BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 1954—1958 (1968)

Organic Syntheses by Means of Noble Metal Compounds. XXXVII.[1] Carbonylation of Allene-Palladium Chloride Complexes

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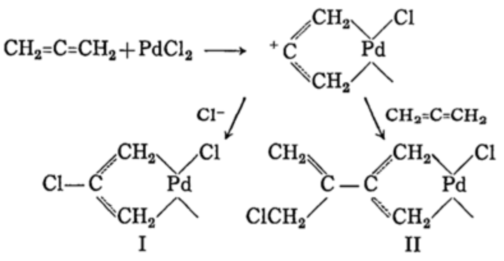
(Received February 22, 1968)

The reaction of allene with palladium chloride and a carboxylate anion gave di-μ-chloro-bis(2-acyloxy-π-allyl) dipalladium which was converted into an acetoacetate by carbonylation. Carbonylation of allene in ethanol in the presence of palladium chloride produced ethyl itaconate. The carbonylation of di-μ-chloro-bis(2-chloro-π-allyl) dipalladium in ethanol formed 3-chloro-3-butenoate. 4-Hydroxy-3,4-dimethyl-2-pentenoic acid γ-lactone, 3-isopropylideneglutarate and 3-(ethoxycarbonylmethyl)-4-methyl-3-hexenedioate were isolated by the carbonylation of di-μ-chloro-bis[2-(1-(chloromethyl)vinyl)-π-allyl] dipalladium. The mechanisms of these reactions are discussed.

Olefinic double bonds react with palladium chloride easily to form π-complexes or π-allyl complexes.[2] Of particular interest is the complex formation with dienes. Thus 1,3-butadiene reacts with palladium chloride to form 1-(chloromethyl)-π-allylpalladium chloride.[3] Allene is a 1,2-diene and its reaction with palladium chloride gives either complex I or II, depending on the reaction conditions.[4,5] The formation of the complexes I and II can be explained in the following way.



By the displacement of a chlorine atom of palladium chloride by one of the double bonds of allene, the center carbon atom of allene becomes cationic and a nucleophilic attack at this carbon is expected. When the displaced chloride anion attacks the carbon, the complex I is formed and this reaction proceeds in a benzene solution. In other words, this reaction is the insertion of the double bond of allene between the Pd–Cl bond. When the reaction is carried out in methanol, the cationic center is somewhat stabilized and another molecule of allene attacks the carbon to give the complex II. The consideration of this mechanism led us to expect that the attack of other nucleophiles at the center carbon of allene in the presence of palladium chloride should give π-allylic complexes substituted at the center carbon. From these considerations, the π-allylic complex formation from allene in the presence of a carboxylate anion and carbon monoxide was studied.

The carbonylation of π-allylic palladium complexes to form β,γ-unsaturated carboxylic acid derivatives is a well established reaction.[6,7] Therefore, it is expected that the carbonylation of the allene complexes should give 3-substituted 3-butenoic acid derivatives. A part of these studies has already been reported.[8]

Results

At first the reaction of allene with palladium chloride in the presence of carboxylate anions

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[1] Part XXXVI. H. Takahashi and J. Tsuji, *J. Am. Chem. Soc.*, **90**, 2387 (1968).

[2] E. O. Fischer and H. Werner, "Metal π-Complexes", Vol. 1, Elsevier Pub. Co., Amsterdam (1966).

[3] S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, **1963**, 4806; 1964, 5002.

[4] R. G. Schultz, *Tetrahedron Lettesrs*, **1964**, 301; *Tetrahedron*, **20**, 2809 (1964).

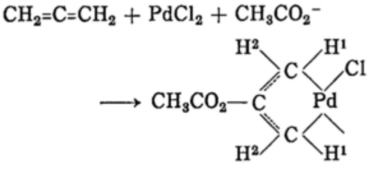
[5] M. S. Lupin and B. L. Shaw, *Tetrahedron Letters*, **1964**, 883; M. S. Lupin, J. Powell, and B. L. Shaw, *J. Chem. Soc.*, *A*, **1966**, 1687.

[6] J. Tsuji, J. Kiji and M. Morikawa, *Tetrahedron Letters*, **1963**, 1811; J. Tsuji, J. Kiji, S. Imamura, and M. Morikawa, *J. Am. Chem. Soc.*, **86**, 4359 (1964).

[7] W. T. Dent, R. Long and G. G. Whitfield, *J. Chem. Soc.*, **1964**, 1588.

[8] J. Tsuji and T. Susuki, *Tetrahedron Letters*, **1965**, 3027.

was studied. When allene was bubbled into acetic acid solution of sodium chloropalladate and sodium acetate, di-μ-chloro-bis(2-acetoxy-π-allyl) dipalladium (complex III) was isolated. Similarly, the reaction in propionic acid gave a propionyl substituted π-allyl complex. Although the reaction was carried out in protic solvents, a complex corresponding to II was not isolated.



III

The structure of the complex III was proved by its NMR spectrum (Fig. 1), which showed a pattern typical of π-allylpalladium chloride. In this spectrum, the peaks at τ 6.90 and 6.00 assignable to H^1 and H^2 appeared as doublets and their coupling constant ($J_{1,2}$) was found to be 2.4 cps. The coupling of H^1 and H^2 is not observed with most of π-allylic complexes and the only exception so far reported is the complex I, which has $J_{1,2}=2.0$.[5] Thus it seems likely that only the π-allyl complexes substituted with electronegative groups at the center carbon show the coupling of H^1 and H^2.

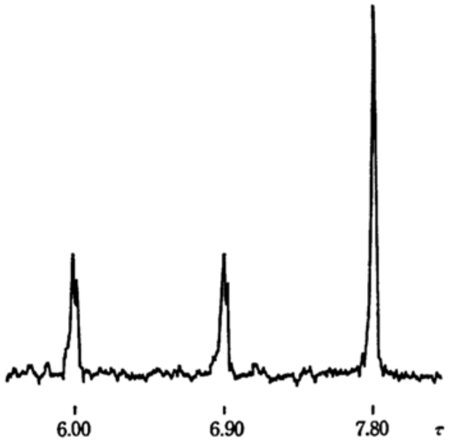
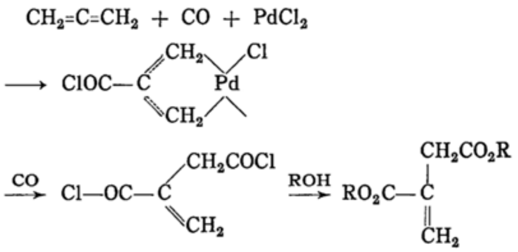
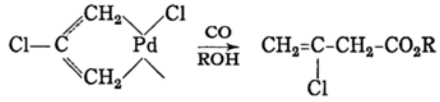


Fig. 1. NMR spectrum of di-μ-chloro-bi (2-acetoxy-π-allyl) dipalladium.

The attack of carbon monoxide on olefins coordinated to palladium to form acid derivatives is well known.[9] It is expected that the attack of carbon monoxide on the center carbon of allene should form a carbonyl substituted π-allyl complex which is further attacked by carbon monoxide to give itaconate as shown below. Based on this assumption, the reaction of allene, carbon monoxide and palladium chloride in ethanol was carried out, and actually itaconate was isolated, although the yield was poor.

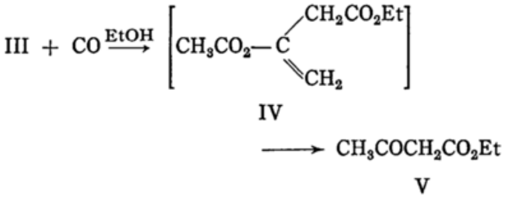


Then the carbonylation of the complexes I, II and III was studied. The product of the carbonylation of the complex I was 3-chloro-3-butenoate as expected.



I

The carbonylation of the complex III was carried out in benzene and the product was treated with ethanol. An ester was isolated by distillation and identified as ethyl acetoacetate (V), which was presumably formed by ethanolysis of ethyl 3-acetoxy-3-butenoate (IV) formed initially.



IV

V

Different from the complexes I and III, which gave 3-substituted 3-butenoates, the carbonylation of the complex II seems to be complicated. In addition to the π-allylic structure, this complex contains allylic chloride and conjugated diene structures, both of which are expected to be carbonylated. Actually the carbonylation of the complex II in ethanol produced three products, which were formed by the stepwise attack of one, two and three molecules of carbon monoxide. The first product was an unsaturated lactone (IR 1750 cm^{-1}) and identified as 4-hydroxy-3,4-dimethyl-2-pentenoic acid γ-lactone (VI) by

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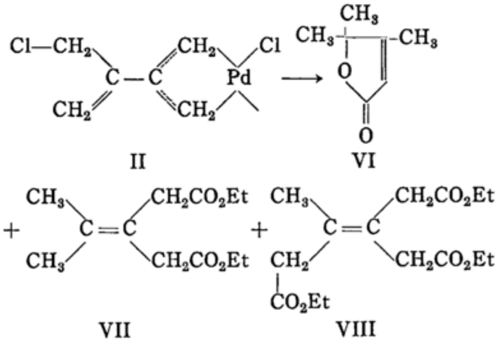
[9] J. Tsuji, M. Morikawa and J. Kiji, *J. Am. Chem. Soc.*, **86**, 4851 (1964).

NMR and IR spectra and mixed melting point measurement with an authentic sample.



The second one was an unsaturated diester. The NMR spectrum showed two singlets due to two methyl groups (6H at τ 8.26) and two methylene groups (4 H at τ 6.94). The ozonization, followed by the treatment with dinitrophenylhydrazine produced two hydrazones. They were the hydrazones of acetone and ethyl 3-oxoglutarate. From these evidences, the ester is determined as ethyl 3-isopropylideneglutarate (VII). The third, higher boiling fraction was a triester. The ozonization gave ethyl acetoacetate and ethyl 3-oxoglutarate, which suggests that the triester is ethyl 3-(ethoxycarbonylmethyl)-4-methyl-3-hexenedioate (VIII). The NMR spectrum supports the structure (Fig. 2).

The formation of these three esters can be explained by the following mechanism. At first carbon monoxide attacks the π-allylic system to form IX, which is converted into the lactone VI by double bond isomerization and hydrogenolysis of the chlorine as shown below. The intermediate lactone X is an allylic lactone and can react with palladium by oxidative addition to form another π-allylic complex XI. The carbonylation of this complex leads to the formation of a diester (XII), which gives VII by hydrogenolysis.

The intermediate diester XII has an allylic chloride structure and can be converted into another π-allylic complex XIII by the reaction with palladium. The carbonylation of this complex gives the triester VIII.

Experimental

Materials. Allene was purchased from the Matheson Co. It was distilled from a cylinder into a glass vessel and its volume was measured. Then it was redistilled into a stainless steel autoclave. The NMR specptra were determined with high resolution spectrometer, models DP 60 and HR 100, the peak positions are expressed in terms of τ values. The molecular weights were determined in benzene using a Mechrolab vapor pressure osmometer, or by mass spectrometer.

Formation of the Complex III. Sodium chloropalladate (9.0 g) and sodium acetate (2 g) were dissolved in acetic acid (220 m*l*) and allene was bubbled into the solution at room temperature with stirring. The deep brown solution turned gradually to pale brown, and the complex began to precipitate slowly. After one hour, the complex was collected by filtration (6.7 g) and recrystallized from a mixture of chloroform and methanol, mp 178.5—179.5°C (decomp).

Found; C, 24.96 ; H, 3.09 ; Cl, 15.15%, mol wt, 478.7. Calcd for $(C_5H_7O_2PdCl)_2$; C, 24.84 ; H, 2.90; Cl, 14.70%, mol wt, 481.8. NMR. Fig. 1.

By the similar procedure, the propionyl complex

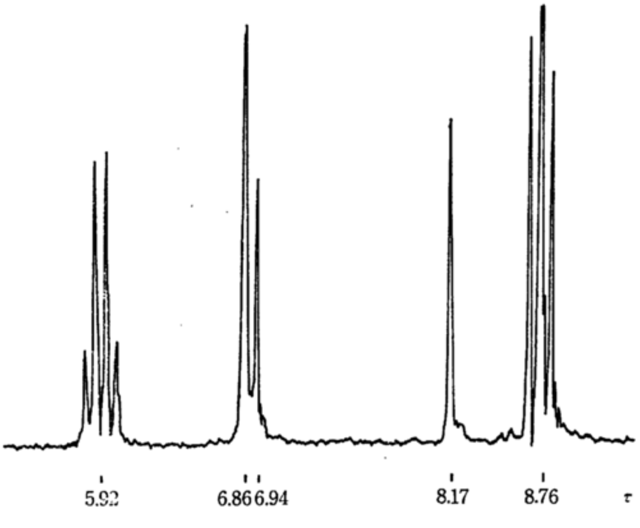
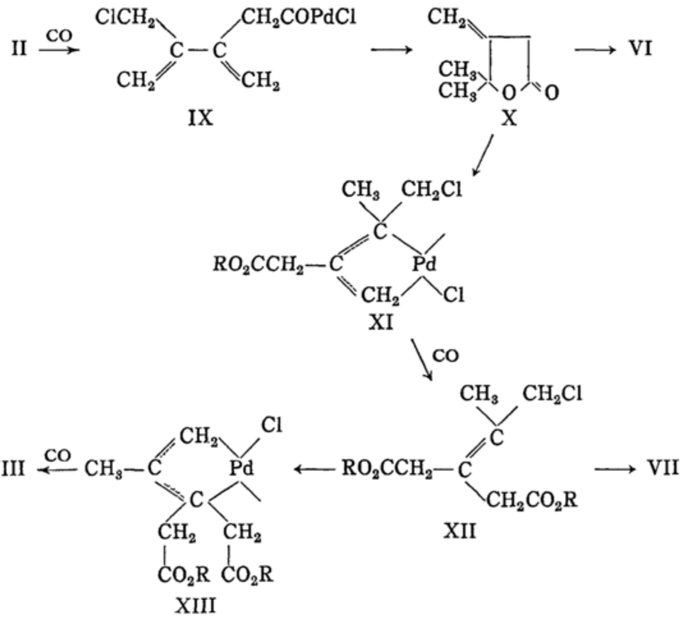


Fig. 2. NMR spectrum of ethyl 3-(ethoxycarbonylmethyl) 4-methyl-3-hexenedioate.



(3.9 g) was obtained from sodium chloropalladate (6.0 g) and sodium propionate in propionic acid (200 m*l*) and methanol (100 m*l*). The complex was recrystallized from chloroform-methanol mixture, mp 169—170°C (decomp).

Found: C, 28.30; H, 3.53; Cl, 14.38%, mol wt, 516. Calcd for $(C_6H_9O_2PdCl)_2$: C, 28.26; H, 3.56; Cl, 13.90%, mol wt, 510. NMR. 8.80 (triplet, CH_3-), 7.51 (quartet, -CH_2-CO-), 6.88, and 5.96 (doublets), $J_{1,2}=2.4$ cps.

Carbonylation of the Complex I. The complex I (9.5 g) in methanol (60 m*l*) was carbonylated at 100°C under carbon monoxide pressure (100 atm) for 15 hr. After the usual work-up, 4.0 g of the product was isolated by distillation at 145—146°C. It was identified as methyl 3-chloro-3-butenoate by the following evidences. IR, 1750 and 1640 cm^{-1}, NMR spectrum, 6.55 (-CH_2-), 6.11 (CH_3), 4.44 (=CH_2).

Found: C, 44.81; H, 5.31; Cl, 26.24%, mol wt, 134. Calcd for $C_5H_7O_2Cl$: C, 44.63; H, 5.24; Cl, 26.35%, mol wt, 134.5.

Carbonylation of the Complex III. The complex (2.5 g) and benzene (40 m*l*) were placed in a glass vessel with a gas inlet capillary, and then the vessel was placed in an autoclave. The carbonylation was carried out at 100°C under carbon monoxide pressure (100 atm) for 16 hr with shaking. The product was heated with 10 m*l* of ethanol and the solvents were removed by distillation. The residue was distilled under reduced pressure (50°C/14 mmHg) to give 0.3 g of the product, which was identified as ethyl acetoacetate by gas chromatography, IR spectrum and the mixed melting point determination of its dinitrophenylhydrazone (mp 95—96°C).

Carbonylation of Allene. Ethanol (50 m*l*) and palladium chloride (3 g) were placed in the glass vessel which was placed in the autoclave. Allene (10 m*l*) was distilled into the autoclave and then carbon monoxide was charged (100 atm). The autoclave was shaken at 150°C for 20 hr. The precipitated palladium was removed by filtration and ethanol was removed by distillaton. The residue was subjected to the distillation under reduced pressure (103°C/9 mmHg) to give 0.5 g of ethyl itaconate. The structure was determined by IR and NMR spectra. IR 1730, 1640 cm^{-1}, NMR 3.76, 4.35 (=CH_2), 5.85 (-CH_2-), 6.76(CH_2) 8.73 (CH_3).

Found: C, 58.32; H, 7.68%, mol wt, 189. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58%, mol wt, 186.2.

Carbonylation of the Complex II. The complex (10 g) was carbonylated in ethanol (60 m*l*) at 110°C under carbon monoxide pressure (110 atm) for 15 hr with shaking, and pressure drop of 13 atm was observed. After the usual work-up, the residue was distilled under reduced pressure to give the following two fractions. The first fraction (80—110°C/3 mmHg, 4.6 g) was found to be a mixture of two compounds and they were separated by preparative gas chromatography. One of them solidified on standing and was recrystallized from ether-hexane mixture, mp 43.5—45°C (reported mp 44.5—46.5°C[10]), yield 24.4%. This compound was identified as 4-hydroxy-3,4-dimethyl-2-pentenoic acid γ-lactone by the following evidence. IR, 1750, 1630 cm^{-1}, NMR 8.53(CH_3), 7.94(CH_3), 4.40 (=CH-).

Found: C, 66.54; H, 7.97%, mol wt, 130. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99%, mol wot, 126.

The compound was identified by the comparison with the authentic sample which was prepared by

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10) J. M. Stewart and D. W. Wooley, *J. Am. Chem. Soc.*, **81**, 4951 (1959).

11) S. G. Matsoyan, G. A. Chukhadzhyan and S. A. Vartanyan, *Zhur. Obshchei. Khim.*, **30**, 1202 (1960); *Chem. Abstr.*, **55**, 374 (1961).

the known method.[10,11] The other one was redistilled (132°C/10 mmHg, 20.2%) and found to be ethyl 3-isopropylideneglutarate by the following evidence. IR, 1740 cm^{-1} NMR, 8.75 (6H, -CH_3), 8.26 (6H, -CH_3), 6.94 (4H -CH_2-), 5.98 (4H, O-CH_2-).

Found : C, 63.01 ; H, 8.79%, mol wt, 220. Calcd for $C_{12}H_{20}O_4$: C, 63.13 ; H, 8.83%, mol wt, 228.

The ester was ozonized in ethyl acetate containing tetracyanoethylene and the ozonide was treated with dinitrophenylhydrazine. The hydrazone was separated by passing through a silica column using benzene as an eluate to give two hydrazones. One of them was recrystallized from ethanol and identified as the hydrazone of acetone, mp 125—126°C. The other was recrystallized from aqueous ethanol, mp 85—86 °C. The hydrazone was identified as that of ethyl 3-oxoglutarate by mixed melting point determination with an authentic sample.

Found: C, 47.20; H, 4.77; N, 14.64%. Calcd for $C_{15}H_{18}N_4O_8$: C, 47.12; H, 4.75; N, 14.66%.

The second fraction was redistilled (125—127°C/3 mmHg) to give 1.1 g of a triester which was identified as ethyl 3-(ethoxycarbonylmethy)-4-methyl-3-hexenedioate by the following evidences. IR, 1735 cm^{-1}, NMR (Fig. 2) 8.76 and 5.92 (3 ethyl groups), 8.17 (methyl), 6.94 and 6.86 (3 methylene groups).

Found : C, 59.84 ; H, 8.04%, mol wt, 306. Calcd for $C_{15}H_{24}O_6$: C, 59.98 ; H, 8.05%, mol wt, 300.

The ester was ozonized as before and the product was converted into dinitrophenylhydrazones, which were separated into two fractions by column chromatography through silica gel using benzene as an eluate. One of them was identified as the hydrazone of ethyl acetoacetate by IR and mixed melting determination (95—96°C) with an authentic sample.

Found : C, 46.51 ; H, 4.45 ; N, 18.07%. Calcd for $C_{12}H_{14}N_4O_6$: C, 46.45 ; H, 4.55 ; N, 18.06%.

The other hydrazone was identified as that of ethyl 3-oxoglutarate (mp 85—86°C).