–1.34 (m, 6H), 1.58–1.73 (m, 5H), 2.24–2.33 (m, 1H), 4.20 (dd, $J = 6.7$, 1.2 Hz, 2H), 5.40 (d, $J = 10.8$ Hz, 1H), 5.49 (dt, $J = 10.8$, 6.7 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 25.8 (2C), 25.9 (2C), 33.4, 36.6, 58.8, 126.5, 139.2.

3.2.3. (*Z*)-4-Ethyl-2-octen-1-ol

(*Z*)-4-Ethyl-2-octen-1-ol was prepared similarly to give (*Z*)-1-cyclohexyl-2-propen-1-ol from 2-ethylhexanal and ethyl (diphenylphosphono)acetate. ^{1}H-NMR (C_6D_6, 400 MHz) δ 0.80 (t, $J = 7.4$ Hz, 3H), 0.87 (t, $J = 7.2$ Hz, 3H), 1.01–1.36 (m, 8H), 2.02–2.08 (m, 2H), 4.03 (br, 2H), 5.04 (t, $J = 10.7$ Hz, 1H), 5.60 (dt, $J = 10.7$, 6.3 Hz, 1H); ^{13}C-NMR (100 MHz, C_6D_6) δ 12.0, 14.2, 23.2, 28.8, 29.9, 35.5, 39.6, 59.0, 129.9, 136.8.

3.3. General procedure for the carbonylation of allylic phosphates

A typical procedure is described (Table 2, entry 7). A mixture of dioxane (10 ml), EtOH (0.691 g, 15 mmol), **1a** (0.811 g, 3 mmol), $[Ir(cod)Cl]_2$ (40.3 mg, 0.06 mmol) and $AsPh_3$ (36.7 mg, 0.12 mmol) was placed in a 50 ml stainless autoclave equipped with a glass liner and a magnetic stirring bar. The reactor was sealed and was flushed with carbon monoxide three times, and then it was pressurized with carbon monoxide to 40 kg cm^{-2}. The mixture was heated at 100 °C for 24 h. The reaction was terminated by rapid cooling. The solvent was evaporated in vacuo. Column chromatography (*n*-hexane–AcOEt = 98/2) of the residue gave **3a** as a colorless oil (yield 90%, 0.514 g).

3.4. Characterization of products

3.4.1. Ethyl (*E*)-4-phenyl-3-butenoate (**3a**) [4h]

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.26 (t, $J = 7.1$ Hz, 3H), 3.22 (dd, $J = 7.1$, 1.4 Hz, 2H), 4.16 (q, $J = 7.1$ Hz, 2H), 6.29 (dt, $J = 15.9$, 7.1 Hz, 1H), 6.47 (d, $J = 15.9$ Hz, 1H), 7.18–7.37 (m, 5H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 14.1, 38.4, 60.6, 121.8, 126.2 (2C), 127.4, 128.4 (2C), 133.3, 136.8, 171.4.

3.4.2. *n*-Hexyl (*E*)-4-phenyl-3-butenoate (**3b**)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.88 (t, $J = 6.8$ Hz, 3H), 1.27–1.38 (m, 6H), 1.63 (quintet, $J = 6.8$ Hz, 2H), 3.23 (dd, $J = 7.1$, 1.3 Hz, 2H), 4.10 (t, $J = 6.8$ Hz, 2H), 6.30 (dt, $J = 15.9$, 7.1 Hz, 1H), 6.48 (d, $J = 15.9$ Hz, 1H), 7.19–7.37 (m, 5H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 13.9, 22.4, 25.5, 28.5, 31.3, 38.4, 64.9, 121.8, 126.2 (2C), 127.4, 128.4 (2C), 133.2, 136.8, 171.5. IR (neat) 1737 cm^{-1}. Anal. Calc. for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00; O, 12.99. Found: C, 78.23; H, 9.10%.

3.4.3. 2-Methylethyl (*E*)-4-phenyl-3-butenoate (**3c**)

^{1}H-NMR ($CDCl_3$, 270 MHz) δ 1.24 (d, $J = 6.3$ Hz, 6H), 3.19 (dd, $J = 7.1$, 1.4 Hz, 2H), 5.03 (seventet, $J = 6.3$ Hz, 1H), 6.29 (dt, $J = 15.9$, 7.1 Hz, 1H), 6.47 (d, $J = 15.9$ Hz, 1H), 7.18–7.37 (m, 5H). ^{13}C-NMR ($CDCl_3$, 67.8 MHz) δ 21.7 (2C), 38.6, 68.0, 122.0, 126.2 (2C), 127.4, 128.4 (2C), 133.1, 136.9, 171.0. IR (neat) 1732 cm^{-1}. Anal. Calc. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90; O, 15.67. Found: C, 76.72; H, 8.14%.

3.4.4. Methoxycarbonylmethyl (*E*)-4-phenyl-3-butenoate (**3d**)

^{1}H-NMR ($CDCl_3$, 270 MHz) δ 3.36 (dd, $J = 7.1$, 1.4 Hz, 2H), 3.75 (s, 3H), 4.65 (s, 2H), 6.30 (dt, $J = 15.9$, 7.1 Hz, 1H), 6.52 (d, $J = 15.9$ Hz, 1H), 7.20–7.38 (m, 5H). ^{13}C-NMR ($CDCl_3$, 67.8 MHz) δ 37.6, 52.1, 60.7, 120.8, 126.2 (2C), 127.5, 128.4 (2C), 133.8, 136.6, 168.0, 170.8. Anal. Calc. for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02; O, 27.32. Found: C, 66.92; H, 6.27%.

3.4.5. Ethyl (*E*)-3-phenyl-2-propenyl ether (**4a**)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.24 (t, $J = 7.0$ Hz, 3H), 3.54 (q, $J = 7.0$ Hz, 2H), 4.12 (dd, $J = 6.0$, 1.4 Hz, 2H), 6.29 (dt, $J = 15.9$, 6.0 Hz, 1H), 6.60 (d, $J = 15.9$ Hz, 1H), 7.19–7.39 (m, 5H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 15.1, 65.6, 71.1, 126.3, 126.4 (2C), 127.5, 128.5 (2C), 132.1, 136.7.

3.4.6. Ethyl (*E*)-4-(4-methylphenyl)-3-butenoate (**6a**)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.26 (t, $J = 7.1$ Hz, 3H), 2.31 (s, 3H), 3.20 (dd, $J = 7.1$, 1.4 Hz, 2H), 4.15 (q, $J = 7.1$ Hz, 2H), 6.23 (dt, $J = 15.9$, 7.1 Hz, 1H), 6.44 (d, $J = 15.9$ Hz, 1H), 7.09 (d, $J = 8.0$ Hz, 2H), 7.25 (d, $J = 8.0$ Hz, 2H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 14.1, 21.0, 38.4, 60.6, 120.7, 126.1 (2C), 129.1 (2C), 133.1, 134.1, 137.2, 171.7. Anal. Calc. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90; O, 15.67. Found: C, 76.17; H, 7.85%.

3.4.7. Ethyl (*E*)-4-(4-fluorolphenyl)-3-butenoate (**6b**)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.27 (t, $J = 7.1$ Hz, 3H), 3.22 (dd, $J = 7.1$, 1.2 Hz, 2H), 4.17 (q, $J = 7.1$ Hz, 2H), 6.21 (dt, $J = 15.9$, 7.1 Hz, 1H), 6.44 (d, $J = 15.9$ Hz, 1H), 6.98 (t, $J = 8.7$ Hz, 2H), 7.32 (dd, $J = 8.7$, 5.4 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 14.1, 38.3, 60.7, 115.3 (d, $J_{C-F} = 21.6$ Hz, 2C), 121.5 (d, $J_{C-F} = 1.9$ Hz), 127.7 (d, $J_{C-F} = 8.0$ Hz, 2C), 132.1, 133.0 (d, $J_{C-F} = 3.3$ Hz), 162.2 (d, $J_{C-F} = 246.6$ Hz), 171.5. Anal. Calc. for $C_{12}H_{13}FO_2$: C, 69.22; H, 6.29; F, 9.12; O, 15.37. Found: C, 68.94; H, 6.17; F, 9.17%.

3.4.8. Ethyl (*E*)-3-decenoate ((*E*)-**8a**)

^{1}H-NMR (C_6D_6, 400 MHz) δ 0.86 (t, $J = 7.1$ Hz, 3H), 0.94 (t, $J = 7.1$ Hz, 3H), 1.13–1.27 (m, 8H), 1.91 (q, $J = 6.7$ Hz, 2H), 2.88 (dd, $J = 6.9$, 1.0 Hz, 2H), 3.93 (q, $J = 7.1$ Hz, 2H), 5.41 (dt, $J = 15.3$, 6.7 Hz, 1H), 5.61 (dt, $J = 15.3$, 6.9 Hz, 1H). ^{13}C-NMR (C_6D_6, 100 MHz) δ 14.0, 14.1, 22.5, 28.7, 29.1, 31.6, 32.4, 38.1, 60.4, 121.5, 134.7, 172.1. IR (neat) 1741 cm^{-1}. Anal. Calc. for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18; O, 16.14. Found: C, 72.74; H, 11.37%.

3.4.9. Ethyl (*Z*)-3-decenoate ((*Z*)-**8a**)

Compound (*Z*)-**8a** could not be isolated in pure form. Partial ^{1}H-NMR spectra was obtained from the mixture of (*E*)-**8a**. ^{1}H-NMR (400 MHz, C_6D_6) δ 2.97 (d, $J = 7.2$ Hz, 2H), 5.48 (dt, $J = 10.8$, 7.3 Hz, 1H), 5.71 (dt, $J = 10.8$, 7.2 Hz).

3.4.10. Ethyl (*E*)-4-cyclohexyl-3-butenoate ((*E*)-**8b**)

^{1}H-NMR (C_6D_6, 400 MHz) δ 0.94 (t, $J = 7.1$ Hz, 3H), 1.00–1.19 (m, 4H), 1.51–1.65 (m, 6H), 1.79–1.83 (m, 1H), 2.88 (d, $J = 6.9$ Hz, 2H), 3.93 (q, $J = 7.1$ Hz, 2H), 5.38 (dd, $J = 15.5$, 6.7 Hz, 1H), 5.58 (dt, $J = 15.5$, 6.9 Hz, 1H). ^{13}C-NMR (C_6D_6, 100 MHz) δ 14.2, 26.3 (2C), 26.4, 33.1 (2C), 38.4, 40.9, 60.2, 120.2, 140.1, 171.3. IR (neat) 1740 cm^{-1}. Anal. Calc. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27; O, 16.30. Found: C, 73.49; H, 10.18%.

3.4.11. Ethyl (*Z*)-4-cyclohexyl-3-butenoate ((*Z*)-**8b**)

Compound (*Z*)-**8b** could not be isolated in pure form. Partial ^{1}H-NMR spectra was obtained from the mixture of (*E*)-**8b**. ^{1}H-NMR (400 MHz, C_6D_6) δ 2.96 (d, $J = 7.2$ Hz, 2H), 5.32 (dd, $J = 11.3$, 7.3 Hz, 1H), 5.58 (dt, $J = 11.3$, 7.2 Hz).

3.4.12. Ethyl (*E*)-5-ethyl-3-nonenoate ((*E*)-**8c**)

^{1}H-NMR (C_6D_6, 400 MHz) δ 0.81–0.88 (m, 6H), 0.95 (t, $J = 6.8$ Hz, 3H), 1.09–1.36 (m, 8H), 1.76–1.78 (m, 1H), 2.88 (dd, $J = 7.0$, 1.3 Hz, 2H), 3.93 (q, $J = 7.1$ Hz, 2H), 5.13 (dd, $J = 15.3$, 8.9 Hz, 1H), 5.53 (dt, $J = 15.3$, 7.0 Hz, 1H). ^{13}C-NMR (C_6D_6, 100 MHz) δ 11.9, 14.2,

14.3, 23.2, 28.3, 29.8, 35.0, 38.3, 44.9, 60.2, 122.5, 138.8, 171.2. IR (neat) 1741 cm^{-1}. Anal. Calc. for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39; O, 15.07. Found: C, 73.60; H, 11.53%.

*3.4.13. Ethyl (Z)-5-ethyl-3-nonenoate ((Z)-**8c**)*

^{1}H-NMR (C_6D_6, 400 MHz) δ 0.78–0.88 (m, 6H), 0.96 (t, $J = 7.1$ Hz, 3H), 1.04–1.36 (m, 8H), 2.01–2.08 (m, 1H), 2.96 (dd, $J = 7.3$, 1.7 Hz, 2H), 3.93 (q, $J = 7.1$ Hz, 2H), 5.12 (t, $J = 10.9$ Hz, 1H), 5.72 (dt, $J = 10.9$, 7.3 Hz, 1H). ^{13}C-NMR (C_6D_6, 100 MHz) δ 11.9, 14.2, 14.3, 23.2, 28.7, 29.9, 33.8, 35.5, 39.5, 60.2, 121.9, 137.9, 171.1. IR (neat) 1741 cm^{-1}. Anal. Calc. for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39; O, 15.07. Found: C, 73.37; H, 11.57%.

*3.4.14. Ethyl (E)-3-nonenoate ((E)-**18**) [4h]*

^{1}H-NMR (C_6D_6, 400 MHz) δ 0.83 (t, $J = 7.1$ Hz, 3H), 0.94 (t, $J = 7.1$ Hz, 3H), 1.10–1.28 (m, 6H), 1.89 (q, $J =$ 6.9 Hz, 2H), 2.88 (d, $J = 6.9$ Hz, 2H), 3.93 (q, $J = 7.1$ Hz, 2H), 5.39 (dt, $J = 15.3$, 6.9 Hz, 1H), 5.59 (dt, $J =$ 15.3, 6.9 Hz, 1H). ^{13}C-NMR (C_6D_6, 100MHz) δ 14.17, 14.2, 22.8, 29.1, 31.6, 32.7, 38.1, 60.2, 122.5, 134.4, 171.3. IR (neat) 1741 cm^{-1}.

*3.4.15. Ethyl (Z)-3-nonenoate ((Z)-**18**) [4h]*

Compound (*Z*)-**18** could not be isolated in pure form. Partial ^{1}H-NMR spectra was obtained from the mixture of (*E*)-**18**. ^{1}H-NMR (400 MHz, C_6D_6) δ 2.95 (d, $J = 7.2$ Hz, 2H), 5.46 (dt, $J = 10.8$, 7.3 Hz, 1H), 5.68 (dt, $J =$ 10.8, 7.2 Hz).

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