Journal of Organometallic Chemistry, 296 (1985) 269–280
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

REACTIONS OF ALLYLIC CARBONATES CATALYZED BY PALLADIUM, RHODIUM, RUTHENIUM, MOLYBDENUM, AND NICKEL COMPLEXES; ALLYLATION OF CARBONUCLEOPHILES AND DECARBOXYLATION-DEHYDROGENATION *

ICHIRO MINAMI, ISAO SHIMIZU, and JIRO TSUJI *
Tokyo Institute of Technology, Meguro Tokyo 152 (Japan)
(Received February 27th, 1985)

Summary

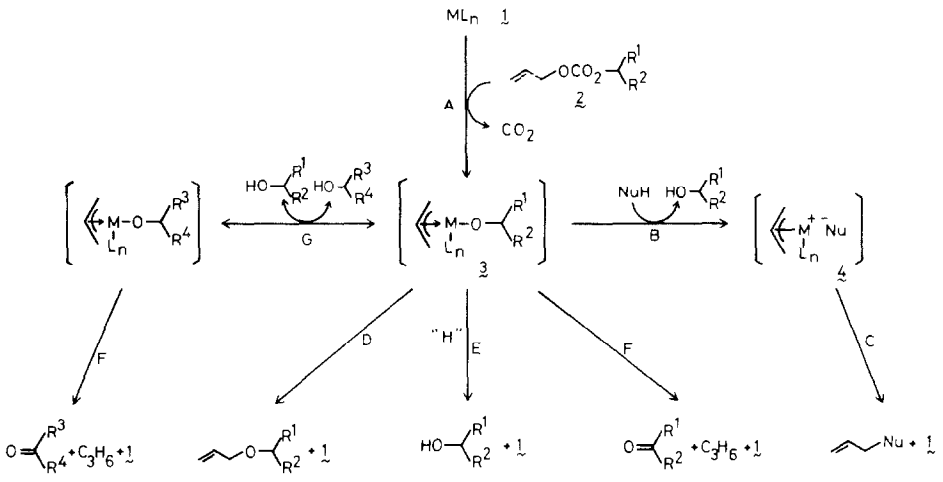
Allylation of carbonucleophiles with allylic carbonates catalyzed by various transition metal complexes has been studied. Palladium, rhodium, ruthenium, nickel, and molybdenum complexes were found to be active catalysts. The rhodium catalyst showed a different regioselectivity from the other catalysts, the reaction can proceed without allylic rearrangement. In the absence of nucleophiles, allyl alkyl carbonates were converted into ketones by decarboxylation-dehydrogenation; the ruthenium catalyst was the most active in this reaction.

Introduction

The chemistry of π-allyl complexes is one of the important aspects of organometallic chemistry. Extensive studies have been carried out in particular on π-allyl complexes of palladium and nickel [1,2], which are used in organic synthesis as stoichiometric reagents and as catalysts. Recently, many useful catalytic reactions involving π-allylpalladium complexes as intermediates have been discovered for such reactions, a number of allylic compounds such as halides, acetates, ethers, alcohols, amines [3], ammonium salts [4], and phosphates [5] has been used as sources of π-allylpalladium complexes. Allylic nitro compounds [6] and sulfones [7] have also been used, but they show different activities and the readily available acetates are used most extensively, generally in the presence of base. Recently, we have found that allylic carbonates are very reactive compounds [8–10]; In particular, they react with active methylene compounds [8], silyl enol ethers [11], ketene silyl acetals [12], and enol acetates [13] to give allylated compounds under neutral conditions even in

* Dedicated to Professor Lamberto Malatesta in recognition of his important contributions to organometallic chemistry.

0022-328X/85/$03.30



SCHEME 1

the absence of a base or Lewis acid. We have also observed the palladium-catalyzed decarboxylation-dehydrogenation of alkyl allyl carbonates [14] to give ketones or aldehydes in the absence of nucleophiles.

In contrast to the extensive studies on the reactions of allylic compounds with palladium and nickel complexes, the use of other transition metal complexes for the reaction of allylic compounds has been rather limited. There are a number of reports on the reaction of allylic esters catalyzed by iron, cobalt [15], molybdenum [16], nickel [17], and tungsten [18] complexes in the presence of base. We thus decided to explore new aspects of π-allyl chemistry of various transition metal complexes by using very reactive allylic carbonates, and we found that allylation of carbonucleophiles can be carried out under neutral conditions with palladium, rhodium, ruthenium, molybdenum, and nickel complexes. We also found that dehydrogenation of alcohols is possible with palladium, rhodium, and ruthenium catalysts. Some of the results have been presented in preliminary communications [8,14,19,20] and details are presented here.

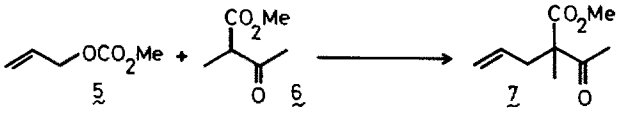
Results and discussion

1. Allylation

Initially allylation of methyl 2-methyl-3-oxobutanoate (**6**) by allyl methyl-carbonate (**5**) was examined, and the results are shown in Table 1. As previously reported, reactions catalyzed by palladium and rhodium complexes took place at 20–25°C without addition of bases [8,19], but those involving use of tetrakis(triethyl phosphite) nickel and molybdenum hexacarbonyl as catalysts required higher temperatures, 65–110°C. The neutral allylation can be understood in terms of the mechanism. Proton transfer between the nucleophile and the π-allyl alkoxide complex **3** (path B in Scheme 1), generated from allyl carbonate **2** and the low-valent transition metal complex **1** (oxidative addition-decarboxylation, path A), gives **4** and alcohol. Then nucleophilic substitution takes place to give allylated nucleophile, and the low-valent transition metal complex **1** is regenerated (path C).

TABLE 1

ALLYLATION WITH VARIOUS CATALYSTS



5 6 7

Run	Catalyst	mol%	Solvent	Temperature (°C)	Time (h)	Yield (%) [a]
1	$Pd_2(dba)_3 \cdot CHCl_3$					
	PPh_3 (1/4)	5	THF	20–25	0.5	97
2	$RhH(PPh_3)_4$					
	P^nBu_3 (1/2)	5	THF	20–25	1	93
3	$RuH_2(PPh_3)_4$	5	pyridine	20–25	24	90
4	$Ni[P(OEt)_3]_4$					
	PPh_3 (1/4)	10	THF	65	2	94
5	$Mo(CO)_6$	10	toluene	110	5	98
6	$W(CO)_3(MeCN)_3$					
	Bpy (1/2)	20	dioxane	100	11	(5)
7	$Co_2(CO)_8$	20	dioxane	100	12	(4)
8	$Fe(CO)_5$	20	dioxane	100	12	(23)
9	$Cr(CO)_6$	20	dioxane	100	12	(1)
10	Cp_2TiCl_2	20	dioxane	100	12	(4)

[a] GLC yields in parentheses.

The ruthenium hydride $RuH_2(PPh_3)_4$ [21] catalyzed the allylation at 20–25°C when pyridine was used as a slovent. In dioxane or toluene the reaction took place at 100°C in 80–90% yields. Almost no allylation was observed with tungsten tricarbonyltris(acetonitrile) under neutral conditions and even when a stoichiometric amount of sodium hydride was added, the reaction did not proceed smoothly (100°C, 10 h, 39%). The addition of sodium hydride results in the presence of sodium methoxide after the reaction and under the conditions used (at 100°C), sodium methoxide may react with **7** to give methyl 2-methyl-4-pentanoate by deacetonylation. Another side reaction is the transesterification of allyl methyl carbonate (**5**) by sodium methoxide. The occurrence of the latter reaction must be the main cause of the ineffective allylation, since a considerable amount of the β-keto ester **6** was recovered after **5** was consumed completely, even though two equivalents of **5** were added for each equivalent of **6**. These results indicate that the π-allyltungsten alkoxide complex is not sufficiently basic to generate complex **4** (path B in Scheme 1). In any case, tungsten complexes seem to be ineffective for the allylation of carbonucleophiles with allylic carbonates; in contrast, smooth allylation by allyl acetates catalyzed by tungsten complexes in the presence of base is known [18].

Carbonyls of cobalt, iron, chromium, and titanocene dichloride showed poor catalytic activities. From these results, the transition metal complexes examined here can be classified into the following three groups in terms of their catalytic activities for the allylation under neutral conditions.

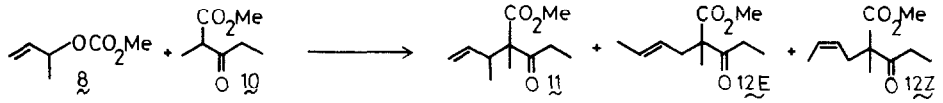
A. Active: Reaction proceeds at 20–25°C; palladium, rhodium, and ruthenium.

B. Moderate: Reaction proceeds at 65–110°C; molybdenum and nickel.

C. Poor: Virtually no reaction; tungsten, cobalt, iron, chromium, and titanium.

TABLE 2

REGIOSELECTIVITY IN THE ALLYLATION OF **10** WITH **8**



Run	Catalyst	Solvent	Temperature (°C)	Time (h)	Yield (%)	11/12*E*/12*Z*
1	$Pd_2(dba)_3 \cdot CHCl_3$					
	PPh_3 (1/4)	THF	20–25	0.5	89	27/65 / 8
2	$RhH(PPh_3)_4$					
	P^nBu_3 (1/2)	dioxane	100	2	81	86/12 / 2
3	$Mo(CO)_6$	toluene	110	6	97	3/57 /40
4	$Ni[P(OEt)_3]_4$					
	PPh_3 (1/4)	dioxane	100	3	64	24/60 /16
5	$RuH_2(PPh_3)_4$	pyridine	100	24	61	32/58 /10

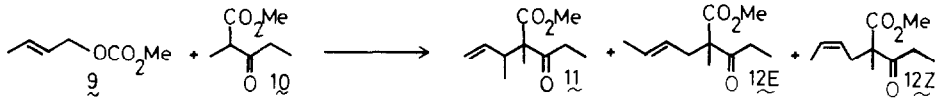
2. Regioselectivity in the allylation reaction

The regioselectivity of the allylation of the β-keto ester **10** with palladium, rhodium, ruthenium, nickel, and molybdenum catalysts was then studied using isomeric allylic carbonates, namely methyl 1-methylallyl carbonate (**8**) and crotyl methyl carbonate (**9**).

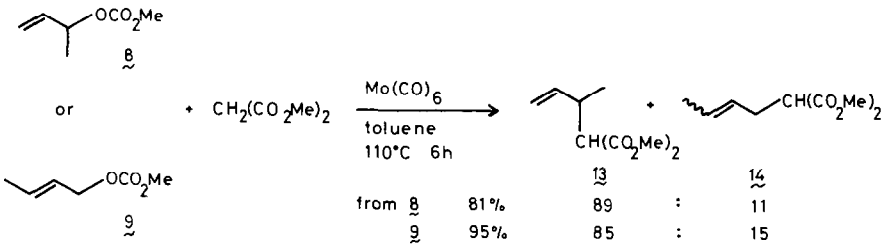
As shown in Table 2 and Table 3, the palladium catalyst gave the same ratio resulting from α-attack, product **12**, and that resulting from γ-attack, product **11** (roughly, **11**/**12** 30/70) from both **8** and **9** (see also Scheme 3). Similarly, palladium catalyzed allylation of active methylene compounds such as acetylacetone, methyl acetoacetate, and dimethyl malonate gave α-attack product **16** as a mixture of *E* and *Z* isomers in 80–95% yields with 60–70% selectivities from both **8** and **9** [22]. Although stereoselectivity for *E* and *Z* forms of **12** was not complete, high regioselectivity was observed in the molybdenum-catalyzed reactions of **8** and **9** with

TABLE 3

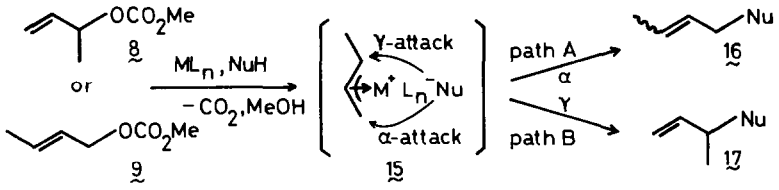
REGIOSELECTIVITY IN THE ALLYLATION OF **10** WITH **9**



Run	Catalyst	Solvent	Temperature (°C)	Time (h)	Yield (%)	11/12*E*/12*Z*
1	$Pd_2(dba)_3 \cdot CHCl_3$					
	PPh_3 (1/4)	THF	20–25	0.5	93	29/63 / 8
2	$RhH(PPh_3)_4$					
	P^nBu_3 (1/2)	dioxane	100	2	97	28/63 / 9
3	$Mo(CO)_6$	toluene	110	15	84	0/72 /28
4	$Ni[P(OEt)_3]_4$					
	PPh_3 (1/4)	dioxane	100	3	(trace)	
5	$RuH_2(PPh_3)_4$	pyridine	100	24	(9)	



SCHEME 2



SCHEME 3

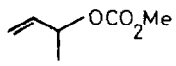
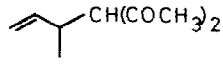
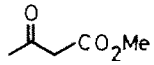
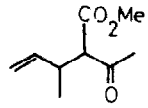
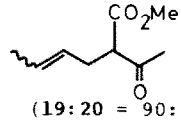
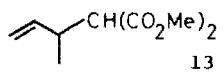
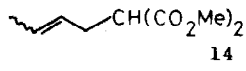
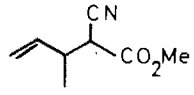
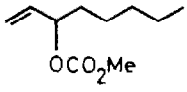
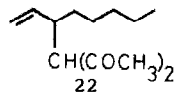
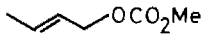
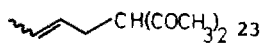
10. Upon changing the nucleophile, regioselectivity in the molybdenum catalyzed reaction greatly changed. For example, reaction of dimethyl malonate with **8** or **9** gave dimethyl 2-(1-methylallyl)malonate (**13**) as a major product (path B in Scheme 3). Similar unusual regioselectivity has been reported for the molybdenum catalyzed allylation of carbonucleophiles with allylic acetates under basic conditions [16a].

Since the same selectivity was observed for both **8** and **9**, the palladium and molybdenum catalyzed reactions can be understood in terms of the formation of the π-allyl complexes **15** as a common intermediate from **8** or **9**, and subsequent nuclephilic substitution at the less hindered site.

In contrast to these two catalysts, the rhodium hydride complex, $RhH(PPh_3)_4$ showed a different selectivity towards **8** and **9** [19]. The major product from **8** was **11** (86% selectivity), and that from **9** was **12** (72% selectivity). This means that the rhodium-catalyzed reaction proceeds without allylic rearrangement. These results can not be explained in terms of the formation of a π-allylrhodium complex similar to the palladium complex as an intermediate, but a σ-allylrhodium complex may be formed as the intermediate [23]. The rhodium-catalyzed allylation of various active methylene compounds was also examined. As shown in Table 4, all the reactions gave the allylated products formed without allylic rearrangement. Acetylacetone and methyl cyanoacetate showed high selectivity, and dimethyl malonate showed a somewhat lower selectivity. Surprisingly, the nickel- and ruthenium-catalyzed reactions hardly proceeded at all when **9** was used as the allylating agent but reaction of **8** with **10** showed a selectivity similar to that of palladium. These results suggest that the π-allyl complex **15** is a possible intermediate.

TABLE 4

REGIOSELECTIVE ALLYLATION WITH RHODIUM CATALYST

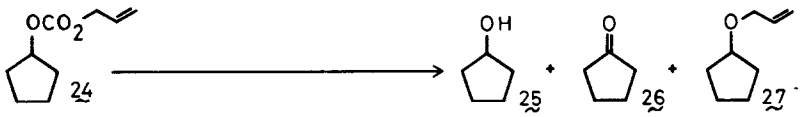
Run	Allylic carbonate	Nucleophile	Product	Yield (%)
1	 **8**	$CH_2(COCH_3)_2$	 **18**	86
2	**8**		 **19**  **20** (**19:20** = 90:10)	74
3	**8**	$CH_2(CO_2Me)_2$	 **13**  **14** (**13:14** = 77 :23)	95
4	**8**	$CH_2(CN)(CO_2Me)$	 **21**	69
5		$CH_2(COCH_3)_2$	 **22**	71
6	 **9**	$CH_2(COCH_3)_2$	**18**  **23** (**18:23** = 28 : 72)	97
7	**9**	$CH_2(CO_2Me)_2$	**13, 14** (**13:14** = 40 :60)	91

3. Dehydrogenation of alcohols

Dehydrogenation of alcohols to the corresponding ketones or aldehydes under mild conditions is an important synthetic reaction. As we have reported previously, alkyl allyl carbonates can be converted into ketones or aldehydes in the absence of nucleophiles by using phosphine-free palladium catalysts in acetonitrile [14]. This reaction can be accounted for in terms of elimination of β-hydrogen from π-allyl

TABLE 5

DECARBOXYLATION-DEHYDROGENATION OF 24



Run	Catalyst	mol%	Solvent	Temperature (°C)	Time	Yield of **25**/**26**/**27**
1	$Pd_2(dba)_3 \cdot CHCl_3$	10	MeCN	80	4	14/86/ 0
2	$Pd(OAc)_2$	10	MeCN	80	4	23/76/ 0
3	$Pd(OAc)_2$					
	PPh_3 (1/4)	5	MeCN	80	4	89/ 7/ 4
4	$Pd(OAc)_2$					
	PPh_3 (1/4)	5	THF	65	4	6/ 0/88
5	$RhH(PPh_3)_4$	5	MeCN	80	10	17/29/ 0
6	$RhH(PPh_3)_4$	5	PhH	80	10	6/88/ 0
7	$RuH_2(PPh_3)_4$	5	MeCN	80	10	27/12/ 0
8	$RuH_2(PPh_3)_4$	5	PhH	100	10	7/93/ 0
9	$Ni[P(OEt)_3]_4$	20	MeCN	80	10	17/58/ 0

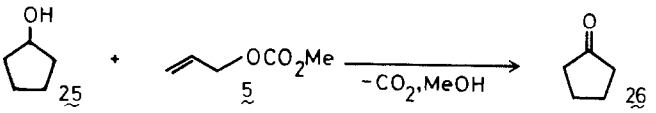
alkoxide complex **3** (path F in Scheme 1). Only CO_2 and propene are produced as by-products, and hence the reaction is very clean. But three competitive reactions are possible for the π-allyl alkoxide complex **3**, namely, allylation (path D), protonation (path E), and β-elimination (Path F) as shown in Scheme 1. With the aim of achieving clean dehydrogenation we examined the catalytic activity of other transition metal complexes using allyl cyclopentyl carbonate (**24**) as a model compound.

As shown in Table 5, the phosphinepalladium catalysts gave allyl ether **27** or alcohol **25** predominantly (runs 3 and 4). Almost no allylation was observed with the phosphine-free palladium catalysts, but protonation took place in about 20% yield (runs 1 and 2). Rhodium and ruthenium hydride complexes showed high selectivity in non polar solvents such as benzene or toluene. Acetonitrile is a good solvent for the dehydrogenation with the palladium catalyst, but it is not suitable for the rhodium and ruthenium catalysts. The reaction proceeded smoothly with 5 mol% of rhodium or ruthenium catalysts. With the palladium-catalyzed reactions 10 mol% of catalyst was usually required; if < 10 mol% was used then palladium black separated during the reaction and the yield of ketone was low. These differences can be accounted for by considering the stabilizing effect of the catalysts by the phosphine ligand. The nickel complex also showed considerable catalytic activity, but the turnover of the catalyst was poorer compared with that of the palladium species. Other transition metal complexes such as chromium, molybdenum, and tungsten carbonyls showed poor reactivities in the dehydrogenation, and almost all the starting material **24** was recovered.

As we have reported previously, conversion of saturated primary alcohols into the corresponding aldehydes is difficult with palladium catalyst [14]. Ruthenium catalyst showed the same feature (reaction of allyl decyl carbonate (**28**) in benzene at 100°C for 22 h gave decyl aldehyde (**29**) in 53% yield). The low reactivity of allyl carbonates of saturated primary alcohols suggests that secondary alcohols must be converted into ketones after alkoxide exchange with ruthenium alkoxide complex (path G in

TABLE 6

DEHYDROGENATION OF **25** WITH **5** [a]



Run	Catalyst	mol%	Solvent	Temperature (°C)	Time	Yield (%)
1	$RuH_2(PPh_3)_4$	5	toluene	100	13	99
2	$RuH_2(PPh_3)_4$	0.5	toluene	100	24	60
3	$RhH(PPh_3)_4$	5	toluene	100	10	76 [b]
4	$Pd_2(dba)_3 \cdot CHCl_3$	5	MeCN	80	22	57

[a] Reaction was carried out using 0.5 mmol of 25 and 1 mmol of 5. [b] Allyl cyclopentyl ether (**27**) was obtained (3%).

Scheme 1); reaction of **28** with cyclopentanol (**25**) did, in fact, give the ketone **26** (54%), rather than the aldehyde **29** (10%), along with n-decyl alcohol.

We furthermore found that effective dehydrogenation of secondary alcohols is possible when excess allyl carbonates of saturated primary alcohol is present. As shown in Table 6, cyclopentanol (**25**) was converted into cyclopentanone (**26**) almost quantitatively by use of two equivalents of allyl methyl carbonate (**5**) and 5 mol% of the ruthenium catalyst. In this reaction, the rhodium catalyst gave a small amount of by-product, allyl cyclopentyl ether (**27**). The phosphine-free palladium catalyst was not effective. By use of the alkoxide exchange-dehydrogenation method, secondary alcohols can be converted directly into ketones under mild conditions without formation of the corresponding allyl carbonates **2**, and this is useful for organic synthesis.

Experimental

General

^1H NMR spectra were recorded on a JEOL Model FX-90Q Fourier transform spectrometer at 90 MHz using $CDCl_3$ solutions containing tetramethylsilane as internal standard. The data are reported in the form: δ value of signal (peak multiplicity, number of protons, coupling constant). ^{13}C NMR spectra were recorded on a JEOL Model FX-90Q at 22.5 MHz in $CDCl_3$ solutions with tetramethylsilane as internal standard. Infrared spectra were recorded on a JASCO Model IRA-2 spectrometer using neat liquids; data are given in cm^{-1}, only the important diagnostic bands being reported. Qualitative and quantitative GLC analyses was performed on a Shimadzu Model GC-4C(PT) gas chromatograph; The column were of 3 m × 3 mm, 15% silicone DC 550 on 60/80 Uniport B. Preparative GC was performed on a Varian Model 920 gas chromatograph; the column was 3 m × 5 mm, 15% silicone DC 550 on 60/80 Uniport B, with He as carrier gas. Transition metal complexes, $Pd_2(dba)_3 \cdot CHCl_3$ [24], $Pd(OAc)_2$ [25], $RhH(PPh_3)_4$ [26], $RuH_2(PPh_3)_4$ [27], $W(CO)_3(MeCN)_3$ [28], Cp_2TiCl_2 [29], and $Ni[P(OEt)_3]_4$ [30], were prepared by standard procedures.

The complexes $Mo(CO)_6$, $Co_2(CO)_8$, $Fe(CO)_5$, $Cr(CO)_6$, PPh_3, P^nBu_3, and

bipyridine were purchased. THF, dioxane, toluene, and benzene were distilled over Na under argon; MeCN was distilled from P_2O_5 under argon, and pyridine was distilled from NaOH under argon. All reactions were carried out under argon. Allylic carbonates were prepared from corresponding alcohols and chloroformates by the method we described previously [8b,31]. Methyl 2-methyl-3-oxobutanoate (**6**) was prepared by a known procedure [32]. Methyl 2-methyl-3-oxopentanoate (**10**) was prepared by Claisen condensation of methyl propionate.

*Reaction of allyl methyl carbonate (**5**) with methyl 2-methyl-3-oxobutanoate (**6**) (Table 1)*

In a screw-capped sealed tube the compounds $Pd_2(dba)_3$ $CHCl_3$ (13 mg, 0.025 mmol) and PPh_3 (26 mg, 0.1 mmol) were placed in a tube, which was flushed with argon. A solution of **5** (116 mg, 1 mmol) and **6** (65 mg, 0.5 mmol) in THF (2 ml) was then added to the above apparatus and the tube was sealed with a screw cap. The solution was stirred for 30 min at 20–25°C. When the reaction was complete (GLC and TLC analyses), the solvent was removed and the residue was chromatographed on silica gel to give pure methyl 2-allyl-2-methyl-3-oxobutanoate (**7**) (82.5 mg, 97%).

^{1}H NMR ($CDCl_3$): δ 1.36 (s, 3H), 2.18 (s, 3H), 2.52 and 2.61 (d, J 5.4 Hz, 2H), 3.75 (s, 3H), 4.90–5.25 (m, 2H) 5.40–5.90 (m, 1H). IR(neat): 2950, 1740, 1710, 1640, 1240, 995, 920 cm^{-1}. Anal. Found: C, 63.69; H, 8.23. $C_9H_{14}O_3$ calcd.: C, 63.51; H, 8.29%.

Rhodium, nickel, ruthenium; and molybdenum-catalyzed reactions were carried out similarly, and the conditions are indicated in Table 1. Reactions catalyzed by tungsten, cobalt, iron, and titanium (runs 6–10) were carried out similarly, but in these cases the yields were determined by GLC analyses without isolation of the product because they were so low.

*Allylation of methyl 2-methyl-3-oxopentanoate (**10**) with methyl 1-methylallyl carbonate (**8**) or crotyl methyl carbonate (**9**) (Table 2, and Table 3)*

Reactions were carried out using **10** (144 mg, 1 mmol) and **8** or **9** (195 mg, 1.5 mmol) by the procedure used for the allylation of **6**. When the reaction was complete, the mixture was analyzed by GLC to give the ratio of 11/12E/12Z, and then chromatographed on silica gel to give the product as a mixture of regioisomers. Pure **11**, 12E, and 12Z were prepared as described below.

*Preparation of methyl 2-methyl-2-(1-methylallyl)-3-oxopentanoate (**11**)*

A solution of **8** (910 mg, 7 mmol), **10** (720 mg, 5 mmol), $RhH(PPh_3)_4$ (115 mg, 0.1 mmol), and P^nBu_3 (40.5 mg, 50 μl, 0.2 mmol) in dioxane (10 ml) was refluxed for 5 h. When the reaction was complete, the solvent was distilled off and pure **11** was isolated by preparative GLC as a mixture of diastereomers.

^{1}H NMR ($CDCl_3$): δ 0.96 and 1.03 (d, J 6.6 Hz, 3H), 1.02 and 1.04 (t, J 7.0 Hz, 3H), 1.29 and 1.30 (s, 3H), 2.46 (q, J 7.0 Hz 2H), 3.09 (dq, J 7.8 Hz and 6.6 Hz, 1H), 3.69 and 3.72 (s, 3H), 4.93–5.16 (m, 2H), 5.66 and 5.78 (ddd, J 17.4, 9.7 and 7.8 Hz, 1H). IR(neat): 2970, 1740, 1715, 1640, 1240, 970, 920 cm^{-1}. Anal. Found: C, 66.83; H, 9.45. $C_{11}H_{18}O_3$ calcd.: C, 66.64; H, 9.15%.

*Preparation of methyl 2-[2(E)-butenyl]-2-methyl-3-oxopentanoate (**12E**) and methyl 2-[2(Z)-butenyl]-2-methyl-3-oxopentanoate (**12Z**)*

A solution of **9** (5.2 g, 40 mmol), **10** (4.3 g, 30 mmol), and $Mo(CO)_6$ (1.3 g, 5

mmol) in toluene (50 ml) was refluxed for 15 h. The solvent was then removed and the stereoisomers **12***E* and **12***Z* were separated by preparative GLC.

12*E* ^{1}H NMR ($CDCl_3$): δ 1.04 (t, *J* 7 Hz, 3H), 1.30 (s, 3H), 1.64 (dd, *J* 5.9 and 0.9 Hz, 3H), 2.44 (q, *J* 7.0 Hz, 2H), 2.52 (dd, *J* 5.5 and 0.9 Hz, 2H), 3.71 (s, 3H), 5.29 (dqt, *J* 15.2, 5.9 and 0.9 Hz, 1H), 5.53 (dtq, *J* 15.2, 5.5 and 0.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 22.5 MHz): 8.0, 18.0, 19.1, 31.8, 38.4, 52.2, 59.5, 125.1, 129.6, 173.4, 207.9. IR(neat) 2950, 1750, 1710, 1460, 1240, 1030, 975 cm^{-1}. Anal. Found: C, 66.59; H, 9.11. $C_{11}H_{18}O_3$ calcd.: C, 66.64; H, 9.15%.

12*Z*. ^{1}H NMR ($CDCl_3$): δ 1.05 (t, *J* 7 Hz, 3H), 1.34 (s, 3H), 1.60 (dd, *J* 6.6 and 1.5 Hz, 3H), 2.46 (q, *J* 7.0 Hz, 2H), 2.60 (dd, *J* 6.8 and 1.5 Hz, 2H), 3.72 (s, 3H), 5.22 (dtq, *J* 11.0, 6.8 and 1.5 Hz, 1H), 5.60 (dtq, *J* 11.0, 6.6 and 1.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 22.5 MHz): 8.1, 12.9, 19.1, 31.7, 32.4, 52.3, 59.4, 124.2, 127.7, 173.4, 208.0. IR(neat): 2950, 1750, 1715, 1460, 1220, 705 cm^{-1}. Anal. Found: C, 66.63; H, 9.05. $C_{11}H_{18}O_3$ calcd.: C, 66.64; H, 9.15%.

*Molybdenum-catalyzed reaction of dimethyl malonate with methyl 1-methylallyl carbonate (**8**) or crotyl methyl carbonate (**9**).*

To avoid diallylation, the reaction was carried out using an excess of dimethyl malonate, and the calculation of the yield was based on the allyl carbonate taken. A solution of dimethyl malonate (264 mg, 2 mmol), **8** or **9** (130 mg, 1 mmol), and $Mo(CO)_6$ (52 mg, 0.2 mmol) in toluene was refluxed for 16 h. The regioselectivity was determined by GLC and the allylated product was isolated by column chromatography. Pure **13** and **14** were isolated by preparative GLC.

Dimethyl 2-(1-methylallyl)malonate (**13**). ^{1}H NMR($CDCl_3$): δ 1.10 (d, *J* 6.6 Hz, 3H), 2.80–3.10 (m, 1H), 3.33 (d, *J* 9.0 Hz, 1H), 3.74 and 3.78 (s, 6H), 4.92–5.20 (m, 2H), 5.78 (ddd, *J* 7.6, 9.9, and 17.3 Hz, 1H). IR(neat): 2950, 1735, 1640, 1020, 920 cm^{-1}.

Dimethyl 2-(2-butenyl)malonate (**14**). ^{1}H NMR($CDCl_3$) 1.62 (d, *J* 7.1 Hz, 3H), 2.56 (dd, *J* 7.1 and 8.6 Hz, 2H), 3.40 (t, *J* 8.6 Hz, 1H), 3.72 (s, 6H), 5.30–5.70 (m, 2H). IR(neat): 2950, 1740, 1440, 965, 920, 735, 640 cm^{-1}.

Rhodium-catalyzed allylation of carbonucleophiles (Table 4)

A solution of allylic carbonate (1 mmol), carbonucleophile (2 mmol), $RhH(PPh_3)_4$ (57 mg, 0.05 mmol) and P^nBu_3 (20 mg, 25 μl, 0.1 mmol) in dioxane (5 ml) was refluxed. After the reaction was complete, the mixture was analyzed by GLC to determine the regioselectivity. The pure products were isolated by column chromatography and (for a mixture of regioisomers) preparative GLC.

3-(1-Methylallyl)-2,4-pentadione (**18**). ^{1}H NMR ($CDCl_3$): δ 0.99 (d, *J* 6.6 Hz, 3H), 2.12 (s, 3H), 2.19 (s, 3H), 2.80–3.20 (m, 1H), 3.60 (d, *J* 10.6 Hz, 1H), 4.93–5.17 (m, 2H), 5.66 (ddd, *J* 9.9, 7.7, and 17.1 Hz, 1H). IR(neat): 2980, 1700, 1640, 1360, 1000, 920 cm^{-1}. Anal. Found: C, 70.11; H, 9.08. $C_9H_{14}O_2$ calcd.: C, 70.10; H, 9.15%.

Methyl 2-(methylallyl)-3-oxobutanoate (**19**). ^{1}H NMR ($CDCl_3$) δ 1.03 and 1.07 (d, *J* 6.6 Hz, 3H), 2.19 and 2.23 (s, 3H), 2.80–2.20 (m, 1H), 3.39 (d, *J* 9.7 Hz, 1H), 3.69 and 3.73 (s, 3H), 4.95–5.20 (m, 2H), 5.50–6.00 (m, 2H). IR(neat): 2950, 1750, 1720, 1645, 1000, 920 cm^{-1}. Anal. Found: C, 63.79; H, 8.34. $C_9H_{14}O_3$ calcd.: C, 63.51; H, 8.29%.

Methyl 2-(2-butenyl)-3-oxobutanoate (**20**). ^{1}H NMR ($CDCl_3$): δ 1.63 (d, *J* 5.1

Hz, 3H), 2.22 and 2.24 (s, 3H), 2.40–2.70 (m, 2H), 3.50 (t, *J* 7.5 Hz, 1H), 3.73 (s, 3H), 5.20–5.70 (m, 2H). IR(neat): 2950, 1740, 1720, 1435, 1360, 965, 715 cm^{-1}. Anal. Found: C, 63.39; H, 8.19. $C_9H_{14}O_3$ calcd.: C, 63.51; H, 8.29%.

Methyl 2-cyano-3-methyl-4-pentenoate (**21**). ^1H NMR ($CDCl_3$): δ 1.21 and 1.25 (d, *J* 6.8 Hz, 3H), 2.75–3.05 (m, 1H), 3.51 and 3.52 (d, *J* 5.1 Hz, 1H), 3.80 and 3.82 (s, 3H), 5.10–5.29 (m, 2H), 5.81 (ddd, *J* 7.3, 9.7, and 17.3 Hz, 1H). IR(neat): 2950, 2250, 1740, 1640, 1000, 930 cm^{-1}. Anal. Found: C, 62.47; H, 7.29; N, 9.04. $C_8H_{11}NO_2$ calcd.: C, 62.73; H, 7.24; N 9.14.

3-(1-Pentylallyl)-2,4-pentadione (**22**). ^1H NMR ($CDCl_3$): δ 0.86 (t, *J* 6.3 Hz, 3H), 1.23 (bs, 8H), 2.10 (s, 3H), 2.19 (s, 3H), 2.60–3.00 (m, 1H), 3.67 (d, *J* 10.6 Hz, 1H), 5.04 (dd, *J* 1.5 and 17.1 Hz, 1H), 5.07 (dd, *J* 1.5 and 10.8 Hz, 1H), 5.50 (ddd, *J* 8.8, 10.8 and 17.1 Hz, 1H). IR(neat): 2950, 1700, 1640, 1360, 995, 920 cm^{-1}. Anal. Found: C, 74.00; H, 10.10. $C_{13}H_{22}O_2$ calcd.: C, 74.24; H, 10.54.

3-(2-Butenyl)-2,4-pentadione (**23**). ^1H NMR ($CDCl_3$): δ 1.63 (dd, $J = 4.9$ and 1.1 Hz, 3H), 2.10 and 2.12 (s, 3H), 2.17 and 2.18 (s, 3H), 2.40–2.70 (m, 2H), 3.75–3.80 (m, 1H), 5.20–5.80 (m, 2H). IR(neat) 2900, 1700, 1360, 1145, 965, 720 cm^{-1}.

*Reaction of allyl cyclopentyl carbonate (**24**) (Table 5)*

$RuH_2(PPh_3)_4$ (29 mg, 0.025 mmol) was placed in a screw-cap sealed tube which was flushed with argon. A solution of **24** in benzene was added and the tube was then sealed with a screw cap. It was kept at 100°C (bath temperature) and the reaction was monitored by GLC. The other reactions listed in Table 5 were carried out similarly. The conditions are indicated in Table 5. Analytically pure allyl cyclopentyl ether (**27**) was obtained from the palladium-catalyzed reaction [9].

*Preparation of allyl cyclopentyl ether (**27**)*

A solution of **24** (850 mg, 5 mmol), $Pd_2(dba)_3$ $CHCl_3$ (130 mg, 0.25 mmol) and PPh_3 (262 mg, 1 mmol) in THF (20 ml) was refluxed for 5 h. When the reaction was complete the solvent was removed by distillation, and **27** was isolated by preparative GLC.

^1H NMR ($CDCl_3$, 90 MHz): δ 1.71 and 1.66 (bs, 8H), 3.93 (dt, *J* 5.4 and 1.4 Hz, 2H), 5.06–5.38 (m, 3H), 5.94 (ddt, *J* 17.1, 9.9 and 5.4 Hz, 1H). IR (neat): 2950, 1640, 1340, 1180, 920 cm^{-1}. Anal. Found, C, 75.91; H, 11.27. $C_8H_{14}O$ calcd.: C, 76.14; H, 11.18.

*Reaction of cyclopentanol (**25**) with allyl methyl carbonate (**5**) (Table 6)*

A solution of **25** (43 mg, 0.5 mmol), **5** (116 mg, 1 mmol), and $RuH_2(PPh_3)_4$ (29 mg, 0.025 mmol) in toluene (2 ml) was stirred at 100°C, and the reaction was monitored by GLC. Palladium- and rhodium-catalyzed reactions were carried out similarly.

Acknowledgement

Financial supports by the Grant-in-Aid for Special Project Research, No. 59104005 from the Ministry of Education and Asahi Glass Foundation for Industrial Technology are deeply appreciated.

References

1 J. Tsuji, Organic Synthesis with Palladium Compounds, Springer-Verlag, Berlin, 1980; B.M. Trost and T.R. Verhoeven, Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982, Vol. 8, p. 799.
2 P.W. Jolly, Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982, Vol. 6, p. 145.
3 K.E. Atkins, W.E. Walker, and R.M. Manyik, Tetrahedron Lett., (1970) 3821.
4 T. Hirao, N. Yamada, Y. Ohshiro, and T. Agawa, J. Organomet. Chem., 236 (1982) 409.
5 Y. Tanigawa, K. Nishimura, A. Kawasaki, and S. Murahashi, Tetrahedron Lett., 23 (1982) 5549.
6 (a) R. Tamura and L.S. Hegedus, J. Am. Chem. Soc., 104 (1982) 3727; (b) N. Ono, I. Hamamoto, and A. Kaji, Chem. Commun., (1982) 821.
7 B.M. Trost, N.R. Schmuff, and M.J. Miller, J. Am. Chem. Soc., 102 (1980) 5979.
8 (a) J. Tsuji, I. Shimizu, I. Minami, and Y. Ohashi, Tetrahedron Lett., 23 (1982) 4809; (b) J. Tsuji, I. Shimizu, I. Minami, Y. Ohashi, T. Sugiura, and K. Takahashi J. Org. Chem., 50 (1985) 1523.
9 F. Guibe, Y.S. M'Leux, Tetrahedron Lett., 22 (1981) 3591.
10 P.D. Jeffrey and S.W. McCombie, J. Org. Chem., 47 (1982) 587.
11 J. Tsuji, I. Minami, and I. Shimizu, Chem. Lett., (1983) 1325.
12 J. Tsuji, K. Takahashi, I. Minami, and I. Shimizu, Tetrahedron Lett., 25 (1984) 4783.
13 J. Tsuji, I. Minami, and I. Shimizu, Tetrahedron Lett., 24 (1983) 4713.
14 J. Tsuji, I. Minami, and I. Shimizu, Tetrahedron Lett., 25 (1984) 2791.
15 J.L. Roustan, J.Y. Merour, and F. Houlihan, Tetrahedron Lett., (1979) 3721.
16 (a) B.M. Trost and M. Lautens, J. Am. Chem. Soc., 104 (1982) 5543; 105 (1983) 3343; (b) T. Tatsumi, K. Hashimoto, H. Tominaga, Y. Mizuta, K. Hata, M. Hidai, and Y. Uchida, J. Organomet. Chem., 252 (1983) 105.
17 T. Cuvigny and M. Julia, J. Organomet. Chem., 250 (1983) C21.
18 B.M. Trost and M.-H. Hung, J. Am. Chem. Soc., 105 (1983) 7757.
19 J. Tsuji, I. Minami, and I. Shimizu, Tetrahedron Lett., 25 (1984) 5157.
20 J. Tsuji, I. Minami, and I. Shimizu, Chem. Lett., (1984) 1721.
21 Y. Hayashi, S. Komiya, T. Yamamoto, and A. Yamamoto, Chem. Lett., (1984) 977.
22 E. Keinan and M. Sahai, Chem. Commun., (1984) 648.
23 D.N. Lawson, J.A. Osborn, and G. Wilkinson, J. Chem. Soc. A, (1966) 1733.
24 T. Ukai, H. Kawazura, Y. Ishii, J.J. Bonnet, and J.A. Ibers, J. Organomet. Chem., 65 (1974) 253.
25 T.A. Stephenson, S.M. Morehouse, A.R. Powell, J.P. Heffer, and G. Wilkinson, J. Chem. Soc., (1965) 3632.
26 N. Ahmad, J.J. Levison, S.D. Robinson, and M.F. Uttley, Inorg. Synth., 15 (1974) 58.
27 J.J. Levison and S.D. Robinson, J. Chem. Soc. A, (1970) 2947.
28 J.W. Faller, D.A. Haitko, R.D. Adams, and D.F. Chodosh, J. Am. Chem. Soc., 101 (1979) 865.
29 G. Wilkinson and J.M. Birmingham, J. Am. Chem. Soc., 76 (1954) 4281.
30 T.M. Balthazor and R.C. Grabiak, J. Org. Chem., 45 (1980) 5425.
31 J. Tsuji, K. Sato and H. Okamoto, J. Org Chem., 49 (1984) 1341.
32 M. Stiles, D. Wolf, and G.V. Hudson, J. Am. Chem. Soc., 81 (1959) 628.