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Aza- and oxacarbonylations of allyl phosphates catalyzed by rhodium carbonyl cluster. Selective synthesis of β,γ-unsaturated amides, esters, and acids *

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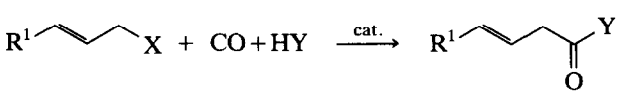
Abstract

Rhodium-catalyzed carbonylation of allyl phosphates under CO (20 atm) at 50°C proceeds very efficiently in the presence of amines, alcohols, and water to give the corresponding β,γ-unsaturated amides, esters, and acids, respectively. These carbonylations occur with high regioselectivity at the less substituted carbon of allyl unit to give linear β,γ-unsaturated acid derivatives.

1. Introduction

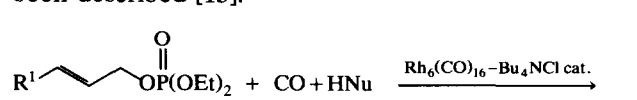
Carbonylation of allylic compounds is of importance [1] because insertion of CO into allylic skeletons gives homoallylic compounds which are synthetically important but not easily accessible. Carbonylation of allylic halides can be performed readily by using nickel [2], cobalt [3], and palladium complex catalysts [4,5] (eqn. (1)). Carbonylations of allylic esters, which are useful



(1)

substrates, require severe reaction conditions [2a,6]. However, palladium-catalyzed carbonylations of allyl alkyl carbonates [7] and allyl phosphates [8] were recently found to proceed under mild reaction conditions. Furthermore, carbonylation of allyl acetates was found to proceed under mild conditions if a co-catalyst of bromide ion was used [8].

We are now in a position to achieve catalytic oxacarbonylations of allyl halides [2–4], carbonates [7], phosphates [8], acetates [8], and ethers [9] by using oxygen nucleophiles such as water and alcohols to give β,γ-unsaturated acids and their esters. However, the azacarbonylations reported for allylic compounds are limited to azacarbonylations of allylamines [10] and allyl carbamates [11] and to only one example of allyl carbonate [7a]. This is because amination of allylic compounds proceeds faster than azacarbonylation. In view of the fact that allylrhodium complexes take the form of η^1-allyl rather than η^3-allyl complexes, we examined rhodium-catalyzed azacarbonylation. We found that rhodium carbonyl-catalyzed azacarbonylation of allyl phosphates proceeds with high efficiency to give β,γ-unsaturated amides (eqn. (2)). These amides are very useful precursors for various compounds such as homoallylamines; however, methods for their synthesis are limited to a few reactions [12]. The present reaction provides a convenient method for preparation of β,γ-unsaturated amides from allyl alcohols. Furthermore, under the same reaction conditions oxacarbonylations proceed readily to give β,γ-unsaturated acids and their esters. Full details of the rhodium-catalyzed aza- and oxacarbonylations of allyl phosphates have been described [13].



(2)

HNu = HNR^2R^3, HOR^2

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* Dedicated to Professor Gian Paolo Chiusoli in recognition of his important contributions to organometallic chemistry and its applications in organic synthesis.

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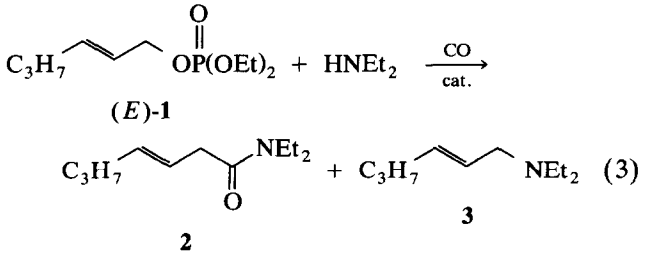
2. Results and discussion

2.1. Azacarbonylation of allyl phosphates

We have found allyl phosphates to be highly reactive substrates for transition metal-catalyzed transformations. Palladium-catalyzed amination and alkylation [14], azidation [15], and hydroxylamination [16] of allyl phosphates all proceed highly efficiently. Furthermore, allyl phosphates can serve as a useful protective group for internucleotide linkage [17]. In considering these results, we investigated azacarbonylation of allyl phosphates.

The catalytic activity of metal complex catalysts has been specifically examined as it applies in the carbonylation of (*E*)-2-hexenyl diethyl phosphate (**1**) in the presence of diethylamine under CO (20 atm) at 50°C (eqn. (3)). $Pd(PPh_3)_4$ is a good catalyst for oxacarbonylation [8], but is very poor for azacarbonylation, as



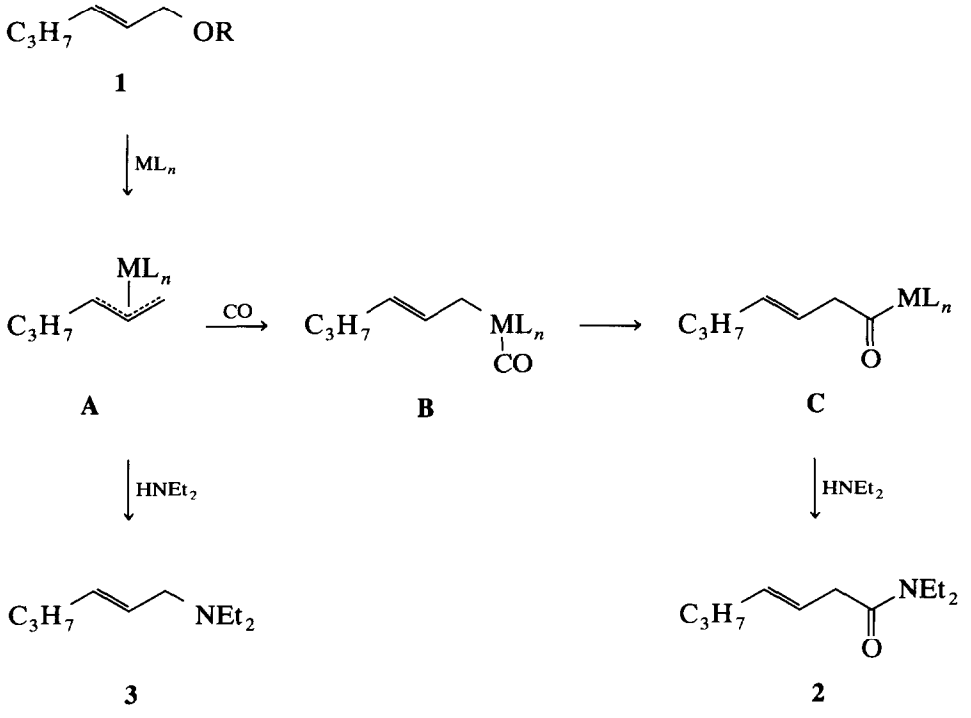
shown in Table 1. Thus, $Pd(PPh_3)_4$-catalyzed reaction of **1** with diethylamine under CO (20 atm) afforded *N*,*N*-diethyl-3-heptenamide (**2**) in 8% yield only along with *N*,*N*-diethyl-2-hexenylamine (**3**) (80% yield; entry 1). This reaction can be rationalized by proposing the mechanism shown in Scheme 1. Oxidative addition of palladium(0) to allyl phosphate **1** gives the π-allylpalladium complex **A** (M = Pd). Co-ordination of CO induces isomerization from η^3-allylpalladium complex **A** to the η^1-allylpalladium complex **B** [18]. The CO migration of **B** gives the acyl complex **C** which reacts with amines to give **2** [19]. The allylamine **3** is derived from the attack of amines on the π-allylpalladium complex **A** [20]. Isomerization of the η^3-allyl complex **A** to the η^1-allyl complex **B** seems to be a key step.

Allylrhodium complexes take the form of η^1-allyl rather than η^3-allyl complexes [21], so we examined

TABLE 1. Catalytic activity in the carbonylation of **1** [a]

Entry	Catalyst (mol%)	co-catalyst	CO, atm	yield, % [b]	
				Amide **2**	Amine **3**
1	$Pd(PPh_3)_4$ (5)	none	20	8	80
2	$Rh_6(CO)_{16}$ (1)	none	20	32	9
3	$Rh_6(CO)_{16}$ (1)	Bu_4NCl	20	83	9
4	$Rh_6(CO)_{16}$ (1)	Bu_4NCl	1	68	21
5	$RhH(CO)(PPh_3)_3$ (5)	Bu_4NCl	20	37	15
6	$Ru_3(CO)_{12}$ (2)	Bu_4NCl	20	20	43
7	$Mo(CO)_5$ (5)	Bu_4NCl	20	12	22

[a] Reaction conditions: substrate 1.0 mmol, catalyst, co-catalyst 0.1 mmol, amine 2.0 mmol, benzene 2 ml, CO 20 atm, at 50°C, 6 h.
[b] Determined by GLC.

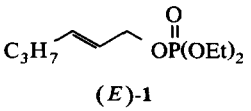
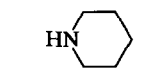
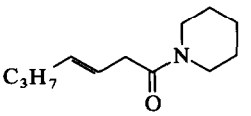
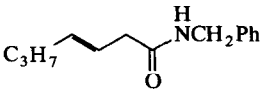
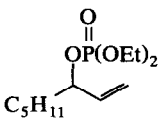
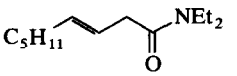
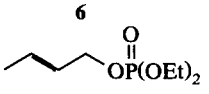
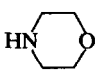
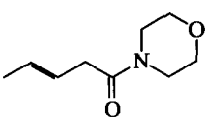
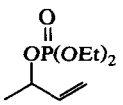
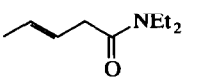
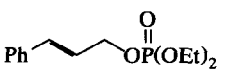
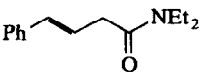


Scheme 1.

rhodium-catalyzed azacarbonylation. We have found that $Rh_6(CO)_{16}$ complex is an excellent catalyst for azacarbonylation of **1**. Using other catalysts such as $RhH(CO)(PPh_3)_2$, $Ru_3(CO)_{12}$, and $Mo(CO)_6$, the amide **2** was obtained in poor yields even under CO pressure (20 atm). Importantly, we found that addition of a co-catalyst Bu_4NCl enhanced the azacarbonylation dramatically and also gave a predominance of the amide **2**. Thus, the $Rh_6(CO)_{16}$–Bu_4NCl-catalyzed reaction of **1** with diethylamine afforded amide **2** in 83% yield along with a small amount of allylamine **3** (9% yield; entry 3). The undesired allylamine **3** can be removed readily by simple extraction with an acid solution. THF and benzene are excellent solvents. Rhodium-catalyzed azacarbonylation of **1** occurs even under CO at atmospheric pressure to give amide **2** in 68% yield (entry 4 in Table 1).

As shown in Table 2, the azacarbonylation of allyl phosphates proceeds to give the corresponding β,γ-unsaturated amides in good yields. Aliphatic, alicyclic, and benzylic amines can be used as nucleophiles. When primary amines are used as nucleophiles, *N*-monosubstituted amides are obtained selectively (entry 2). Insertion of CO takes place with high regioselectivity at the less substituted terminal carbon atom of allyl units to give linear amides rather than branched isomers regardless of the positional identity of the initial leaving group. Thus, 3-buten-2-yl phosphate (**10**) was converted into 3-pentenamide **11** exclusively (entry 5). It is noteworthy that α,β-unsaturated amides could not be detected among the products, although isomerization of β,γ-unsaturated amides to α,β-unsaturated amides occurs readily [22]. The (*E*)-isomers of β,γ-unsaturated amides are obtained preferentially. The car-

TABLE 2. Rhodium-catalyzed azacarbonylation of allyl phosphates [a]

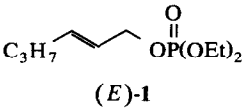
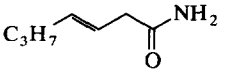
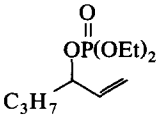
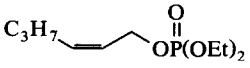
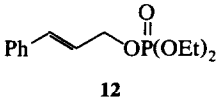
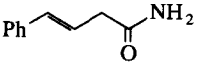
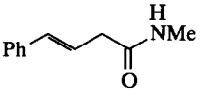
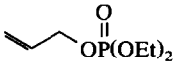
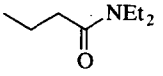
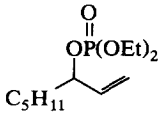
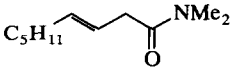
Entry	allyl phosphate	amine	β,γ-unsaturated amide	yield, % [b]	*E* : *Z* ratio [c]
1	 (*E*)-**1**		 **4**	82	86:14
2	(*E*)-**1**	H_2NCH_2Ph	 **5**	80	90:10
3	 **6**	$HNEt_2$	 **7**	83	88:12
4	 **8**		 **9**	74	75:25
5	 **10**	$HNEt_2$	 **11**	84	80:20
6	 **12**	$HNEt_2$	 **13**	77	100:0

[a] Reaction conditions: substrate 1.0 mmol, $Rh_6(CO)_{16}$ 0.01 mmol, Bu_4NCl 0.1 mmol, amine 2.0 mmol, benzene 2 ml, CO 20 atm, at 50°C, 6 h.
[b] Isolated yield.
[c] Determined by ^1H and ^{13}C NMR and GLC.

bonylation of cinnamyl phosphate (**12**) with diethylamine gave (*E*)-*N*,*N*-diethyl-4-phenyl-3-butenamide (**13**) stereoselectively (entry 6).

Next, we examined the preparation of primary β,γ-unsaturated amides, which are important precursors of primary homoallylamines and β-lactams [23]. When aqueous ammonia solution was used as a nucleophile, a mixture of β,γ-unsaturated acids and amides was obtained. However, a combination of ammonium chloride and triethylamine was found to be very effective for azacarbonylation. Thus, azacarbonylation of 1-octen-3-yl phosphate (**6**) with 2 equivalents of ammonium chloride and triethylamine in the presence of 1 mol% of $Rh_6(CO)_{16}$ gave 3-nonenamide (**14**) exclusively (eqn. (4)). For the carbonylation of **6**, $Rh_6(CO)_{16}$ cluster is again an effective catalyst in comparison with the other catalysts such as $RhH(CO)(PPh_3)_2$, $Ru_3(CO)_{12}$, $Mo(CO)_6$, and $Pd(PPh_3)_4$. The effect of solvent is quite remarkable; reaction in DMSO gave excellent results, and DMF and acetonitrile can be used, but other solvents such as toluene, THF, and chloroform gave poor results. Ammonium chloride and liberated triethylamine hydrochloride seem to play a role as co-catalyst, and hence Bu_4NCl is not required. Combination

TABLE 3. Rhodium-catalyzed azacarbonylation of allyl phosphates by using amine hydrochloride [a]

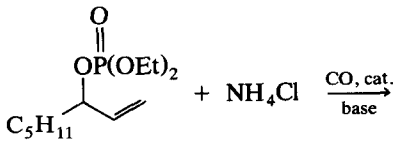
Entry	allyl phosphate	amine hydrochloride	β,γ-unsaturated amide	yield, % [b]	*E* : *Z* ratio [c]
1	 (*E*)-**1**	NH_4Cl	 **15**	87	87:13
2	 **16**	NH_4Cl	**15**	70	87:13
3	 (*Z*)-**1**	NH_4Cl	**15**	72	73:27
4	 **12**	NH_4Cl	 **17**	72	100:0
5	**12**	$H_2NMe \cdot HCl$	 **18**	80	100:0
6	 **19**	$HNEt_2 \cdot HCl$	 **20**	92	–
7	 **6**	$HNMe_2 \cdot HCl$	 **21**	84	87:13

[a] Reaction conditions: substrate 1.0 mmol, $Rh_6(CO)_{16}$ 0.01 mmol, amine hydrochloride 2.0 mmol, triethylamine 2.0 mmol, DMAP 0.2 mmol, DMSO 2 ml, CO 20 atm, at 50°C, 6 h.

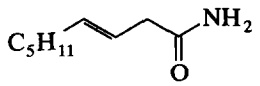
[b] Isolated yield.

[c] Determined by ^1H and ^{13}C NMR and/or GLC.

of a catalytic amount of 4-*N*,*N*-dimethylaminopyridine (DMAP) and triethylamine resulted in rather high yields of amide **14**.



6

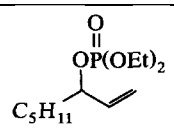
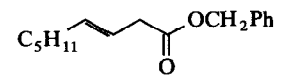
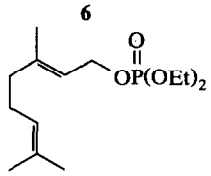
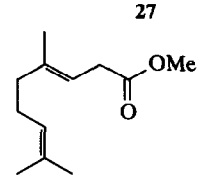
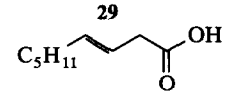
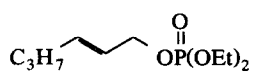
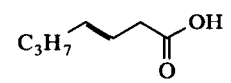
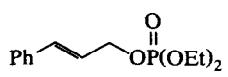
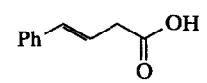
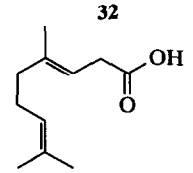


14 (4)

A variety of primary β,γ-unsaturated amides can be obtained upon treatment of allyl phosphates with CO (20 atm) in DMSO in the presence of $Rh_6(CO)_{16}$ (1 mol%) catalyst, ammonium chloride, and triethylamine at 50°C as shown in Table 3. Linear β,γ-unsaturated primary amides are obtained regioselectively without formation of α,β-unsaturated isomers. The loss of stereochemistry of carbon–carbon double bonds of β,γ-unsaturated amides seems to be due to *syn-anti* isomerization of intermediate π-allylrhodium complexes involving σ-intermediate [24]. Amines with low boiling points can also be used for the present procedure. Thus, the carbonylation of cinnamyl phosphates (**12**) with methylamine hydrochloride gave (*E*)-*N*-methyl-4-phenyl-3-butenamide (**18**) stereoselectively in 80% yield (entry 5).

Allylic acetates can also be used as substrates for $Rh_6(CO)_{16}$-catalyzed azacarbonylation (eqn. (5)). The carbonylation of 1-octen-3-yl acetate (**22**) did not proceed under the conditions as optimized for the car-

TABLE 4. Rhodium-catalyzed oxacarbonylation of allyl phosphates [a]

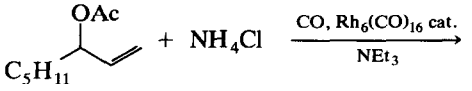
Entry	allyl phosphate	nucleophile	β,γ-unsaturated ester	yield, % [b]	*E*:*Z* ratio [c]
1	 **6**	$PhCH_2OH$	 **27**	77	92:8
2	 **28**	MeOH	 **29**	72	76:24
3	**6**	H_2O	 **30**	64	84:16
4	 (*E*)-**1**	H_2O	 **31**	64	87:13
5	 **12**	H_2O	 **32**	97	100:0
6	**28**	H_2O	 **33**	71	77:23

[a] Reaction conditions: substrate 1.0 mmol, $Rh_6(CO)_{16}$ 0.01 mmol, alcohols or water 2.0 mmol, triethylamine 2.0 mmol, Bu_4NCl 0.1 mmol, DMSO 2 ml, CO 20 atm, at 50°C, 10 h.

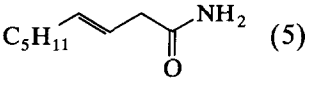
[b] Isolated yield.

[c] Determined by ^1H and ^{13}C NMR and/or GLC.

bonylation of allyl phosphates. However, when the reaction was carried out under 60 atm of CO at 80°C,



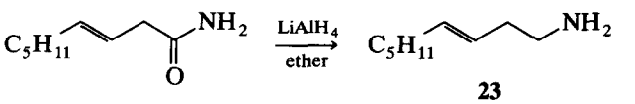
22



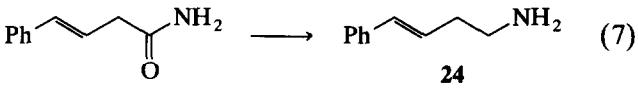
14 (5)

amide **14** was obtained in 41% yield. It is noteworthy that the addition of NaBr as a co-catalyst enhanced the present azacarbonylation reaction. Thus, the reaction of allyl acetates **22** with ammonium chloride in the presence of 1 mol% of $Rh_6(CO)_{16}$, 10 mol% of NaBr, and triethylamine in DMSO under the pressure of CO (60 atm) at 80°C gave amide **14** in 64% yield without formation of α,β-unsaturated isomer. We have found that the addition of a catalytic amount of NaBr enhanced the palladium-catalyzed carbonylation of allyl acetates [8]. Although the role of NaBr is not clear, the ligand exchange of intermediate π-allyl complex seems to occur.

The primary β,γ-unsaturated amides are readily converted into the corresponding primary homoallylamines with $LiAlH_4$ [25]. Typically, the reaction of 3-nonenamide (**14**) with $LiAlH_4$ gave 3-nonenylamine



14 23 (6)



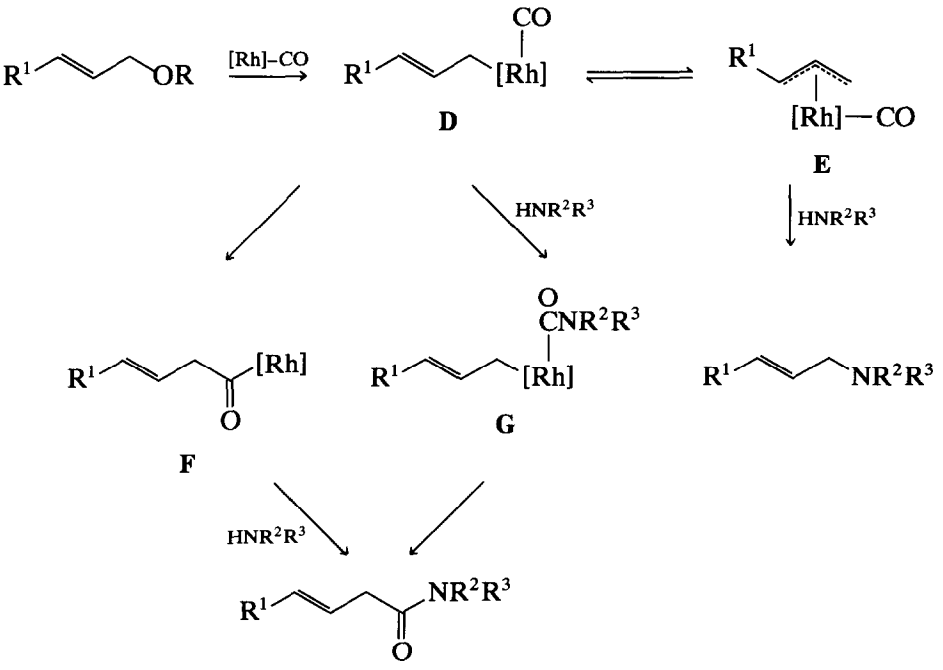
17 24 (7)

(**23**) in 69% yield (eqn. (6)). Similar treatment of (*E*)-4-phenyl-3-butenamide (**17**) afforded (*E*)-4-phenyl-3-butenylamine (**24**) in 71% yield (eqn. (7)). Furthermore, dehydration of primary amides gives the corresponding nitriles [26]. Thus, the treatment of amide **14** with thionyl chloride in benzene at 80°C afforded 3-nonenonitrile (**25**) in 99% yield (eqn. (8)).

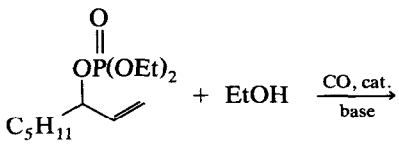
14 25 (8)

2.2. *Oxacarbonylation of allyl phosphates*

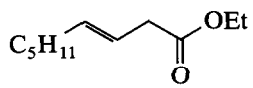
Oxacarbonylation of allyl phosphate **6** to give ethyl 3-nonenoate (**26**) has been examined in the presence of ethanol (eqn. (9)). The combination of $Rh_6(CO)_{16}$ and



Scheme 2.



6

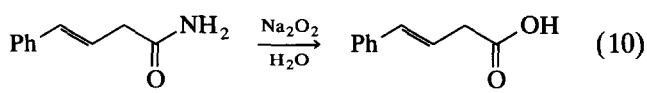


(9)

26

Bu_4NCl is again the best catalyst among those examined. $[RhCl(cod)]_2$ is a good catalyst, and other catalysts such as $RhH(CO)(PPh_3)_2$, $RhHCl(PPh_3)_2$, and $Ru_3(CO)_{12}$ showed low catalytic activity. DMSO is again an excellent solvent. The reaction of allyl phosphate **6** with 2 equivalents of ethanol in the presence of 1 mol% of $Rh_6(CO)_{16}$, 10 mol% of Bu_4NCl, and triethylamine in DMSO under the pressure of CO (20 atm) at 50°C gave **26** in 72% yield.

Representative results of the oxacarbonylations are shown in Table 4. β,γ-Unsaturated acids can be prepared upon treatment with water (entries 3–6). Further, β,γ-unsaturated acids have been prepared by nickel- [2b,c] and palladium-catalyzed [4e] carbonylation of allyl halides in alkaline conditions. The present reaction provides a convenient method for the direct synthesis of β,γ-unsaturated acids from allyl esters. Homogeranic acid (**33**) thus obtained is a useful precursor of actinidiolide and loliolide [27]. (*E*)-4-Phenyl-3-butenoic acid (**32**) was obtained from **12** in 97% yield. It is noteworthy that **32** was obtained by hydrolysis of the amide **17** (eqn. (10)).



(10)

17 32

2.3. Mechanisms

Since CO insertion occurs selectively at the less hindered carbon atom of an allylic system irrespective of the regiochemistry of the starting substrates, carbonylation seems to proceed via the π-allylrhodium intermediate. The active species seems to be anionic cluster carbonyl, $[Rh_6(CO)_{15}Cl]^- \cdot Bu_4N^+$, derived from $Rh_6(CO)_{16}$ and $Bu_4N^+Cl^-$ [28]. Anionic rhodium carbonyl complex $[Rh(CO)(PEt_3)(mnt)]^-$ (mnt = malenonitriledithiolate) reacts with allyl chloride to give acyl complex of $Rh(COC_3H_5)(PEt_3)_2(mnt)$ [29]. The present reaction can be rationalized with the mechanism shown in Scheme 2. Labile $[Rh_6(CO)_{15}Cl]^-$ undergoes oxidative addition to allyl phosphate to give η^1-allylrhodium complex **D**. Although η^1-allyl complex **D** is in equilibrium with the η^3-allyl complex **E**, the equilibrium lies to η^1-allylrhodium complex **D** [21]. Migration of allyl group onto the co-ordinated CO gives the acylrhodium complex **F** [29], which reacts with amine to give β,γ-unsaturated amide. Allylamines are derived from direct amination of π-allyl complex **E**. Since $Rh_6(CO)_{16}$ reacts with primary amine to give $[RNH_3]^+[Rh_6(CO)_{15}(CONHR)]^-$ [28], an alternative pathway which involves reductive elimination of (carbamoyl)(σ-allyl)rhodium complex **G** cannot be excluded. Oxacarbonylation proceeds according to the same mechanism, which involves reaction of acylrhodium complex **F** with an alcohol to give β,γ-unsaturated ester.

3. Experimental section

3.1. General

All melting points were measured in capillary tubes and are uncorrected. NMR spectra were recorded on JEOL PMX-60-SI (^1H at 60 MHz), JEOL JNM-FX-100 (^1H at 100 MHz, ^{13}C at 25 MHz), JEOL JNM-GSX-270 (^1H at 270 MHz, ^{13}C at 68 MHz), and JEOL JNM-GX-500 (^1H at 500 MHz) spectrometers in $CDCl_3$ solutions. IR spectra were recorded with Hitachi 215 and Shimadzu FTIR-4100 spectrometers; data are given in cm^{-1}, only the important diagnostic bands being reported. Analytical GLC evaluations of product mixtures were carried out on Shimadzu GC-9A and GC-8A flame ionization chromatographies by using a 1 m × 3 mm stainless steel column (10% SE-30 on 80–120 mesh Uniport HP) and Shimadzu GC-Mini 2 flame ionization chromatography by using a 25 m × 0.25 mm chemical bonded on a glass capillary column (PEG-20M). Mass spectra were obtained with a Shimadzu GCMS QP-1000 by using a glass column packed with SE-30 on Uniport HP and JEOL JMS-DX303 mass spectrometers. Elemental analyses were carried out with a Yanagimoto MT-3 CHN instrument.

$Rh_6(CO)_{16}$ was commercially obtained (N. E. Chemcat) and used as received. Benzene, toluene, and THF were distilled over benzophenone ketyl. Dimethylsulfoxide (DMSO) was distilled over calcium hydride under argon. Allylic phosphates were prepared from corresponding allyl alcohols and chloro diethyl phosphate by the method we described previously [14].

3.2. Azacarbonylation of (E)-2-hexenyl diethyl phosphate ((E)-1) with diethylamine

3.2.1. Influence of metal catalyst and co-catalyst

In a 10 ml stainless-steel autoclave were placed allyl phosphate **1** (0.236 g, 1.0 mmol), diethylamine (0.146 g, 2.0 mmol), metal catalyst (0–0.05 mmol), Bu_4NCl (0–0.1 mmol), and benzene (2 ml). After CO was intro-

duced up to 20 atm, the mixture was stirred at 50°C for 6 h. The yields of *N,N*-diethyl-3-heptenamide (**2**) and *N,N*-diethyl-2-hexenylamine (**3**) were determined by GLC analysis using dodecane as an internal standard. These results are listed in Table 1.

3.2.2. Influence of solvent

In a 10-ml autoclave were placed **1** (1.0 mmol), diethylamine (2.0 mmol), $Rh_6(CO)_{16}$ (0.011 g, 0.01 mmol), Bu_4NCl (0.028 g, 0.1 mmol), and solvent (2 ml). The mixture was stirred under CO (20 atm) at 50°C for 6 h. The yields of **2** and **3** determined by GLC are as follows: Solvent benzene (83, 9%), THF (84, 7%), acetonitrile (61, 27%), benzene–water (4, 0%).

3.2.3. Influence of CO pressure

In a 10 ml autoclave were placed **1** (1.0 mmol), diethylamine (2.0 mmol), $Rh_6(CO)_{16}$ (0.01 mmol), Bu_4NCl (0.1 mmol), and benzene (2 ml). The mixture was stirred under CO or argon at 50°C for 6 h. In case of the reaction under argon or atmospheric pressure of CO, a 25 ml side armed flask equipped with a rubber balloon filled with argon or CO was used. The yields of **2** and **3** determined by GLC are as follows: P_{CO} 0 (under argon) (0, 83%), 1 (68, 21%), 20 (83, 9%), 50 (85, 7%) atm.

3.2.4. N,N-Diethyl-3-heptenamide (2)

^1H NMR (270 MHz) δ 0.89 (t, $J = 7.3$ Hz, 3H, H-7), 1.11 (t, $J = 7.1$ Hz, 3H, CH_3), 1.18 (t, $J = 7.1$ Hz, 3H, CH_3), 1.25–1.48 (m, 2H, H-6), 2.02 (dt, $J = 5.2$, 6.8 Hz, 2H, H-5), 3.06 (d, $J = 5.1$ Hz, 2H, H-2), 3.32 (q, $J = 7.1$ Hz, 2H, NCH_2), 3.37 (q, $J = 7.1$ Hz, 2H, NCH_2), 5.50 (dt, $J = 15.3$, 5.2 Hz, 1H, H-4), 5.59 (dt, $J = 15.3$, 5.2 Hz, 1H, H-3) for (*E*)-**2**: 3.10 (d, $J = 4.9$ Hz, 2H, H-2) for (*Z*)-**2**; $^{13}C\{^1H\}$ NMR (68 MHz) δ 13.0 (CH_3), 13.6 (C-7), 14.4 (CH_3), 22.4 (C-6), 34.7 (C-5), 37.7 (C-2), 40.1 (NCH_2), 42.2 (NCH_2), 123.5 (C-3), 133.5 (C-4), 170.9 (C=O) for (*E*)-**2**; 29.7 (C-5), 32.6 (C-2), 122.8 (C-3), 132.2 (C-4) for (*Z*)-**2**; IR (neat) 1640 (C=O), 970 (CH=CH) cm^{-1}; Mass spectrum, *m/e* (relative intensity) 183 (M^+, 28), 168 (13), 154 (25), 111 (13), 83 ($M^+ - C(O)NEt_2$, 100); High resolution mass spectrum for $C_{11}H_{21}NO$, Calcd 183.1624, Found 183.1615. Anal. Calcd for $C_{11}H_{21}NO$: C, 72.08; H, 11.55; N, 7.64. Found: C, 71.98; H, 11.60; N, 7.62%.

3.2.5. N,N-Diethyl-2-hexenylamine (3)

^1H NMR (60 MHz) δ 0.63–2.27 (m, 7H), 1.02 (t, $J = 7$ Hz, 6H, CH_3), 2.51 (q, $J = 7$ Hz, 4H, NCH_2), 3.03 (d, $J = 5$ Hz, 2H, H-1), 5.10–5.87 (m, 2H, H-2 and H-3). $^{13}C\{^1H\}$ NMR (68 MHz) δ 11.5 (CH_3), 13.4 (C-6), 22.3 (C-5), 34.4 (C-4), 46.3 (NCH_2), 55.1 (C-1), 127.0, 133.4; IR (neat) 1200 (C–N), 970 (CH=CH) cm^{-1}. Anal. Calcd for $C_{10}H_{21}N$: C, 77.35; H, 13.62; N, 9.02. Found: C, 77.07; H, 13.72; N, 8.88%.

3.3. General procedure for rhodium-catalyzed azacarbonylation of allyl phosphates

In a 10-ml stainless-steel autoclave were placed $Rh_6(CO)_{16}$ (0.011 g, 0.01 mmol), Bu_4NCl (0.028 g, 0.1 mmol), allyl phosphate (1.0 mmol), amine (2.0 mmol), and dry benzene (2 ml). Then, CO was introduced up to 20 atm, and the mixture was stirred at 50°C for 6 h. The product was extracted with ether, and the extracts were washed with 1 M HCl and brine and dried ($MgSO_4$). Evaporation followed by column chromatography or thin layer chromatography on silica gel gave pure amide. Stereoisomeric ratio (*E* : *Z*) of the products was determined on the basis of ^1H and ^{13}C NMR and/or capillary GLC analyses. These results are summarized in Table 2.

3.3.1. N-3-Heptenoylpiperidine (4)

^1H NMR (60 MHz) δ 0.70–1.77 (m, 11H), 1.80–2.23 (m, 2H, H-5), 3.05 (dd, $J = 3$, 1 Hz, 2H, H-2), 3.23–3.67 (m, 4H, NCH_2), 5.07–5.83 (m, 2H, H-3, H-4); IR (neat) 1640 (C=O), 970 (CH=CH) cm^{-1}. Anal. Calcd for $C_{12}H_{21}NO$: C, 73.80; H, 10.84; N, 7.17. Found: C, 73.62; H, 10.90; N, 7.09%.

3.3.2. N-Benzyl-3-heptenamide (5)

^1H NMR (270 MHz) δ 0.85 (t, $J = 7.3$ Hz, 3H, H-7), 1.38 (tq, $J = 7.1$, 7.3 Hz, 2H, H-6), 2.00 (dt, $J = 7.3$, 7.1 Hz, H-5), 2.98 (d, $J = 6.5$ Hz, 2H, H-2), 4.40 (d, $J = 6.5$ Hz, 2H, $PhCH_2N$), 5.53 (dt, $J = 16$, 7.3 Hz, 1H, H-4), 5.62 (dt, $J = 16$, 6.5 Hz, 1H, H-3), 6.05 (br, 1H, NH), 7.21–7.42 (m, 5H, Ph) for (*E*)-**5**; 3.06 (d, $J = 7.0$ Hz, 2H, H-2) for (*Z*)-**5**; $^{13}C\{^1H\}$ NMR (68 MHz) δ 13.7 (C-7), 22.4 (C-6), 34.6, 40.5, 43.6, 122.7 (C-4), 127.5 (*p*), 127.7, 128.7, 136.4 (C-3), 138.3 (*i*), 171.3 (C=O) for (*E*)-**5**; 121.8 (C-4), 135.3 (C-3) for (*Z*)-**5**; IR (neat) 3280 (N–H), 1640 (C=O), 962 (CH=CH) cm^{-1}. Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.30; H, 9.01; N, 6.40%.

3.3.3. N,N-Diethyl-3-nonenamide (7)

^1H NMR (270 MHz) δ 0.88 (t, $J = 6.6$ Hz, 3H, H-9), 1.11 (t, $J = 7.1$ Hz, 3H, CH_3), 1.17 (t, $J = 7.1$ Hz, 3H, CH_3), 1.23–1.40 (m, 6H), 2.03 (dt, $J = 5.5$, 7.0 Hz, 2H, H-5), 3.05 (d, $J = 5.5$ Hz, 2H, H-2), 3.31 (q, $J = 7.1$ Hz, 2H, NCH_2), 3.37 (q, $J = 7.1$ Hz, 2H, NCH_2), 5.50 (dt, $J = 15.5$, 5.5 Hz, 1H, H-4), 5.58 (dt, $J = 15.5$, 5.5 Hz, 1H, H-3) for (*E*)-**7**; 3.12 (d, $J = 5.5$ Hz, 2H, H-2) for (*Z*)-**7**; $^{13}C\{^1H\}$ NMR (68 MHz) δ 12.9 (CH_3), 13.9 (C-9), 14.3 (CH_3), 22.4 (C-8), 28.9 (C-7), 31.4 (C-6), 32.4 (C-5), 37.6 (C-2), 40.0 (NCH_2), 42.0 (NCH_2), 123.1 (C-3), 133.7 (C-4), 170.8 (C=O) for (*E*)-**7**; 122.3 (C-3),

132.4 (C-4) for (*Z*)-**7**; IR (neat) 1640 (C=O), 960 (CH=CH) cm^{-1}. Anal. Calcd for $C_{13}H_{25}NO$: C, 73.88; H, 11.92; N, 6.63. Found: C, 73.77; H, 11.84; N, 6.38%.

3.3.4. N-3-Pentenoylmorphorine (9)

^1H NMR (270 MHz) δ 1.69 (ddt, $J = 1.4$, 3.4, 1.4 Hz, 3H, H-5), 3.07 (ddq, $J = 1.4$, 3.4, 1.4 Hz, 2H, H-2), 3.46 (br-t, $J = 5$ Hz, 2H, NCH_2), 3.55–3.70 (m, 6H), 5.47–5.70 (m, 2H, H-3, H-4) for (*E*)-**9**; 1.66 (ddt, $J =$ 1.4, 6.0, 1.4 Hz, 3H, H-5), 3.13 (ddt, $J = 1.4$, 6.0, 1.4 Hz, 2H, H-2) for (*Z*)-**9**; $^{13}C\{^1H\}$ NMR (68 MHz) δ 17.8 (C-5), 37.4 (C-2), 41.9 (NCH_2), 46.2 (NCH_2), 66.5 (OCH_2), 66.8 (OCH_2), 123.5 (C-3), 128.8 (C-4), 170.2 (C=O) for (*E*)-**9**; 32.2 (C-2), 122.5 (C-3), 127.0 (C-4) for (*Z*)-**9**; IR (neat) 1638 (C=O), 964 (CH=CH) cm^{-1}. Anal. Calcd for $C_9H_{15}NO_2$: C, 63.88; H, 8.93; N, 8.28. Found: C, 63.66; H, 8.94; N, 8.07%.

3.3.5. N,N-Diethyl-3-pentenamide (11)

^1H NMR (60 MHz) δ 1.11 (t, $J = 7$ Hz, 3H, CH_3), 1.16 (t, $J = 7$ Hz, 3H, CH_3), 1.53–1.83 (m, 3H, H-5), 2.98–3.10 (m, 2H, H-2), 3.31 (q, $J = 7$ Hz, 2H, NCH_2), 3.34 (q, $J = 7$ Hz, 2H, NCH_2), 5.17–5.87 (m, 2H, H-3, H-4); $^{13}C\{^1H\}$ NMR (25 MHz) δ 13.0 (CH_3), 14.4 (CH_3), 17.8 (C-5), 37.5 (NCH_2), 40.2 (C-2), 42.1 (NCH_2), 124.5 (C-3), 128.0 (C-4), 170.7 (C=O) for (*E*)-**11**; 32.3 (C-2), 123.6 (C-3), 126.2 (C-4) for (*Z*)-**11**; IR (neat) 1640 (C=O), 968 (CH=CH) cm^{-1}. Anal. Calcd for $C_9H_{17}NO$: C, 69.63; H, 11.04; N, 9.03. Found: C, 69.77; H, 10.72; N, 8.92%.

3.3.6. (E)-N,N-Diethyl-4-phenyl-3-butenamide (13)

^1H NMR (270 MHz) δ 1.14 (t, $J = 7.1$ Hz, 3H, CH_3), 1.20 (t, $J = 7.1$ Hz, 3H, CH_3), 3.28 (d, $J = 5.4$ Hz, 2H, H-2), 3.35 (q, $J = 7.1$ Hz, 2H, NCH_2), 3.40 (q, $J = 7.1$ Hz, 2H, NCH_2), 6.37 (dt, $J = 16$, 5.6 Hz, 1H, H-3), 6.41 (d, $J = 16$ Hz, 1H, H-4), 7.15–7.38 (m, 5H, Ph); $^{13}C\{^1H\}$ NMR (68 MHz) δ 13.0 (CH_3), 14.4 (CH_3), 37.8 (NCH_2), 40.2 (C-2), 42.2 (NCH_2), 123.8, 126.2, 127.3, 128.5, 132.4, 137.1 (*i*), 170.1 (C=O); IR (neat) 1630 (C=O), 970 (CH=CH) cm^{-1}. Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.10; H, 9.00; N, 6.35%.

3.4. Azacarbonylation of 1-octen-3-yl diethyl phosphate (6) using ammonium chloride

3.4.1. Influence of solvents

In a 10 ml autoclave were placed allyl phosphate **6** (0.264 g, 1.0 mmol), NH_4Cl (0.11 g, 2.0 mmol), solvent (2 ml), $Rh_6(CO)_{16}$ (0.011 g, 0.01 mmol), NEt_3 (0.20 g, 2.00 mmol), and 4-dimethylaminopyridine (DMAP) (0.024 g, 0.20 mmol). Then CO was introduced up to 20 atm, and the mixture stirred at 50°C for 10 h. The conversion of allyl phosphate **6** and the yield of 3-nonenamide (**14**) based on the consumed **6** were determined by GLC using undecane as an internal standard. The results were: solvent DMSO (99, 99%), DMSO without DMAP (99, 87%), DMF (96, 98%), acetonitrile (99, 71%), methanol (99, 45%), toluene (96, 39%), chloroform (99, 27%), THF (70, 41%).

3.4.2. Influence of catalyst

In a 10 ml autoclave were placed **6** (1.0 mmol), NH_4Cl (2.0 mmol), DMSO (2 ml), NEt_3 (2.0 mmol), DMAP (0.20 mmol), and metal catalyst. The mixture was stirred under CO (20 atm) at 50°C for 6 h. The conversion of **6** and the yield of **14** determined by GLC were: catalyst (mol%) $Rh_6(CO)_{16}$ (1) (99, 95%), $RhH(CO)(PPh_3)_2$ (5) (99, 23%), $Pd(PPh_3)_4$ (5) (99, 16%), $Ru_3(CO)_{12}$ (2) (29, 0%), $Mo(CO)_6$ (5) (5, 0%), none (5, 0%).

3.4.3. Influence of CO pressure

In a 10 ml autoclave were placed **6** (1.0 mmol), NH_4Cl (2.0 mmol), DMSO (2 ml), NEt_3 (2.0 mmol), DMAP (0.20 mmol), and $Rh_6(CO)_{16}$ (0.01 mmol). The mixture was stirred under CO or argon at 50°C for 6 h. In case of the reaction under argon or atmospheric pressure of CO, a 25 ml side armed flask equipped with a rubber balloon filled with argon or CO was used. The conversion of **6** and the yield of **14** determined by GLC are as follows: P_{CO} 0 (46, 0%), 1 (51, 63%), 5 (91, 60%), 10 (99, 91%), 20 (99, 95%) atm.

3.4.4. Temperature dependency

In a 10 ml autoclave were placed **6** (1.0 mmol), NH_4Cl (2.0 mmol), DMSO (2 ml), NEt_3 (2.0 mmol), DMAP (0.20 mmol), and $Rh_6(CO)_{16}$ (0.01 mmol). The mixture was stirred under CO (20 atm) for 6 h. The conversion of **6** and the yield of **14** determined by GLC analysis are as follows: *T* 25 (39, 0%), 50 (99, 95%), 100 (99, 77%) °C.

3.4.5. 3-Nonenamide (14)

Mp 62–64°C; ^1H NMR (100 MHz) δ 0.88 (t, $J = 7.5$ Hz, 3H, H-9), 1.04–1.56 (m, 6H), 2.02 (dt, $J = 7.1$, 7.0 Hz, 2H, H-5), 2.93 (d, $J = 6.8$ Hz, 2H, H-2), 5.47 (dt, $J = 18.5$, 7.1 Hz, 1H, H-4), 5.59 (dt, $J = 18.5$, 6.8 Hz, 1H, H-3), 5.20–6.56 (br-d, 2H, NH_2); $^{13}C\{^1H\}$ NMR (25 MHz) δ 14.0 (C-9), 22.5 (C-8), 28.8 (C-7), 31.4 (C-6), 32.5 (C-5), 40.0 (C-2), 122.4 (C-3), 136.3 (C-4), 174.8 (C=O) for (*E*)-**14**; 27.3 (C-5), 34.6 (C-2), 121.6 (C-3), 136.3 (C-4), 174.5 (C=O) for (*Z*)-**14**; IR (KBr) 3350 (N–H), 1640 (C=O), 970 (CH=CH) cm^{-1}. Anal. Calcd for $C_9H_{17}NO$: C, 69.63; H, 11.04; N, 9.02. Found: C, 69.44; H, 10.86; N, 8.98%.

3.5. General procedure for preparation of β,γ-unsaturated amides using amine hydrochloride

In a 10 ml stainless-steel autoclave were placed allyl phosphate (1.0 mmol), amine hydrochloride (2.0 mmol), and DMSO (2 ml). After the autoclave was flushed with CO, $Rh_6(CO)_{16}$ (0.011 g, 0.01 mmol), NEt_3 (0.202 g, 2.0 mmol), and DMAP (0.024 g, 0.20 mmol) were added. Then CO was introduced up to 20 atm, and the mixture was stirred at 50°C for 6 h. The product was extracted with ether, and the extracts were washed with 2 M HCl, aqueous $NaHCO_3$ solution, and brine and dried (Na_2SO_4). Evaporation followed by column chromatography or thin layer chromatography on silica gel gave pure amide. Stereoisomeric ratio ($E:Z$) of the products was determined on the basis of ^1H and ^{13}C NMR and/or capillary GLC analyses. These results are summarized in Table 3.

3.5.1. 3-Heptenamide (15)

Mp 76°C; ^1H NMR (270 MHz) δ 0.91 (t, $J = 7.3$ Hz, 3H, H-7), 1.41 (tq, $J = 7.3$, 7.3 Hz, 2H, H-6), 2.04 (dt, $J = 6.8$, 7.3 Hz, 2H, H-5), 2.97 (d, $J = 6.8$ Hz, 2H, H-2), 5.54 (dt, $J = 15.2$, 6.8 Hz, 1H, H-4), 5.70 (dt, $J = 15.2$, 6.8 Hz, 1H, H-3), 5.4–6.0 (br, 2H, NH_2) for (*E*)-**15**; 0.92 (t, $J = 7.3$ Hz, 3H, H-7), 3.04 (d, $J = 7.1$ Hz, 2H, H-2) for (*Z*)-**15**; $^{13}C\{^1H\}$ NMR (25 MHz) δ 13.7 (C-7), 22.5 (C-6), 34.6 (C-5), 40.0 (C-2), 122.6 (C-3), 136.0 (C-4), 174.8 (C=O) for (*E*)-**15**; 121.8 (C-3), 134.7 (C-4), 174.6 (C=O) for (*Z*)-**15**; IR (KBr) 3360 (N–H), 1670 (C=O), 975 (CH=CH) cm^{-1}. Anal. Calcd for $C_7H_{13}NO$: C, 66.10; H, 10.30; N, 11.02. Found: C, 65.81; H, 10.11; N, 10.82%.

3.5.2. (E)-4-Phenyl-3-butenamide (17)

Mp 129–130°C; ^1H NMR ($CDCl_3$–CD_3OD, 270 MHz) δ 3.18 (dd, $J = 1.3$, 7.2 Hz, 2H, H-2), 5.73 (br, 2H, NH_2), 6.31 (dt, $J = 15.9$, 7.2 Hz, 1H, H-3), 6.56 (dt, $J = 15.9$, 1.3 Hz, 1H, H-4), 7.22–7.40 (m, 5H, Ph); IR (KBr) 3370 (N–H), 1650 (C=O), 960 (CH=CH) cm^{-1}. Anal. Calcd for $C_{10}H_{11}NO$: C, 74.50; H, 6.88; N, 8.69. Found: C, 74.15; H, 6.88; N, 8.62%.

3.5.3. (E)-N-Methyl-4-phenyl-3-butenamide (18)

^1H NMR (60 MHz) δ 2.73 (s, 3H × 0.4, *anti*-NCH_3), 2.82 (s, 3H × 0.6, *syn*-NCH_3), 3.29 (d, $J = 6$ Hz, 2H, H-2), 6.15 (dt, $J = 6$, 15 Hz, 1H, H-3), 6.50 (d, $J = 15$ Hz, 1H, H-4), 7.07–7.47 (m, 6H, Ph, NH). Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 8.00. Found: C, 75.31; H, 7.49; N, 7.79%.

3.5.4. N,N-Diethyl-3-butenamide (20)

^1H NMR (60 MHz) δ 1.11 (t, $J = 7$ Hz, 3H, CH_3), 1.17 (t, $J = 7$ Hz, 3H, CH_3), 3.10 (ddd, $J = 1$, 1, 6 Hz, 2H, H-2), 3.29 (q, $J = 7$ Hz, 2H, NCH_2), 3.36 (q, $J = 7$ Hz, 2H, NCH_2), 4.80–5.50 (m, 2H, H-4), 5.98 (ddt, $J = 9$, 18, 6 Hz, 1H, H-3); IR (neat) 1640 (C=O), 996 (CH_2=CH) cm^{-1}. Anal. Calcd for $C_8H_{15}NO$: C, 68.05; H, 10.71; N, 9.92. Found: C, 67.77; H, 10.72; N, 9.82%.

3.5.5. N,N-Dimethyl-3-nonenamide (21)

Bp 122–125°C (3 mmHg; Kugelröhr); ^1H NMR (60 MHz) δ 0.88 (t, $J = 5$ Hz, 3H, H-9), 1.07–1.67 (m, 6H), 1.83–2.27 (m, 2H, H-5), 2.93 (s, 3H, NCH_3), 2.99 (s, 3H, NCH_3), 3.02 (d, $J = 6.4$ Hz, 2H, H-2), 5.40–5.69 (m, 2H, H-3, H-4); IR (neat) 1630 (C=O), 970 (CH=CH) cm^{-1}.

3.6. Rhodium-catalyzed azacarbonylation of 1-octen-3-yl acetate (22)

In a 10 ml stainless-steel autoclave were placed $Rh_6(CO)_{16}$ (0.011 g, 0.01 mmol), NaBr (0.010 g, 0.1 mmol), 1-octen-3-yl acetate (**22**) (0.17 g, 1.0 mmol), NH_4Cl (0.11 g, 2.0 mmol), NEt_3 (0.20 g, 2.0 mmol), and DMSO (2 ml). Then CO was introduced up to 60 atm, and the mixture was stirred at 80°C for 12 h. Usual work-up followed by column chromatography on silica gel gave amide **14** in 61% yield. When the reaction was performed without NaBr, amide **14** was obtained in 41% yield.

3.7. Reduction of 3-nonenamide (14)

To a suspension of $LiAlH_4$ (0.152 mg, 4.0 mmol) in dry ether (6 ml), a solution of amide **14** (0.155 g, 1.0 mmol) in ether (6 ml) was added dropwise at room temperature. After the mixture was stirred at room temperature for 3 h, water was added. The product was extracted with 2 M HCl. The combined aqueous solutions were made strongly basic with 2 M NaOH and extracted with dichloromethane. The extracts were washed with brine and dried ($MgSO_4$). The filtrate was evaporated to give 3-nonenylamine (**23**) (0.097 g, 69%): ^1H NMR (270 MHz) δ 0.88 (t, $J = 7.1$ Hz, H-9), 1.22–1.40 (m, 8H), 2.00 (dt, $J = 6.8$, 6.9 Hz, 2H, H-5), 2.47 (dt, $J = 7.3$, 6.9 Hz, 2H, H-2), 3.00 (t, $J = 7.3$ Hz, 2H, H-1), 5.34 (dt, $J = 15.1$, 6.9 Hz, 1H, H-4), 5.61 (dt, $J = 15.1$, 6.8 Hz, 1H, H-3); $^{13}C\{^1H\}$ NMR (68 MHz) δ 14.1 (C-9), 22.5 (C-8), 28.9 (C-7), 30.6 (C-6), 31.4 (C-5), 32.5 (C-2), 39.7 (C-1), 123.5 (C-3), 135.6 (C-4); IR (neat) 3250 (N–H), 1570 (C=C), 970 (CH=CH) cm^{-1}; High resolution mass spectrum for $C_9H_{19}N$, Calcd 141.1517, Found 141.1515.

3.7.1. (E)-4-Phenyl-3-butenylamine (24)

The reduction of amide **17** according to the procedure described above gave homoallylamine **24** in 71% yield: ^1H NMR (60 MHz) δ 1.45 (s, 2H, NH_2), 2.40 (dt, $J = 6$, 6 Hz, 2H, H-2), 2.45–2.93 (m, 2H, H-1), 6.14 (dt, $J = 16$, 6 Hz, 1H, H-3), 6.48 (d, $J = 16$ Hz, 1H, H-4),

7.00–7.67 (m, 5H, Ph); IR (neat) 3300 (N–H), 1600 (C=C), 960 (CH=CH) cm^{-1}; High resolution mass spectrum for $C_{10}H_{13}N$, Calcd 147.1048, Found 147.1039.

3.8. Dehydration of 3-nonenamide (14)

In a 25 ml side-armed flask were placed amide **14** (0.081 g, 0.52 mmol), dry benzene (2 ml), and thionyl chloride (0.100 g, 0.84 mmol). The mixture was stirred at 80°C for 4 h. The reaction mixture was cooled in an ice bath, and 1 ml of water added to decompose the excess thionyl chloride. Cold 2 M NaOH solution was added to make the mixture alkaline. The product was extracted with ether, and the combined extracts washed with 1% aqueous Na_2CO_3 solution and water (10 ml) and dried ($MgSO_4$). Evaporation of the filtrate gave nitrile **25** (0.071 g, 99%): ^1H NMR (60 MHz) δ 0.58–1.72 (m, 9H), 1.75–2.32 (m, 2H, H-5), 3.30 (d, $J = 5.0$ Hz, 1H, H-2), 5.28 (dt, $J = 14.0$, 5.0 Hz, 1H, H-3), 5.82 (dt, $J = 14.0$, 7.0 Hz, 1H, H-4); IR (neat) 2260 (C≡N), 970 (CH=CH) cm^{-1}.

3.9. Oxacarbonylation of 1-octen-3-yl diethyl phosphate (6) using ethanol

3.9.1. Influence of catalyst

In a 10 ml autoclave were placed allyl phosphate **6** (0.264 g, 1.0 mmol), NEt_3 (0.20 g, 2.0 mmol), Bu_4NCl (0.028 g, 0.1 mmol), catalyst (0.01–0.05 mmol), ethanol (2.0 mmol), and DMSO (2 ml). Then CO was introduced up to 20 atm, and the mixture was stirred at 50°C for 5 h. The conversion of allyl phosphate **6** and the yield of ethyl 3-nonenoate (**26**) based on consumed **6** were determined by GLC analysis using undecane as an internal standard. These results are as follows: Catalyst (mol%) $Rh_6(CO)_{16}$ (1) (99, 70%), $Rh_6(CO)_{16}$ (1) without Bu_4NCl (99, 36%), $[RhCl(cod)]_2$ (5) (99, 60%), $RhCl(CO)(PPh_3)_2$ (5) (99, 25%), $RhH(CO)(PPh_3)_2$ (5) (99, 21%), $Ru_3(CO)_{12}$ (3) (79, 37%), $Pd(PPh_3)_4$ (5) (97, 23%), none (22, 0%).

3.9.2. Influence of solvent

In a 10 ml autoclave were placed **6** (1.0 mmol), NEt_3 (2.0 mmol), Bu_4NCl (0.1 mmol), $Rh_6(CO)_{16}$ (0.01 mmol), ethanol (2.0 mmol), and solvent (2 ml). The mixture was stirred under CO (20 atm) at 50°C for 5 h. The conversion of **6** and the yield of **26** determined by GLC analysis are as follows: Solvent DMSO (99, 70%), THF (99, 50%), toluene (99, 40%), acetonitrile (99, 39%), dichloromethane (99, 26%).

3.9.3. Ethyl-3-nonenoate (26)

Bp 70–71°C (4 mmHg); ^1H NMR (270 MHz) δ 0.88 (t, $J = 6.9$ Hz, 3H, H-9), 1.26 (t, $J = 6.9$ Hz, 3H, CH_3), 1.30–1.45 (m, 6H), 1.96–2.08 (m, 2H, H-5), 3.01 (d, $J = 5.4$ Hz, 2H, H-2), 4.13 (q, $J = 6.9$ Hz, 2H, OCH_2), 5.51 (dt, $J = 15.6$ and 5.6 Hz, 1H, H-4), 5.57 (dt, $J = 15.6$, 5.4 Hz, 1H, H-3) for (*E*)-**26**; 3.09 (d, $J = 5.4$ Hz, 2H, H-2) for (*Z*)-**26**; IR (neat) 1740 (C=O), 1250 (C–O), 970 (CH=CH) cm^{-1}. Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.62; H, 10.90%.

3.10. General procedure for oxacarbonylation of allyl phosphate

In a 10 ml stainless-steel autoclave were placed allyl phosphate (1.0 mmol), NEt_3 (0.202 g, 2.0 mmol), Bu_4NCl (0.028 g, 0.10 mmol), alcohol or water (2.0 mmol), DMSO (2 ml), and $Rh_6(CO)_{16}$ (0.011 g, 0.01 mmol). CO was introduced up to 20 atm, and the mixture was stirred at 50°C for 10 h. The product was extracted with ether, and the combined extracts were washed with 2 M HCl and brine and dried (Na_2SO_4). Evaporation followed by column chromatography or thin layer chromatography on silica gel. Stereoisomeric ratio ($E:Z$) of the products was determined on the basis of ^1H and ^{13}C NMR and/or capillary GLC analyses. Oxacarbonylation using water as above afforded β,γ-unsaturated carboxylic acids. Stereoisomeric ratio ($E:Z$) of carboxylic acids was determined on the basis of ^1H and ^{13}C NMR analyses and/or capillary GLC analyses of its methyl esters obtained by treating with diazomethane. These results are summarized in Table 4.

3.10.1. Benzyl 3-nonenoate (27)

^1H NMR (270 MHz) δ 0.88 (t, $J = 6.8$ Hz, 3H, H-9), 1.22–1.38 (m, 6H), 2.02 (dt, $J = 5.3$, 7.7 Hz, 2H, H-5), 3.06 (d, $J = 5.3$ Hz, 2H, H-2), 5.11 (s, 2H, OCH_2Ph), 5.53 (dtt, $J = 18.5$, 1.1, 5.3 Hz, 1H, H-4), 5.58 (dtt, $J = 18.5$, 1.1, 5.3 Hz, 1H H-3), 7.22–7.36 (m, 5H, Ph), for (*E*)-**27**; 3.13 (d, $J = 5.3$ Hz, 1H, H-2), 5.16 (s, 2H, OCH_2Ph) for (*Z*)-**27**; IR (neat) 1735 (C=O), 1240 (C–O), 965 (CH=CH) cm^{-1}.

3.10.2. Methyl 4,8-dimethyl-3,7-nonadienoate (29)

^1H NMR (60 MHz) δ 1.53–1.97 (m, 9H, CH_3), 1.97–2.17 (m, 4H), 3.05 (d, $J = 7.0$ Hz, 2H, H-2), 3.67 (s, 3H, OCH_3), 4.80–5.20 (m, 1H, H-7), 5.30 (t, $J = 7.0$ Hz, 1H, H-3); IR (neat) 1750 (C=O) cm^{-1}.

3.10.3. 3-Nonenoic acid (30)

^1H NMR (60 MHz) δ 0.70–1.83 (m, 9H), 1.83–2.50 (m, 2H, H-5), 3.08 (d, $J = 4.0$ Hz, 2H, H-2), 5.43–5.93 (m, 2H, H-3, H-4), 11.58 (s, 1H, OH); $^{13}C\{^1H\}$ NMR (25 MHz) δ 14.0 (C-9), 22.5 (C-8), 28.8 (C-7), 31.4 (C-6), 32.5 (C-5), 37.9 (C-2), 120.7 (C-3), 135.5 (C-4), 178.7 (C=O) for (*E*)-**30**; 27.4 (C-5), 32.7 (C-2), 119.9 (C-3), 134.1 (C-4), 178.6 (C=O) for (*Z*)-**30**; IR (neat) 3200 (O–H), 1710 (C=O), 970 (CH=CH) cm^{-1}.

3.10.4. 3-Heptenoic acid (31)

^{1}H NMR (60 MHz) δ 0.88 (t, J = 5.0 Hz, 3H, H-7), 1.07–1.77 (m, 2H, H-6), 1.80–2.27 (m, 2H, H-5), 3.05 (d, J = 5.0 Hz, 2H, H-2), 5.45–5.67 (m, 2H, H-3, H-4), 10.53 (br, 1H, OH); ^{13}C{^{1}H} NMR (25 MHz) δ 13.6 (C-7), 22.3 (C-6), 34.6 (C-5), 37.9 (C-2), 120.9 (C-3), 135.3 (C-4), 178.9 (C=O) for (*E*)-**31**; 32.8 (C-5), 120.2 (C-3), 133.8 (C-4), 178.7 (C=O) for (*Z*)-**31**; IR (neat) 3200 (O–H), 1710 (C=O) cm^{-1}.

3.10.5. (E)-4-Phenyl-3-butenoic acid (32)

^{1}H NMR (60 MHz) δ 3.27 (d, J = 6.0 Hz, 2H, H-2), 6.10 (dt, J = 15.0, 6.0 Hz, 1H, H-3), 6.51 (d, J = 15.0 Hz, 1H, H-4), 7.00–7.67 (m, 5H, Ph), 11.42 (s, 1H, OH); IR (KBr) 3400 (O–H), 1705 (C=O), 1225 (C–O), 975 (CH=CH) cm^{-1}.

3.10.6. 4,8-Dimethyl-3,7-nonadienoic acid (33)

^{1}H NMR (60 MHz) δ 1.47–1.77 (m, 9H, CH_3), 1.87–2.23 (m, 4H), 3.08 (d, J = 7.0 Hz, 2H, H-2), 4.86–5.20 (m, 1H, H-7), 5.30 (t, J = 7.0 Hz, 1H, H-3), 10.83 (bs, 1H, OH); ^{13}C{^{1}H} NMR (25 MHz) δ 16.4, 17.7, 25.7, 26.5, 33.6, 39.6 (C-2), 115.0 (C-7), 123.9 (C-3), 131.6, 139.7, 179.1 (C=O) for (*E*)-**33**; 40.0 (C-2), 115.7 (C-7), 123.7 (C-3) for (*Z*)-**33**; IR (neat) 3200 (OH), 1710 (C=O) cm^{-1}.

3.11. Hydrolysis of (E)-4-phenyl-3-butenamide (17)

To the suspension of amide **17** (0.089 g, 0.55 mmol) in water (3 ml) on the steam bath was added Na_2O_2 (0.043 g, 0.55 mmol) as portions. The mixture was heated at 85–100°C for 2 h. After cooling to 0°C, 12 M HCl was added, and the product extracted with dichloromethane. The combined extracts were dried (Na_2SO_4) and evaporated to give (*E*)-4-phenyl-3-butenoic acid (**32**) (0.086 g, 97%).

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