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Carbon–oxygen bond cleavage in allylic esters promoted by low-valent transition-metal hydride complexes

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$CoH(N_2)(PPh_3)_3$ promotes carbon–oxygen (C–O) bond cleavage in allylic carboxylates to give the corresponding olefins at room temperature. On the other hand, $RuH_2(PPh_3)_4$ and $RhH(PPh_3)_4$ are mainly active for C–O bond cleavage at elevated temperature. Reaction proceeds through a mechanism involving predissociation of one of the tertiary phosphines from the $RuH_2(PPh_3)_4$ and $RhH(PPh_3)_4$ and competitive coordination of allylic carboxylates and PPh_3 to the vacant site on ruthenium and rhodium. A new six-membered metallocyclic complex, $Co(OCOCH_2COCH_3)(PPh_3)_2$, has been isolated.

Keywords: Carbon–oxygen bond, cleavage, cobalt, rhodium, ruthenium, phosphine

INTRODUCTION

Cleavage of carbon–halogen bonds in aryl halides and carbon–oxygen bonds in allylic esters and carboxylates promoted by transition-metal complexes has been extensively utilized in organic synthesis.[1-7] Although the decarboxylation reaction has been observed in the formation of Vaska's complex from alcohols and $IrCl_3$,[8,9] and cleavage of the allyl-oxygen bond in allyl carboxylates[10-13] and allyl ethers[14] was noted about a decade ago. In spite of increasing interest concerning transition-metal promoted C–O bond cleavage of esters, a detailed study of the reaction process was made relatively late.[15-20] Selective cleavage of the C–O bond in aryl carboxylates promoted by nickel(0) complexes,[19-21] in alkenyl carboxylates by nickel,[19,20] palladium[22] and ruthenium[21] complexes, and in allyl ethers by nickel complexes, has been reported by Yamamoto's group. We have previously reported the selective cleavage of C–O and Si–O bonds in trimethylsilyl ethers promoted by transition-metal hydride complexes.[23]

As an extension of this study we now report the interactions of hydrido-cobalt, -rhodium and -ruthenium complexes with esters.

RESULTS AND DISCUSSION

Table 1 summarizes the reaction products of $CoH(N_2)(PPh_3)_3$ (**1**), $RhH(PPh_3)_4$ (**2**) and $RuH_2(PPh_3)_4$ (**3**) with esters. The esters (**A–E**) used for examining the reactivities of the transition metal hydrides are shown in Fig. 1.

The metal hydrides under discussion undergo ligand dissociation in solution and readily afford coordinatively unsaturated species.[24]

Reaction of allylic esters with $CoH(N_2)(PPh_3)_3$ (1)

Reaction of allylic ester **A** proceeded smoothly at room temperature with evolution of nitrogen and propene. A new six-membered metallocyclic compound was isolated by the reaction of **1** with **A** (Fig. 2). The compound was fully characterized by spectroscopic methods (see the Experimental section).

Similar C–O bond cleavage was also observed in the reaction of **1** with allylic esters **B–D**, affording nitrogen, propene, and cobalt complexes corresponding to the esters used. However, the reaction between **1** and **E** yielded butene-2 as main product. The resulting cobalt complexes were characterized on the basis of their elemental analysis, IR and ^1H NMR spectra. The spectra of all the complexes obtained in the reactions

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Table 1 Reaction of esters with $CoH(N_2)(PPh_3)_3$, $RhH(PPh_3)_4$ and $RuH_2(PPh_3)_4$

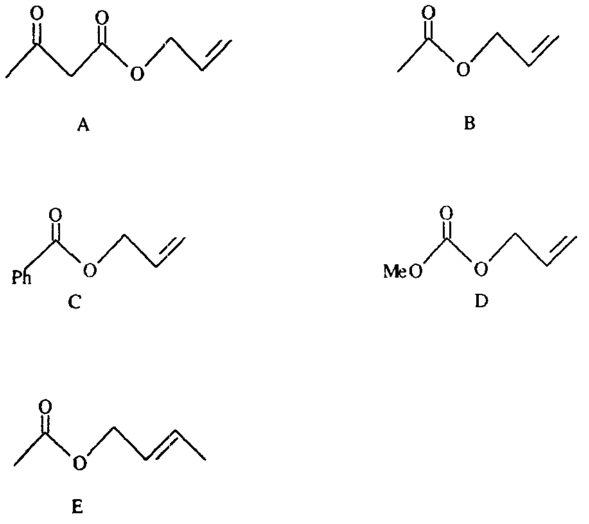
Run	Ester (mmol)	Temp. (°C)	Time (h)	Reaction products (mmol)
$CoH(N_2)(PPh_3)_3$ (**1**)				
1	**A** (1.18)	rt[a]	72	C_3H_6 (0.101), $Co(OCOCH_2COCH_3)(PPh_3)_2$ (0.22), N_2 (0.18)
2	**B** (1.16)	rt	72	C_3H_6 (0.108), $Co(OCOCH_3)$ $(PPh_3)_3$ (0.25), N_2 (0.20)
3	**C** (1.20)	rt	72	C_3H_6 (0.106), $Co(OCOPh)$ $(PPh_3)_3$ (0.20), N_2 (0.22)
4	**D** (1.10)	rt	72	C_3H_6 (0.98), N_2 (0.18)
5	**E** (1.20)	rt	72	C_4H_8 (0.017), C_4H_{10} (0.107), N_2 (0.21)
$RhH(PPh_3)_4$ (**2**)				
6	**A** (1.27)	100	80	CH_4 (0.001), C_2H_4 (0.023), C_3H_6 (0.136)
7	**B** (1.20)	100	80	CH_4 (trace), C_3H_6 (0.141)
8	**C** (1.22)	100	80	CH_4 (trace), C_3H_6 (0.138)
9	**D** (1.24)	100	80	C_3H_6 (0.140)
10	**E** (1.22)	100	80	2-C_4H_8 (0.139)
$RuH_2(PPh_3)_4$ (**3**)				
11	**A** (1.14)	80	72	CH_4 (trace), C_3H_6 (0.120), $RuH_2(CO)$ $(PPh_3)_3$ (0.26)
12	**B** (1.24)	80	72	CH_4 (trace), C_3H_6 (0.146), $RuH_2(CO)(PPh_3)_3$[b]
13	**C** (1.28)	80	72	CH_4 (trace), C_3H_6 (0.138), $RuH_2(CO)(PPh_3)_3$[b]
14	**D** (1.26)	80	72	C_3H_6 (0.128), $RuH_2(CO)$ $(PPh_3)_3$[b]
15	**E** (1.20)	80	72	2-C_4H_8 (0.148), $RuH_2(CO)(PPh_3)_3$[b]

The solvent was benzene.

[a] Abbreviation: rt, room temperature. [b] Not measured.

showed ν(C–O) and ν(C=O) bands at 1260 and 1800 cm^{-1} respectively.

It was observed that removal of nitrogen from the reaction system accelerated the reaction, indicating that the prior liberation of nitrogen from **1** seems to be an essential factor for the cleavage reactions to proceed.[19,20] In the presence of excess PPh_3, the reaction was strongly hindered and formation of propene was severely suppressed.



A B C D E

Figure 1

Reaction of allylic esters with $RhH(PPh_3)_4$ (2)

Contrary to the high reactivity of complex **1**, which cleaves the C–O bond in allylic esters at room temperature, complex **2** does not react at all with any allylic esters at room temperature. However, reaction proceeds at 100 °C to liberate propene. A small amount of ethylene was also observed. The resulting complexes appear to be $RhH(CO)(PPh_3)_3$ and other rhodium carbonyl complexes,[25] supported on the basis of the IR spectra to the recovered solids (see the Experimental section). Addition of free tertiary phosphine to the reaction system strongly suppressed the formation of the C_3 entity.

Reaction of allylic esters with $RuH_2(PPh_3)_4$ (3)

The reaction of **3** with allylic esters (**A–D**) proceeds smoothly at 80 °C liberating propene as a major gaseous product along with trace amounts of methane. The reaction of **3** with **E** produces butene-2 as a major product. The resulting solid complexes appear to be a mixture of $RuH_2(CO)(PPh_3)_3$, and probably complexes of the type $RuH(OCOCH_2COCH_3)(PPh_3)_3$. The nature of the recovered complexes was revealed by their IR spectra (see the Experimental section).

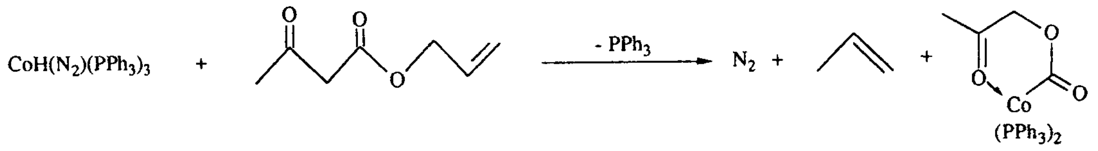


Figure 2

It can be seen then that in the reactions of allylic esters with Group 8 and 9 transition-metal hydrides, the C–O bond in allylic esters is cleaved, as indicated by the formation of C_3 olefins.

Interestingly, the cobalt hydride complex(**1**) primarily cleaves the C–O bond at room temperature, whereas the rhodium hydride (**2**) and ruthenium hydride (**3**) cleaves the C–O bond in allylic esters at 100 and 80 °C respectively, a considerably higher temperature than that required for similar C–O bond cleavage in aryl carboxylates by nickel(0) compounds.

The two reaction mechanisms (Mechanisms I and II) are consistent with the products and stoichiometry of the reactions. In both Mechanisms I and II we presume predissociation of one of the PPh_3 ligands from $RhH(PPh_3)_4$ (reaction 1a) and coordination of $CH_3COCH_2COOCH_2CH{=}CH_2$ to the vacant site of the coordinatively unsaturated rhodium complex (reaction 1b). This assumption is in agreement with the literature.[21] The dissociation of one PPh_3 ligand from **2** in the solution is also supported by ^{31}P NMR spectrum of $RhH(PPh_3)_4$ in diphenylmethane at 25 °C,[26] which shows a broad (half-width *ca* 500 Hz) signal 35 ppm downfield from external PPh_3, indicating that the PPh_3 ligand in $RhH(PPh_3)_3$ formed by the dissociation is exchanged rapidly with PPh_3 in solution. The position of the broad signal shifts upfield on addition of PPh_3 according to the equilibrium expressed in reaction 1a.

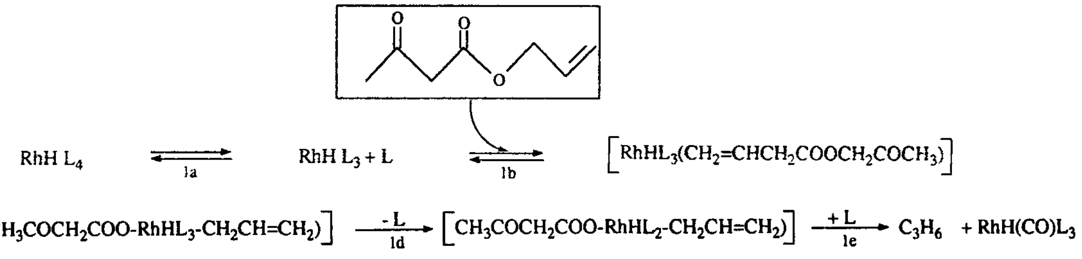
Mechanism I resembles that proposed for the C–O bond cleavage of aryl carboxylates promoted by nickel(0) compounds[19,20] and of aryl acetates with rhodium and ruthenium hydride complexes. Mechanism I involves the oxidative additation of the esters to rhodium (reaction 1c) followed by reductive elimination of C_3H_6 (reaction 1e). Observation of a similar trend for C–O bond cleavage by nickel(0) complexes having no metal–hydrogen bonds and the present rhodium(I) hydride complex, may be taken as an indication that the present C–O bond cleavage proceeds by a similar mechanism to that observed in nickel(0)-promoted reactions. Use of a solvent having a high coordinating ability [e.g. quinoline and (methylsulphinyl)methane] retards the reactions between esters and the rhodium hydride complex, and is in accordance with the assumption that the reaction proceeds through coordination of ester at the vacant site of $RhH(PPh_3)_3$.

On the other hand, an S_N2' type of mechanism (Mechanism II) involving a double-bond shift have also been proposed, similar to the sigmatropic rearrangement of allylic compounds.

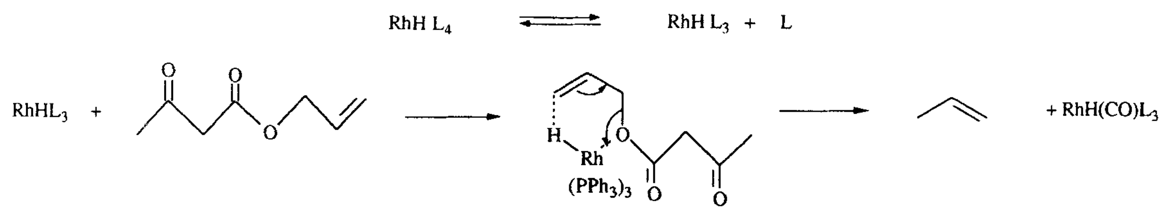
The actual reaction of **2** with allylic esters may proceed through the interaction of the allylic double bond with the Rh–H bond followed by β-elimination of the C_3 entity of olefins.

EXPERIMENTAL

All manipulations were carried out under nitrogen, argon or vacuum. Solvents were dried and distilled. IR spectra were measured on a Hitachi-295 spectrometer. ^1H NMR spectra were recorded on a JEOL-XL-100 spectrometer. The analyses of gaseous and liquid products were carried out by using Shimadzu GC-3BT and



Mechanism 1



Mechanism 2

GC-6A gas chromatographs. GCMS spectra were recorded on a Hitachi M-80 spectrometer. Microanalyses were performed with a Yanagimoto CHN autorecorder type MT-2.

Complexes $CoH(N_2)(PPh_3)_3$,[27] $RhH(PPh_3)_4$[26,27] and $RuH_2(PPh_3)_4$[28] were prepared by the methods reported in the literature. Esters **A**–**E** were prepared by the usual methods using sodium hydride.

Reactions of various allylic esters with cobalt, rhodium and ruthenium hydride complexes

Typical experimental procedures are described below. Details of reaction conditions and results are summarized in Table 1.

Reaction of 1 with allylic esters

To a Schlenk-type flask containing **1** (0.46 mmol) and benzene (2.0 cm^3) was added allylic ester **A** (1.18 mmol) by trap-to-trap distillation. After the mixture was stirred for 72 h at room temperature, nitrogen (0.18 mmol) and propene (0.101 mmol) were generated. After volatile substances had been removed, a pink solid, $Co(OCOCH_2COCH_3)(PPh_3)_2$ was recrystallized with a toluene–hexane mixture. IR (KBr): ν(C–O) 1260, ν(C=O) 1686 cm^{-1}, diamagnetic. ^1H NMR (CD_2Cl_2): $\delta = 1.8$, (3H, s, CH_3); $\delta = 4.2$ (2H, s, CH_2); $\delta = ca\,7.75$ (30H, m, PPh_3). Analysis: Found (calcd. for $C_{40}H_{35}O_3P_2Co$): C, 69.55 (70.17), H, 5.30 (5.15); Co, 9.2% (8.60%).

Reaction of **1** with **B** was performed analogously. The resulting compound was characterized by IR, magnetic moment and elemental analysis as $Co(OCOCH_3)(PPh_3)_3$. IR (KBr): ν(C=O) 1700 cm^{-1}, diamagnetic. Analysis: Found (calcd for $C_{56}H_{48}O_2P_3Co$): C, 74.88 (74.33); H, 5.72 (5.34); Co 6.32% (6.51%).

Reaction of **1** with **C** was also carried out analogously. The isolated compound was characterized by IR, magnetic susceptibility and elemental analysis as $Co(OCOPh)(PPh_3)_3$. IR (KBr) ν(C—O) 1272, ν(C=O) 1690 cm^{-1}, diamagnetic. Analysis: Found (calcd for $C_{61}H_{50}O_2P_3Co$); C, 75.68 (75.77); H, 5.40 (5.21); Co, 6.02% (6.09%).

Reaction of 2 with allylic ester A

A mixture of **2** (0.49 mmol) and **A** (1.27 mmol) in benzene (2.0 cm^3) was degassed. After the mixture was stirred for 80 h at 100 °C, propene (0.102 mmol), ethene (0.228 mmol) and methane (trace) were detected. Evaporation of volatile substances *in vacuo* afforded a yellow solid. The IR spectrum of this solid showed ν(C=O) and $C\equiv O$ 1800 (m), 1970 (s) and 2000 (sh) cm^{-1}, possibly due to a mixture of $RhH(CO)(PPh_3)_3$ and other carbonyl complexes of rhodium.

Reaction of 3 with allylic ester A

Allylic ester **A** (1.14 mmol) was added to a Schlenk tube containing **3** (0.44 mmol) in benzene (2.0 cm^3). The reaction mixture was stirred at 80 °C under vacuum. After 70 h, propene (0.12 mmol) and methane (trace) were detected by GC. A dirty white solid was obtained after removal of volatile substances by trap-to-trap distillation, washed with ether three times and dried under vacuum to yield 0.24 g. (59%) of a whitish solid, which was characterized as $RuH_2(CO)(PPH_3)_3$ by comparing its IR $\nu(C\equiv O)$, 1940 cm^{-1} and ^1H NMR (CD_2Cl_2) $\delta = -7.2$ (1H, dtd, $J = 72$, 24, 7 Hz, Ru–H_a), $\delta = -5.4$ (1H, tdd, $J = 25$, 18, 9 Hz, Ru–H_b), $\delta = ca\,7$ (45H, m, PPh_3) data with literature data.[29–31] This crude product, obtained initially from the reaction mixture, seems to contain some ruthenium carbonyl complex. However, isolation of the complex was not feasible since the proportion of the complex contained in the crude product was too small, as suggested by weak ν(Ru–H) and ν(C=O) bands in the IR spectrum of the crude product.

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