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ORGANIC SYNTHESES BY MEANS OF NOBLE METAL COMPOUNDS XVI[1].

CARBONYLATION OF ALLENE-PALLADIUM CHLORIDE COMPLEXES

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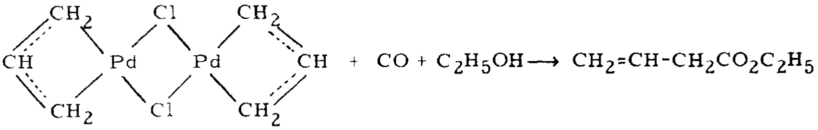
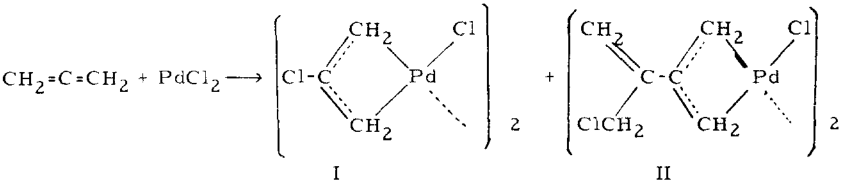
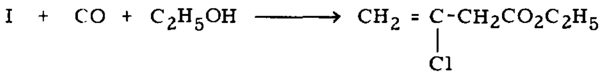
We have reported that π-allylpalladium chloride can be carbonylated in ethanol to form ethyl 3-butenoate[2].



Recently the preparation of palladium chloride complexes from allene was reported[3, 4]. These complexes (I and II) have π-allylic structures and it might be expected that the complexes can likewise be carbonylated to form β, γ -unsaturated esters.



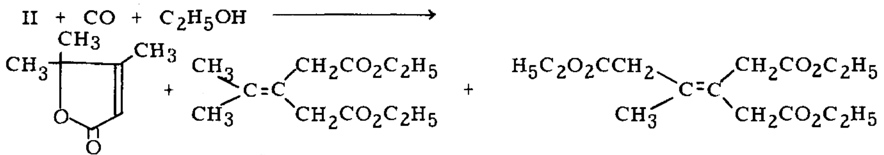
Actually ethyl 3-chloro-3-butenoate (III) was obtained by carbonylation of the complex I which is a chloro-substituted π-allylpalladium chloride.



$$\mathrm{I} + CO + C_2H_5OH \longrightarrow CH_2 = \underset{\displaystyle Cl}{C}\text{-}CH_2CO_2C_2H_5$$

III

The carbonylation of the complex II seemed to be interesting, since there existed several possibilities. The following three products, IV, V, and VI, were obtained as a result of mono-, di-, and tricarbonylations. In a typical example, 10g. of the complex II was mixed with ethanol (60 ml.) in a glass vessel equipped with a gas inlet capillary. The vessel was set in an autoclave and carbon monoxide was introduced (100 kg./cm^2.). The reaction was carried out at 110° for 15 hours. After the usual work-up, the products were separated and purified by preparative gas chromatography (yields ; IV, 24.4, V, 20.2, and VI, 9.5%).



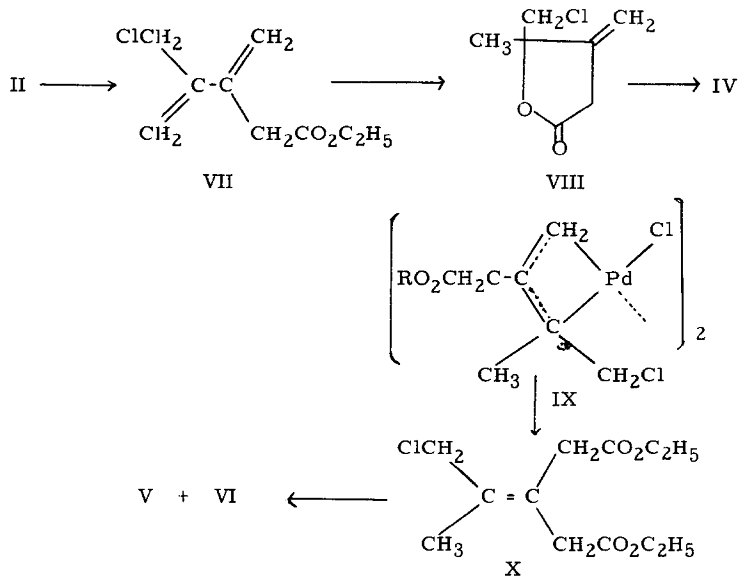
IV V VI

4-Hydroxy-3,4-dimethyl-2-pentenoic acid lactone (IV) was identified with an authentic sample prepared by the known method[5] by the IR and NMR spectra and mixed melting point determination (43.5 -45°). The structure of ethyl 3-isopropylideneglutarate (V) was derived from the NMR spectrum which showed the following peaks ; 8.75τ (triplet, 6 methyl protons), 8.26τ (singlet, 6 methyl protons), 6.94τ (singlet, 4 methylene protons), 5.98τ (quartet, 4 methylene protons). Further convincing evidence of V was obtained by ozonization. The ozonized product was treated with 2,4-dinitrophenylhydrazine and the 2,4-dinitrophenylhydrazones of acetone (m.p. 125 - 126°) and of ethyl 3-oxoglutarate (m.p. 85 - 86°, mixed m.p.

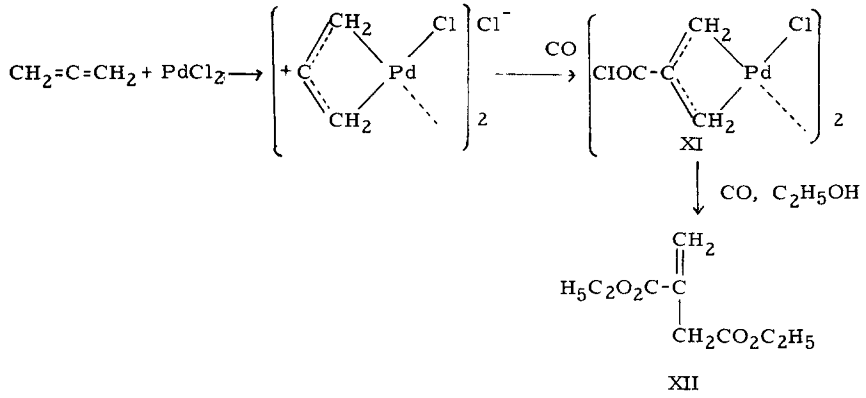
determination with an authentic sample) were obtained after chromatographic separation through a silica gel column. Ethyl 3-ethoxycarbonylmethyl-4-methyl-3-hexenedioate (VI, Anal. Found : C, 59.98, H, 8.05 ; Calcd. for $C_{15}H_{24}O_6$: C, 59.84, H, 8.04%.) showed the following NMR peaks ; 8.76τ (triplet 9 methyl protons), 8.17τ(singlet, 3 methyl protons), 6.94τ (singlet, 2 methylene protons), 6.86τ (singlet, 4 methylene protons), 5.92τ (quartet, 6 methylene protons). Ethyl acetoacetate (m.p. of 2,4-dinitrophenylhydrazone, 95 - 96°) and ethyl 3-oxoglutarate (m.p. of 2,4-dinitrophenylhydrazone, 85 - 86°) were obtained by ozonization, giving convincing support for the structure VI.

There are several possible mechanisms for the formation of these products, among which the most probable one seems to be the following. The first attack of carbon monoxide at π-allylic system of II undoubtedly forms ethyl 5-chloro-3,4-dimethylenepentanoate (VII). The conversion of VII into the unsaturated lactone (IV) by hydrogenolytic removal of chlorine and double bond migration under acidic aconditions is understandable.
A lactone (VIII), formed from VII, seems to be the possible intermediate of V and VI through an allylic complex IX. The lactone (VIII) is an allylic lactone and it can form the π-allylic complex (IX), which is then carbonylated to form X. Hydrogenolytic removal of chlorine of X produces V. X has an allylic chlorine which is susceptible to carbonylation. Thus the formation of VI from X is understandable.

The carbonylation of allene without prior formation of the complex was then carried out. According to the mechanism of the complex formation, the central carbon of allene becomes cationic. Under the usual conditions



of complex formation, the cation attracts chlorine to form the complex I. It was therefore expected that carbon monoxide might attack the cationic center when the complex formation was carried out under carbon monoxide pressure. This actually happened. Attack of carbon monoxide at the central carbon with formation of chloroformyl-substituted π-allylpalladium chloride (XI), was followed by carbonylation in the usual way to give ethyl itaconate (XII), which was thus isolated in low yield as the sole product.



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