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ORGANIC SYNTHESES BY MEANS OF NOBLE METAL COMPOUNDS*

V. REACTION OF BUTADIENEPALLADIUM CHLORIDE COMPLEX WITH CARBON MONOXIDE

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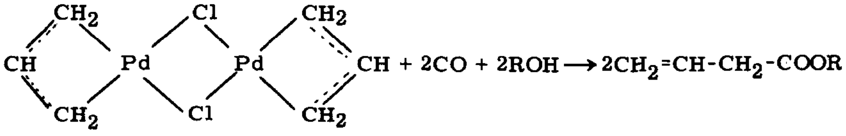
In a previous paper of this series,[1] we have reported the reaction of π-allylpalladium chloride complex (I) with carbon monoxide in ethanol to form ethyl vinylacetate (II) as shown below.



I II

The formation of β-chloroacyl chloride by the reaction of olefinpalladium chloride complex with carbon monoxide has also been reported.[2] As an another well characterized complex of palladium chloride with an unsaturated compound, butadienepalladium chloride complex is known, and the following structure (III) was proposed for the complex based mainly on NMR studies.[3] It is apparent that the structure of the butadiene complex (III) is in essence

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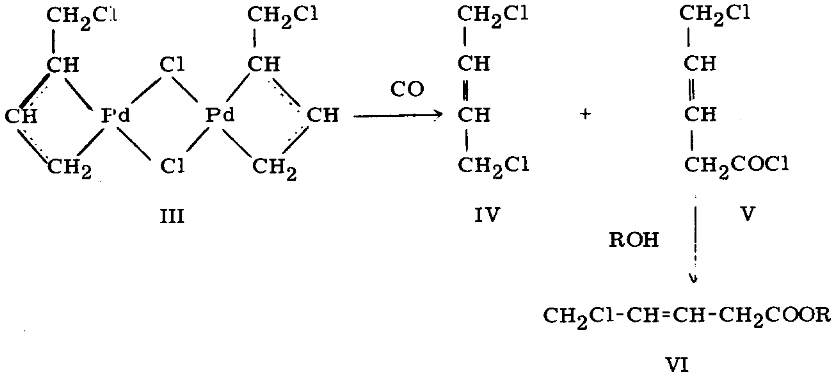
* Part IV. J. Tsuji, M. Morikawa and T. Nogi, Chem. Ind. in press (1964).

similar to that of π-allyl complex (I) in having chlorine bridged structure, and hence the same type of the reaction with carbon monoxide is expected for both of the complexes. In the present communication, we wish to report the reaction of the butadiene complex with carbon monoxide. Following reaction was confirmed to occur in benzene.



The reaction was carried out in the following way. The complex (III, 20 g.), suspended in benzene (100 ml.), was allowed to react in a stainless steel pressure reactor with carbon monoxide (50 kg./cm^2. pressure) at a room temperature for 10 hours. Crude benzene solution, separated from yellow precipitate of palladium by centrifugation, showed an IR band at 1800 cm^{-1} indicating that an acid chloride was formed. The solution was then refluxed with 10 ml. of methanol to convert the acid chloride into the corresponding methyl ester. After the usual work-up, two products (total yield 2.5 g., b.p. 90-95°/80 mm. and 100-120°/50 mm.) were obtained, and purified by preparative gas chromatography.

The lower boiling fraction was found to be 1,4-dichloro-2-butene (IV) from the following evidences. (Found : C, 38.37; H, 4.81; Cl, 56.22%. Calcd. for $C_4H_6Cl_2$: C, 38.40; H, 4.80; Cl, 56.80%.) Ozonization gave chloroacetaldehyde as a sole product identified as its 2, 4-dinitrophenylhydrazone (m. p. 158°, reported m. p. 155°[4], Found : C, 37.45; H, 2.75; N, 21.69%. Calcd. for $C_8H_7O_4N_4Cl$: C, 37.14; H, 2.71; N, 21.66%.) Bromination gave 2, 3-dibromo-1, 4-dichlorobutane (m. p. 97°). The structure of the higher boiling fraction was determined as methyl 5-chloro-3-pentenoate (VI) in the following way. (Found : C, 48.45; H, 6.03; Cl, 23.41%. Calcd. for $C_6H_9O_2Cl$; C, 48.48; H, 6.06; Cl, 23.88%) Ozonization gave chloroacetaldehyde; its 2, 4-dinitrophenylhydrazone being identified with that mentioned above. Absorbing 2 moles of hydrogen, the ester was converted into methyl valerate by hydrogenation. Further convincing evidence was obtained by NMR spectrum of the ethyl ester, which showed the following peaks; 5.96 τ (doublet, $ClCH_2$-), 4.20 τ (multiplet, -CH=CH-), 6.95 τ (doublet, $-CH_2COOR$), 5.88 and 8.76 τ ($-OCH_2CH_3$). The formation of these two products seems to be competitive and their relative ratio varied with the reaction conditions.

Concerning the reaction mechanism, the first step of this reaction seems to be the coordination of carbon monoxide on palladium, followed by the formation of acylpalladium complex by rearrangement. The acyl complex is finally decomposed into acyl chloride under high carbon monoxide pressure. The driving force of the reaction is the coordination of carbon monoxide on palladium either by the splitting of the chlorine bridge structure or the expansion of the coordination shell of palladium.

When the carbonylation of the complex was carried out in ethanol at 70°, 1, 4-dichloro-2-butene and ethyl 3-pentenoate were obtained. It was also found that ethyl 3-pentenoate was formed from butadiene in the presence of a catalytic amount of palladium chloride. Furthermore, it was confirmed that the catalytic reaction in ethanol can be carried out by the addition of metallic palladium such as palladium on carbon and a small amount of hydrogen chloride.

From these evidences and the result described in the previous paper[1] that ethyl vinylacetate is obtained by the carbonylation of allyl chloride in ethanol in the presence of metallic palladium, it is quite reasonable to assume that butadiene forms the complex with metallic palladium and hydrogen chloride as an intermediate for the carbonylation reaction. As an supporting evidence, although indirect, the formation of π-allylpalladium bromide complex from palladium black and allyl bromide reported by Fischer et al.[5] should be mentioned.

Thus, it can be said that this reaction chemically supports the correctness of the structure of the complex expressed by III.

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1. J. Tsuji, M. Morikawa and J. Kiji, Tetrahedron Letters No. 26, 1811 (1963).
2. J. Tsuji, J. Kiji and M. Morikawa, ibid. 1061.
3. B. L. Shaw, Chem. Ind. 1190 (1962).
4. C. C. Price, A. Pohland and B. H. Velzen, J. Org. Chem. **12** 308 (1947).
5. E. O. Fischer and G. Burger, Z. Naturforsch. **16** b, 702 (1961).