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DEHYDROGENATION OF ALCOHOLS WITH ALLYL CARBONATES CATALYZED BY PALLADIUM OR RUTHENIUM COMPLEXES

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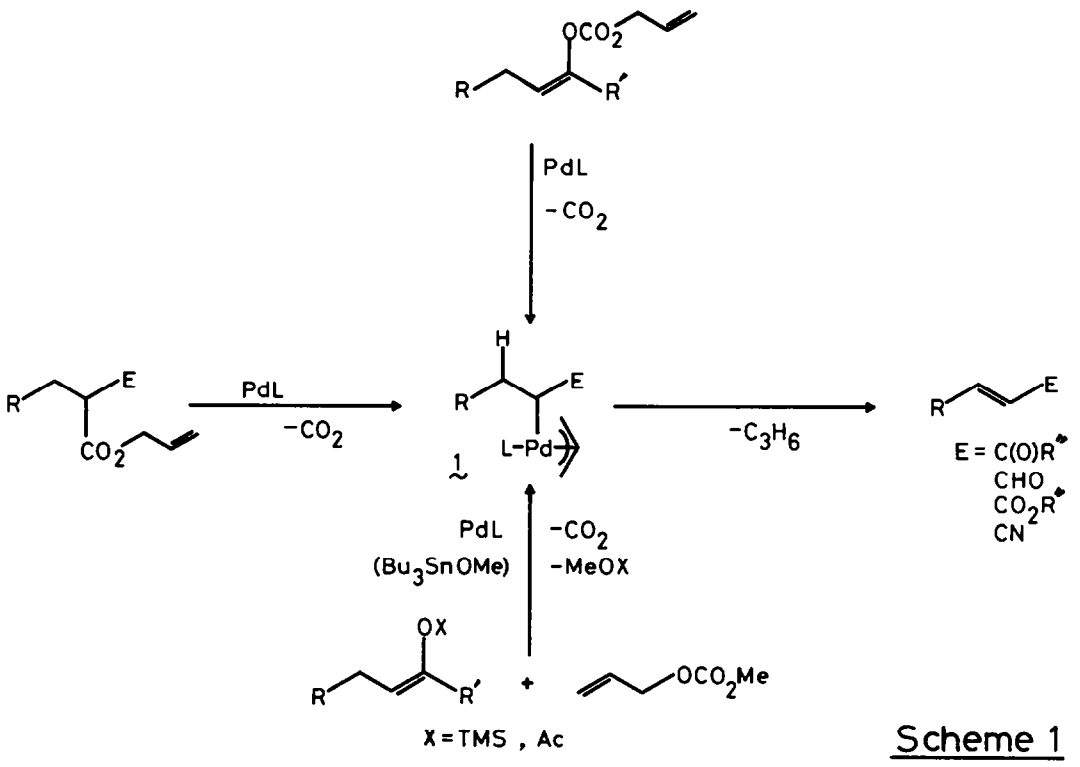
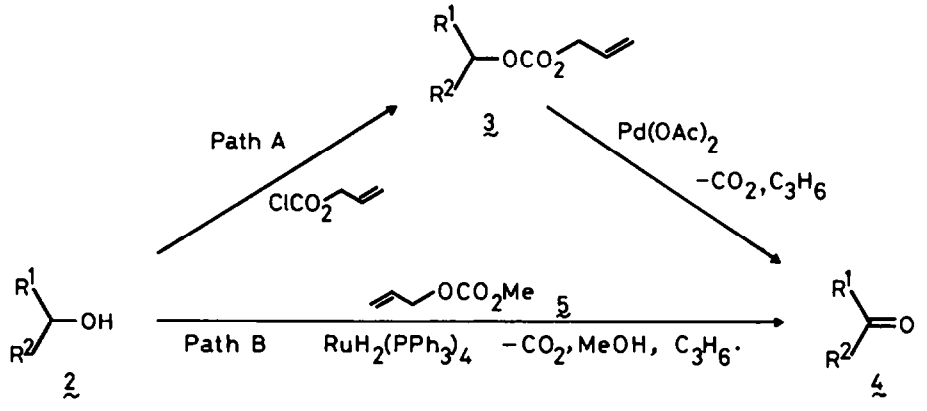
Abstract - Treatment of alkyl allyl carbonates with a phosphine-free palladium catalyst in acetonitrile affords ketones or aldehydes in high yields. This new method of oxidation of alcohols via allyl carbonates can be applied to various alcohols except simple primary alcohols. The reaction proceeds under neutral conditions and hence various acid- or base-sensitive functional groups are not affected during the reaction. Ruthenium hydride complex is also an effective catalyst. Direct dehydrogenation of secondary or allylic alcohols was carried out by the reaction with allyl methyl carbonate by the catalysis of the ruthenium complex. 1,4-Diols and 1,5-diols are converted to lactones with excess allyl methyl carbonate.

INTRODUCTION

Oxidation of alcohols is one of the most important reactions in organic synthesis. Generally, inorganic compounds such as chromium or manganese compounds[1] are used as oxidants, but separation of inorganic salts, after the reaction, is sometimes poses a problem. We have previously reported the palladium-catalyzed decarboxylation-dehydrogenation of allyl β-keto carboxylates, allyl vinylic carbonates, enol silyl ethers, enol acetates, or allyl α-cyanocarboxylates to give α,β-unsaturated ketones, aldehydes, esters, lactones, or nitriles.[2] As expressed by (SCHEME 1), these unique dehydrogenation reactions proceed via the (π-allyl)palladium intermediate **1**, which is converted into propene and Pd(0) species after the reaction. In other words, the (π-allyl)palladium complex **1** acts as a dehydrogenating agent or a proton acceptor. In our continuing work on the dehydrogenation of various organic compounds with (π-allyl)palladium complex, we have found that allyl alkyl carbonates **3**, derived from alcohols **2** and allyl chloroformate, can be converted into ketones **4** with phosphine-free palladium catalyst (Path A in Scheme 2).[3] This reaction is clean and facile since only CO_2 and propene are generated as by-products. But turnover of the palladium catalyst was not very high (usually 5-10 times). Later, we have found that a ruthenium catalyst is more effective than the palladium catalyst for the same reaction. Turnover of the catalyst increased to higher than 100 times. Furthermore, we have found that direct oxidation of secondary or allylic alcohols **2** with allyl methyl carbonate (**5**) proceeds with the ruthenium catalyst (Path B in Scheme 2).[4] The oxidation proceeds under neutral conditions, and hence tolerates many kinds of functional groups. A part of studies has already been reported as communications,[3,4] and details of the reaction are presented in this paper. We have discovered several synthetic methods based on palladium-catalyzed reaction of allyl alkyl carbonates,[5] and shown the usefulness of allyl alkyl carbonates. The reaction reported in this paper presents another useful palladium- and ruthenium-catalyzed reaction of allyl alkyl carbonates.



Scheme 1



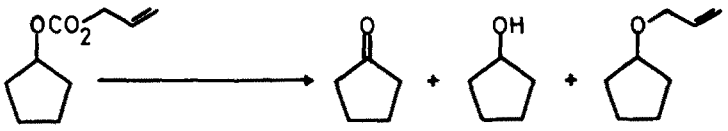
Scheme 2

RESULTS AND DISCUSSION

Dehydrogenation of allyl alkyl carbonates

Reaction of allyl cyclopentyl carbonate (6) as a model compound was examined with various palladium catalysts. As shown in (TABLE 1), the phosphine-free palladium catalyst gave satisfactory results. In the presence of PPh_3, the allylation or protonation takes place rather than the dehydrogenation. Nitriles are the most effective solvents. In THF, with palladium-phosphine catalyst, allyl cyclopentyl ether (9) was the major product (runs 4 and 5). Palladium-catalyzed alkyl allyl ether formation from allyl alkyl carbonates has been reported.[6] When the phosphine-free palladium catalyst was used in THF, palladium-black deposited and almost no reaction took place. Thus the coordinative solvents such as MeCN act as a weak ligand to stabilize the Pd(0) species during the reaction. The reaction proceeds at a refluxing temperature of MeCN.

Table 1. Dehydrogenation of 6 with Palladium Catalyst[a)]



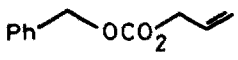
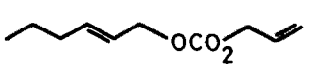
6 7 8 9

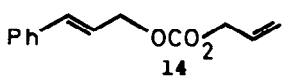
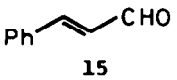
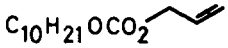
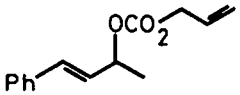
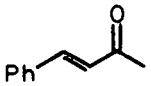
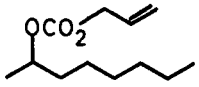
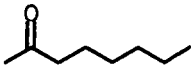
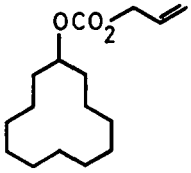
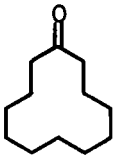
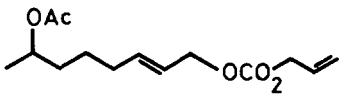
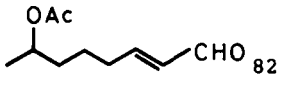
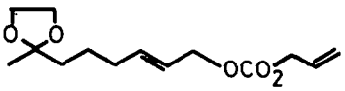
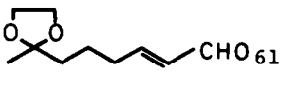
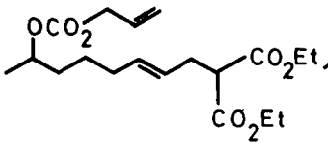
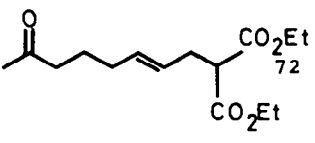
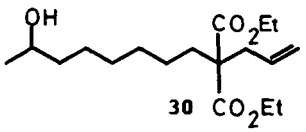
Run	Catalyst	Solvent	Yield[b)] of 7 : 8 : 9
1	$Pd_2(dba)_3 \cdot CHCl_3$	MeCN	86 : 14 : 0
2	$Pd(OAc)_2$	MeCN	76 : 23 : 0
3	$Pd(OAc)_2$-PPh_3	MeCN	7 : 89 : 4
4	$Pd_2(dba)_3 \cdot CHCl_3$-PPh_3	THF	0 : 7 : 92
5	$Pd(OAc)_2$-PPh_3	THF	0 : 6 : 88
6	$RuH_2(PPh_3)_4$	PhH	93 : 7 : 0
7	$RhH(PPh_3)_4$	PhH	88 : 6 : 0

a) Reactions were carried out using 6 (0.5 mmol), Pd catalyst (0.05 mmol) in a solvent (2 mL) at 80°C (bath) under argon. b) Calculated by GLC analysis.

The reaction can be applied to allyl carbonates of various alcohols except saturated primary alcohols. From allyl carbonate of a saturated primary alcohol, corresponding aldehyde was obtained in a low yield (run 4). When unsymmetrical biallylic carbonates were subjected to the oxidation, (runs 2,3, and 5), the less hindered simple allyl group was cleaved and accepted proton to form α,β-unsaturated ketones or aldehydes from a larger allyl group. Base- or acid-sensitive functional groups are not affected during the reaction (runs 8 and 9). Complete chemoselectivity was observed in the reaction of **28**, which has a malonate moiety in the same molecule. With the phosphine-free palladium catalyst, no allylation took place and the ketone **29** was a sole product (run 10). On the othe hand, the intramolecular allylation of the malonate moiety proceeded predominantly with palladium-phosphine catalyst to afford **30** without the oxidation and allyl ether formation (run 11).

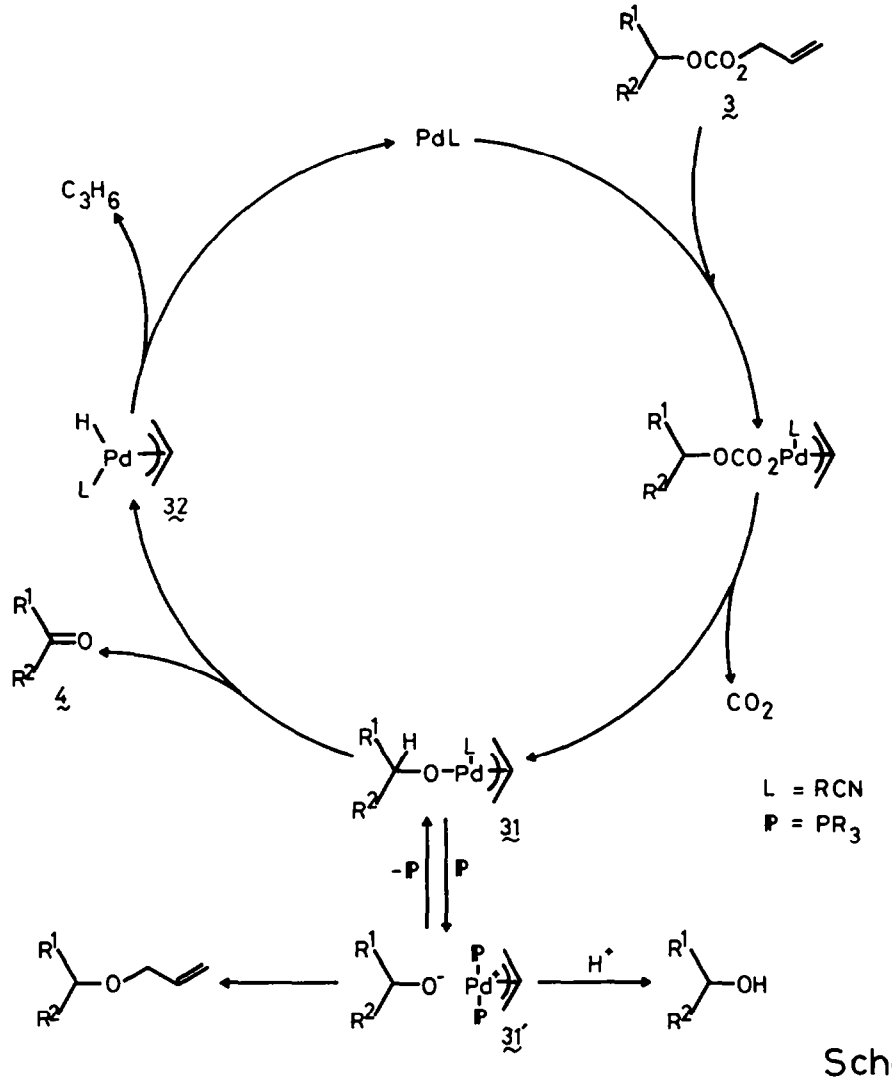
Table 2. Palladium Catalyzed Dehydrogenation of Allyl Alkyl Carbonate[a)]

Run	Allyl Carbonate	Product	Yield(%)[b)]
1	 **10**	PhCHO **11**	76
2	 **12**	 **13**	(95)

3	 **14**	 **15**		69
4	 **16**	$^{n}C_9H_{19}CHO$	**17**	(27)
5	 **18**	 **19**		88
6	 **20**	 **21**		(96)
7	 **22**	 **23**		77
8	 **24**	 **25**		82
9	 **26**	 **27**		61
10	 **28**	 **29**		72
11[c]	**28**	 **30**		89

a) Reactions were carried out using allyl carbonate (1 mmol) and $Pd(OAc)_2$ (0.1 mmol) in MeCN (5 mL) at 80°C for 1-2 h under argon. b) Isolated yield. GLC yield in parenthesis. c) PPh_3 (0.4 mmol) was added.

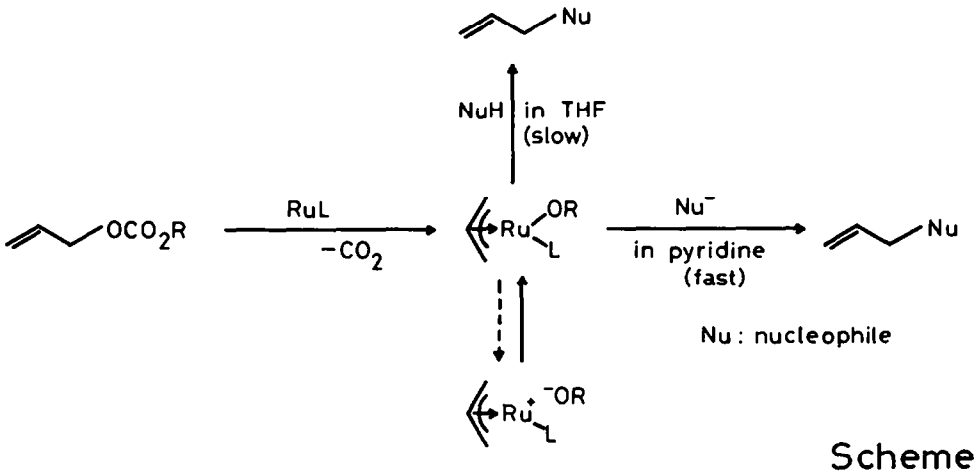
As expressed by (SCHEME 3), the reaction proceeds by the following mechanism. Oxidative addition of allyl carbonate 3 to Pd(0) species, followed by decarboxylation gives (π-allyl)-palladium alkoxide complex 31, which is in equilibrium with cationic one 31'. Subsequently, β-hydrogen elimination from 31 takes place to give the ketone 4 and (π-allyl)palladium hydride complex 32. Finally, reductive elimination of 32 gives propene and regenerates the active Pd(0) species. From a mechanistic consideration, equilibrium of the neutral complex 31 with the cationic complex 31' is important in this reaction. In the presence of the phosphine ligand, formation of the cationic complex 31' is more preferential[7] to the neutral complex 31 and hence the allylation or protonation takes place.



Scheme 3

So far, three examples for the dehydrogenation of alcohols based on -elimination from palladium alkoxide complexes have been reported. In these reactions, generation of palladium alkoxide intermediates remains a problem. The $PdCl_2$-$CuCl_2$ catalyzed dehydrogenation[8] starts by exchange of counter anion of palladium atom. At the same time, HX is generated. In this reaction, Pd(II) species itself is the oxidant and $CuCl_2$ is the reoxidant of Pd(0) to Pd(II). Another type of dehydrogenation starts by the oxidative addition of RX to Pd(0), followed by exchange reaction of the anion to give palladium alkoxide complex and HX.[9,10] In this case, organic halides such as aryl bromide or CCl_4 are the hydrogen-acceptors to afford HX and the reaction proceeds in the presence of bases. Only the carbonate method can be carried out under mild neutral conditions and hence it is clean.

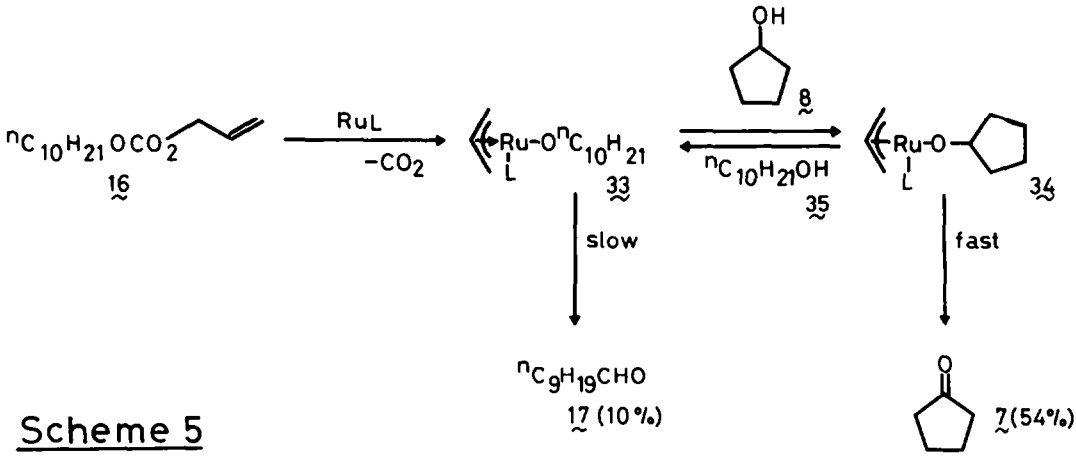
Similar to the palladium-catalyzed preparation of α,β-unsaturated ketones, esters, and nitriles,[2] the turnover of the phosphine-free palladium catalyst is not always satisfactory. For a smooth reaction, usually 10 mol% of the catalyst is required. Otherwise Pd-black slowly deposits during the reaction and the dehydrogenation is not complete. To overcome this problem, various transition metal catalysts were examined to find the most effective catalyst. By a brief survey shown in (TABLE 1), $RuH_2(PPh_3)_4$ was found to be effective. Also $RhH(PPh_3)_4$ gave satisfactory results, but its catalytic activity was slightly inferior to the ruthenium catalyst. We also observed an interesting solvent effect. The palladium-catalyzed dehydrogenation reaction proceeds only in coordinative solvents such as MeCN or PhCN, while the ruthenium-catalyzed reaction proceeds smoothly in non-polar solvents such as benzene or toluene. In these solvents, the neutral (π-allyl)ruthenium complex may be much more preferential to the cationic one. The results indicate that the neutral complex is favorable even in the presence of phosphine ligand. The same tendency was observed in the allylation of β-keto esters with allylic carbonates. For the smooth and mild allylation, ruthenium catalyst requires basic solvents such as pyridine. In neutral solvents, the allylation proceeds by heating.[4]



Scheme 4

Oxidation of alcohols with allyl methyl carbonate catalyzed by the ruthenium complex.

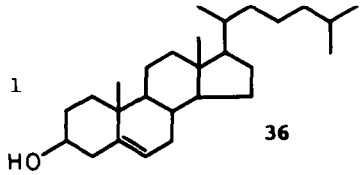
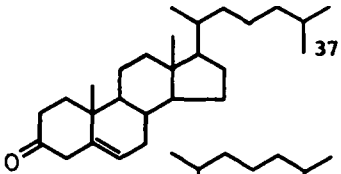
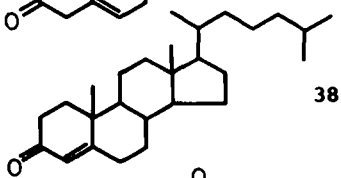
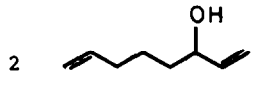
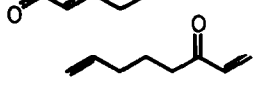
As shown in (TABLE 2), allyl carbonates of saturated primary alcohols are hardly oxidized to saturated aldehydes with palladium catalyst. The ruthenium catalyst showed the same tendency. In other words, elimination of β-hydrogen from primary carbon is very slow. This is one limitation, but we thought it can be useful from a different point of view. In other words, we speculated that secondary alcohols may be oxidized with allyl carbonate of primary alcohol by the following mechanism. Oxidative addition of ruthenium(II) species to allyl carbonate of primary alcohol, followed by decarboxylation gives (π-allyl)ruthenium alkoxide complex **33**, which is ready to react with a secondary alcohol to give another (π-allyl)ruthenium complex **34** by alkoxide exchange reaction rather than undergoing dehydrogenation to give aldehydes **17**. Then, β-hydrogen elimination gives ketone. We were pleased to find that reaction of cyclopentanol (**8**) with allyl decyl carbonate (**16**) in the presence of the ruthenium catalyst gave cyclopentanone (**7**, 54%) and decanal (**17**, 10%) (SCHEME 5).[4] When the dehydrogenation of **8** was carried out using two equivalents of allyl methyl carbonate (**5**), **7** was obtained quantitatively with 1 mol% of the ruthenium catalyst. With 10 mol% of the palladium catalyst, Pd-black deposited during the reaction and the reaction was not complete (57%). The rhodium catalyst gave a small amount of allyl cyclopentyl ether as a by-product (3%). As the hydrogen acceptor, allyl methyl carbonate (**5**) is used most conveniently since it gives propene, methanol, and CO_2 as by-products. Removal of excess **5** (b.p. 127-130°C) is also easy. Other allylic compounds such as allyl acetate, allyl phenyl ether, N,N'-dicyclohexyl-O-allylisourea,[11] allyl carbamates,[12] and allyl formate have moderate reactivities in this reaction.

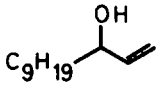
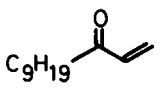
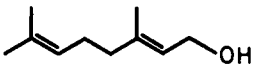
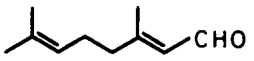
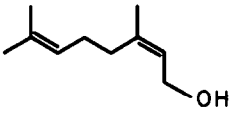
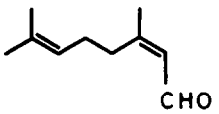
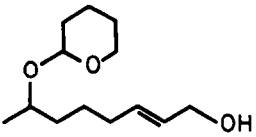
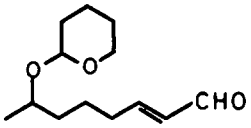
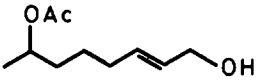
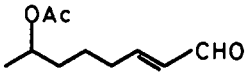
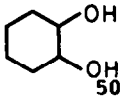
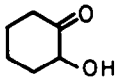
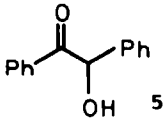
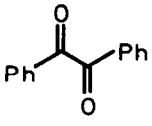
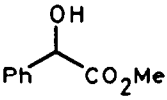
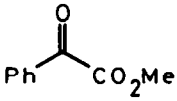


Scheme 5

Application of the oxidation was examined with various allylic and secondary alcohols using 1 mol% of the ruthenium catalyst. Results are shown in (TABLE 3). Cholesterol was converted to 5-cholesten-3-one. But 4-cholesten-3-one was obtained in a considerable amount by thermally induced isomerization. With chromium or manganese compounds, oxidation of secondary allylic alcohols is sometimes difficult because of allylic rearrangement. The ruthenium-allyl carbonate method gave α,β-unsaturated ketones in good yields (runs 2 and 3). E- and Z- allylic alcohols were converted to the corresponding enals with retention of the configuration (runs 4 and 5). Allylic alcohols which have acid-sensitive functional groups or base-sensitive functional groups underwent smooth oxidation without affecting these functional groups (runs 6 and 7). Reaction of 1,2-diol gave α-hydroxy ketone in moderate yields with two equivalents of 5. Also α-hydroxy ketone and ester were converted to the corresponding β-dicarbonyl compounds in satisfactory yields with five equivalents of 5 (runs 9 and 10). So far, several methods for ruthenium catalyzed dehydrogenation of alcohols with various hydrogen acceptor have been reported.[13] In the present reaction, allyl methyl carbonate (5) is used as the hydrogen acceptor which is converted to propene, carbon dioxide, and methanol. Thus the reaction is clean and facile. As a stoichiometric reaction, decarboxylation-dehydrogenation-decarbonylation of allyl ethyl carbonate with $RuH_2(PPh_3)_4$ to give $RuH_2(CO)(PPh_3)_3$ has been reported.[14] But in the present catalytic reaction, we could not detect the same reaction.

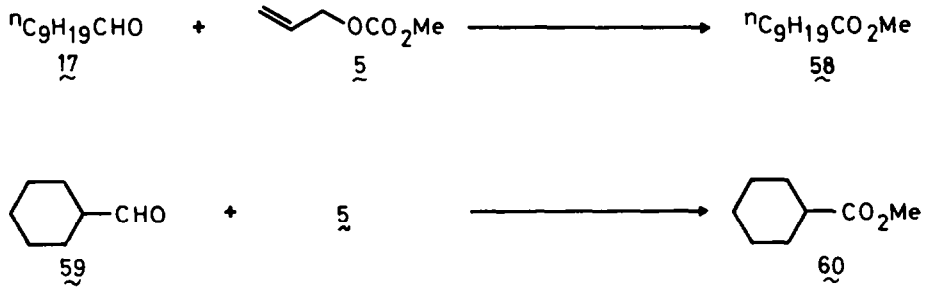
Table 3. Dehydrogenation of Various Alcohols with Allyl Methyl Carbonate[a]

Run	Alcohol	Time(h)	Product	Yield[b]
1		2		52
				18
2		4		(95)

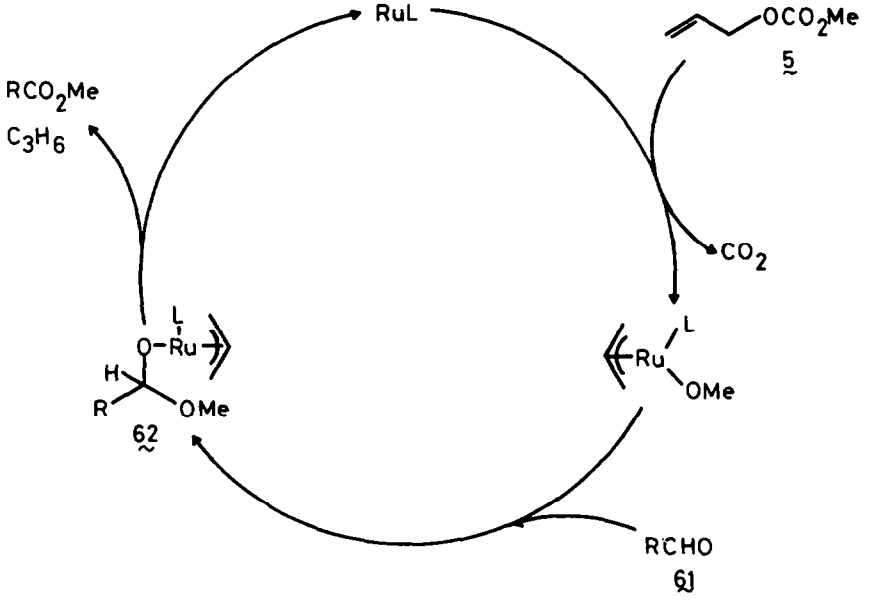
3	 **41**	2	 **42**	81	
4[c]	 **43**	3.5	 **44**	79	**44 : 46 = 96 : 4**
5[c]	 **45**	3.5	 **46**	75	**44 : 46 = 1 : 9**
6[c]	 **47**	8	 **48**	85	
7[c]	 **49**	8	 **25**	80	
8	 **50**	12	 **51**	55	
9[c]	 **52**	24	 **53**	98	
10	 **54**	24	 **55**	61	
11[c]	 **56**	10	PhCHO **11**	(60)	
			$PhCO_2Me$ **57**	(20)	

a) Reactions were carried out using alcohol (1 mmol), **5** (2 mmol), and $RuH_2(PPh_3)_4$ (0.01 mmol) in toluene under argon. b) GLC yields in parenthesis. c) 5 mmol of **5** was used.

Some primary alcohols were converted to methyl esters with excess 5 under rather drastic conditions. In this reaction, the first step must be the dehydrogenation of alcohols to give aldehydes. Conversion of aldehydes to the corresponding esters was confirmed by the reaction of 17 with 5. Reactivity of aldehydes for the esterification decreases dramatically by steric hindrance. For example, the yield of 58 was lower than 30% by the reaction of 17 with 5 under the same conditions. Reaction of 17 with allyl ethyl carbonate did not give the corresponding ethyl ester, indicating that this esterification is limited to preparation of methyl esters. The mechanism for the ester formation is explained by (SCHEME 7), which involves the nucleophilic attack of methoxide anion to aldehyde 61, to form hemiacetal followed by β-elimination of the ruthenium complex 62. Limitation of the esterification indicates that the nucleophilic attack of methoxide anion is the rate determining step.



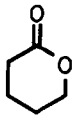
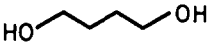
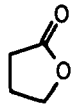
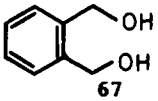
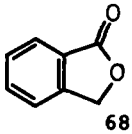
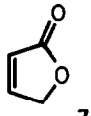
Scheme 6



Scheme 7

When 1,4- or 1,5-diols were subjected to the oxidation with allyl methyl carbonate, facile intramolecular nucleophilic attack of alkoxide anion takes place to afford a cyclic hemiacetal, which is oxidized to a lactone. In fact, 1,4- or 1,5-diols were converted to five- or six-membered lactones respectively in good yields.

Table 4. Reaction of 1,5- or 1,4-Diols

Run	Diol	Time(h)	Lactone	Yield(%)
1	 **63**	2	 **64**	83
2	 **65**	3.5	 **66**	79
3	 **67**	3	 **68**	93
4	 **69**	6	 **70**	77

Reactions were carried out using $RuH_2(PPh_3)_4$ (0.01 mmol), allyl methyl carbonate (5 mmol), diol (1 mmol) in boiling toluene (5 mL) under argon.

CONCLUSION

The intramolecular decarboxylation-dehydrogenation of allyl carbonates affords ketones or α,β-unsaturated aldehydes with phosphine-free palladium catalyst in MeCN. With palladium-phosphine catalyst, competitive allylation and protonation take place. Turnover of the phosphine-free palladium catalyst is somewhat unsatisfactory. Catalytic activity of the ruthenium-phosphine complex, $RuH_2(PPh_3)_4$ is superior to that of phosphine-free palladium catalyst. Usually the reactions were carried out with 10 mol% of $Pd(OAc)_2$ or 1 mol% of $RuH_2(PPh_3)_4$ as a catalyst. With these catalysts, dehydrogenation of allyl carbonates of saturated primary alcohols is difficult. Taking advantage of the difference of reactivities between primary alcohols and secondary alcohols, we found the direct dehydrogenation of secondary alcohols. For this reaction, ruthenium catalyst is the most effective. As for the dehydrogenating agents, allyl methyl carbonate (5) was chosen as the most convenient one. By using 5, CO_2, MeOH, and propene are generated as by-products. These by-products are easily removed by evaporation, and the procedure is simple. Furthermore, this reaction proceeds under neutral conditions and hence acid- or base-sensitive functional groups are not affected at all during the reaction. Also allylic alcohols and α-hydroxy carbonyl compounds are easily dehydrogenated by the present method. The reaction offers a facile and effective method of oxidation of secondary and allylic alcohols.

EXPERIMENTAL SECTION

General: ^{1}H NMR spectra were recorded on a JEOL Model FX-90Q Fourier transform spectrometer in $CDCl_3$ solution at 90 MHz or Hitachi Model R24A spectrometer in CCl_4 at 60 MHz using tetramethylsilane as an internal standard. Infrared spectra were obtained on a JASCO Model IRA-2 spectrometer as a neat liquid. GLC analyses were performed on a Shimadzu Model GC-4C(PT) gas chromatograph. The instrument was equipped with a thermal conductivity detector and herium carrier gas. The column was 3 m X 3φ, 15% silicone DC 550 on 60/80 Uniport B. Peak areas were obtained on a Shimadzu Model C-ELB automatic integrator.

THF and toluene were dried over Na, distilled, and stored under argon. Acetonitrile was dried over P_2O_5, distilled, and stored under argon.

Transition metal complexes, $Pd(OAc)_2$[15] $Pd_2(dba)_3\ CHCl_3$[16] $RuH_2(PPh_3)_4$,[17] and $RhH(PPh_3)_4$,[18] were prepared by the known procedures.

Preparation of allyl methyl carbonate (5)

A solution of allyl alcohol (58 g, 1 mol) and pyridine (79 g, 1 mol) in dry ether (1 L) was cooled to 0°C under nitrogen. To this solution, methyl chloroformate (94.5 g, 1 mol) was added dropwise through a dropping funnel over 30 min. White precipitate appeared and the resultant suspension was stirred for 5 h at 25-30°C. After the reaction was complete, (GLC analysis), the suspension was filtered through celite and the filtrate was washed with saturated $CuSO_4$ to remove excess pyridine. Then the solution was dried over $MgSO_4$ and distilled to obtain pure **5** (100 g, 86%): ^{1}H NMR(CCl_4) δ 3.70 (s, 3H), 4.52 (d, J=6 Hz, 2H), 5.00-5.50 (m, 2H), 5.50-6.20 (m, 1H); IR(neat) 2950, 1740, 1440, 1260, 790 cm^{-1}; b.p. 127-130°C.

Other allylic carbonates were prepared from alcohols and allyl chloroformate by the same procedure.[19]

Reaction of allyl cyclopentyl carbonate (6) (TABLE 1)

Typical procedure (run 1): In a screw capped sealed tube, $Pd_2(dba)_3\ CHCl_3$ (26 mg, 0.025 mmol) was placed and the apparatus was flushed with argon. A solution of **6** in MeCN (5 mL) was added and the tube was sealed. The tube was heated at 80°C (bath temperature) and the reaction was monitored by GLC. Other reactions were carried out similarly.

Palladium-catalyzed dehydrogenation of allyl carbonates (TABLE 2)

Typical procedure (run 1): In a 30 mL two-necked flask, fitted with a reflux condenser and a rubber cap, $Pd(OAc)_2$ (22 mg, 0.1 mmol) was placed and the flask was filled with argon. Acetonitrile (2 mL) was added and the catalyst was dissolved. To this solution a solution of **10** (232 mg, 1 mmol) in acetonitrile (3 mL) was added and the resultant solution was refluxed for 1 h under argon. After the reaction was judged to complete (TLC and GLC analyses), the reaction mixture was filtered through florisil. Then **11** (128 mg, 88%) was isolated by column chromatography on silica gel. Other reactions were carried out by the same procedure. The products, **11**, **13**, **15**, **17**, **21**, and **23** were identified by NMR, IR, and GLC analyses with authentic samples.

1-Phenyl-1-buten-3-one (**19**): ^{1}H NMR(CCl_4) δ 2.20(s, 3H), 6.34 (d, J=16.8 Hz, 1H), 7.15 (d, J=16.8 Hz, 1H), 6.80-7.30 (m, 5H); IR(neat) 1670, 1625, 1610, 1580, 1500, 1260, 980, 750, 690 cm^{-1}

7-Acetoxy-2-octenal (**25**): ^{1}H NMR($CDCl_3$) 1.21 (d, J=6.6 Hz, 3H), 1.28-1.99 (m, 4H), 2.03 (s, 3H), 2.25-2.74 (m, 2H), 3.65-4.94 (m, 1H), 6.09 (ddt, J=15.7, 7.5, and 1.4 Hz, 1H), 6.83 (dt, J=15.7 and 6.6 Hz, 1H), 9.49 (d, J=7.5 Hz, 1H); IR(neat) 2950, 1730, 1695, 1640, 1250, 1020, 980, 960, 740 cm^{-1}

2-Methyl-2-(6-oxo-4-hexenyl)-1,3-dioxolane (**27**): ^{1}H NMR($CDCl_3$) δ 1.31 (s, 3H), 1.60-1.70 (m, 4H), 2.33-2.39 (m, 2H), 3.93 (s, 4H), 6.11 (dd, J=7.7 and 15.6 Hz, 1H), 6.84 (dt, J=15.6 and 6.7 Hz, 1H), 9.49 (d, J=7.7 Hz, 1H); IR(neat) 2950, 2850, 1680, 1375 cm^{-1}

Diethyl (E)-7-oxo-2-octenylmalonate (**29**): ^{1}H NMR ($CDCl_3$) δ 1.26 (t, J=7 Hz, 6H), 1.60 (tt, J=7 and 7 Hz, 2H), 1.82-2.12 (m, 2H), 2.12 (s, 3H), 2.41 (t, J=7 Hz, 2H), 2.56 (dd, J=5 and 7 Hz, 2H), 3.36 (t, J=7 Hz, 1H), 4.18 (q, J=7 Hz, 4H), 5.42 (dt, J=5 and 15 Hz, 1H), 5.44 (dt, J=5 and 15 Hz, 1H); IR (neat) 1745, 1715, 970 cm^{-1}; Anal. Calcd for $C_{15}H_{24}O_5$. C 63.36; H 8.51. Found, C 63.34; H 8.43.

2-Allyl-2-(7-hydroxy-2-octenyl)malonate (**30**): ^{1}H NMR($CDCl_3$) δ 1.17 (d, J=6.2 Hz, 3H), 1.24 (t, J=7.3 Hz, 3H), 1.26 (t, J=7.3 Hz, 3H), 1.40 (bs, 4H), 1.79 (bs, 1H), 2.40-2.75 (m, 6H), 3.80-3.95

(m, 1H), 4.19 (q, J=7.3 Hz, 2H), 4.17 (q, J=7.3 Hz, 2H), 4.86-5.65 (m, 5H); IR(neat) 3250, 2950, 1725, 740 cm^{-1}

Dehydrogenation of alcohols with the ruthenium catalyst (TABLE 3)

Typical procedure (run 3): In a 30 mL two-necked flask, fitted with a reflux condenser and a rubber cap, $RuH_2(PPh_3)_4$ (11.5 mg, 0.01 mmol) was placed and the apparatus was flushed with argon. A solution of **41** (184 mg, 1 mmol) and **5** (232 mg, 2 mmol) in toluene (5 mL) was added to the above apparatus and the catalyst was dissolved. The resultant solution was refluxed for 2 h under argon. After the reaction was complete (TLC and GLC analyses), **42** (148 mg, 81%) was isolated by column chromatography on silica-gel. Other reactions were carried out by the same procedure. The products, **11**, **40**, **44**, **46**, **51**, **53**, **55**, and **57** were identified by NMR, IR, and GLC analyses with authentic samples.

5-Cholesten-3-one (**37**): ^1H NMR($CDCl_3$) δ 0.68-3.48 (m, 43H), 5.28-5.40 (m, 1H); IR(KBr) 2850, 1680, 1610, 1460, 1380, 1270, 1230, 870, 730 cm^{-1}

4-Cholesten-3-one (**38**): ^1H NMR($CDCl_3$) 0.74-2.68 (m, 42H), 5.76 (d, J=6 Hz, 1H), 6.12 (s, 1H); IR(KBr) 2850, 1670, 1610, 1470, 1380, 1260, 1220, 870, 730 cm^{-1}

1-Dodecen-3-one (**42**): ^1H NMR(CCl_4) 0.65-1.05 (m, 3H), 1.05-1.88 (m, 14H), 2.05-2.65 (m, 2H), 5.58 (dd, J=6.0,13.5 Hz, 1H), 6.00-6.20 (m, 2H); IR(neat) 2850, 1680, 1620, 1460, 1400, 1270, 990, 960, 720 cm^{-1}

7-(2-Tetrahydropyranyl)oxy-2-octenal (**48**): ^1H NMR($CDCl_3$) δ 1.12 (d, J=6.2 Hz, 3H), 1.35-1.98 (m, 10H), 1.98-2.55 (m, 2H), 3.20-4.04 (m, 3H), 4.50 (bs, 1H), 6.13 (dd, J=7.9, 15.5 Hz, 1H), 6.79 (dt, J=6.6, 15.5 Hz, 1H), 9.49 (d, J=7.9 Hz, 1H); IR(neat) 2860, 1695, 1640, 1205, 1135, 1080, 1060, 870 cm^{-1}; Hi-Mass M/e = 225.1465 ($M-1^+$).

Reaction of 1,4- or 1,5-diol (TABLE 4)

Typical procedure (run 1): In a 30 mL two-necked flask, fitted with a reflux condenser and a rubber cap, $RuH_2(PPh_3)_4$ (11.5 mg, 0.01 mmol) was placed and the apparatus was flushed with argon. A solution of **63** (104 mg, 1 mmol) and **5** (1.16 g, 10 mmol) in toluene (5 mL) was added to the above apparatus and the catalyst was dissolved. The resultant solution was refluxed for 2 h under argon. After the reaction was complete (TLC and GLC analyses), the lactone **64** (83 mg, 83%) was isolated by column chromatography on silica-gel. Other reactions were carried out by the same procedure. The lactones **64**, and **66** were identified by NMR, IR, and GLC analyses with authentic samples.

Phthalide (**68**): ^1H NMR(CCl_4) δ 5.14 (s, 2H), 7.10 (m, 3H), 7.58-7.90 (m, 1H); IR(KBr) 1740, 1040, 995, 730 cm^{-1}; m.p. 72-73°C; reported m.p. 72-73°C.[20]

2,5-Dihydro-2H-furanone (**70**): ^1H NMR($CDCl_3$) 4.91 (dd, J=2.2 and 1.7 Hz, 2H), 6.18 (dt, J=6.0 and 2.2 Hz, 1H), 7.59 (dt, J=6.0 and 1.2 Hz, 1H); IR(neat) 2900, 1730, 1160, 1030 cm^{-1}

Reaction of **17** with **5** (SCHEME 6)

A solution of **17** (93 mg, 0.5 mmol), **5** (290 mg, 2.5 mmol), and $RuH_2(PPh_3)_4$ (29 mg, 0.025 mmol) in toluene (2 mL) was stirred at 140°C (bath temperature) in a sealed tube. Formation of **58** (95%) was detected by GLC analysis.

Reaction of **59** with **5** was carried out by the same procedure and formation of **60** (27%) was confirmed.

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