

Palladium-Catalysed Carbonylation of Unsaturated Compounds*

D. Medema, R. van Helden, and C. F. Kohll

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The oxidative carbonylation of olefins in the presence of palladium(II)/copper(II) as catalyst yields β -substituted and/or α - β unsaturated carboxylic acid derivatives. The palladium-catalysed carbonylation of allylic compounds affords β - γ unsaturated carboxylic acid derivatives, while tertiary allylamines can be converted into γ -amino acids.

The interaction of conjugated and cumulated dienes with π -allylic palladium complexes is described as part of the palladium-catalysed synthesis of polyunsaturated carboxylic acid derivatives from a diene, an alcohol and carbon monoxide or from a diene, an allylic compound and carbon monoxide.

The kinetics and mechanisms of these reactions are discussed.

Introduction

Some time ago (1960) it was found in our Laboratory¹ and elsewhere^{2,3} that ethylene, in the presence of acetates, reacts with palladium salts in non-aqueous solvents (e.g. acetic acid) to produce vinyl acetate. Our work was based on the assumption that coordination of an olefin to palladium salts should facilitate the attack of free or coordinated nucleophilic agents (OCOR, OR, CO, CN, etc.) at the olefinic carbon atoms.

It initiated a general study of the interaction of Pd-olefin and Pd- π -allyl complexes with various nucleophilic compounds in nonaqueous solvents^{1,4,9}. The present paper describes work carried out in 1963-1965 and reported mainly in the patent literature¹⁰ on synthetic and mechanistic aspects of the interaction of unsaturated compounds and carbon monoxide in the presence of Pd complexes. On this subject only a

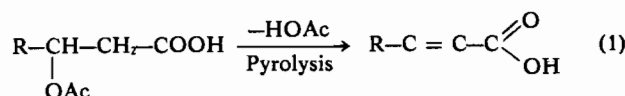
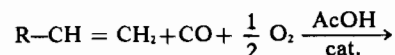
few studies have been published by other workers; for a discussion of this work the reader is referred to the literature.¹¹⁻¹⁶

I. The Carbonylation of Olefins. When the yellow $C_2H_4 \cdot PdCl_2$ complex is reacted with CO (1 atm, 20 °C) in various solvents (e.g. benzene) β -chloropropionyl chloride is formed (50%). The Pd part of the complex is converted into $(PdCOCl_2)_2$ and $(Pd_2Cl(CO)_2)_n$ complexes (cf. Section II.3). The rate is increased considerably when the reaction is carried out under pressure; for instance, at 40 atm the reaction is complete within 15 minutes. Interaction of ethylene and CO with palladium acetate in acetic acid yields β -acetoxypropionic acid.

With propylene and vinyl chloride (90 °C, 90 atm) β -chlorobutyryl chloride and β, β -dichloropropionyl chloride are obtained, respectively (42%). This stands in contrast to the reaction with OH^{-18} and OAc^{-7} , where the most highly substituted carbon atom is attacked.

We found that the reaction between α -olefins, CO and $Pd(OAc)_2$ can be made catalytic. A one-step reaction of ethylene, carbon monoxide and oxygen at 140-150 °C in acetic acid/acetic anhydride with a catalyst combination of LiCl (0.50 mole/l), $Pd(OAc)_2$ or $PdCl_2$ (0.014 mole/l) and $CuCl_2$ (0.25 mole/l) produced β -acetoxy-propionic acid at a rate of 2 mole $\cdot l^{-1} \cdot h^{-1}$ with a selectivity of 85% at 60 atm. The reaction can also be performed at 1 atm and 90 °C (rate 0.2 mole $\cdot l^{-1} \cdot h^{-1}$).

With α -olefins similar results were obtained; butadiene yielded vinylacrylic acid.



The presence of alkali ion in the system is essential for a high rate and high selectivity.

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(7) C. F. Kohll and R. van Helden, *Rec. Trav. Chim.*, **87**, 481 (1968) cf. Shell Internat. Research Mij. N. V., Brit. pat. 1010024 (1965).

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(9) D. Medema and R. van Helden, paper presented at the symposium « Homogeneous Catalytic Reaction Involving Palladium », 157th Nat. Meeting, Am. Chem. Soc., Petrol. Div. Minneapolis, April 1969.

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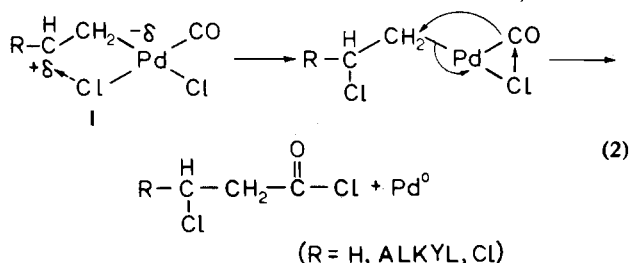
(14) A. U. Blackham (Nat. Dist. and Chem. Corp.), U.S.P. 3119861 (1964).

(15) A. Aguiló in: F.G.A. Stone and R. West (ed.), « Advances in organometallic chemistry », Academic Press, New York 1967, Vol. 5 and references given there.

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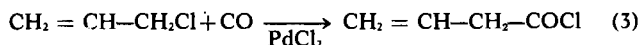
In analogy to the synthesis of vinyl acetate¹⁷ it may be assumed that the carbonylation proceeds via species of the type $C_2H_4 \cdot PdCl_2CO$ (I).

The results with the substituted olefins¹ suggest that the attack on the olefin starts with chloride—being more nucleophilic than CO—followed by attack of CO on the other olefinic carbon atom:



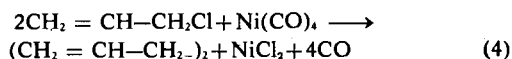
A detailed account of our studies on the carbonylation of olefins will be published separately.¹⁷

II. Carbonylation of Allylic Compounds. When the reaction outlined in the previous section was performed with allyl chloride the result was remarkable: carbon monoxide entered between the carbon-halogen bond, yielding vinylacetyl chloride in a catalytic reaction:



This result led to the hypothesis that reaction (3) proceeds via π -allyl PdCl complexes. In fact, the latter were found to be excellent catalysts for this type of reaction.

The carbonylation of allylic chlorides is also possible in the presence of $\text{Ni}(\text{CO})_4$ in hydroxylic solvents.^{19,20} In this case the yield was low, because side reaction (4) destroyed the catalyst:



Evidence has been obtained that this reaction also proceeds via π -allyl Ni complexes.²¹

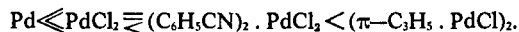
With tris[tris(*p*-fluorophenyl)phosphine]platinum²² only the carbonylation of allyl alcohol was studied. Very low yields (1-5%) were obtained. In this case, too, π -allyl complexes were assumed to be intermediates in the carbonylation.

1. Interaction of allyl chloride and carbon monoxide in the presence of palladium compounds.

a. Preliminary experiments. In a typical experiment allyl chloride (2.2 mole/l) was reacted with carbon monoxide (90 °C, 85 atm) in dimethoxyethane (DMC) as solvent, $(\pi\text{-C}_3\text{H}_5 \cdot \text{PdCl})_2$ being used as catalyst (0.028 mole/l). After 1½ hours the con-

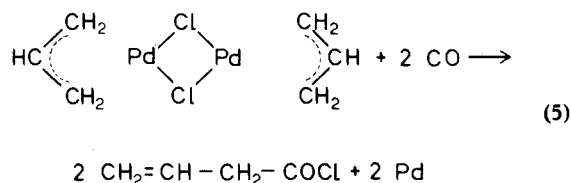
version was 90% with a selectivity towards vinylacetyl chloride of 95%. $[\pi\text{-Allyl} \cdot \text{RhCl}_2]_n$ and $[(\pi\text{-allyl})_2 \cdot \text{RhCl}]_2$ ²³ can also be used as catalysts, but then the activity is much lower owing to the formation of the stable complex $(\text{Rh}(\text{CO})_2\text{Cl})_2$. The reaction can be carried out in various solvents (CCl_4 , benzene, DMC), or in the absence of a solvent (*cf.* Section II.1b).

Other palladium compounds can also be used as catalysts, the reaction rate increasing in the order (Table I):



With π -allylpalladium chloride the carbonylation started immediately, whereas with Pd, PdCl_2 and even with the benzene-soluble bis(benzonitrile)palladium chloride $(\text{PhCN})_2\text{PdCl}_2$ an induction period of about 20 minutes was observed. This can be explained by assuming that the true catalyst in this reaction was a π -allyl-palladium complex, which in the experiments with Pd, PdCl_2 and $(\text{PdCN})_2\text{PdCl}_2$ was not present at the beginning of the reaction. A confirmation of this assumption may be that both Pd and PdCl_2 react with allyl chloride to form π -allylpalladium chloride.

The assumption that the latter is the actual catalyst is also indicated by the fact that this complex (0.16 mole/l) reacts with CO under the same conditions to yield vinylacetyl chloride (45 % m) and palladium metal:



Long reaction periods in the catalytic carbonylation (> 6 h) led to the formation of small amounts of the more stable conjugated crotonyl chloride in addition to vinylacetyl chloride.

b. Influence of concentration of allyl chloride, carbon monoxide and $(\pi\text{-allyl} \cdot \text{PdCl})_2$; solvent effect. The reaction was studied kinetically by measuring the CO consumption as a function of time. Using 1,2-dimethoxyethane (DMC) as solvent we found the reaction to be first-order with respect to the allyl chloride and the $(\pi\text{-C}_3\text{H}_5 \cdot \text{PdCl})_2$ concentration (Figure 1 and 2). With benzene and particularly with carbon tetrachloride as solvent the deviation from first-order at high conversions (Figure 1) is related to the formation of insoluble complexes (*cf.* Section II.3), which separate during the reaction. When the latter complexes are used in a subsequent carbonylation experiment they show a somewhat lower activity than in the one starting with $(\text{C}_3\text{H}_5\text{PdCl})_2$.

It was further found that the rate of reaction is proportional to the square of the carbon monoxide pressure (Figure 3a and 3b).

From Figure 1 and 4 it will be seen that type and amount of solvent have a pronounced influence on

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Table I. Effect of type of palladium catalyst on rate of carbonylation of allyl chloride

Substrate: 0.2 mole of allyl chloride Initial pressure: 76.8 atm
 Amount of solvent: 75 ml of benzene Reaction temperature: 90°C

		Conversion into vinyl acetylchloride, %m				
		10 min	30 min	1 h	3 h	5 h
$[\pi\text{-C}_3\text{H}_5 \cdot \text{PdCl}]_2$,	2.5 mmole	12	36	48	70	80
$(\text{PhCN})_2 \cdot \text{PdCl}_2$,	5 mmole	<2	4	12	59	71
PdCl_2 ,	5 mmole	<2	6	13	38	65
Pd,^{**}	5 mat	0	<2	<2	4	6*

* After 24 h: 35 %m. ** Finely divided Pd metal, freshly prepared.

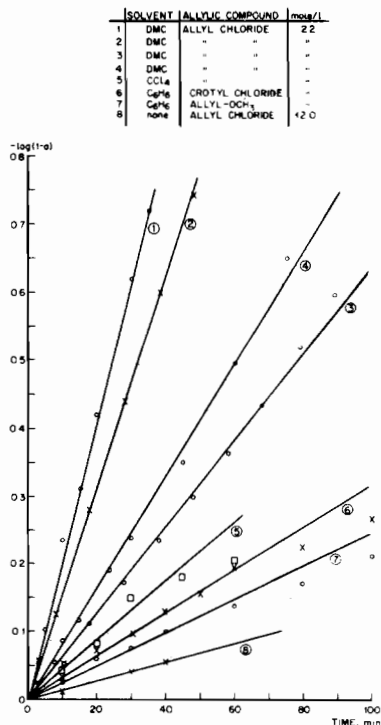


Figure 1. Carbonylation of various allylic compounds. Dependence of rate on concentration of allylic compound. a = fraction of allylic compound converted into unsaturated acid derivative. Conditions: 1, 2, 3 see Figure 2. 4, 5, 6, 7, 8 temperature: 90°C; initial CO pressure: 76.8 atm; corresponding π -allylic PdCl catalyst: 0.028 mole/l.

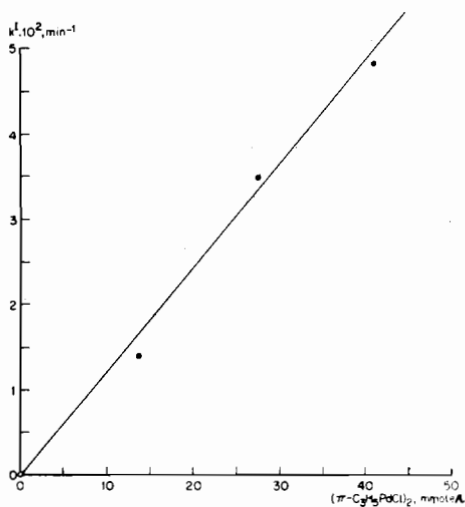


Figure 2. Carbonylation of allyl chloride. Dependence of rate on catalyst concentration. k' = first-order rate constant (cf. Figure 1). Conditions: temperature: 95°C; CO pressure: 94 atm; allyl chloride: 2.2 mole/l; solvent: dimethoxyethane.

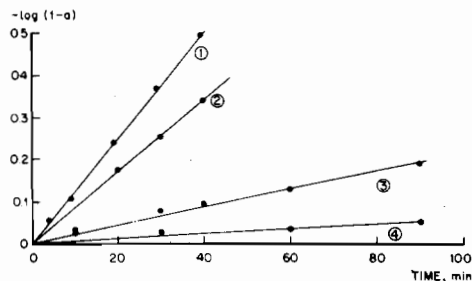


Figure 3a. Carbonylation of allyl chloride. Dependence of rate on allyl chloride concentration at various carbon monoxide pressures. a = fraction of allyl chloride converted into vinylacetylchloride. Conditions: pressure: ①-90 atm, ②-76 atm, ③-40 atm, ④-20 atm, allyl chloride: 2.2 mole/l; π -allyl PdCl: 0.028 mole/l; temperature: 94-95°C; solvent: DMC.

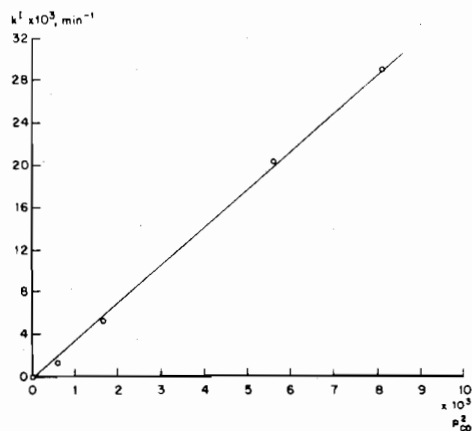


Figure 3b. Carbonylation of allyl chloride. Dependence of rate on carbon monoxide pressure k' = first-order rate constant (cf. Figure 3a), plotted versus square of CO pressure..

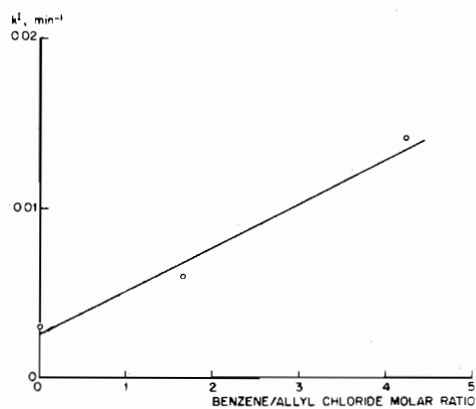


Figure 4. Carbonylation of allyl chloride. Dependence of rate on benzene/allyl chloride molar ratio. Conditions: temperature: 90°C; initial CO pressure: 76.8 atm; (π -C₃H₅PdCl)₂: 0.028 mole/l.

the rate. The difference in rate in DMC, benzene and CCl_4 may be related to the basicity of the solvent; the rate decreases in the order:

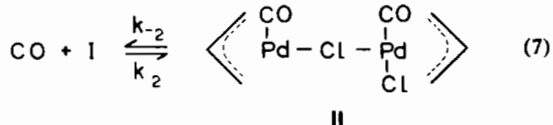
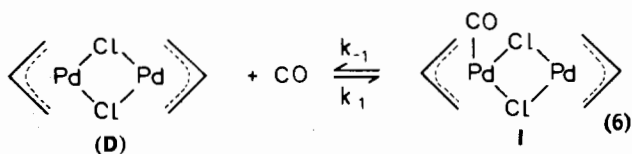
$$k^1(\text{min}^{-1}) \quad \text{DMC} > \text{benzene} > \text{CCl}_4$$

0.019	0.014	0.010
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$(\pi\text{-C}_3\text{H}_5, \text{PdCl})_2$: 0.028 mole/l; 90°C ; 76.8 atm CO).

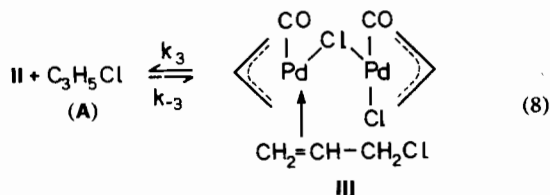
The differences between the various solvents cannot be explained by a difference in solubility of carbon monoxide, because the latter increases in the order: benzene $<$ CCl_4 $<$ DMC.

The results may be described by the following mechanism. In two consecutive fast steps a five-coordinated species is formed. The latter — having 18 electrons in the outer shells of the Pd atoms — is unstable and transforms into a four-coordinated species (II) by splitting the PdCl_2Pd bridge.

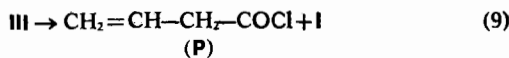


In a more basic solvent the formation of II may be enhanced through the formation of weak bonds between the four-coordinated Pd atom and a solvent molecule.

In the presence of allylchloride the solvent molecules in II are displaced by allylchloride, yielding III:



The five-coordinated species III gives vinylacetyl chloride + I:



If it is assumed that (8) is the rate-determining step and that the stationary-state principle holds for the intermediates I, II and III, the rate equation is given by:

$$\frac{dP}{dt} = \frac{k_1 k_2 k_3}{k_{-1} k_{-2}} [\text{D}]_0 [\text{CO}]^2 [\text{A}] \quad (11)$$

At constant $[\text{CO}]$ and $[\text{D}]$ this leads to:

$$\frac{dP}{dt} = k^1 [\text{A}] \quad (12)$$

in which:

$$k^1 = K_1 K_2 k_3 [\text{D}] [\text{CO}]^2 \quad (13)$$

It must be pointed out, however, that a similar relationship is found when (9) is assumed to be rate-determining (cf. Section II.2a).

c. Effect of triphenylphosphine. It was found that a strong donor like PPh_3 has a pronounced influence on the reaction rate. In the presence of PPh_3 the reaction is also first-order with respect to the allyl chloride concentration (Figure 5). The rate — expres-

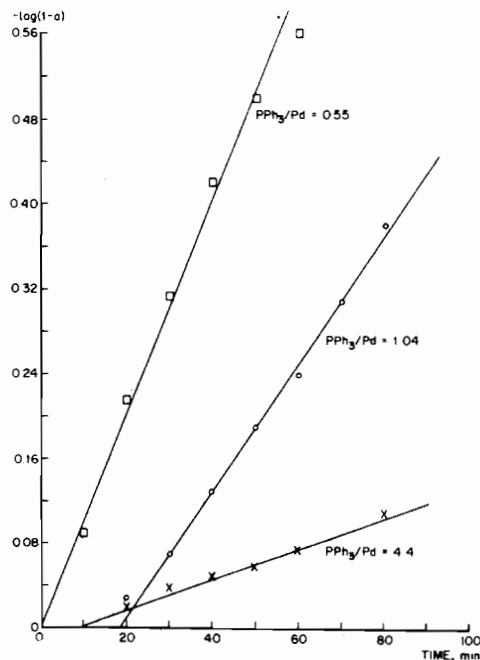


Figure 5. Carbonylation of allyl chloride in benzene solution. Effect of triphenylphosphine on rate. Conditions: temperature: 90°C ; initial CO pressure: 76.8 atm; allyl chloride: 2.2 mole/l; $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2$: 0.028 mole/l.

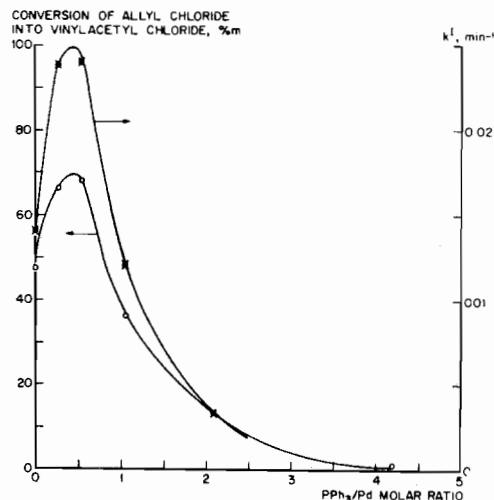
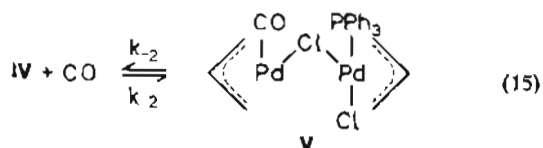
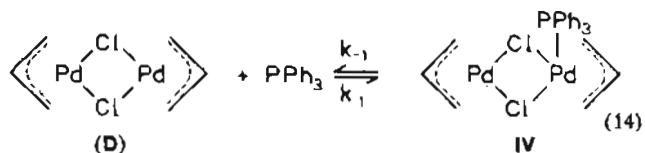


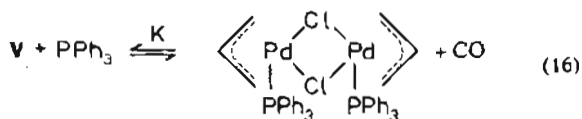
Figure 6. Carbonylation of allyl chloride. Effect of PPh_3/Pd molar ratio on rate and conversion k^1 = first-order reaction constant. Reaction time: 50 min.

sed by the first-order rate constant — passes through a maximum at a PPh_3/Pd molar ratio of 0.5 (Figure 6). At higher PPh_3/Pd molar ratios an induction period is observed (Figure 5) and the rate becomes nearly zero at ratios higher than four.

In the presence of PPh_3 — being a very effective donor — the reaction rate is about proportional to its concentration up to a PPh_3/Pd ratio of 0.5. In this region the role of CO is partly taken over by PPh_3 :



At higher ratios another molecule of PPh_3 can be taken up, leading to a species which is inactive for carbonylation:

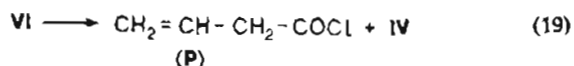
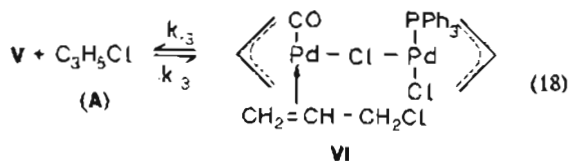


The effective catalyst concentration is then given by:

$$[\text{D}] = \frac{[\text{D}_0]}{1 + K_1 K_2 K [\text{PPh}_3]^2} \quad (17)$$

with $\text{D}_0 =$ intake of $(\pi\text{-C}_3\text{H}_5)_2\text{PdCl}_2$.

The further steps are the same as in the previous section:

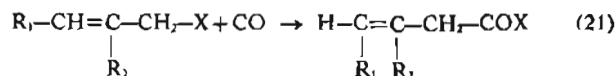


This leads to the following relationship between the first-order rate constant and the molar ratio of PPh_3/D_0 :

$$k' = K_1 K_2 k_3 [\text{CO}] \frac{\left[\frac{\text{PPh}_3}{\text{D}_0} \right]}{\frac{1}{[\text{D}_0]^2} + K_1 K_2 K \left(\frac{[\text{PPh}_3]}{[\text{D}_0]} \right)^2} \quad (20)$$

The results (Figure 6) fit this relationship quite well. When PBU_3 or SnCl_2 is used instead of PPh_3 (molar ratio 0.5) the rate of the carbonylation is reduced*.

2. *Carbonylation of other allylic compounds.* The reaction described in the previous section was found to be a general π -reaction for allylic compounds; the corresponding π -allyl Pd chlorides were used as catalysts:

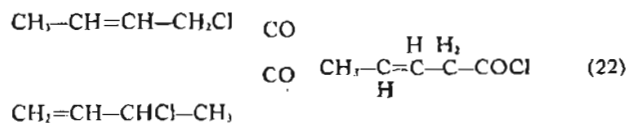


($\text{R}_1 = \text{Cl, alkyl, H; R}_2 = \text{alkyl, H;}$
 $\text{X} = \text{halogen, OH, OR, OCOR.}$)

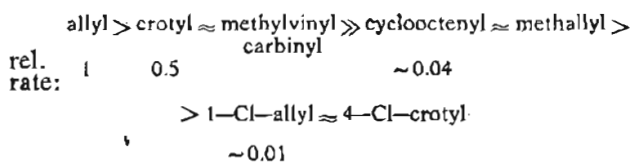
Under the same conditions as for allyl chloride conversions of 4-80% were obtained in reaction periods of 6 hours (Tables II and III). Cycloalkenyl chlorides could also be converted into the corresponding acid chlorides. The rate was found to be proportional to the concentration of the allylic compound. This is shown in Figure 1 for crotyl chloride and allylmethyl ether with benzene as solvent. Here, too, the deviation from the first-order relationship at high conversions is related to the formation of insoluble complexes (*cf.* Section II.3).

Structural factors in the allylic compound were found to have a strong influence on the carbonylation rate.

a. *Effect of substituents in the allyl fragment.* It was found that CO always enters at the least substituted carbon atom in the allyl fragment. For instance, from crotyl chloride or its isomer methylvinyl carbonyl chloride the same acid chloride (*trans*-pent-3-enoyl chloride) was obtained at about the same rate. The same was found for 3,3- or 1,3-dichloro-1-propene; only 4-chloro-3-butenoyl chloride (*cis/trans* ratio = 2) was formed.



For the allylic chlorides the rate decreased in the order (Table II):



The order of reactivities is generally in line with the ease with which these compounds are coordinated to the metal (*cf.* Section II.1b). In the case of the slowly reacting allylic chlorides the conversion could

(*) Studies on the effect various phosphines and arsines on the rate and NMR studies on the interaction of π -allylic Pd halides with carbon monoxide will be presented in a separate paper by H. C. Volger, K. Vrieze, J. W. F. M. Lemmers and A. P. Praet (*J. Organomet. Chem.*, in press).

Table II. Carbonylation of allylic chlorides with CO with the corresponding π -allylic Pd chloride complexes as catalysts
 Conditions: allylic chloride: 0.2 mole benzene: 75 ml π -allylic PdCl: 2.5 mmole
 initial pressure: 76.8 atm temperature: 90°C

Starting material	Time h	Product	Conversion %m	$k^1 \cdot 10^{***} \text{ min}^{-1}$
allyl chloride	5	vinylacetyl chloride	80	140
crotyl chloride	6	trans-pent-3-enoyl chloride	72	75
methylvinyl carbinyl chloride	5	trans-pent-3-enoyl chloride	75	80
cycloocten-2-enyl chloride	6	cyclooct-2-enoyl chloride	17	5***
methallyl chloride	5	isopropenylacetyl chloride	10*	4***
3,3-dichloro-1-propene	6	4-chlorovinylacetyl chloride	8	2***
1,4-dichlorobutene	5	5-chloropent-3-enyl chloride	3.5	1***

* In CCl_4 as solvent a 30% conversion was obtained in 18 hours. ** First-order rate constant given by $k^1 = \frac{-\ln(1-a)}{t}$, a being the fraction of allylic compound converted into the corresponding acid chloride. *** Values were derived from the amount of product isolated at the end of the experiments.

Table III. Influence of X in allyl-X with π -allyl. PdCl as catalyst

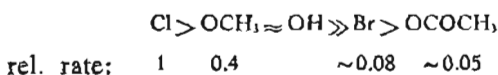
Conditions: see Table II; reaction time 5 h.

Starting material	Reaction products	Conversion, % m	$k^1 \cdot 10^4 \text{ min}^{-1}$
allyl-OH	allyl ester of vinylacetic acid + vinylacetic acid	60 (ester) 12 (acid)	—
allyl-OCH ₃	methylester of vinylacetic acid	92***	54
allyl-O-C(=O)-CH ₃	vinylacetic and acetic anhydrides	20*	7****
allyl-Br	vinylacetyl and crotonyl bromides	25**	10****

* After 12 h 50% conversion. ** π -allyl. PdBr as catalyst. *** Selectivity > 95%. **** Values were derived from the amount of product isolated at the end of the experiments.

be increased by using longer reaction times (>20 h) and higher catalyst concentrations; however, at the same time isomerization occurred. For instance, part of the product obtained from methallyl chloride under these conditions was isomerized to β,β -dimethyl acryloyl chloride. When methallyl chloride was carbonylated with π -allyl. PdCl as catalyst it was found that the π -allyl group in the catalyst is displaced by π -methallyl: at the end of the experiment π -methallyl. PdCl and π -methallyl. Pd carbonyl chloride (**VII**) were isolated (10 and 50%, respectively). It must be mentioned that in the absence of CO exchange did not occur.

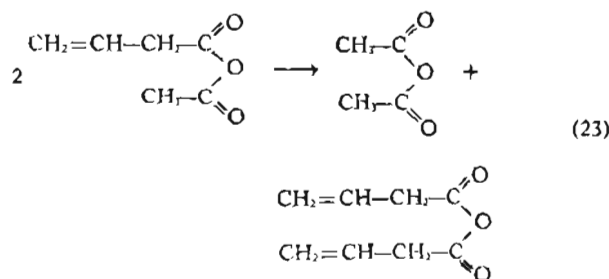
b. *Effect of X in allyl-X.* The carbonylation reaction can be extended to allyl derivatives other than allyl chloride (Table III). The effect of X on the rate cannot easily be understood:



With X = OCH₃, OH, OCOCH₃, π -allyl. PdCl was used as catalyst. It was found to be essential that halide is present in the system. Thus, with allyl acetate in the presence of π -allyl Pd acetate carbonylation did not occur; the catalyst decomposed into allyl acetate and Pd metal.

The carbonylation products of allyl acetate, vinylacetic and acetic anhydride are presumably formed by disproportionation of the unstable mixed anhy-

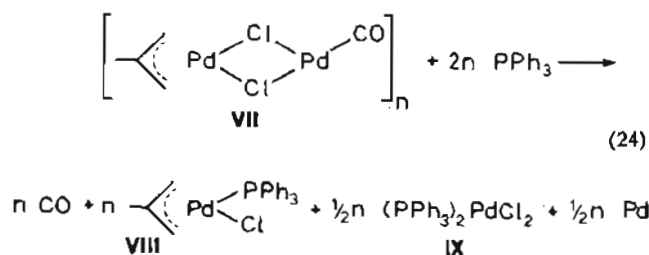
dride:



3. *Composition and structure of π -allylic carbonyl Pd complexes.* The composition and structure of the yellowish green palladium complexes isolated at the end of carbonylation experiments were determined by elemental analysis, IR and chemical reactions. With methallyl chloride a complex of type **VII** was isolated. IR indicated π -methallyl groups (3070, 1460, 1333, 830, 780 cm^{-1}), terminal CO groups (1934 and 625 cm^{-1}) and bridged PdCl bonds (258 and 233 cm^{-1}). The elemental analysis of the complex tallied well with $(\text{C}_4\text{H}_7\text{Pd}_2\text{Cl}_2\text{CO})_n$. Mass-spectroscopic analysis of the pyrolysis products of this complex showed the presence of methallyl chloride, pointing to a methallyl group. Reaction of the complex with CO afforded isopropenyl acetyl chloride, which also shows that a methallyl group is present in the complex.

Reaction of **VII** with PPh_3 produced — in virtually quantitative yields — Pd metal, carbon monoxide and

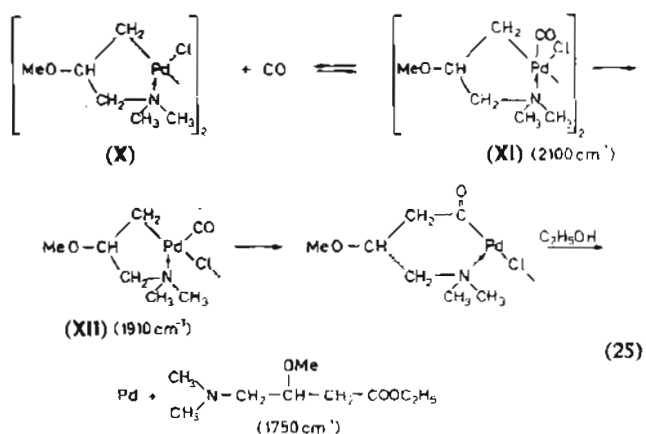
the two Pd complexes **VIII** and **IX**:



With allyl and crotyl chlorides similar complexes could be isolated. Depending on the conversion of allyl chloride another absorption band appears (1975 cm^{-1}) in the spectrum of the insoluble complex isolated. At high conversion a complex with the composition $(\text{Pd}_2\text{Cl}(\text{CO}))_n$ can be isolated. This complex shows a lower activity in a subsequent carbonylation experiment. An analogous complex of type **VII** was isolated by Tsuji and co-workers.²⁴

4. Formation of γ -amino acids starting from tert-allyl amines. Further evidence of the formation of intermediates of type II was obtained from experiments with the complex X. The latter is formed from PdCl_2 and N,N-dimethyl allyl amine in methanol solution.²⁵

Interaction of a benzene solution of complex X in benzene with carbon monoxide at room temperature and atmospheric pressure indicated that 2 mole CO/mole I was absorbed in 3 minutes. This fast absorption was followed by slow formation of Pd metal, which was complete after standing overnight. Working-up yielded the hydrochloride of β -methoxy- γ -N,N-dimethyl-aminobutyric acid (yield 50 %m on X).

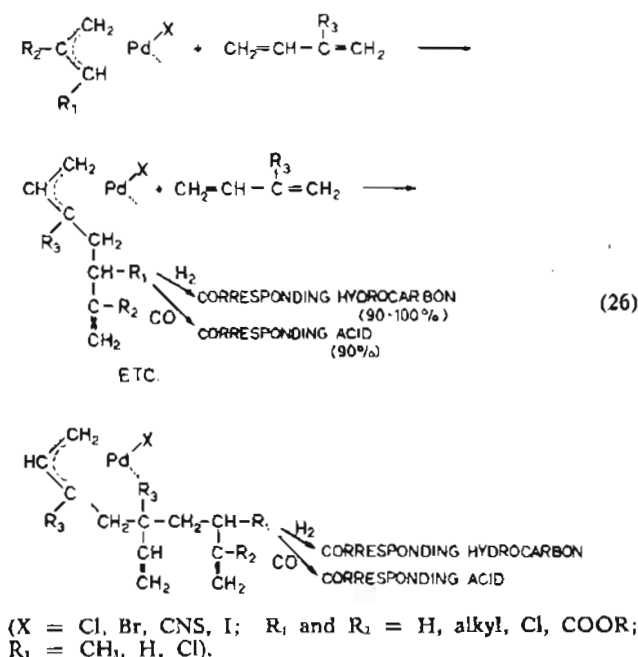


The reaction was followed by IR in chloroform solution. The carbonyl absorption at 2100 cm^{-1} (five-coordinated **XI**) gradually decreased to zero (20 h). After 20 minutes two other CO absorptions were observed (1910 and 1750 cm^{-1}), which can be attributed to the four-coordinated species **XII** and the product, respectively. The concentration of the species corresponding to 1910 cm^{-1} also decreased to zero.

Upon addition of PPh_3 to **XI** (2 mole/mole **XI**) CO is immediately and quantitatively released; subsequently it is absorbed very slowly. The latter is presumably due to slow displacement of PPh_3 bound to Pd by CO.

III. Formation of polyunsaturated Acids from an Allylic compound, a Diene and Carbon Monoxide. We found that π -allyl Pd halides react with butadiene by addition of the π -allyl fragment to the diene, yielding a new π -allyl complex with seven carbon atoms. A striking result is obtained when allyl chloride, butadiene and CO are reacted in the presence of catalytic amounts of $(\pi\text{-C}_3\text{H}_5)_2\text{PdCl}_2$: 3,7-octadienoyl chloride is obtained besides vinylacetyl chloride; with excess butadiene more diene molecules can be built in, leading to a triple-unsaturated C_{12} acid. We have studied this reaction and the addition of dienes to allyl PdX complexes separately.

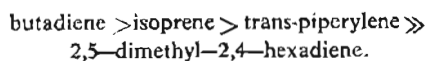
1. Interaction of π -allylic Pd-X complexes with dienes*. π -Allylic Pd halides (0.03 mole/l) react with conjugated dienes (4 mole/l) in benzene solution (1 atm., 20°C) to form new π -allylic Pd complexes via addition of the allyl fragment to the diene molecules. We succeeded in isolating these complexes and determining their structure (elemental analysis, IR, NMR, chemical reactions):



Experiments in which we followed the reaction by IR showed that the rate increases with increasing electronegativity of the bridging ligand, viz.:



For the dienes the sequence in reactivity is:



(24) J. Tsuji and S. Hosaka, *J. Am. Chem. Soc.*, **87**, 4077 (1965).
(25) A. C. Cope et al., *J. Am. Chem. Soc.*, **89**, 287 (1967).

(* A detailed account of this work will be presented by D. Medema in a thesis.

It was further found that the conjugated diene always enters the π -allyl moiety at the most substituted carbon atom. Further addition of butadiene only occurred upon the temperature being raised and at higher butadiene concentrations. Evidently, substitution of an alkyl group on a terminal carbon atom of the π -allyl group greatly retards further addition of the diene. Under the more stringent conditions a mixture of complexes is formed. With $R_1, R_2, R_3 = H$ hydrogenation yields *n*-heptane, 5-ethyl nonane (no *n*-undecane could be detected) and a C_{15} and C_{19} hydrocarbon.

In agreement with these results it was found that the rate of reaction (26) increased with increasing electron-withdrawing properties of substituents present in the π -allyl fragment:



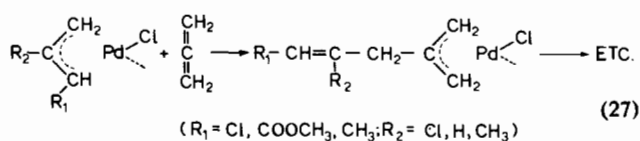
rel. rate: 10^5 1

Kinetic studies with $(\pi\text{-methallyl-PdBr})_2$ (**C**) and isoprene (**I**) showed that the rate of disappearance of **C** is represented by (Figure 7):

$$-dC/dt = k_2[C][I] = k_1[C]$$

($E = 13.8 \text{ kcal/mole}, A = 10^{5.83} \text{ mole}^{-1} \text{ l min}^{-1}$)

With allene as diene the reaction was found to proceed as follows:



CONC OF ISOPRENE, mole/l	CONC OF COMPLEX (C), mole/l	TEMP, °C	$10^3 k_2$, mole ⁻¹ l min ⁻¹
Δ 1.85	2.14×10^{-2}	70.1	1.18
\square 2.82	2.45×10^{-2}		
\circ 3.70	2.14×10^{-2}	79.6	2.01
\times 3.70	2.14×10^{-2}	59.5	0.62
$+$ 3.70	2.14×10^{-2}		

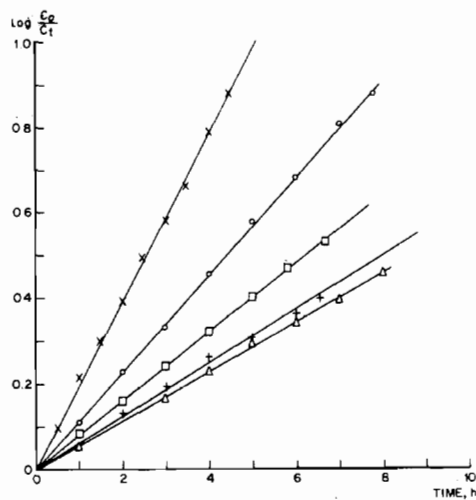


Figure 7. Pseudo first-order kinetics for the reaction of π -methallyl-palladium bromide with isoprene. Influence of isoprene concentration and temperature.

Here, too, the complexes formed could be isolated and identified by IR, NMR and chemical reactions. The rate decreased in the same order as for the conjugated dienes.

The results indicate that the rate-determining step is the coordination of the diene to the π -allyl Pd complex (Figure 8, **XIII**). This is further supported by the fact that in the presence of PPh_3 ($\text{Pd/PPh}_3 = 1$) no reaction with dienes occur.

Butadiene adds on to the substituent-carrying carbon atom, contrary to the attack of allene and CO (*cf.* Section II). This difference can be explained by the fact that butadiene can act as a bidentate ligand, whereas allene and CO can only act as monodentate ligands for a single metal atom. It may be expected that the bridge is split at that chlorine atom which is opposite to the carbon atom which forms a σ bond with Pd in the dynamic allyl form (*trans* effect). A σ bond will preferentially be formed between Pd and the unsubstituted carbon atom of the π -allyl group. As a result, the second double bond of butadiene is coordinated in the *cis* position relative to the carbon atom carrying the substituent

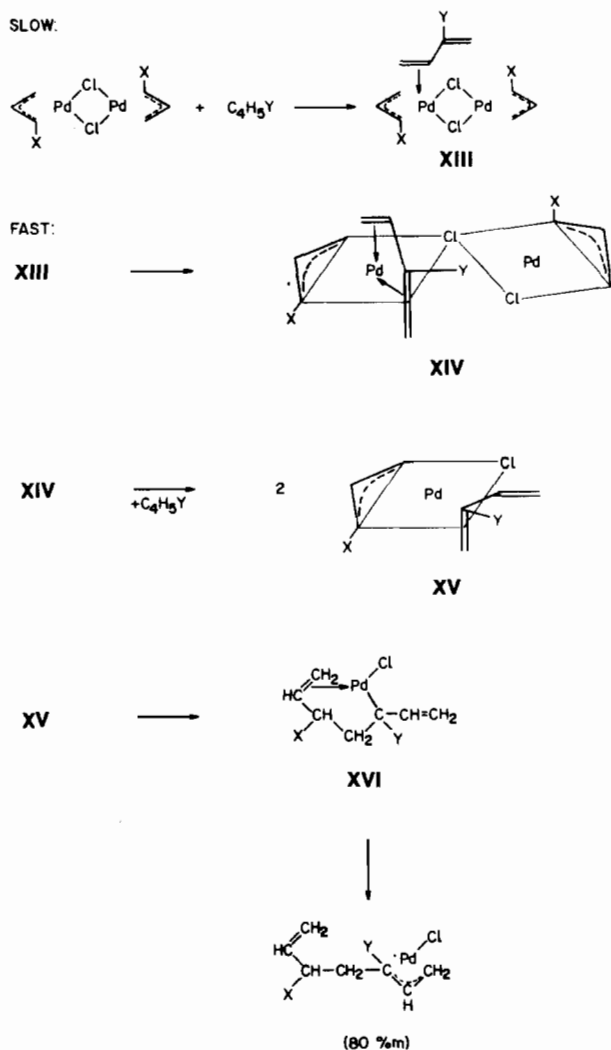


Figure 8. Mechanism of addition of π -allyl to conjugated dienes

X = CH₃, Cl, H, COOR
Y = H, Cl, CH₃

(Figure 8, **XIV**). With allene and CO the most likely structure of the four-coordinate intermediate will be the one in which, for steric and polar reasons, the attacking molecule is in the *trans* position relative to the carbon atom carrying the substituent:



From Figure 8 it is also clear why the π -allyl group reacts with the less readily coordinated double of isoprene.

2. *Effect of acetate as bridging ligand.* With π -allyl Pd acetate (nitrate, trifluoroacetate) and butadiene (5 h, 1 atm) the same reaction takes place as with the halide (Figure 9). However, by allowing the reaction to continue for another 24 h displacement of the C_7 ligands occurs and a complex of type **XVIII** (Figure 9) is formed (75%). The structure of the

latter could be derived from elemental analysis, IR, NMR and chemical reactions (*cf.* Figure 9).

When the reaction is carried out at 50°C and higher butadiene concentration (5 mole/l) n-dodecatetraene-1,3,6,10 is formed in a catalytic reaction. In addition, the complex **XVIII** can be isolated at the end of the reaction and used as catalyst for linear trimerization.

Minor amounts of 1,3,7-octatriene were also obtained. This product became the main one when PPh_3 was added ($Pd/PPh_3 = 1$). This may be explained by the blocking effect of the latter in **XVIII**.

Displacement of the allylic ligands in **XVIII** by butadiene molecules took also place when starting from β -carboxymethyl- π -allyl Pd acetate and π -crotyl Pd acetate: **XVIII** was obtained together with the 5-carboxymethyl and 5-methyl derivatives of **XIX** and **XX**, respectively.

The difference in behaviour of the acetates versus the halides can be nicely explained on the basis of the difference in structure.⁵ In hydroxylic solvents (alcohols, aliphatic acids) the reaction with π -allyl Pd acetate (nitrate, sulfate) was found to take a

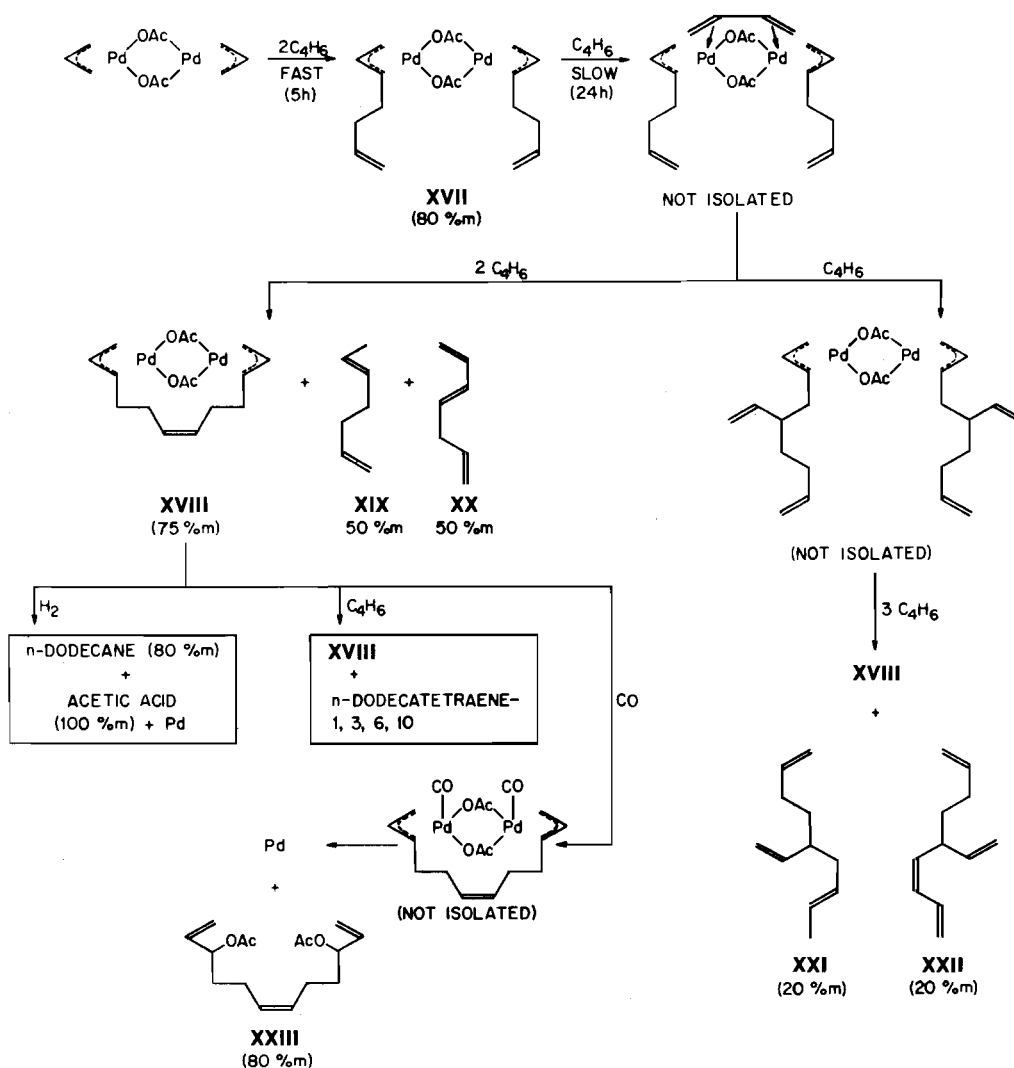
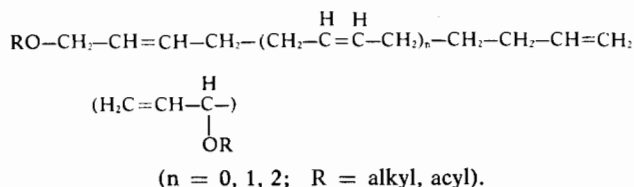


Figure 9. Mechanism of linear trimerization of butadiene.

different course: polyunsaturated alcohols, ethers or esters were obtained with the structure:



In the beginning of the reaction a complex with the structure **XXIV** could be isolated (Figure 10). An analogous intermediate is formed as found by Wilke²⁶ and co-workers starting from $(\pi\text{-allyl})_2\text{Pd}$ and by Smutny²⁷ in the reaction of dienes with phenols in the presence of Pd compounds and Na phenolate. The proposed mechanism (Figure 10) is in agreement with the fact that $(\pi\text{-allyl})_2\text{Pd}$ upon reaction with CH_3OH yields propylene, allyl-methylether and Pd.

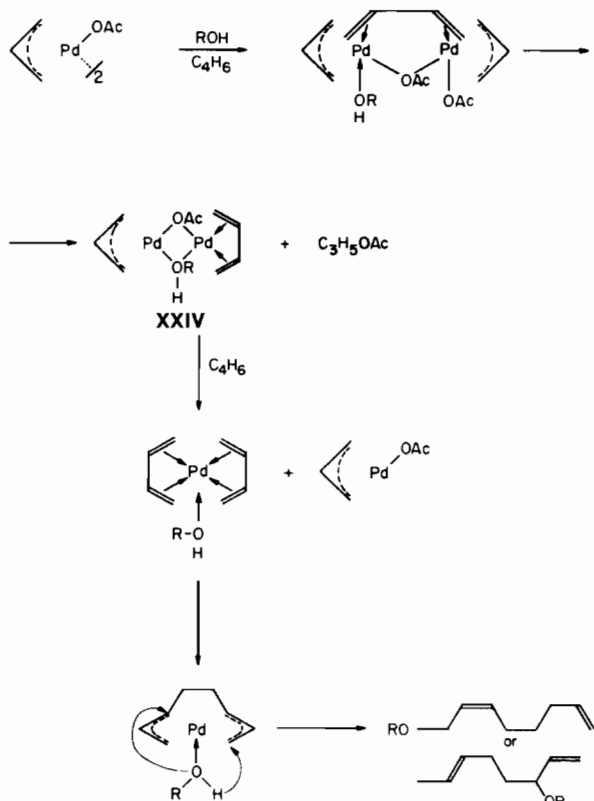
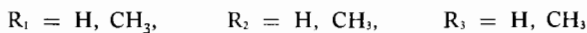
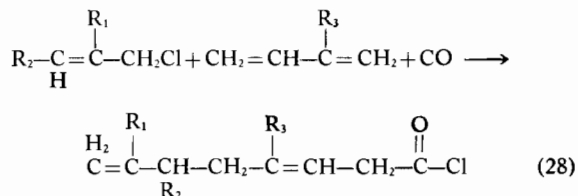


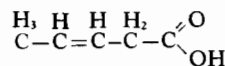
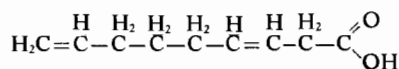
Figure 10. Mechanism of formation of unsaturated ethers (esters) with π -allyl Pd acetate as catalyst.

3. Synthesis of long-chain unsaturated acids. In the foregoing sections one of the steps involved in the reaction of a diene, an allylic compound and CO has been described. In Section III.1 it has already been shown that complexes of the type formed in reaction (26) react with carbon monoxide to form the corresponding acid chloride. The catalytic reaction bet-

ween a diene, an allylic compound and CO was found to yield the same products:



In a typical experiment allyl chloride (0.83 mole/l) was reacted at 90°C with butadiene (3.33 mole/l) and CO (initial pressure 52 atm) in benzene solution, with $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2$ as catalyst (16.7 mmole/l). After 6 h the conversion of allyl chloride amounted to 71% and the yield of 3,7-octadienoyl chloride + vinylacetyl chloride (mol. ratio 0.8) amounted to 90%. In addition, small amounts of a C₉ acid and a C₅ acid were obtained:



The latter are presumably formed from butadiene (via crotyl chloride) and a butadiene dimer.

The C₈ acid/C₄ acid molar ratio was found to be proportional to the ratio $[\text{butadiene}]/[\text{CO}][\text{allyl chloride}]$ (Figure 11). This indicates that in the competition between CO and butadiene (Figure 12) the reaction of $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2$ with the diene is the slowest step. The results further indicate that in

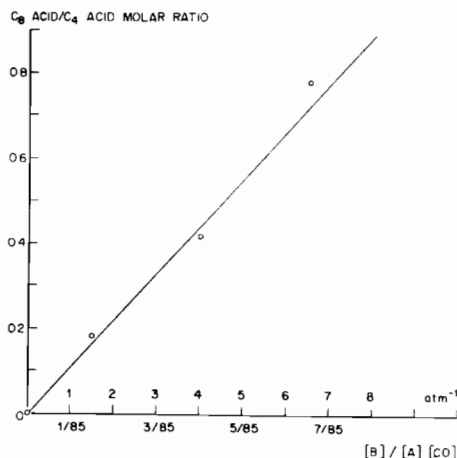
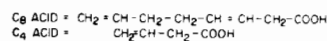


Figure 11. Effect of butadiene, allyl chloride and CO concentrations on C₈ acid/C₄ acid molar ratio. Conditions: temperature: 90°C; initial CO pressure: 52-85 atm; butadiene (B): 2.5-3.33 mole/l; allyl chloride (A): 0.83-1.67 mole/l; $(\pi\text{-allyl PdCl})_2$: 16.7 mmole/l.

(26) G. Wilke *et al.*, *Angew. Chem.*, 75, 10 (1963); *ibid.*, 78, 15 (1966).

(27) E. J. Smutny, *J. Am. Chem. Soc.*, 89, 6793 (1967).

the carbonylation of allylic compounds the bonded π -allylic fragment is displaced by the incoming allylic chloride (*cf.* Section II.2a).

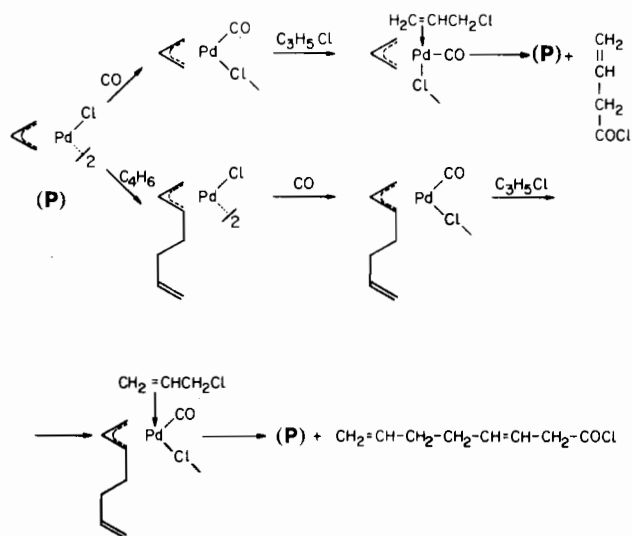


Figure 12. Carbonylation of allyl chloride in the presence of butadiene.

IV. Mechanistic Considerations. It seems very reasonable to assume that the first step in the carbonylation is coordination of carbon monoxide to the palladium atoms to form a five-coordinated palladium complex (I), i.e. in analogy with the reaction of π -allylic Pd halides with conjugated dienes (Figure 8). The complex formed — having 18 electrons in the outer shells of the Pd atom — is unstable and transforms into a four-coordinated species (II). In the presence of allyl chloride III is formed in a rate-determining step (Figure 13) (*cf.* Section II.b).

The fact that methallyl chloride reacts much more slowly than allyl chloride is also in agreement with this supposition: methallyl chloride may be expected to coordinate to Pd with much more difficulty. The low rate of Cl-allyl chloride, too, may be explained on this basis: in the interaction of vinyl chloride with acetate anions catalysed by PdCl₂ indications were obtained that the lower rate of this reaction as compared with the same reaction with ethylene is due to the fact that the formation of the vinyl chloride/PdOAcCl₂ complex proceeds less readily than that of the corresponding ethylene complex.^{1,7}

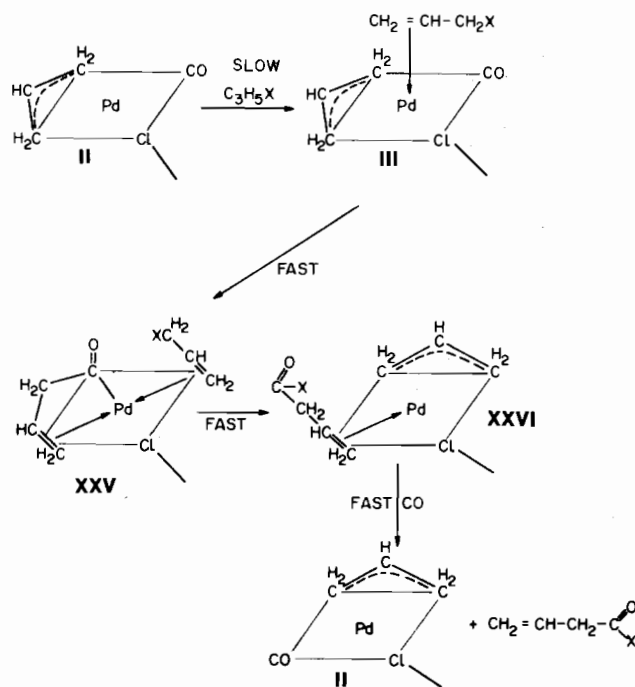


Figure 13. Mechanism of the carbonylation.

Insertion of carbon monoxide between the palladium atom and the π -allyl moiety gives **XXV**, in which for steric reasons the double bond has to be in the non-conjugated position, since otherwise coordination to the palladium atom is not possible. This species with a σ -bonded vinylacetyl group is not stable. While a new π -allyl group is formed and the coordinatively bonded vinylacetyl chloride is displaced by carbon monoxide the original species is restored (Figure 13). The latter is indicated by the results with methallyl chloride with C₃H₅PdCl as catalyst and with the results obtained in the synthesis of octadienoyl chloride. It is seen that the chlorine in the intermediate **XXVI** remains bonded to Pd, whereas X from allyl-X enters the final product. This may be the reason why the presence of halide in the system is essential. That the CO molecule enters *trans* to the substituent in the allyl group may be due to steric and polar effects, since the same is found with triphenylphosphine.²⁸

(28) F. A. Cotton *et al.*, *Inorg. Chem.*, 6, 179 (1967).