Tetrahedron Letters No.49, pp. 4387-4388, 1965. Pergamon Press Ltd.
Printed in Great Britain.

ORGANIC SYNTHESES BY MEANS OF NOBLE METAL COMPOUNDS

XVII. REACTION OF π-ALLYLPALLADIUM CHLORIDE WITH NUCLEOPHILES[1]

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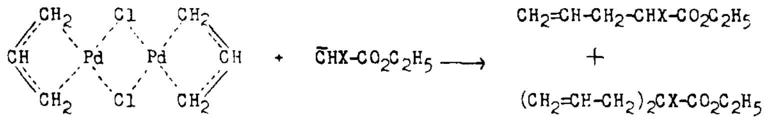
(Received 24 August 1965)

Reaction of olefin-palladium chloride complex with water to form a carbonyl compound is well known. By the elaborate work of Smidt et al. on the mechanism of the reaction, it was firmly established that the first step of the reaction is a nucleophilic attack of hydroxide ion to the complex.[2] Consideration of this reaction mechanism led us to the expectation that a carbanion can also attack various palladium chloride complexes, giving a new possibility of carbon-carbon bond formation. We have reported that cyclooctadiene-palladium chloride complex reacts with carbanions derived from ethyl malonate and acetoacetate.[3]

In this paper, we wish to report that π-allylpalladium chloride (I) reacts smoothly with ethyl malonate and acetoacetate as shown below.



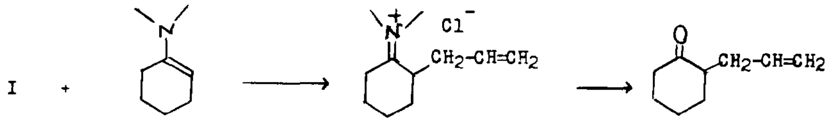
I

X= $CO_2C_2H_5$, $COCH_3$

The complex I(3.7 g.) was dissolved in a mixture of ethanol(10 ml.) and dimethyl sulfoxide(15 ml.). To the solution was added a solution of sodium

(0.5 g.) and ethyl malonate(3.6 g.) in ethanol(20 ml.) and dimethyl sulfoxide (20 ml.) at room temperature with stirring. Soon metallic palladium separated. After the usual work-up, ethyl allylmalonate(1.5 g.) and ethyl diallylmalonate (1.9 g.) were obtained.

As another nucleophile, an enamine was found to react with the complex. The complex(3.7 g.) was dissolved in a mixture of dimethyl sulfoxide(15 ml.) and ethanol(10 ml.). To the solution was added 1-morpholino-1-cyclohexene (3.5 g.) and the mixture was warmed on a steam bath with stirring. The reaction mixture was subjected to hydrolysis with hydrochloric acid. After the usual work-up, 1.1 g. of 2-allylcyclohexanone was obtained(m.p. of 2,4-dinitrophenylhydrazone, 143-144°, reported m.p. 144°.[4])



Thus it was established that the carbanions can attack the carbon atom of the palladium complex giving allyl derivatives in high yield. In contrast with these results, the reactions of acetate and alcoholate anions with the complex gave allyl acetate and ether in low yield. In the latter case, a main reaction path seemed to be the oxidation of alcohol into carbonyl compound.[5]

References

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