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CONVERSION OF CYCLOOCTA-1,5-DIENE-PALLADIUM (II) CHLORIDE TO 6-EXO-CHLORO-2-ENDO-ACETOXYBICYCLO [3.3.0] OCTANE BY LEAD TETRAACETATE IN ACETIC ACID

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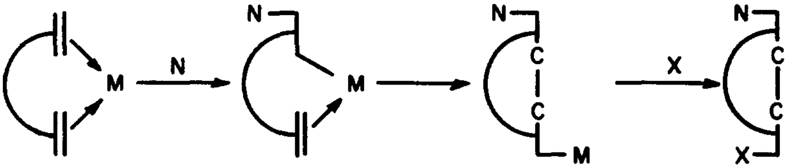
In connection with a general synthetic scheme where dienes are converted to carbocyclic compounds *via* transition metal-diene complexation as illustrated below, we examined an oxidative decomposition of 1,5-cyclooctadiene-$PdCl_2$ complex. It was recently reported that oxidation of 1,5-cyclooctadiene by $PdCl_2$-$Pb(OAc)_4$ in HOAc gave 2,6-diacetoxy bicyclo [3.3.0] octane (**4**), exclusively as the di-*endo* isomer.[1] The authors rationalized that the π-complex **1** formed under the reaction conditions, underwent *trans*-nucleophilic addition of acetate followed by *cis*-insertion of Pd(II) and another S_N2 substitution by acetate.



When the preformed 1,5-cyclooctadiene-$PdCl_2$ complex (**1**)[2] was treated with $Pb(OAc)_4$ in HOAc at r.t. for 20 hr, the major product isolated in 60% yield was not **4** but 6-*exo*-chloro-2-*endo*-acetoxy bicyclo [3.3.0] octane (**2**) [ir, 1725 cm^{-1}, nmr δ 1.2-2.1 (m, 8H), 2.14 (s, 3H), 2.9 (br. m, 2H), 4.2 (q, 1H), 5.4 (q, 1H), m/e 202, 187, 167, 159, 142]. The chloroacetate **2** was hydrolyzed (KOH/MeOH, r.t.) and oxidized (CrO_3/H_2SO_4-acetone) to give the chloro ketone **3** [ir, 1735 cm^{-1}, nmr δ 1.6-2.6 (m, 8H), 3.0 (m, 2H), 4.2 (m, 1H), Analysis found: C, 60.49, H, 6.89, Cl, 22.29. $C_8H_{11}OCl$ requires C, 60.57, H, 6.94, Cl 22.02%]

The nmr spectrum of **2** showed considerably smaller couplings for the carbinyl proton at δ 4.2 than the carbinyl H at δ 5.4 suggesting that the Cl substituent has the *exo* stereochemistry. Definitive evidence for the structure **2** was obtained by its smooth conversion to the known **4** with AgOAc in refluxing HOAc.

When 1,5-cyclooctadiene was treated with $PdCl_2$-$Pb(OAc)_4$ as reported[1], the presence of **2** in *ca* 10% yield could be detected. These results seem to suggest that σ-bonded complex **5** rather than π-complex **1** was formed as the major intermediate in the $PdCl_2$-$Pb(OAc)_4$ conditions, and that *cis*-intramolecular ligand transfer from the metal to the olefin carbon is considerably faster than the well-established addition of nucleophile to olefin-Pd (II) complex[3,4] under these conditions.

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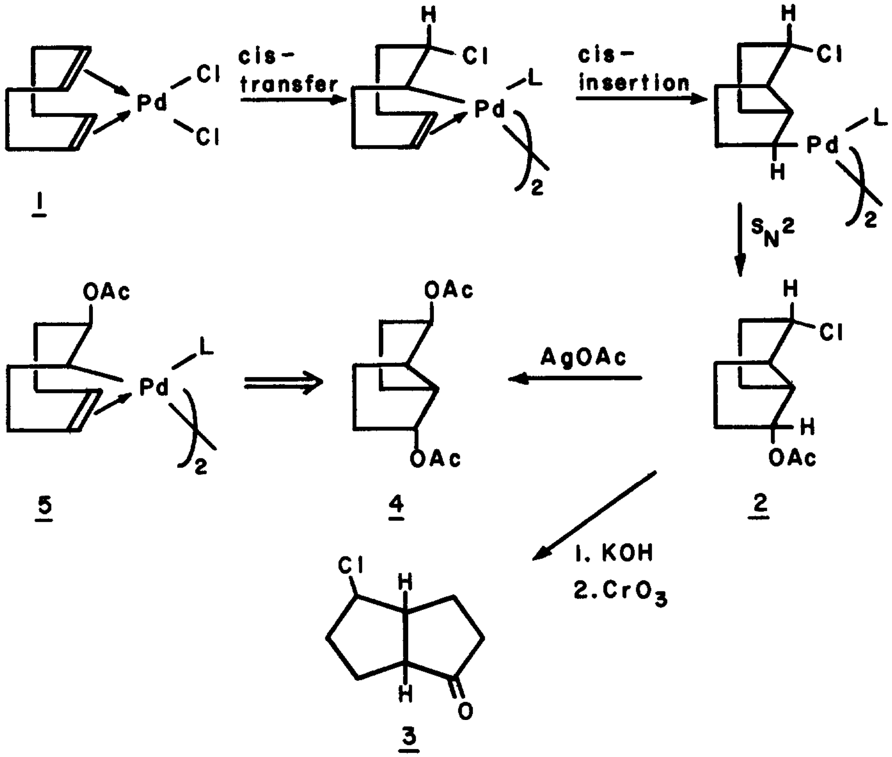

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