

The Carbonylation of Dienes with Palladium Catalysts

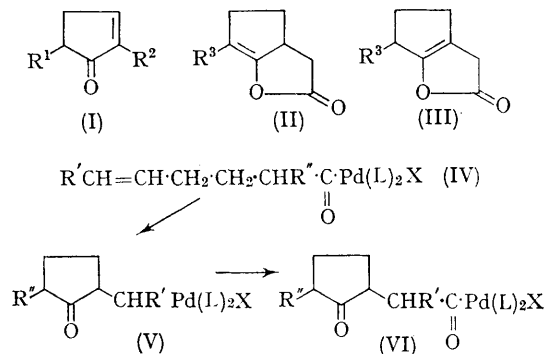
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SYNTHESES of unsaturated esters, saturated diesters, and cyclic- γ -keto-esters from dienes, carbon monoxide, and alcohols using palladium complexes as catalysts have been described recently.^{1,2} It has also been shown that cyclo-octa-1,5-diene reacts with carbon monoxide in the presence of palladium complexes to give bicyclo[3,3,1]non-2-en-9-one.³ We now report the reactions of $\alpha\omega$ -dienes with carbon monoxide at 200° and 1000 atm. over 2 hr. using a 2% solution of di-iodobis(tributylphosphine)palladium(II) in tetrahydrofuran as catalyst.

Penta-1,4-diene gave 2-methylcyclopent-2-enone (I; R¹ = H, R² = Me) and a mixture of enol-lactones (II and III; R³ = H) in an overall yield of less than 4%. Hexa-1,5-diene gave 2,5-dimethylcyclopent-2-enone (I; R¹ = R² = Me) in 6% yield and the enol-lactones (II and III; R³ = Me) in 10% yield. Hepta-1,6-diene afforded 5-ethyl-2-methylcyclopent-2-enone (I; R¹ = Et, R² = Me) and 2-ethyl-5-methylcyclopent-2-enone (I; R¹ = Me, R² = Et) in an overall yield of 16%. These products are probably obtained from hepta-1,5-diene formed by the isomerisation of hepta-1,6-diene. A mixture of enol-lactones was also obtained. Octa-1,7-diene did not react. The products were identified by elemental analysis, molecular weight determination, and n.m.r. and infrared spectra. The enol-lactones reacted with methanolic 2,4-dinitrophenylhydrazine to give the 2,4-dinitrophenylhydrazones of the corresponding methyl γ -ketoesters.³

This work demonstrates that palladium complexes will catalyse the addition of one or two molecules of carbon monoxide to 1,4- or 1,5-dienes. The addition of one molecule leads to unsaturated cyclic ketones, and the addition of two molecules leads to enol-lactones. Our studies suggest that the proposed rearrangement of the alkenoylpalladium intermediates (IV \rightarrow V)^{2,3} only occurs when the palladium acyl is an alk-5-enoylpalladium complex as in (IV). We propose that the unsaturated ketones are formed through the elimination of HPd(L)₂X from (V) followed by isomerisation of the unsaturated ketone, and that the enol-lactones are formed by the cleavage of the palladium acyl (VI) by the enol form of the neighbouring keto-group.



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

² S. Brewis and P. R. Hughes, *Chem. Comm.*, 1965, 489.

³ S. Brewis and P. R. Hughes, *Chem. Comm.*, 1966, 6.