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ORGANIC SYNTHESES BY MEANS OF NOBLE METAL COMPOUNDS

III. REACTION OF π-ALLYLPALLADIUM CHLORIDE COMPLEX WITH CARBON MONOXIDE

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In the first paper of this series[1], the carboxylation reaction of olefin-palladium chloride complex to form β-chloroacyl chloride has been reported. In the present paper, we wish to report the formation of ethyl 3-butenoate by the reaction of π-allylpalladium chloride complex with carbon monoxide in ethanol. The π-allylpalladium chloride complex is unusally stable for organometallic halide, and its structure was fully established by several workers.[2,3]

The reaction of the complex with carbon monoxide was carried out in a stainless steel autoclave. To an ethanolic solution of the complex in the autoclave, carbon monoxide was charged up to the pressure of 100 kg/cm^2 and the reaction mixture was stirred at 70° for 5 hours, during that time gradual absorption of carbon monoxide was observed. After the

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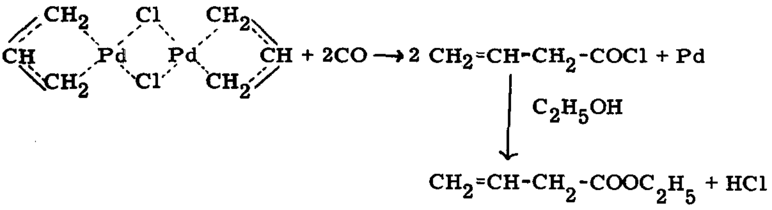
[1] J. Tsuji, M. Morikawa and J. Kiji, Tetrahedron Letters No. 16, 1061 (1963).

[2] R. Huttel, J. Kratzer and M. Bechter, Chem. Ber. 94, 766(1961).

[3] H. C. Dehm and J. C. W. Chien, J. Am. Chem. Soc. 82, 4429(1960).

usual work-up, ethyl 3-butenoate was obtained as a main product accompanied with a small amount of ethyl crotonate presumably formed by the rearrangement of the double bond by the catalytic action of hydrogen chloride generated during the reaction. The total yield of the both esters was 58%.



That the initial product of the carboxylation reaction is 3-butenoyl chloride was confirmed by carrying out the reaction in a benzene solution. The infrared absorption spectrum of the reaction mixture showed a strong carbonyl band at 1800 cm^{-1} due to 3-butenoyl chloride, identified by converting it to ethyl 3-butenoate.

Considering the fact that π-allylpalladium chloride complex is formed (65% yield) with violent heat evolution simply by mixing palladium chloride with excess allyl alcohol,[4] the carboxylation reaction was carried out without prior formation of the complex, and it was found that only catalytic amount of palladium chloride is necessary. Thus, ethanolic solution of allyl chloride or allyl alcohol(0.18 mole) was reacted with carbon monoxide (100 kg/cm^2) in the presence of a catalytic amount of palladium chloride (0.02 mole) at 120° for 10 hours. The yield of ethyl 3-butenoate based on

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[4] R. Huttel and J. Kratzer, <u>Angew. Chem.</u> <u>71</u>, 456(1959).

allyl chloride was 52% and 43.5% based on allyl alcohol. In these cases, ethyl crotonate and ethyl iso-butyrate were detected in the reaction mixture. The amount of these byproduct varies depending on the reaction conditions.

Interestingly, it was found that, not only palladium chloride, but also palladium metal itself is an active catalyst. Palladium on carbon or palladium metal obtained by the reduction of palladium chloride by any means can be used for the reaction, although its activity is somewhat lower than that of palladium chloride. In addition, platinum and rhodium compounds were found to be effective.

The same type of the reaction of allyl chloride by using nickel carbonyl as catalyst has been extensively studied by Chiusoli et al.,[5] and its reaction mechanism has been discussed by Heck.[6] Although palladium carbonyl complex corresponding to butenoylnickel dicarbonyl chloride detected by Heck has not been definitely characterized, the palladium carbonyl complex formed from palladium metal may be an active catlyst. The catalytic activity of palladium metal for carboxylation of olefin[7] and acetylene[8] has been reported. Mechanistic studies of carboxylation reaction by palladium are in progress. The application of this reaction to the other type of allyl compounds will be given in detail in a forthcoming paper.

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5 G. P. Chiusoli and S. Merzoni, Z. Naturforsch. **17b**, 850(1962). and the references cited therein.

6 R. F. Heck, J. Am. Chem. Soc. **85**, 2014(1963).

7 J. Tsuji, M. Morikawa and J. Kiji, Tetrahedron Letters 1437 (1963).

8 G. Jacobsen and H. Spathe, Ger. Pat. 1, 138, 760, 1962; C.A. **58** 6699(1963).