Organic and Biological Chemistry

Organic Syntheses by Means of Noble Metal Compounds. XIII.[1] Carbonylation of Butadiene– and Isoprene–Palladium Chloride Complexes

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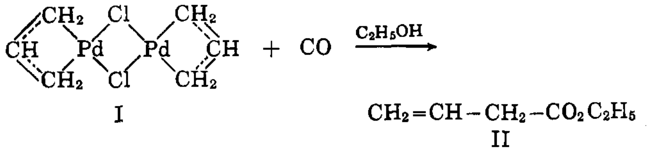
Carbonylation of butadiene– and isoprene–palladium chloride complexes has been studied. It was found that there are two sites of carbon monoxide attack in the complexes, giving different unsaturated carboxylic acid derivatives depending on reaction conditions. The mechanism of the reaction is discussed.

Introduction

In a previous paper of this series,[2] we reported the reaction of π-allylpalladium chloride (I) with carbon monoxide in ethanol to form ethyl 3-butenoate (II). The reaction was assumed to proceed through the formation of acylpalladium dicarbonyl chloride, by analogy with carbonylations catalyzed by nickel carbonyl.[3]

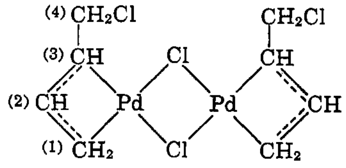

I

$CH_2{=}CH-CH_2-CO_2C_2H_5$

II

Butadiene is known to form a well-characterized complex III with palladium chloride. The complex III is a chloromethyl-substituted π-allylpalladium chloride,[4] and a reaction similar to that of π-allylpalladium chloride with carbon monoxide attacking at C-1 is expected. In addition, the chlorine of the complex III is known to be quite reactive and can be replaced easily with a nucleophilic reagent such as an alkoxy radical through a carbonium ion intermediate.[5] It is expected, therefore, that carbon monoxide as a nucleophilic reagent can replace the chlorine at C-4. Because of these two possible sites of carbon monoxide attack, carbonylation of the diene complex seemed interesting for mechanistic studies of carbonylation of dienes catalyzed by palladium. A preliminary account of part of this work has already been given.[6]

$CH_2{=}CH{-}CH{=}CH_2 + PdCl_2 \longrightarrow$

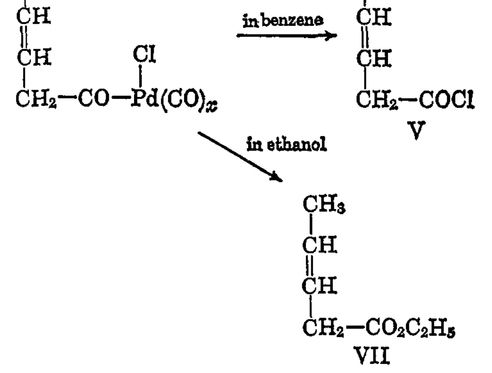

III

Results and Discussion

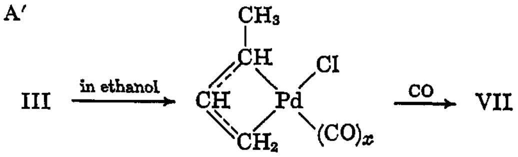
The butadiene and isoprene complexes were carbonylated under various conditions to yield different products. The reaction conditions and products are summarized in Table I.

Carbonylation of the Butadiene Complex. μ,μ-Dichlorobis(4-chloro-2-butenyl)dipalladium (III), prepared from butadiene and palladium chloride–benzonitrile complex,[7] gave 1,4-dichloro-2-butene (IV) and 5-chloro-3-pentenoyl chloride (V) in a ratio of 3:2 when treated with carbon monoxide at room temperature in

Path A


VI IV V VII

Path A′



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[1] Part XII: J. Tsuji and H. Takahashi, *J. Am. Chem. Soc.*, 87, 3275 (1965).

[2] J. Tsuji, J. Kiji, S. Imamura, and M. Morikawa, *ibid.*, 86, 4350 (1964).

[3] R. F. Heck, *ibid.*, 85, 2013 (1963).

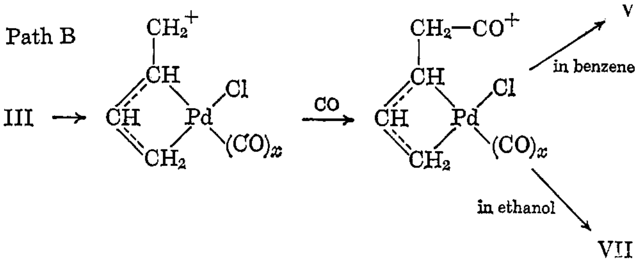
[4] B. L. Shaw, *Chem. Ind.* (London), 1190 (1962).

[5] S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 4806 (1963).

[6] J. Tsuji, J. Kiji, and S. Hosaka, *Tetrahedron Letters*, 605 (1964).

[7] P. E. Slade and H. B. Jonassen, *J. Am. Chem. Soc.*, 79, 1277 (1957).

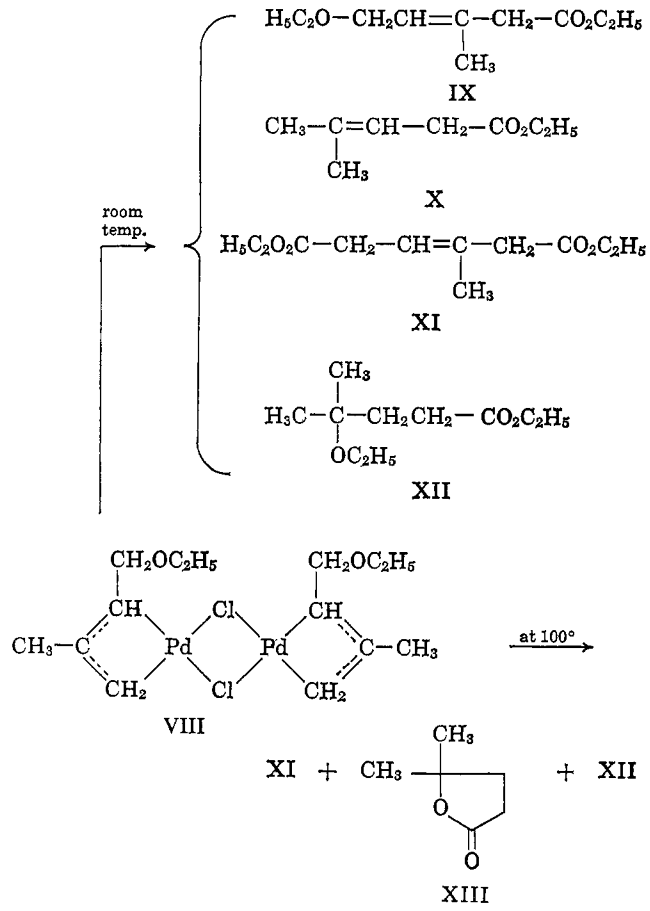
benzene. The first step of the reaction seems to be the coordination of carbon monoxide on palladium to form π-allylpalladium carbonyl chloride (VI). Then the coordinated chlorine and carbon monoxide competitively attack C-1 to give IV and V, respectively (path A). Thus, attack at C-1 seems to predominate under these conditions. At the same time, however, as another possibility, V can be formed by carbon monoxide attack at C-4 through a carbonium ion intermediate and chlorine attack at C-1 (path B).



When the reaction was carried out in ethanol at 70°, 1,4-dichloro-2-butene (IV) and ethyl 3-pentenoate (VII) were obtained in a ratio of 1:2. In addition, a small amount of higher boiling products was obtained. The amount of IV decreased when the reaction was carried out at higher temperature. VII is the product of carbonylation and hydrogenolysis. Hydrogenolysis is commonly observed in many cases of carbonylation carried out in ethanol catalyzed by palladium. It seems possible that VII is formed by carbon monoxide attack at C-1, followed by hydrogenolytic removal of the chlorine at C-4 (path A). Alternatively, VII could be formed by carbon monoxide attack at C-4, followed by hydrogenolysis at C-1 through the path B as shown above. It might be possible that the hydrogenolytic removal of the chlorine can proceed before carbonylation through path A′.

It is not easy to determine which is the true reaction path. This consideration leads us to undertake a more thorough study of the carbonylation of diene complexes. For this study, butadiene is not suitable because of its symmetry, and thus we selected μ,μ-dichlorobis(4-ethoxy-2-butenyl)dipalladium (VIII) derived from isoprene, which is unsymmetrical.

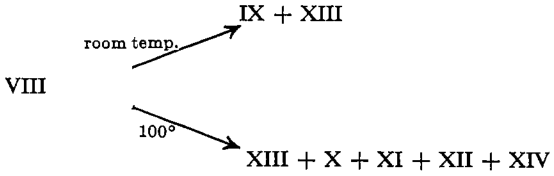
Carbonylation of the Isoprene Complex VIII in Benzene. C-1 and C-4 attacks of this complex should give different products. In this complex, the ethoxy group at C-4, like the chlorine of III, is known to split off easily to give a carbonium ion.[5] Actually, we have confirmed that there are two sites of carbon monoxide attack in this complex depending on the reaction conditions. When the reaction was carried out in benzene at room temperature, a mixture of acid chlorides and esters was obtained. The reaction mixture was treated with ethanol and distilled. Further purification of the distilled products was done by preparative gas chromatography. C-1 attack was found to be predominant and ethyl 5-ethoxy-3-methyl-3-pentenoate (IX) was obtained as a main product. The minor products were identified as ethyl 4-methyl-3-pentenoate (X), ethyl 3-methyl-3-hexenedioate (XI), and ethyl 4-ethoxy-4-methylvalerate (XII). These minor products are formed by C-4 attack. When the reaction temperature was raised to 100°, ethyl 3-methyl-3-hexenedioate (XI) was a main product, accompanied by γ,γ-dimethylbutyrolactone (XIII) and ethyl 4-ethoxy-4-methylvalerate (XII).

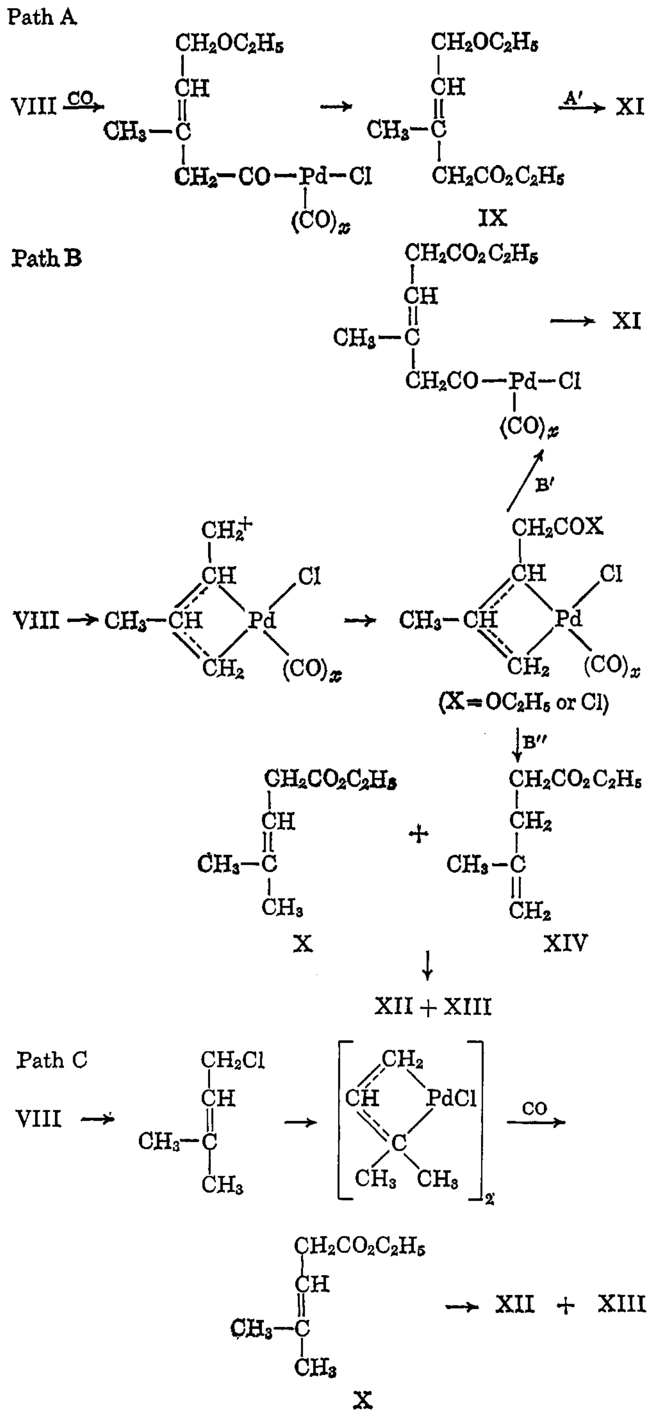


The diester XI can be formed by two reaction paths. In path A, which seems to be the most probable one, the first carbon monoxide attack forms ethyl 5-ethoxy-3-methyl-3-pentenoate (IX). The allylic ether bond of IX is then carbonylated to form XI. It is known that an allylic ether can be carbonylated in the presence of palladium chloride at higher temperature.[2] In path B–B′, carbon monoxide attacks the carbonium ion at C-4 and C-1 at the same time or separately to form XI. The present data do not appear to provide any basis for selecting between these two alternative possibilities.

It is not easy for path B and A′ to take place at room temperature. It became apparent that in benzene the main site of attack was C-1 to form IX (path A) in the reaction carried out at room temperature and that both C-1 and C-4 were attacked equally at higher temperatures.

Carbonylation of the Isoprene Complex in Ethanol. In ethanol, a different reaction was observed. Thus, at room temperature, the product from C-1 attack was predominant and ethyl 5-ethoxy-3-methyl-3-pentenoate (IX) was obtained as a main product, γ,γ-dimethylbutyrolactone (XIII) being a minor product. When the reaction temperature was raised to 100°, the latter was a main product. In addition, several products (X,

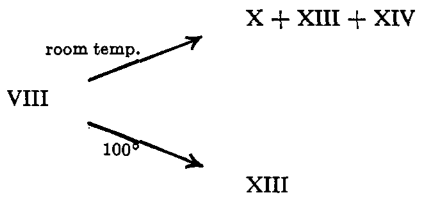




XI, XII, and XIV) formed by C-4 attack were obtained as minor products. Among these products, ethyl 4-methyl-3-pentenoate (X) is a normal product from C-4 attack and hydrogenolysis. Ethyl 4-methyl-4-pentenoate (XIV) is also a product from C-4 attack. These two esters can be formed through path B–B″ by hydrogenolysis at either C-1 or C-3. The lactone XIII, which is a main product at 100°, can be derived from these unsaturated esters by the catalytic action of hydrogen chloride generated during the reaction. The saturated ester XII was undoubtedly formed by the addition of ethanol to either X or XIV. The diester XI was formed by C-1 and C-4 attacks, probably through the reaction path B–B′ mentioned above. In this case, the attack of the second carbon monoxide (path B′) is competing with hydrogenolysis (path B″) to form X and XIV, and the yield of the diester XI is lower than that observed in benzene at 100°. Although the diester can be obtained by path B–B′, path A seems to be more important.

As another possibility, path C should be considered. In this path, the complex VIII is converted to 1,1-dimethyl-substituted π-allyl complex. The latter is then carbonylated to form X. By this path, however, the formation of XIV cannot be explained unequivocally. Interconversion of unsymmetrical π-allylic complex as shown in path C seems to be interesting and needs further elaboration.

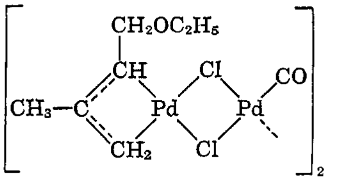
When hydrogen chloride was added to the reaction medium, exclusive attack at C-4 and hydrogenolysis were observed even at room temperature. Thus at room temperature two esters (X and XIV) and the lactone (XIII) were obtained. At 100°, the only product was the lactone (XIII). Thus we can say that,



under these conditions, path B–B″, or path C, is predominant to form the unsaturated esters (X and XIV), and the lactone (XIII) was formed from X and XIV in the presence of hydrogen chloride. It seems reasonable that the addition of hydrogen chloride and the higher temperature assist the formation of the carbonium ion at C-4, and the unsaturated esters (X and XIV) were formed.

From the experimental results mentioned above, we can conclude that the diene complex can be carbonylated at two sites, giving different products. Under the conditions favorable for carbonium ion formation, C-4 attack is preferred. Also it should be emphasized that these conditions favor hydrogenolysis and hence the extent of dicarbonylation decreases. These results give important information on the mechanism of carbonylation of dienes catalyzed by palladium, which will be described in a forthcoming paper.

When the reaction was carried out at room temperature in benzene or ethanol, a new yellowish complex was obtained which had a molecular formula of $C_7H_{13}OPd_2Cl_2CO$. The complex is insoluble in ordinary solvents and stable under dry conditions. The analytical data are in reasonable agreement with this formula despite the lack of any means of purification. Carbon monoxide was evolved when triphenylphosphine was added. We tentatively propose the following structure for the complex although it has an infrared absorption band at 1970 cm.$^{-1}$ instead of one below 1900 cm.$^{-1}$, which is assigned for a bridged carbonyl.



The n.m.r. spectrum of ethyl 4-methyl-4-pentenoate (XIV) needs comment (Figure 1). Assignment of the

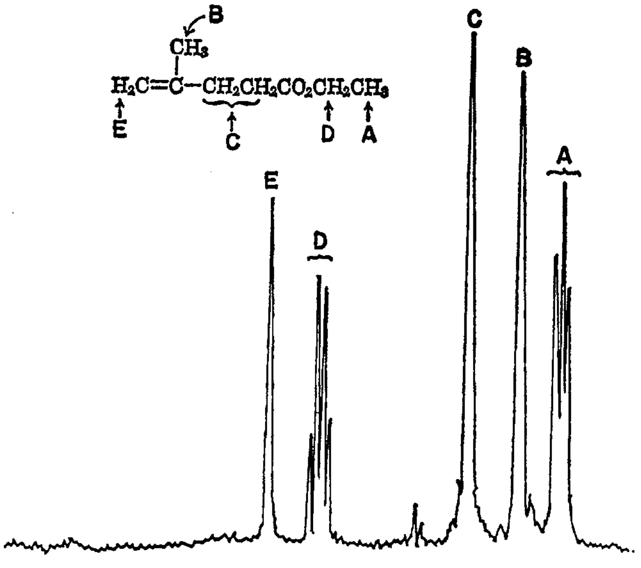


Figure 1. N.m.r. spectrum of ethyl 4-methyl-4-pentenoate (100 Mc.).

peaks shown in the figure is straightforward except for peak C. Interestingly, four protons at C-2 and C-3, although they are under different environments, showed one peak at τ 7.7 (4 H). This was rather surprising, and hence further confirmation of the structure of the ester was carried out as described in the Experimental section.

Experimental

The n.m.r. spectra were determined with high resolution spectrometer Models DP 60 and HR 100 using tetramethylsilane as an internal standard. Gas chromatographic analyses were carried out on a Silicone DC 550 column, 2 m. in length, at 180°. All boiling points are uncorrected.

Materials. Butadiene (99%) and isoprene (99%) are commercial products and were used without purification. μ,μ-Dichlorobis(4-chloro-2-butenyl)dipalladium was prepared by Slade's method.[7] μ,μ-Dichlorobis(4-ethoxy-2-methyl-2-butenyl)dipalladium was prepared by Robinson's method[5] and recrystallized from ethanol, m.p. 124–125°.

General Procedure for Reaction of the Complexes with Carbon Monoxide. The amounts of materials used and reaction conditions are summarized in Table I. To avoid an effect of the metal surface of the autoclave (200 ml.), the reactions were carried out in a glass vessel having a gas inlet capillary. The vessel was set in the autoclave. After the reaction, precipitated palladium was separated by centrifugation or filtration. When the reaction was carried out in benzene, the crude reaction product was boiled with ethanol. In all cases, the crude reaction product was separated by distillation after the usual work-up. In a few cases, the reaction was repeated twice and the products were combined before distillation. Further separation and purification of the distilled crude product were carried out by preparative gas chromatography.

Structural determination of all products is described below.

1,4-Dichloro-2-butene (IV). The product boiling at 90–95° (80 mm.) was brominated with bromine in carbon tetrachloride to give 2,3-dibromo-1,4-dichlorobutane; its melting point (96–97°) was undepressed with an authentic sample prepared by bromination of reagent grade 1,4-dichloro-2-butene.

Anal. Calcd. for $C_4H_6Cl_2$: C, 38.40; H, 4.80; Cl, 56.80. Found: C, 38.37; H, 4.81; Cl, 56.22.

Ethyl 5-Chloro-3-pentenoate. The crude ester boiling at 100–120° (50 mm.) and purified by preparative gas chromatography was converted to ethyl valerate by reduction with palladium on carbon and identified with an authentic sample by gas chromatography and the infrared spectrum.

Chloroacetaldehyde was obtained by ozonolysis and its 2,4-dinitrophenylhydrazone had m.p. 158–159°. Further confirmation was by the n.m.r. spectrum which showed peaks at τ 8.75 (triplet, CH_3), 6.95 (diffused doublet, CH_2CO–), 6.0 (doublet, $ClCH_2$), 5.80 (quartet, OCH_2), and 4.25 (multiplet, vinyl protons).

Anal. Calcd. for $C_6H_9O_2Cl$: C, 48.48; H, 6.06; Cl, 23.88. Found: C, 48.45; H, 6.03; Cl, 23.34.

Ethyl 3-Pentenoate (VII). Ethyl valerate was obtained by hydrogenation and identified with an authentic sample by infrared and n.m.r. spectra and gas chromatography. Acetaldehyde was obtained by ozonolysis and its 2,4-dinitrophenylhydrazone had m.p. 163–164°. The n.m.r. spectrum of the ester showed peaks at τ 8.76 (triplet, methyl protons), 8.31 (doublet, methyl protons), 7.06 (multiplet, CH_2CO), 5.87 (quartet, OCH_2), and 4.52 (multiplet, two vinyl protons).

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.66; H, 9.45.

Ethyl 5-Ethoxy-3-methyl-3-pentenoate (IX). Two isomers (A and B) were separated by preparative gas chromatography; they seem to be *cis* and *trans* isomers. Their n.m.r. spectra were similar but showed somewhat different τ-values as shown below; isomer A, 8.84 and 8.73 (overlapping triplets, methyl protons of the ethyl ester and ether), 8.26 (singlet, methyl protons), 7.02 (somewhat diffuse singlet, two protons, CH_2CO_2), 6.62 (quartet, two ether protons), 6.10 (doublet, two protons, $OCH_2C{=}$), 5.92 (quartet, two protons of the ethyl ester), and 4.56 (triplet, one vinyl proton); isomer B, 8.86, 8.76, 8.31, 7.10, 6.63, 6.08, 5.94, and 4.63.

Anal. Calcd. for $C_{10}H_{18}O_3$: mol. wt., 186. Found: mol. wt., 186 (mass spectroscopy, isomers A and B).

Ethyl 4-Methyl-3-pentenoate (X). Ethyl 4-methylvalerate was obtained by hydrogenation. Acetone was obtained by ozonolysis and identified in the form of its 2,4-dinitrophenylhydrazone, m.p. 126°.

Anal. Calcd. for $C_9H_{10}O_4N_4$: C, 45.39; H, 4.20; N, 23.50. Found: C, 45.42; H, 4.29; N, 23.35.

The n.m.r. spectrum showed peaks at 8.81 (triplet, methyl protons), 8.39 and 8.27 (singlets, two terminal methyls), 7.04 (doublet CH_2CO), 5.97 (quartet, OCH_2), and 4.75 (multiplet, $=CH$).

Ethyl 3-Methyl-3-hexenedioate (XI). Two isomers A and B (probably *cis* and *trans*) were obtained. Confirmation was by n.m.r. spectrum which showed peaks at (for isomer A) 8.76 (triplet, methyl protons of two ethyl ester groups), 8.19 (singlet, three methyl protons), 7.06–7.03 (overlapping singlet and doublet, four protons due to CCH_2CO_2 and $O_2CCH_2CH{=}$), 5.94 (quartet, protons of two ethyl ester groups), and 4.51 (triplet,

Table I. Reactions of Butadiene and Isoprene Complexes with Carbon Monoxide

Expt.[a]	Complex, g.	Solvent, ml.	Reaction		Product compn.,[b] %		Total yield,[c] g.
			Temp., °C.	Time, hr.			
1	12	Benzene, 60	18	22	IV V[d]	60 40	1.5
2	10	Ethanol, 40	70	17	IV VII	35 65	1.5
3	8	Benzene, 40	20	16	IX A A X XII XI A B	8.4 72.5 7.6 3.9 2.1 5.8	1
4	10	Ethanol, 40	18	18	IX A B XIII X	27 60 12.5 Trace	0.7
5	10	Ethanol, 30	100	24	XIII X XII XIV XI A B	58.4 14.1 8.8 2.5 5.9 10.3	2.5
6	10	10% HCl in ethanol, 40	27	15	X XIII XIV	49.5 36.1 14.4	3.5
7	8.2	10% HCl in ethanol, 30	100	18	XIII X	94 3.9	2.4
8	10	Benzene, 40	100	16	XI A B XIII XII X	33.3 50.2 13 3.4 Trace	3

[a] Runs 1 and 2, butadiene complex; runs 3–8, isoprene complex; initial carbon monoxide pressure, 100 kg./cm.^{2} at room temperature. [b] Estimated by gas chromatography. [c] Weights of distilled mixture; no attempt was made to optimize the yields. [d] Ethyl ester.

one vinyl proton); and (for isomer B) 8.75, 8.29, 7.06–7.02, 5.92, and 4.55.

Anal. Calcd. for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47; mol. wt., 214. Found (isomer A): C, 61.39; H, 8.47. Found (isomer B): C, 61.38; H, 8.51; mol. wt., 214 (mass spectroscopy).

Ethyl 4-Ethoxy-4-methylvalerate (XII). The structure was confirmed by its n.m.r. spectrum which showed peaks at 8.78–8.91 (multiplet, due to four kinds of methyls), 8.15–8.44 (multiplet, CCH_2C), 7.58–7.85 (multiplet, CH_2CO), 6.70 (quartet, OCH_2), and 5.95 (quartet, CO_2CH_2).

Anal. Calcd. for $C_{10}H_{20}O_3$: C, 63.79; H, 10.71. Found: C, 63.56; H, 10.63.

γ,γ-Dimethylbutyrolactone (XIII). An authentic sample was prepared by Arnold's method[8] and identified by n.m.r. and infrared spectra; infrared bands: 1760 cm.$^{-1}$ (five-membered lactone); n.m.r. spectrum: 8.64 (singlet, six methyl protons), 7.50 (triplet, $COCH_2$) and 7.99 (triplet, CH_2); mol. wt., 114 (mass spectroscopy).

Ethyl 4-Methyl-4-pentenoate (XIV). An infrared spectrum showed the presence of a terminal olefin (895 cm.$^{-1}$).

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.93; mol. wt., 142. Found: C, 67.21; H, 9.76; mol. wt., 142 (mass spectroscopy).

The ester was converted to ethyl 4-methylvalerate by hydrogenation and identified with an authentic sample. In addition, formaldehyde was obtained by ozonolysis and identified in the form of the 2,4-dinitrophenylhydrazone. An authentic sample was prepared by the method of Ritter and Kaniecki by reaction of methallyl chloride with ethyl acetoacetate, followed by deacetylation.[9] The authentic sample showed exactly the same n.m.r. and infrared spectra as those of the carbonylation product.

Isolation of the Complex $C_7H_{18}O\cdot Pd_2Cl_2CO$. After the reaction at room temperature, a yellowish complex, admixed with black metallic palladium, was obtained by filtration and washed with ethanol. Since the complex was insoluble in any organic solvents, separation of the complex from metallic palladium was done mechanically. Its infrared spectrum showed the strong absorption band at 1970 cm.$^{-1}$. The complex is stable under dry conditions at room temperature; after 2 weeks it showed the same infrared spectrum.

Anal. Calcd. for $C_7H_{18}O\cdot Pd_2Cl_2\cdot CO$: C, 22.59; H, 3.08; Cl, 16.68; Pd, 50.07. Found: C, 22.90; H, 3.07; Cl, 16.66; Pd, 50.0.

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(8) R. T. Arnold, J. S. Buckley, and J. Richter, *J. Am. Chem. Soc.*, **69**, 2322 (1947).

(9) J. J. Ritter and T. J. Kanieki, *J. Org. Chem.*, **27**, 622 (1962).