Conversion of Cyclo-octa-1,5-diene into 2,6-Diacetoxybicyclo[3,3,0]octane by Palladium(II) Chloride-Lead Tetra-Acetate in Acetic Acid; X-Ray Determination of the Structure of the Product

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Summary Oxidation of cyclo-octa-1,5-diene by $PdCl_2$ -Pb-(OAc)₄ in acetic acid gave as main product a 2,6-diacetoxybicyclo[3,3,0]octane which X-ray crystal analysis showed to be exclusively the di-*endo*-isomer.

PALLADIUM(II) salts alone in acetic acid oxidize monoolefins to vinyl or allylic acetates.¹ However, addition of certain oxidants to the reaction mixture changes the products to saturated diacetates.² We have now found that a mixture of PdCl₂ and Pb(OAc)₄ in HOAc converts cycloocta-1,5-diene into the 2,6-diacetoxybicyclo[3,3,0]octane. Further, only one of six possible isomers are formed.

Cyclo-octa-1,5-diene was treated for 24 h with catalytic amounts of $PdCl_2$ (0.04 mol. equiv.) in the presence of $Pb(OAc)_4$ (1 M) in acetic acid at 25°. The main product (ca. 70%) was a solid, m.p. 36°. Its n.m.r. spectrum was consistent with a bicyclic saturated diacetate. The ester was hydrolysed and the alcohol converted into its diphenylurethan derivative, m.p. 188°.† A crystal structure determination on the diphenylurethan derivative, C₂₂H₂₄N₂O₄, indicated the structure to be di-endo-2,6-diphenylurethancis-bicyclo[3,3,0]octane.

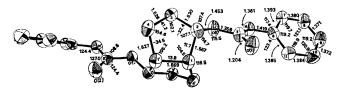
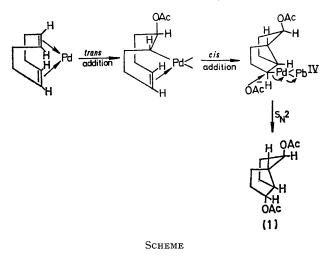


FIGURE. A view of the di-endo-2,6-diphenylurethan-cis-bicyclo-[3,3,1]octane molecule. The two-fold symmetry axis passes through the centre of the C(1)–C(1') bond. Bond lengths (mean $\sigma = 0.006$ Å), bond angles (mean $\sigma = 0.2^{\circ}$) are shown as well as torsion angles (°) within the five-membered ring.

A view of the molecule together with details of molecular geometry is shown in the Figure. The oxygen substituents on the bicyclo[3,3,0]octane ring are clearly endo, and there is marked puckering of the five-membered rings (see torsion angles in the Figure).

The crystals are orthorhombic, space group F2dd (C¹⁹_{2v}); a = 5.289(7), b = 12.948(9), c = 55.15(4) Å; $D_m = 1.34$ g cm⁻³ consistent with Z = 8 (C₂₂H₂₄N₂O₄ molecules); in space group F2dd this demands that each molecule lie on a diad axis. Using $Cu-K_{\alpha}$ radiation 699 reflexions were measured with a Hilger and Watts Y-290 computer-controlled diffractometer by the θ -2 θ scan technique. The structure was solved from an analysis of the three-dimensional Patterson function and refined by full-matrix least-squares with anisotropic thermal parameters. The conventional R-factor is 3.3% for the 583 'observed' reflexions.

Three cis-isomers are possible. A reaction sequence for exclusive formation of one of these, compound (1), which is consistent with known Pd^{Π} chemistry is in the Scheme.



Thus, oxypalladation of cyclo-octa-1,5-diene has been shown to be *trans*³ while the insertion of PdIL-C across double bonds has been shown to be cis.4 Finally, stereochemical studies with $[3,3,6,6-^{2}H_{4}]$ cyclohexene indicate that Pd^{II} is displaced in an $S_N 2$ fashion with inversion of configuration.⁵

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[†] Both the diacetate and diphenylurethan derivative gave satisfactory elemental analyses.

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