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ORGANIC SYNTHESES BY MEANS OF NOBLE METAL COMPOUNDS—XL[1]

PALLADIUM-CATALYSED CARBONYLATION OF ALLYLIC ETHERS

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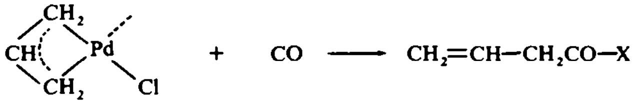
Abstract—Palladium catalysed carbonylation of allylic ethers, especially 1,4-diethoxy-2-butene has been carried out. Hexenedioate, 5-ethoxy-3-pentenoate, 2-ethoxymethyl-3-butenoate, 3-pentenoate, pentadienoate were obtained and the mechanism of the allylic carbonylation and competing reactions are discussed.

INTRODUCTION

We have reported the carbonylation of π-allylpalladium chloride to form 3-butenoic acid derivatives.[2]



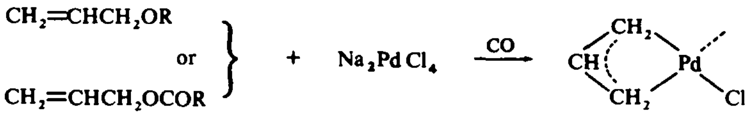
Furthermore, allyl chloride can be carbonylated in the presence of a catalytic amount of palladium chloride, palladium complexes or even metallic palladium.[3] In this catalytic carbonylation, π-allyl complex formation as an intermediate of the carbonylation reaction is assumed. The complex formation from palladium chloride and allyl chloride or allyl alcohol is a reported reaction.[4, 5] Especially, allyl chloride and palladium chloride form the complex most easily by the action of carbon monoxide.[6] In addition, the complex formation by oxidative addition of allyl bromide to metallic palladium has been reported.[7]

We have investigated the carbonylation of allyl ethers catalysed by palladium chloride and the results are reported in this paper.

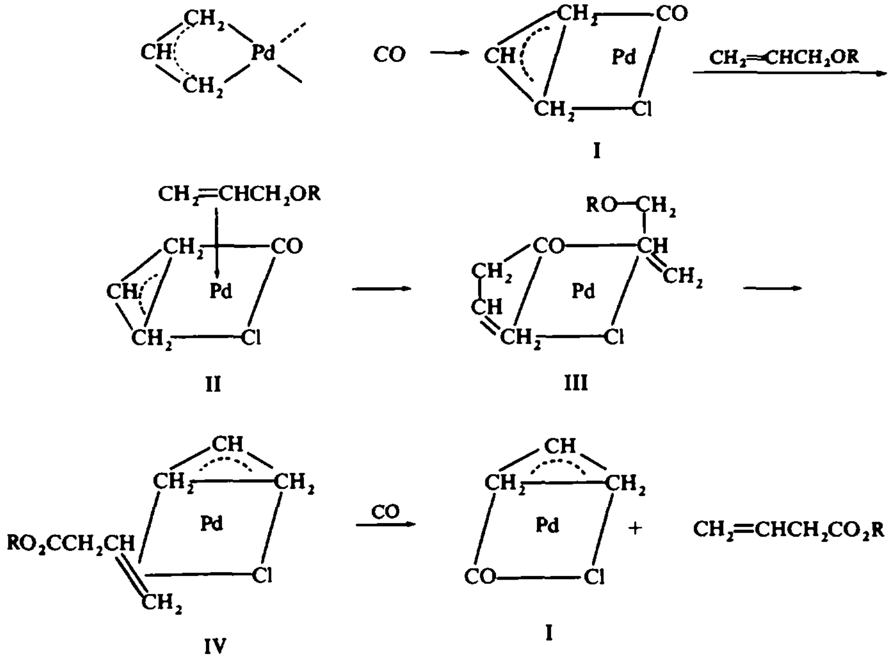
RESULTS AND DISCUSSION

Carbonylation of allyl ethers. In addition to allyl chloride and alcohol, we have briefly reported that allyl ethers, allyl esters can be carbonylated in the presence of a catalytic amount of palladium chloride.[3] Carbon monoxide is inserted into the allylic position to form β,γ-unsaturated esters from allyl ethers and acid anhydrides from allyl esters in an aprotic solvent. In these catalytic carbonylations of allylic compounds, the presence of chloride ion source is essential, and palladium chloride, π-allylpalladium chloride or metallic palladium combined with hydrogen chloride are suitable catalysts.

For the catalytic cycle, π-allylic complex formation from allyl ether or ester seems to be essential, but the π-allyl complex formation from allyl ether and allyl ester is not known. Therefore, at first the possibility of the π-allyl complex formation by the reaction of allyl ether or allyl ester with palladium chloride in methanol in the presence of carbon monoxide was investigated, and facile formation of the π-allyl complex was confirmed.



Thus the catalytic cycle in the carbonylation of allyl ether can be explained by the following scheme. Similar mechanism was proposed for the carbonylation of allyl chloride by Helden.[8]



At first, π-allylcarbonylpalladium chloride (I) is formed. Coordination of the olefinic bond of the allyl ether is accompanied with carbon monoxide insertion into the π-allyl system (II → III). Formation of a new π-allyl system (IV), followed by carbon monoxide coordination regenerates π-allylcarbonylpalladium chloride (I), with liberation of 3-butenoate. During this process, the alkoxy group is intermolecularly transfered from one to the other (III → IV). From this mechanism, it is expected that the allylic carbonylation reaction of allyl ether is not a simple carbon monoxide insertion at the allylic position. Instead, the allylic C—O bond should be cleaved to form the allyl complex. In order to prove this possibility, the carbonylation of an equimolecular mixture of allyl ethyl ether and crotyl methyl ether was carried out in benzene. If the reaction is the simple carbon monoxide insertion, ethyl 3-butenoate and methyl 3-pentenoate should be formed selectively. The experiment, however, showed that the four possible esters were formed in nearly equal amounts showing that the carbonylation proceeds through the cleavage of the C—O bonds with complete exchange of MeO and EtO.

$$\begin{array}{l} CH_2{=}CHCH_2OEt \\ CH_3CH{=}CHCH_2OMe \end{array} + CO \xrightarrow{PdCl_2} \left\{ \begin{array}{l} CH_2{=}CHCH_2CO_2Et \\ CH_2{=}CHCH_2CO_2Me \\ CH_3CH{=}CHCH_2CO_2Et \\ CH_3CH{=}CHCH_2CO_2Me \end{array} \right.$$

These experimental results can be explained by the mechanism of the carbonylation of the allylic ether shown above.

Carbonylation of 1,4-*diethoxy*-2-*butene*. The carbonylation of 1,4-diethoxy-2-butene in the presence of palladium catalyst was then carried out in ethanol. This compound has two allylic ether groups and the catalytic dicarbonylation is expected

TABLE 1. CARBONYLATION OF 1,4-DIETHOXY-2-BUTENE (V)

Vg	Solvent ml	Catalyst g	Reaction temp	Products (g)						
				V	VI	VII	VIII	IX	X	XI
6	EtOH 20	$PdCl_2$ 0·5	60	4·9		0·2	0·1		0·2	0·7
6	20	$PdCl_2$ 0·5	90		2·1		0·5	1·4	0·9	
6	20	$PdCl_2$ 0·5	110		1·8		0·4	1·8	0·7	
6	20	$PdCl_2$ 0·5	130		1·7		0·4	1·4	0·5	
6	20	$Pd(acac)_2$ 1·0	160	1·4	0·7	2·6	0·5			0·8
10	30	$PdCl_2$ 0·5	110		5·2	1·0	0·8	1·3	1·0	
6	benzene* 20	Pd/c (10%) 0·5	90	0·2	1·5	2·7	0·3	0·3	0·7	0·1
10	benzene 30	$PdCl_2$ 1	125	0·5	2·4	5·5	0·3	0·6		
10	benzene 40	$PdCl_2$ 2	115	0·2	2·0	2·6	0·3	1·5	0·2	

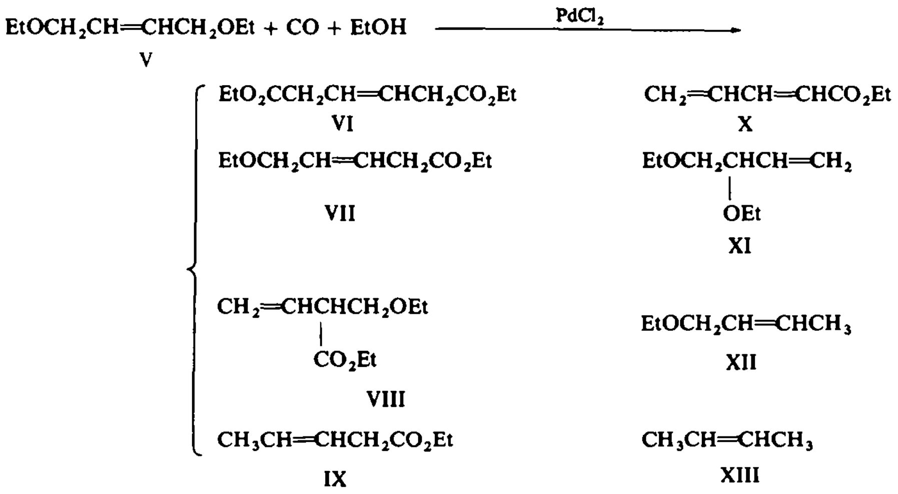
[1] All reactions were carried out CO pressure 100 atm for 20 hr.

[2] When benzene was used as the solvent, the products were treated with EtOH before isolation.

[3] The products were determined by gas chromatography (Silicone DC, 550, 180° and/or 120°; Squalene, 120°; Apiezone, 120°).

* Saturated with HCl.

to form diester. We have found that the reaction carried out under various conditions gave several products shown below. The results are shown in Table 1.



$\mathrm{EtOCH_2CH{=}CHCH_2OEt + CO + EtOH \xrightarrow{PdCl_2}}$

V

$\mathrm{EtO_2CCH_2CH{=}CHCH_2CO_2Et}$ VI

$\mathrm{EtOCH_2CH{=}CHCH_2CO_2Et}$ VII

$\mathrm{CH_2{=}CHCH(CO_2Et)CH_2OEt}$ VIII

$\mathrm{CH_3CH{=}CHCH_2CO_2Et}$ IX

$\mathrm{CH_2{=}CHCH{=}CHCO_2Et}$ X

$\mathrm{EtOCH_2CH(OEt)CH{=}CH_2}$ XI

$\mathrm{EtOCH_2CH{=}CHCH_3}$ XII

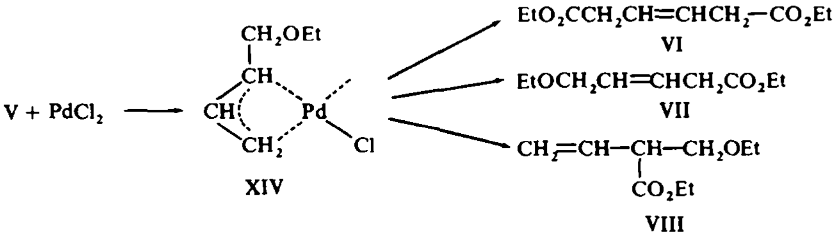
$\mathrm{CH_3CH{=}CHCH_3}$ XIII

Apparently the reaction was not a simple dicarbonylation. The reaction actually occurred can be classified into the following competitive reactions.

1. Dicarbonylation to give hexenedioate (VI).
2. Monocarbonylation to give 5-ethoxy-3-pentenoate (VII) and 2-ethoxymethyl-3-butenoate (VIII).
3. Monocarbonylation, followed by hydrogenolysis to give 3-pentenoate (IX).
4. Monocarbonylation, followed by 1,4-elimination to give pentadienoate (X).
5. Allylic rearrangement of 1,4-diethoxy-2-butene to 1,2-diethoxy-3-butene (XI).
6. Hydrogenolysis of 1,4-diethoxy-2-butene to give 1-ethoxy-2-butene (XII) and 2-butene (XIII).

All these reactions are catalysed by the palladium catalyst and the mechanism of these reactions are discussed in the following.

At first the π-allylic complex (XIV) is assumed to be formed from 1,4-diethoxy-2-butene (V). Carbon monoxide attack on the complex should give the 5-ethoxy-3-pentenoate (VII) as a main product and 2-ethoxymethyl-3-butenoate (VIII) as a minor product by the simple carbon monoxide attack on the allylic complex. Also (VI) is formed by the dicarbonylation.



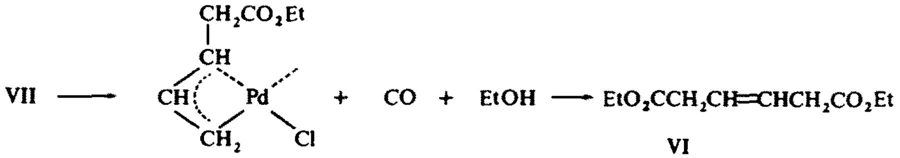
In order to prove the intermediacy of the complex XIV, the complex was synthesized from butadiene in ethanol.[11] The carbonylation of the complex gave hexenedioate (VI), 3-pentenoate (IX) and pentadienoate (X) accompanied by a small amount of 2-ethoxymethyl-3-butenoate (VIII), showing that the complex is the intermediate of the formation of these esters in the carbonylation of diethoxybutene.

$$CH_2{=}CH{-}CH{=}CH_2 + PdCl_2 + EtOH \rightarrow XIV \xrightarrow{CO/ROH} VI, IX, X$$

In this case, 5-ethoxy-3-pentenoate (VII) was not obtained. That VII is the intermediate of VI, IX and X was shown by the following experiment. When 5-ethoxy-3-pentenoate (VII) was subjected to the palladium chloride catalyzed carbonylation, the above shown three esters were actually obtained.

$$EtOCH_2CH{=}CHCH_2CO_2Et \xrightarrow{CO/PdCl_2} VI, IX, X$$

Formation of VI, IX, X from VII can be explained in the following way. The ester VII is an allylic ether and can form another π-allylic complex (XV). Carbon monoxide attack on this complex gave hexenedioate (VI).



$$VII \longrightarrow XV + CO + EtOH \longrightarrow EtO_2CCH_2CH{=}CHCH_2CO_2Et$$

XV

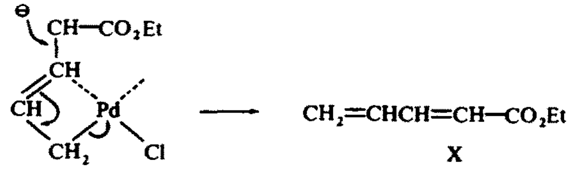
VI

In addition to the carbon monoxide attack, the complex XV undergoes following competitive reactions. 3-Pentenoate (IX) is formed by hydrogenolysis and this reaction is more predominant in the medium containing higher concentration of hydrogen chloride. Exact source of hydrogen is not known.

$$XV \rightarrow CH_3CH{=}CHCH_2CO_2Et$$

IX

1,4-Elimination is another possible reaction. Elimination of proton next to the carbonyl produces 2,4-pentadienoate. Characteristic NMR spectrum of this ester is shown in Fig. 1.



$$XV \longrightarrow CH_2{=}CHCH{=}CH{-}CO_2Et$$

XV

X

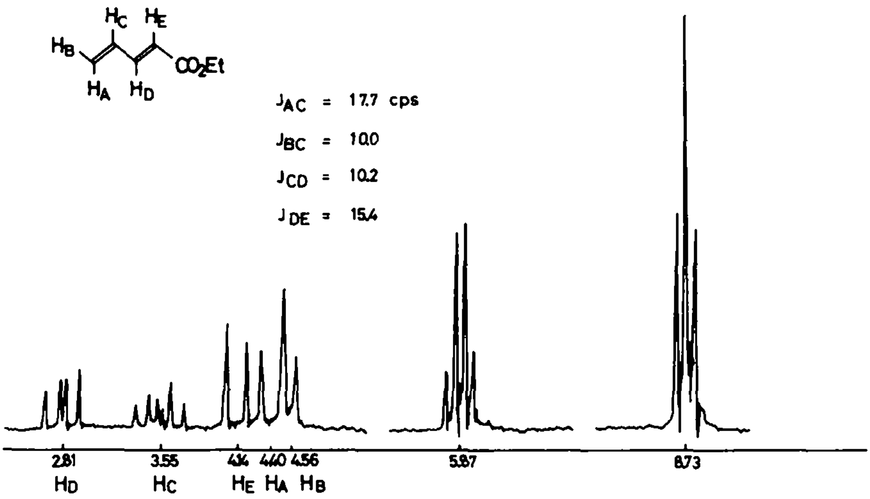


FIG. 1 NMR Spectrum of ethyl 2,4-pentadienoate.

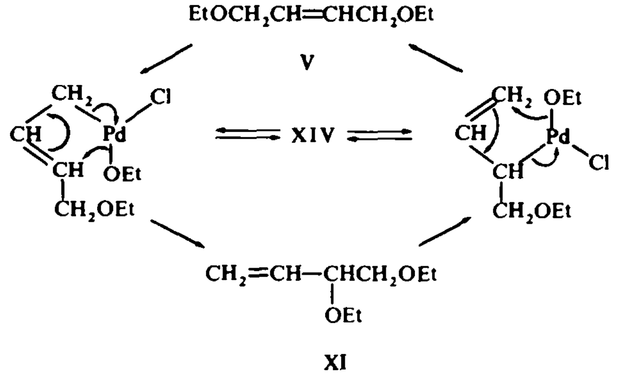
The 1,4-elimination is a general reaction for this type of ester. We reported the formation of 2,4-hexadien-1,6-dioate from 3-hexen-1,6-dioate by the 1,4-elimination reaction through π-allylic complex formation.[9]

The allylic rearrangement is another important reaction catalysed by palladium. It was confirmed that 1,4-diethoxy-2-butene rearranges easily to 1,2-diethoxy-3-butene as shown in Table 2. For this rearrangement, the presence of carbon monoxide and alcohol is not necessary and palladium is an essential catalyst. Recently the palladium catalysed allylic rearrangement of 1,4-dichloro-2-butene to 1,2-dichloro-3-butene was reported.[10] The allylic rearrangement seems to be possible by the following mechanism through palladium complex formation.

TABLE 2. REARRANGEMENT OF 1,4-DIETHOXY-2-BUTENE IN ETHANOL

A g	EtOH ml	$PdCl_2$ g	Temp	Products %	
				A	B
6	20	0·5	60	54	46
6	20	0·5	90	29	34
10	30	1	80	45	30

A. 1,4-diethoxy-2-butene;
B. 1,2-diethoxy-3-butene.
All reactions were carried out under N_2 pressure (20 atm) for 20 hr.



Thus all reactions observed in the carbonylation of diethoxybutene (V) can be explained by the formation of π-allylic complex from the allyl ether. Carbonylation carried out in benzene was somewhat slower than in ethanol. Carbonylation in benzene, followed by ethanolysis gave similar products, except less extensive hydrogenolysis.

EXPERIMENTAL

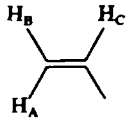
Apparatus and materials. 1,4-Diethoxy-2-butene was synthesized from 1,4-dichlorobutene by Williamson's ether synthesis, b.p. 118–120°/130 mmHg. The NMR spectra were determined on Varian high resolution spectrometer model DP 60 using TMS as an internal standard, and expressed by τ. They are summarized in Table 3. The carbonylation was carried out using a glass vessel having a gas inlet capillary, which was placed in a stainless steel autoclave.

π-Allyl complex formation from allyl ether. Allyl ethyl ether (2 g) and sodium chloropalladate (2 g) were dissolved in MeOH (30 ml) and water (1 ml) was added. CO was passed until brown color of the soln disappeared. After removing a small amount of precipitated Pd, CH_2Cl_2 (30 ml) was added. The soln was washed with water and dried. When the solvent was evaporated, π-allylpalladium chloride (0·9 g) was obtained as yellow crystals and identified by IR spectrum and m.p. Similarly the complex was obtained from allyl acetate.

Carbonylation of allyl ethyl ether and crotyl methyl ether. Allyl ethyl ether (3 g) and crotyl methyl ether (3 g), benzene (17·5 g) and $PdCl_2$ (0·5 g) were subjected to carbonylation at 130° under CO press (150 atm) for 20 hr. By gas chromatography, the formation of methyl vinylacetate (1·21 g, 0·012 mole), ethyl vinylacetate (1·43 g, 0·013 mole), methyl 3-pentenoate (1·45 g, 0·013 mole), ethyl 3-pentenoate (1·53 g, 0·012 mole) was confirmed. Each ester was separated by preparative gas chromatography and identified by IR and gas chromatography with an authentic sample.

Carbonylation of 1,4-diethoxy-2-butene in ethanol. Diethoxybutene (10 g) EtOH (30 ml) and $PdCl_2$ (1 g) were placed in the glass vessel and the reaction was carried out in a 300 ml autoclave under CO press (150 atm) at 110° for 20 hr with shaking. The reaction mixture was poured into ether, and the ethereal soln was washed with water and dried with $MgSO_4$. Ether was evaporated and the residue was subjected to distillation to give two fractions; A (90°/100 mmHg ~ 100°/27 mmHg) 4·2 g and B (85 95°/4 mmHg) 5·2 g. The fraction B was redistilled and pure ethyl 3-hexendioate was obtained. b.p. 95°/4 mmHg. (Found: C, 59·62; H, 8·20; Mol. Wt., 206: Calc. for $C_{10}H_{16}O_4$: C, 5·98; H, 8·05%; Mol. Wt., 200). Ethyl hexendioate was hydrogenated and hydrolysed to give adipic acid, m.p. 152°. The fraction A was found to contain 5 components by gas chromatography (Apiezone and silicone DC 550) and these components were separated by preparative gas chromatography to give 3,4-diethoxy-1-butene, ethyl 3-pentenoate (1·3 g), ethyl 2,4-pentadienoate (1·0 g), ethyl 2-ethoxymethyl-3-butenoate (0·8 g), and ethyl 5-ethoxy-3-pentenoate (1·0 g). These products were confirmed by the following way. NMR spectra are summarized in Table 3.

TABLE 3. NMR SPECTRA

Compound	NMR τ (multiplicity)							
	Ester group		Ether group		Olefinic		Allylic	
	CH_3—	—CH_2—	CH_3—	—CH_2—		—CH=CN—	$=CH-\overset{R}{C}HCO$	$=CH-\overset{R}{C}H-O-$
1,4-Diethoxy-2-butene			8·86 (3)	6·58 (4)		4·30 (m)		6·12 (4)
1,2-Diethoxy-3-butene			8·86 (3)	6·55 (2) 6·53 (4)	H_A 4·80 (4) H_B 4·87 (4) H_C 4·23 (8)			6·20 (4)
Ethyl hexenedioate	8·70 (3)	5·87 (4)				4·34 (m)	6·92 (m)	
Ethyl 5-ethoxy-3-pentenoate*	8·76 (3)	5·91 (4)	8·85 (4)	6·59 (4)		4·34 (6)	7·00 (2)	6·11 (2)
Ethyl 2-ethoxymethyl-3-butenoate	8·77 (3)	5·88 (4)	8·87 (3)	6·52 (4) 6·56 (4)	H_A 4·87 (4) H_B 4·88 (4) H_C 4·18 (8)		6·66 (m)	
Ethyl 3-pentenoate	8·77 (3)	5·92 (4)				4·50 (m)	7·06 (m)	
Ethyl pentadienoate*	8·74 (3)	5·87 (4)			H_A 4·40 (2) H_B 4·56 (2) H_C 3·55 (6)	H_D 2·81 (4) H_E 4·14 (2)		

* 100 Mc.

Ethyl trans-3-*pentenoate.* Identified with an authentic sample obtained by the carbonylation of butadiene by IR and NMR spectra. On hydrogenation, ethyl valerate was obtained. (Found: C, 65·32; H, 9·40; Mol. Wt., 144. Calc. for $C_7H_{12}O_2$: 65·59; H, 9·44%; Mol. Wt., 128·2); IR 1740, 1660, 965 cm^{-1}.

Ethyl 2,4-pentadienoate. (Found: C, 66·32; H, 8·02; Mol. Wt., 143. Calc. for $C_7H_{10}O_2$: C, 66·64; H, 7·99%); Mol. Wt., 126·2); UV λ_{max}^{MeOH} 247 mμ $\varepsilon = 24{,}300$; IR; 1715, 1650, 1600, 1265 cm^{-1}. Characteristic NMR spectrum of the diene system of this ester is shown in Fig. 1. By hydrogenation, ethyl valerate was obtained.

Ethyl-2-ethoxymethyl-3-butenoate. (Found: C, 63·01; H, 9·18; Mol. Wt., 171·5. Calc. for $C_9H_{16}O_3$: C, 62·76; H, 9·36%); Mol. Wt., 172·2); IR: 1740, 1645, 1105, 990, 910 cm^{-1}.

Ethyl 5-ethoxy-3-pentenoate. (Found: C, 62·58; H, 9·31, Mol., Wt., 173·5; Calc. for $C_9H_{16}O_3$: C, 62·76; H, 9·36%); Mol. Wt., 172·2); IR: 1740, 1105, 965 cm^{-1}. By hydrogenation, ethyl valerate was obtained.

Carbonylation of 1-ethoxymethyl-π-allylpalladium chloride. The complex was prepared by the Shaw's method.[11] The complex (4·2 g) was mixed with EtOH (20 ml) in the glass vessel. The carbonylation was carried out at 60° for 20 hr under CO press (150 atm). After the usual work-up, formation of the following compounds was confirmed by gas chromatography: ethyl 3-pentenoate (0·6 g), ethyl 2,4-pentadienoate (0·2 g), ethyl 3-hexenedioate (0·7 g), ethyl 2-ethoxymethyl-3-butenoate (trace).

Carbonylation of ethyl 5-ethoxy-3-pentenoate. The ester (5 g), EtOH (20 ml) and $PdCl_2$ (0·5 g) were placed in the glass vessel. The carbonylation was carried out at 90° for 20 hr under CO press (150 atm). Formation of the following compounds was confirmed by gas chromatography: ethyl 3-pentenoate (0·3 g), ethyl 2,4-pentadienoate (0·6 g), ethyl 3-hexenedioate (4·8 g).

Allylic rearrangement of 1,4-diethoxy-2-butene. 1,4-Diethoxy-2-butene (6 g) $PdCl_2$ (0·5 g) and EtOH (20 ml) were placed in the autoclave and heated at 60° under N_2 (30 atm) for 20 hr. After usual work-up, 3,4-diethoxy-1-butene and 1,4-diethoxy-2-butene were separated by preparative gas chromatography.

3,4-*Diethoxy*-1-*butene.* (Found: C, 66·81; H, 11·03, Mol. Wt., 144. Calc. for $C_8H_{16}O_2$: C, 66·63; H, 11·18%, Mol. Wt., 144); IR: 1650, 1105, 995, 910 cm^{-1}.

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