# 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; $\boldsymbol{X}$-Ray Determination of the Structure of the Product 

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Summary Oxidation of cyclo-octa-1,5-diene by $\mathrm{PdCl}_{2}-\mathrm{Pb}-$ ( 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 $\mathrm{PdCl}_{2}$ and $\mathrm{Pb}(\mathrm{OAc})_{4}$ in HOAc converts cyclo-octa-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 $\mathrm{PdCl}_{2}$ ( 0.04 mol . equiv.) in the presence of $\mathrm{Pb}(\mathrm{OAc})_{4}$ ( 1 m ) in acetic acid at $25^{\circ}$. The main product (ca. $70 \%$ ) was a solid, m.p. $36^{\circ}$. Its n.m.r. spectrum was consistent with a bicyclic saturated diacetate. The ester was hydrolysed and the alcohol converted into its diphenyl-
urethan derivative, m.p. $188^{\circ} . \dagger$ A crystal structure determination on the diphenylurethan derivative, $\mathrm{C}_{22} \mathrm{H}_{24} \mathrm{~N}_{2} \mathrm{O}_{4}$, indicated the structure to be di-endo-2,6-diphenylurethan-cis-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 $C(1)-C\left(1^{\prime}\right)$ bond. Bond lengths (mean $\sigma=0.006 \AA$ ), bond angles (mean $\sigma=0.2^{\circ}$ ) are shown as well as torsion angles $\left({ }^{\circ}\right)$ 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 ( $\mathrm{C}_{2 v}^{19}$ ); $a=5.289(7), b=12.948(9), c=55.15(4) \AA ; D_{\mathrm{m}}=1.34 \mathrm{~g}$ $\mathrm{cm}^{-3}$ consistent with $Z=8\left(\mathrm{C}_{22} \mathrm{H}_{24} \mathrm{~N}_{2} \mathrm{O}_{4}\right.$ molecules); in space group $F 2 d d$ this demands that each molecule lie on a diad axis. Using $\mathrm{Cu}-K_{\alpha}$ radiation 699 reflexions were measured with a Hilger and Watts Y-290 computer-controlled diffractometer by the $\theta-2 \theta$ 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 $\mathbf{3 . 3} \%$ for the 583 'observed' reflexions.

Three $c i s$-isomers are possible. A reaction sequence for exclusive formation of one of these, compound (1), which is consistent with known $\mathrm{Pd}{ }^{I I}$ chemistry is in the Scheme.


## Scheme

Thus, oxypalladation of cyclo-octa-1,5-diene has been shown to be trans ${ }^{3}$ while the insertion of PdILC across double bonds has been shown to be cis. ${ }^{4}$ Finally, stereochemical studies with $\left[3,3,6,6-{ }^{2} \mathrm{H}_{4}\right]$ cyclohexene indicate that $\mathrm{Pd}^{I I}$ is displaced in an $S_{\mathrm{N}} 2$ fashion with inversion of configuration. ${ }^{5}$
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$\dagger$ Both the diacetate and diphenylurethan derivative gave satisfactory elemental analyses.
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