

The Carbonylation of Dienes with Palladium Catalysts

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THE synthesis of $\beta\gamma$ -unsaturated esters from conjugated dienes, carbon monoxide, and alcohols using palladium complexes as catalysts was reported recently by us.¹ We now described the reactions of some non-conjugated dienes with carbon monoxide and methanol at 150° and 1000 atm. using 2% di-iodobis(tributylphosphine)-palladium(II) as catalyst.

The non-conjugated dienes reacted faster than the corresponding conjugated dienes to give unsaturated monoesters together with saturated diesters. For example cyclo-octa-1,5-diene gave methyl cyclo-oct-4-ene-1-carboxylate (I) in 45% yield* and the saturated dicarboxylic esters (II) in 30% yield whereas, in a comparable experiment, cyclo-octa-1,3-diene gave methyl cyclo-oct-2-ene-1-carboxylate in 14% yield and diesters in 3% yield. A detailed study of the change in product distribution during the carbonylation of cyclo-octa-1,5-diene showed that the diesters were

formed in a stepwise manner. As the reaction proceeded the concentration of the unsaturated monoester (I) increased rapidly to a maximum, and then gradually decreased as the concentration of diesters (II) increased.

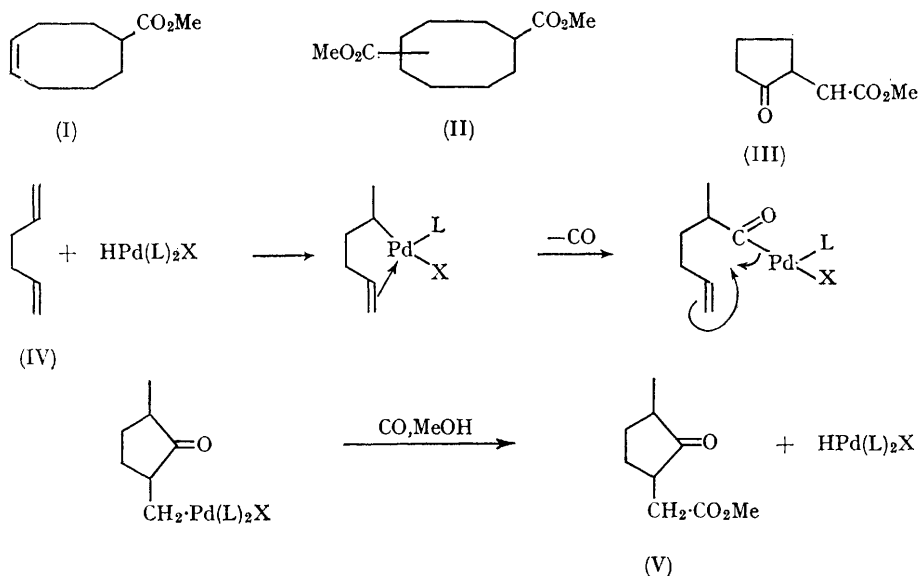
$\alpha\omega$ -Dienes gave unsaturated monoesters and saturated diesters, but in some cases unexpected cyclic products also were obtained. Butadiene gave methyl pent-3-enoate and no cyclic product, but penta-1,4-diene formed a cyclic γ -keto-ester (III) in 5–10% yield as well as the expected ester products. Hexa-1,5-diene produced the cyclic γ -keto-ester (V) in 40–50% yield, whereas hepta-1,6-diene afforded only traces of ketonic products. We suggest that this unusual cyclisation reaction proceeds through the mechanism shown for hexa-1,5-diene (IV \rightarrow V). A study of the product distribution during the carbonylation of hexa-1,5-diene demonstrated that the keto-ester (V) was formed from the diene without the

* All yields are based on the diene charged to the reaction mixture.

¹ S. Brewis and P. R. Hughes, *Chem. Comm.*, 1965, 157.

formation of an intermediate organic product, in contrast with the carbonylation of cyclo-octa-1,5-diene described above, and this observation is consistent with the proposed mechanism. The

of acids enhances the rate of reaction whereas bases, such as sodium acetate, reduce the rate. The reactions described in this and the previous communication¹ may be carried out adequately



products mentioned in this communication were identified by comparison with authentic synthetic samples.

It was observed that the rate of the palladium-catalysed carbonylation reactions depends on the acidity of the reaction medium; thus the presence

at 250 atm., instead of 1000 atm., by using toluene-*p*-sulphonic acid in addition to the palladium catalysts. The lower reaction pressure should enhance the synthetic utility of these carbonylation reactions.

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