The Transannular Addition of Carbon Monoxide to Cyclo-octa-1,5-diene

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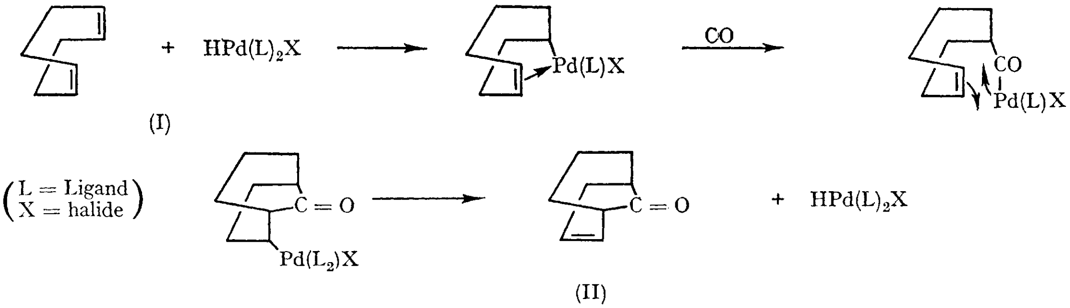
WE have recently reported the reactions of conjugated and non-conjugated dienes with carbon monoxide and alcohols in the presence of palladium catalysts such as di-iodobis(tributylphosphine)palladium(II).[1,2] Most dienes gave unsaturated monoesters and saturated diesters as products, but some αω-dienes, for example hexa-1,5-diene, also gave cyclic-γ-keto-esters in addition to the expected esters.[2]

During our studies we observed that palladium complexes will catalyse the transannular addition of carbon monoxide to cyclo-octa-1,5-diene.

Thus cyclo-octa-1,5-diene in tetrahydrofuran reacted with carbon monoxide at 150° and 1000 atm. in the presence of 1% di-iodobis(tributylphosphine) palladium(II) to give bicyclo[3,3,1]non-2-en-9-one (II) in 40—45% yield* after 8 hr., corresponding to approximately 100 moles of product per gram atom of palladium present. Cyclo-octa-1,3-diene was also obtained in 45—50% yield. We suggest that the ketone is formed by the mechanism outlined (I → II).



The ketone, a waxy solid m.p. 94—96°, analyses for $C_9H_{12}O$ and has a molecular weight of 136·0883 (theoretical 136·0888) as measured by mass spectrometry. The infrared spectrum shows the presence of a *cis*-double bond and a six-membered-ring carbonyl. The

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

ketone forms an orange 2,4-dinitrophenylhydrazone, m.p. 194—195·5°, and corresponds to the description given by Woodward and Foote[3] who synthesised the compound from a cyclohexanone-enamine and acraldehyde.

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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] C. S. Foote and R. B. Woodward, *Tetrahedron*, 1964, **20**, 687.