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RHODIUM-CATALYZED AZACARBONYLATION OF ALLYL PHOSPHATES. THE PREPARATION OF β,γ-UNSATURATED AMIDES FROM ALLYL ALCOHOLS

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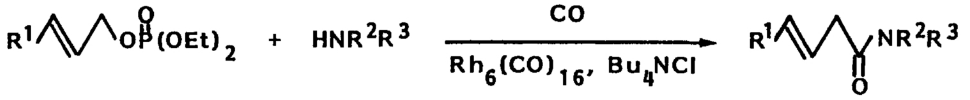
Allyl phosphates undergo a smooth azacarbonylation reaction with amines to afford β,γ-unsaturated amides at 50 °C under CO atmosphere (20 atm) in the presence of $Rh_6(CO)_{16}$ catalyst and Bu_4NCl co-catalyst.

We have found that allyl phosphates are highly active substrates, which undergo palladium(0) catalyzed alkylation and amination quite efficiently.1) In our continuing effort to study the scope of the reaction of allylic phosphates, we have studied the azacarbonylation of allylic phosphates. Although the palladium(0) catalyzed carbonylation of allylic esters to give β,γ-unsaturated esters has been explored by Tsuji recently, only one example of the azacarbonylation of allylic esters has been reported on the palladium catalyzed reaction of ethyl 1-hepten-3-yl carbonate.2)

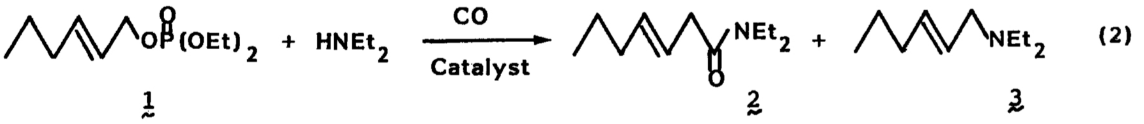
We wish to report that azacarbonylation of allylic phosphates catalyzed by rhodium cluster, $Rh_6(CO)_{16}$, in the presence of Bu_4NCl as co-catalyst gives β,γ-unsaturated amides efficiently as depicted in Eq 1.



(1)

As a typical example, the catalytic reaction of (E)-2-hexenyl diethyl phosphate (1) with diethylamine was examined. The representative results are shown in Table 1. When phosphate 1 was treated with 2 equiv. of diethylamine in the presence of 1 mol% of $Rh_6(CO)_{16}$ and 10 mol% of Bu_4NCl in benzene under CO atmosphere (20 atm) at 50 °C, (E)-N,N-diethyl-3-heptenamide (2) (83%) and

N,N-diethyl-2-hexenylamine (3) (9%) were obtained (Entry 1). The addition of Bu_4NCl as a co-catalyst enhanced the reaction dramatically and also induced high selectivity of the formation of β,γ-unsaturated amide (Entries 1 and 2). The co-catalyst provides solid-liquid phase transfer conditions to accelerate the reaction$^{3)}$ and to increase the chemoselectivity. Higher CO pressure induced higher selectivity of the amide formation (Entries 1 and 3). In the absence of CO, the amination product, allylamine 3 was obtained exclusively (83%) (Entry 4).



The azacarbonylation of allyl phosphates proceeds smoothly only with $Rh_6(CO)_{16}$ catalyst under mild conditions. Using other catalysts such as $RhH(CO)(PPh_3)_3$, $Ru_3(CO)_{12}$, $Mo(CO)_6$, and $Pd(PPh_3)_4$ the reaction gave β,γ-unsaturated amides in poor yields (Entries 5-8) and gave allylamines mainly (Entries 6-8). Benzene is the best solvent among those examined such as MeOH, acetonitrile, and THF. The presence of a small amount of water retarded the reaction strongly. Allyl acetates do not undergo the azacarbonylation. Control experiment showed that the amide 2 is not derived from the amine 3 under the reaction condition.

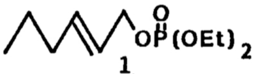
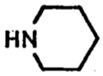
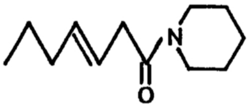
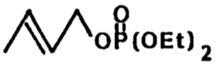
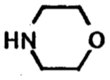
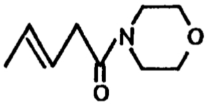
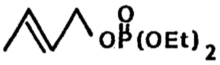
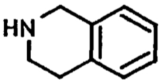
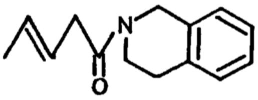
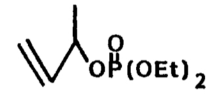
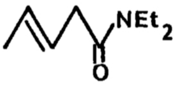
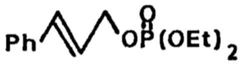
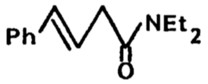
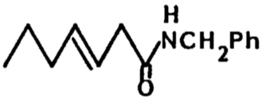
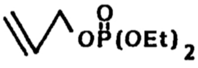
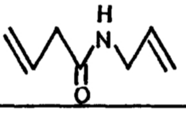
Table 1. Azacarbonylation of 2-Hexenyl Diethyl Phosphate (1)$^{a)}$

Entry	Catalyst	mol%	CO Pressure atm	Additive	Yield$^{b)}$/% Amide 2	Amine 3
1	$Rh_6(CO)_{16}$	1	20	Bu_4NCl	83	9
2	$Rh_6(CO)_{16}$	1	20	none	32	9
3	$Rh_6(CO)_{16}$	1	1	Bu_4NCl	68	21
4	$Rh_6(CO)_{16}$	1	$0^{c)}$	Bu_4NCl	0	83
5	$RhH(CO)(PPh_3)_3{}^{d)}$	5	20	Bu_4NCl	37	15
6	$Ru_3(CO)_{12}{}^{d)}$	2	20	Bu_4NCl	20	43
7	$Mo(CO)_6{}^{d)}$	5	20	Bu_4NCl	12	22
8	$Pd(PPh_3)_4{}^{d)}$	5	20	Bu_4NCl	8	80

a) The reaction was performed according to the procedure described in the text unless otherwise noted. b) Determined by GLC. c) The reaction was carried out under argon atmosphere. d) The reaction time was 12 h.

A typical procedure for the azacarbonylation is as follows: In a 10 mL autoclave were placed phosphate 1 (0.236 g, 1.0 mmol), diethylamine (0.146 g, 2.0 mmol), $Rh_6(CO)_{16}$ (0.011 g, 0.01 mmol), Bu_4NCl (0.028 g, 0.1 mmol), and benzene (2 mL). The autoclave was flushed with carbon monoxide three times and then pressurized to 20 atm with carbon monoxide. The reaction mixture was stirred at 50 °C for 3 h. After cooling to room temperature, the reaction mixture was diluted with ether and washed with 1 M HCl solution and then with brine. The organic layer was dried over $MgSO_4$. Evaporation followed by column chromatography on Florisil gave amide 2 (0.147 g, 81%). The removal of the side products of the allylamines is easily performed by the extraction with a HCl solution.

Table 2. Rhodium Catalyzed Azacarbonylation of Allylic Phosphates[a)]

Entry	Substrate	Amine	Product[b)]	Yield[c)]/%
1	 1	$HNEt_2$		81
2	1			82
3				74
4				84
5		$HNEt_2$		86
6		$HNEt_2$		77
7	1	H_2NCH_2Ph		80
8				62

a) The reaction was carried out according to the typical procedure described in the text. b) The products gave satisfactory IR, NMR, and mass spectral data. c) Isolated yields by column chromatography.

The representative results of the azacarbonylation are summarized in Table 2. α-Methylallyl phosphate was converted into the corresponding (E)-3-pentenamide selectively (Entry 5). It is important that generally (E)-β,γ-unsaturated amides are obtained selectively. Although a few papers reported the synthetic methods of β,γ-unsaturated amides, they are limited to the preparation of N,N-disubstituted amides.4,5) Using the present reaction, N-monosubstituted β,γ-unsaturated amides can be prepared easily (Entries 7 and 8).

The reaction can be rationalized by assuming the mechanism which involves π-allylrhodium complexes.6,7) Either $Rh_6(CO)_{16}$ or labile $[Rh_6Cl(CO)_{15}]^-$, which is derived from the reaction of $Rh_6(CO)_{16}$ with Bu_4NCl,8) undergoes oxidative addition to give a π-allylrhodium complex, which undergoes carbonylation. The acylrhodium complexes thus obtained react with amines to give the corresponding amides. Although the catalytic activity of Pd(0) complex towards allyl acetates is high in comparison with that of Rh(I) complexes,9) the palladium catalyzed azacarbonylation does not proceed efficiently. This is due to the reductive elimination of the π-allylpalladium complexes induced by carbon monoxide10) and also the high reactivity of π-allylpalladium intermediates toward amine nucleophiles.

References

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