ORGANIC SYNTHESES BY MEANS OF NOBLE METAL COMPOUNDS—XLVI

CATALYTIC CARBONYLATION OF CONJUGATED DIENES

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Abstract—Palladium catalysed carbonylation in alcohol of butadiene, isoprene, piperylene and chloroprene has been studied. 3-Pentenoate was obtained from butadiene and similarly 4-methyl-3-pentenoate from isoprene, 2-methyl-3-pentenoate from piperylene and 4-chloro-3-pentenoate from chloroprene were obtained with high selectivity.

INTRODUCTION

In a previous paper of this series,[1] we reported the reaction of butadiene with carbon monoxide in the presence of a catalytic amount of palladium chloride in EtOH to form ethyl 3-pentenoate. In general,
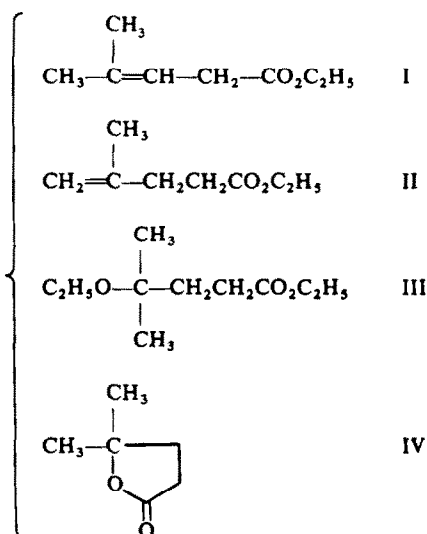
$$CH_2{=}CH\text{-}CH{=}CH_2 + CO + C_2H_5OH \xrightarrow{\ PdCl_2\ } CH_3\text{—}CH{=}CH\text{—}CH_2\text{—}CO_2C_2H_5$$
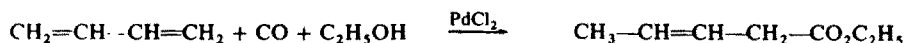
conjugated dienes react in a similar way to give β.γ-unsaturated esters. For example 1.3-cyclohexadiene gave 2-cyclohexenecarboxylate and 1.3-cyclooctadiene gave 2-cyclooctenecarboxylate.[2] However, in the carbonylation of an assymetric conjugated diene, the expected product is not single because CO attack may ocur at two positions. We have investigated such cases, and found 4-methyl-3-pentenoate[3] was formed from isoprene, 2-methyl-3-pentenoate[3] from piperylene and 4-chloro-3-pentenoate[4] from chloroprene almost selectively. In this paper we wish to report results of carbonylation of the conjugated dienes catalysed by Pd. After we have finished our work Brewis and Hughes[5] obtained similar results with isoprene and piperylene. Bordenca and Marsico[6] also reported the same reaction of piperylene.

RESULTS AND DISCUSSION

Carbonylation of isoprene. When isoprene was allowed to react with CO in EtOH at 100° in the presence of a catalytic amount of PdCl₂, ethyl 4-methyl-3-pentenoate (I) was produced as a main product, accompanied by ethyl 4-methyl-4-pentenoate (II), ethyl 4-ethoxy-4-methylvalerate (III) and γ.γ-dimethylbutyrolactone (IV). (Table 1). Ethyl 4-ethoxy-4-methylvalerate

$$CH_2{=}\overset{\overset{\displaystyle CH_3}{\displaystyle |}}{C}\text{—}CH{=}CH_2 + CO + C_2H_5OH \xrightarrow[100°]{PdCl_2}$$
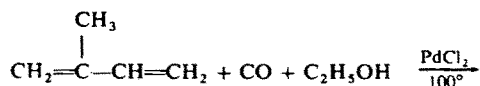
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$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CO_2C_2H_5 \quad \text{I}$$

$$CH_2=\underset{\underset{CH_3}{|}}{C}-CH_2CH_2CO_2C_2H_5 \quad \text{II}$$

$$C_2H_5O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_2CO_2C_2H_5 \quad \text{III}$$

$$CH_3-\underset{\underset{O}{|}}{\overset{\overset{CH_3}{|}}{C}}\quad \text{IV}$$

was undoubtedly formed by the addition of EtOH to either ethyl 4-ethyl-3-pentenoate or ethyl 4-methyl-4-pentenoate. The lactone can be derived from these unsaturated esters by the catalytic action of HCl generated during the reaction. All these products were formed by CO attack at the terminal carbon farther from the Me group. Under the present conditions. a negligible amount of 3-methyl-3-pentenoate was formed which Brewis and Hughes[5] claimed as a minor product.

When the reaction was carried out in MeOH. the corresponding Me esters and the same lactone were produced. These results are summarized in Table 1 together with those of piperylene and chloroprene.

Carbonylation of butadiene. The results obtained under various conditions are shown in Table 2. When butadiene was carbonylated by $PdCl_2$. 3-pentenoate was formed selectively. We investigated some other factors using this conjugated diene.

As shown in Table 2. $PdBr_2$ catalyzes the reaction in a similar way to $PdCl_2$. On the other hand. when PdI_2 was used as catalyst. considerable amounts of n-valerate. 2-methyl butyrate. γ-methyl butyrolactone and diesters were formed diminishing the selectivity of the reaction. Seemingly. formation of the saturated esters such as n-valerate and 2-methyl butyrate suggests the generation of $HPdI_2$ in the reaction system catalyzed by PdI_2. The diesters were formed by the further carbonylation of the unsaturated ester.

Pd on carbon or Pd acetylacetonate catalyzes the carbonylation reaction in the presence of HCl and are inactive in the absence of HCl. At higher HCl concentration selectivity of the reaction was no more observed.

Carbonylation of piperylene. When piperylene was carbonylated under the same conditions as isoprene. 2-methyl-3-pentenoate (V) was formed almost selectively.[3]
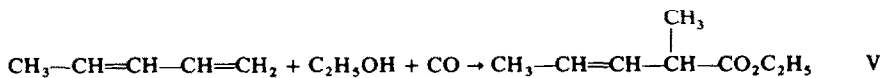
$$CH_3-CH=CH-CH=CH_2 + C_2H_5OH + CO \rightarrow CH_3-CH=CH-\underset{\underset{CH_3}{|}}{CH}-CO_2C_2H_5 \quad \text{V}$$

TABLE 1. REACTIONS OF ISOPRENE, PIPERYLENE AND CHLOROPRENE WITH CARBON MONOXIDE

Diene (ml)	Solv (ml)	PdCl$_2$ (g)	Reaction Temp	Time (hr)	Product Compn[b] (wt %)		Total Yield[c] (g)
Isoprene 20	Ethanol 30	1	100	24	I	82·4	21·1
					II	9·9	
					III	7·8	
					IV	trace	
Isoprene 20	Methanol 30	3	100	13	I'[d]	22·8	19·4
					II'[d]	4·8	
					III'[d]	59·5	
					IV	12·9	
Piperylene 20	Ethanol 30	1	100	26	V	84·0	14·2
					unidentified	16·0	
Chloroprene 20	Ethanol 30	3	110	15	VI-A	71·5	21·1
					VI-B	7·0	
					VII	6·7	
					VIII	7·6	
					high b.p. substances	7·3	

[a] Initial CO pressure; 100 kg/cm^2 at room temperature
[b] Estimated by gas chromatography
[c] Weight of the distilled mixture; no attempt was made to optimize the yield
[d] Me ester corresponding to I, II and III

Carbonylation of chloroprene. In a previous paper of this series.[7] it was reported that 3-butenoate is formed by the Pd catalyzed reaction of allyl halide with CO in EtOH. On the other hand it was reported by Tsutsumi *et al.* that the carbonylation of vinyl chloride by Pd gives acrylate and propionate.[8] We were interested in the carbonylation of chloroprene because it is not only a conjugated diene system but also a vinylic chloride. Therefore in this case. the addition of CO either to the conjugated diene or the substitution of the Cl with CO is expected.

Our experimental results have revealed that the main reaction is the additive carbonylation although the substitution reactions partially take place. When chloroprene was allowed to react with CO in EtOH at 100° in the presence of PdCl$_2$. the *cis* and *trans* forms of ethyl 4-chloro-3-pentenoate (VI) were obtained as main products (Table 1). *Cis* and *trans* isomers were separated by prep GLC. Their structures were assigned by comparing their NMR spectra with those of *cis* and *trans* 2-chloro-2-butenes.[9] In Table 3. A represents the isomer of smaller retention volume in gas chromatography (Silicone DC 550/C-22 or PEG 6000/C-22). and B the other. It is reasonable to assign that the isomer A is *trans* and isomer B is *cis* from the chemical shifts and coupling constants. The ratio of *cis/trans* is *ca* 1/10.

Apparently. 2-methyl-3-butenoate (VII) and tiglate (VIII) were formed by a mechanism different from the main reaction. The formation of the former is analogous to the production of propionate from vinyl chloride. the mechanism of which is unknown. The formation of tiglate is explained by the isomerization of 2-methyl-3-butenoate. Furthermore. a small amount of high boiling substances was produced.
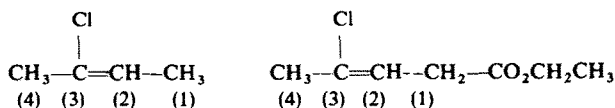
TABLE 2. CARBONYLATION OF BUTADIENE

Butadiene (g)	Solv (ml)		Cat (g)		Temp	Time (hr)	Conv (%)	Products Compn (%)				
								Ethyl 3-pentenoate	Ethyl 2-methyl-butyrate	Ethyl n-valerate	γ-Methyl-butyro-lactone	Diesters
13	EtOH	30	Pd/Cl$_2$	3	100	24	23·7	92·7	3·8	1·5	0	2·0
5·2	EtOH	12	PdBr$_2$	1·2	100	24	29·5	92·2	1·7	2·7	trace	3·4
5·2	EtOH	12	PdI$_2$	1·2	100	24	72·5	36·8	15·8	15·6	12·4	19·5
13	3%HCl/EtOH	30	Pd(acac)$_2$	1	100	24	16·0	97·8	2·2	trace	0	0
13	10%HCl/EtOH	30	Pd(acac)$_2$	1	100	24	29·9	90·2	3·1	3·0	0	3·7
13	30%HCl/EtOH	30	Pd(acac)$_2$	1	100	24	36·5	47·4	22·8	20·9	0·3	8·6
13	30%HCl/EtOH	30	10%Pd/C	5	100	5·5	19·7	24·4	35·9	25·0	trace	14·7
13	EtOH	30	PdCl$_2$	0·5	100	48	32·0	96·4	2·2	trace	trace	1·4
13	10%HCl/EtOH	30	PdCl$_2$	0·5	100	3·5	22·4	52·0	20·3	15·2	0·	12·4
13	30%HCl/EtOH	30	PdCl$_2$	0·5	50	3	21·4	28·5	29·1	29·6	0	12·9

* Initial carbon monoxide pressure: 100 kg/cm² at room temperature

TABLE 3. THE NMR SPECTRA OF THE ALKENYL CHLORIDES

Compound		1	τ 2	4	J_{12} (Hz)
3-Chloro-2-	cis	8·35	4·40	7·98	7·2
butene[9]	trans	8·30	4·53	7·93	6·7
Ethyl 4-chloro-	A	6·86	4·30	7·87	6·4
3-pentenoate	B	7·01	4·28	7·94	7·4

[a] The numbering system is as follows

$$\underset{(4)\ \ \ (3)\ \ \ (2)\ \ \ (1)}{\overset{\overset{\displaystyle Cl}{|}}{CH_3-C{=}CH-CH_3}} \qquad \underset{(4)\ \ \ (3)\ \ (2)\ \ \ (1)}{\overset{\overset{\displaystyle Cl}{|}}{CH_3-C{=}CH-CH_2-CO_2CH_2CH_3}}$$

However, their structures were not identified due to the difficulty of isolation. It is interesting that high polymer was not produced in spite of the high tendency of chloroprene to polymerize.

$$\underset{CH_2{=}\overset{\overset{\displaystyle Cl}{|}}{C}-CH{=}CH_2 + CO + C_2H_5OH \rightarrow}{}$$

VI-A

VI-B

VII

VIII

Higher Boiling Substances
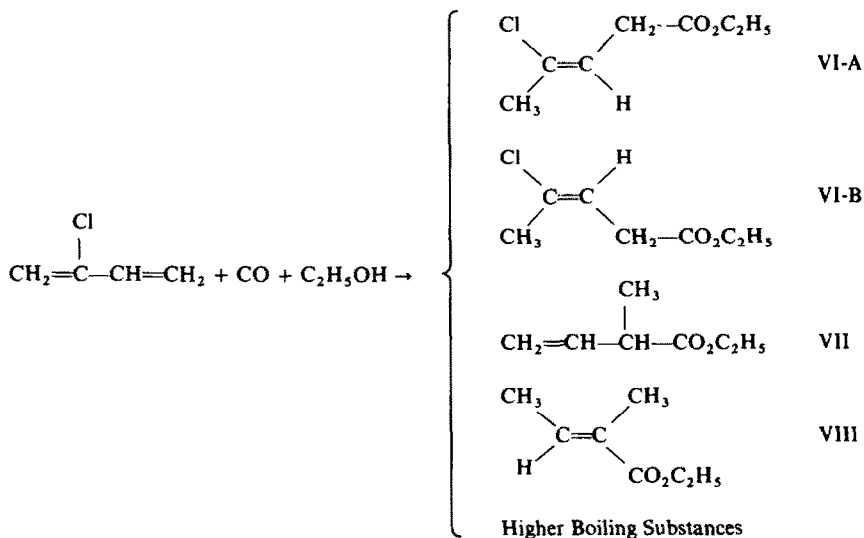
Reaction mechanism. The following mechanisms are tentatively proposed for the reactions. We already reported that **8** and **9** were formed by the reaction of the complex **2** with CO when R_1 was H or Me. and R_2 H.[10] In that case we assumed the reaction proceeds by the mechanism **2 → 5 → 7 → 8 + 9**. Further. it was confirmed that the complex **2** is formed by the direct reaction of isoprene with PdCl$_2$ in EtOH. Therefore the path through the carbonium ion **5** seems reasonable. In the catalytic carbonylation reactions. however. another reaction path **1 → 4 → 6 → 8** should be considered. Chatt and Shaw[11] reported the formation of HPdX(L)$_2$ in the presence of phosphine. The formation of HPdX$_2$ might be possible in our experiment even in the absence of phosphine. Further. **4** might be formed from **2** through **3**.

TABLE 4. THE NMR SPECTRA AND ANALYTICAL DATA

Compound	NMR	Splitting (Hz)[e]	Assignment	Found (Calcd) C(%)	H(%)	Cl(%)	M.W. Found[d] (Calcd)
CH₃ (4) │ CH₃-C=CH-CH₂CO₂CH₃ (3) (2) (1)	8·37, 8·27 7·08 4·77	s, s d (7·0) t (7·0)[b]	3, 4 1 2	—	—	—	128 (128)
CH₃ (4) │ CH₂=C-CH₂CH₂CO₂CH₃ (3) (2) (1)	8·27 7·67 5·31	s s s	4 1, 2 3	—	—	—	128 (128)
CH₃ (4) │ CH₃-C-CH₂CH₂CO₂CH₃ (3) (2) (1) OCH₃ (5)	8·89 8·13-8·44 7·60-7·94 6·90	s m[c] m[c] s	3, 4 2 1 5	59·71 (60·00)	10·02 (10·05)	—	162 (160·2)[c]
CH₃ (5) CH₃-CH=CH-CH-CO₂C₂H₅ (4) (3) (2) (1)	8·83 8·37 7·00 4·35-4·71	d (7·3) d (5·6) quin (7) m	5 4 1 2, 3				
(1) CH₂-CO₂C₂H₅ Cl C=C H CH₃ (2) (3)	7·87 6·86 4·30	s d (6·4) t (6·4)	3 1 1	51·55 (51·71)	6·83 (6·82)	21·50 (21·81)	162 (162)

Compound	NMR	Splitting (Hz)[a][b]	Assignment	C(%)	Found (Calcd) H(%)	Cl(%)	M.W. Found[d] (Calcd)
(structure **1**) Cl, CH₃, H, CH₂CO₂C₂H₅	7·94	s	3	51·68 (51·71)	6·83 (6·82)	20·80 (21·81)	162 (162)
	7·01	d (7·4)	1				
	4·28	t (7·4)	2				
(structure **5**) CH—CO₂C₂H₅, CH₃	8·78	d (6·8)	5	65·49 (65·59)	9·41 (9·44)	—	128 (128)
	6·90	quin (6·8)	1				
	4·95	d (9·6)	3				
	4·92	d (16·0)	4				
	4·13	m	2				

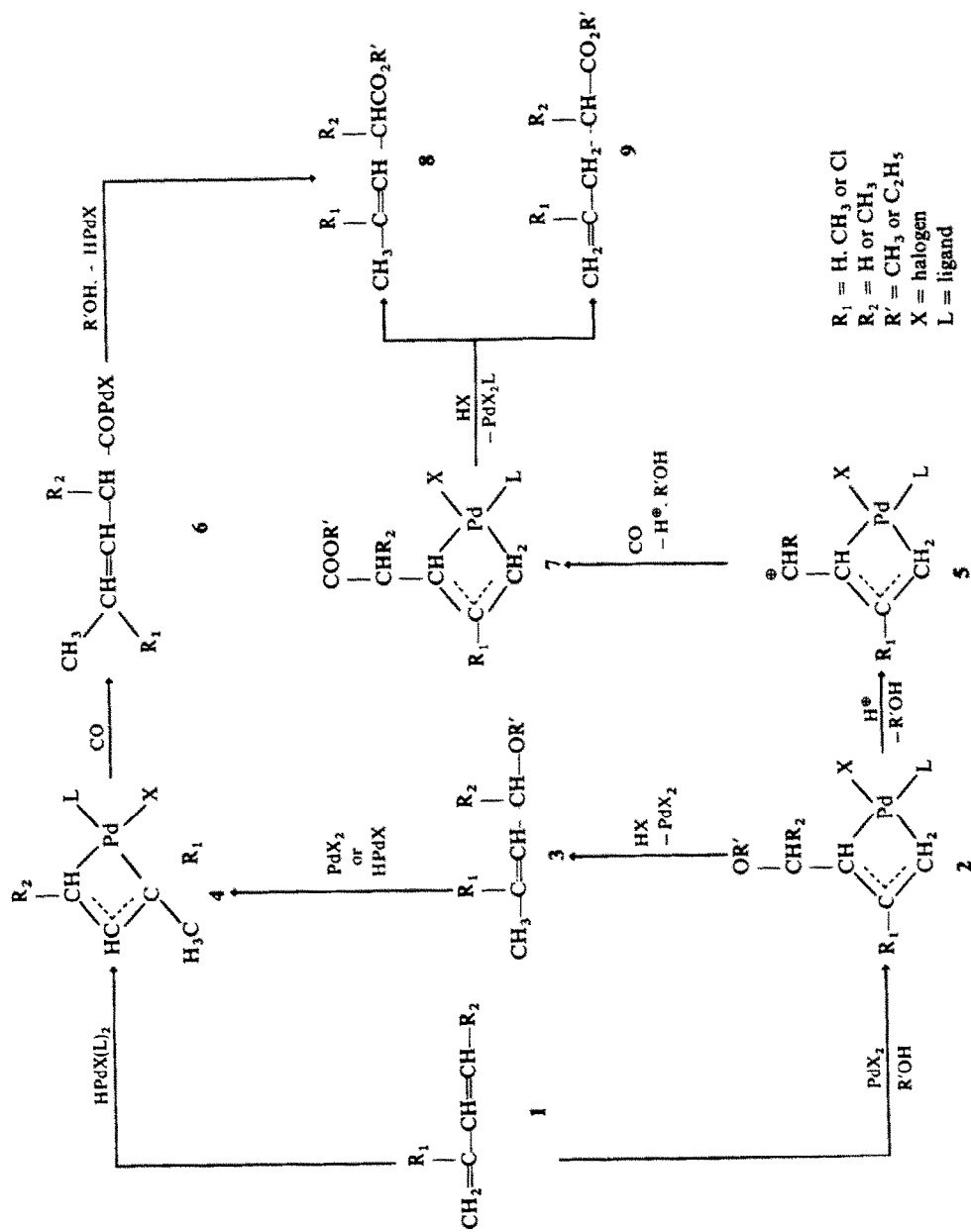[a] s : singlet; d : doublet; t : triplet; quin : quintet; m : multiplet
[b] The hyper-fine structure is observed
[c] Mirror image of each other
[d] Measured by mass spectrometry unless particularly noted
[e] Measured by Mechrolab

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Scheme a

$R_1 = H, CH_3$ or Cl
$R_2 = H$ or CH_3
$R = CH_3$ or C_2H_5
$X =$ halogen
$L =$ ligand

Although the intermediate **3** was not detected in the reaction of the acyclic conjugated dienes. the formation of 3-ethoxycyclooctene was confirmed in the carbonylation of 1.3-cyclooctadiene.[2] Thus three reaction routes seem possible. However. it is difficult to determine which is correct from the experimental results reported here.

EXPERIMENTAL

Butadiene. isoprene piperylene. and chloroprene are commercial products and were used without purification.

General procedure for reaction of the dienes with carbon monoxide. To avoid any effect of the metal surface of an autoclave (100 or 200 ml). the reactions were carried out in a glass vessel equipped with a gas inlet capillary. which was set in the autoclave. After reaction. precipitated Pd was separated by centrifugation or filtration. In all cases. the crude product was distilled after the usual work up. Further separation and purification of the distilled crude product was by prep GLC.

NMR spectra were determined with high resolution spectrometer models DP 60 or HR 100 using TMS as an internal standard. The peak positions are expressed in τ values. The MW's were determined in C_6H_6 using a Mechrolab or by mass spectrometry.

Gas chromatographic analyses were carried out using Silicone DC 550. polyethyleneglycol 6000 or Apiezon grease L as stationary phases. All boiling points were uncorrected.

The structure of the products were confirmed mainly by NMR spectra. elemental analyses and MW's. These data are summarized in Table 4 except those which were reported in the previous papers. Other additional data are described below.

Methyl 4-methyl-4-pentenoate (II'). The IR showed the presence of a terminal CH_2 (3085. 1655. 895 cm^{-1}). The structure was confirmed by comparing its NMR spectrum with that of ethyl 4-methyl-4-pentenoate reported previously.[7]

Ethyl 2-methyl-3-pentenoate (V). Ethyl 2-methyl valerate was obtained by hydrogenation with Pd/C. Acetaldehyde was obtained by ozonolysis and identified in the form of its 2.4-dinitrophenylhydrazone. m.p. 165°. Calcd for $C_8H_8N_4O_4$: C. 42·88; H. 3·53; N. 25·00. Found: C. 42·75; H. 3·85; N. 24·46%).

Ethyl 2-methyl-3-butenoate. The IR showed the presence of $CH_2\!\!=\!\!CH\!-\!$ group (3080. 1640. 995. 920 cm^{-1}). Confirmation was by NMR.

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