Mechanism of the Cope Rearrangement of Acyclic 1,5-Dienes and of the Wacker Oxidation of Alk-1-enes catalysed by Palladium Complexes

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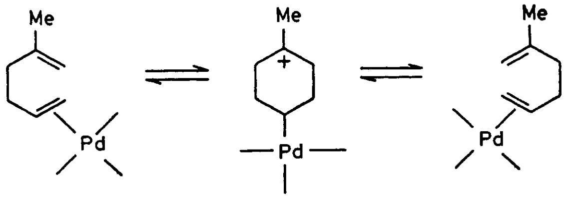
Summary Hexa-1,5-diene is catalytically converted into acetone in an aqueous solution of $(PhCN)_2PdCl_2$, $CuCl_2$, and CuCl at 60 °C in the presence of oxygen, thereby revealing a hitherto unsuspected role of η^3-allylic intermediates in both the Pd^{II}-catalysed Cope rearrangements of 1,5-dienes and the selective Wacker oxidation of propene and higher alk-1-enes to ketones.

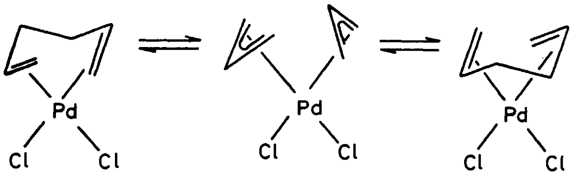
RECENTLY it has been reported[1] that $(PhCN)_2PdCl_2$ under very mild conditions catalyses the Cope rearrangement of several acyclic 1,5-dienes. A mechanism involving formation and cleavage of a cyclohexyl carbonium ion complexed to Pd^{II} was suggested[1] (equation 1). However, when we



(1)

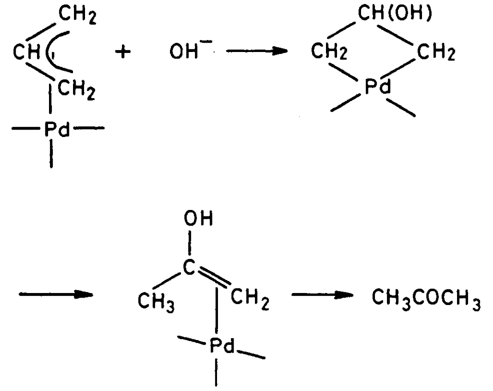
had read this paper[1] we realized that some of our results arising out of studies of the reaction products obtained from oxidative addition of a variety of xanthates to certain noble metal compounds[2] supported a quite different mechanism. Specifically, we had found that when hex-1-en-5-yl-*S*-methylxanthate was added at 90 °C to $Pd(PPh_3)_4$, which had previously partially oxidized to $Pd(O_2)(PPh_3)_2$, with no precaution taken to exclude air, substantial quantities of acetone were obtained in addition to hexa-1,5-diene and other products. When pure $Pd(PPh_3)_4$ was used under dry anaerobic conditions acetone was not produced. Acetone was also formed, but in much smaller amounts, when partially oxidized $Pt(PPh_3)_4$ was allowed to react with this xanthate. These results indicated that a hexa-1,5-diene Pd complex is formed from the xanthate followed by scission of the diene ligand to give a bis(η^3-allyl)Pd compound. The η^3-allyl ligands are then oxidized and the product eventually released is acetone.

In order to test this hypothesis we made up a Wacker catalyst[3] consisting of $(PhCN)_2PdCl_2$, $CuCl_2$, and CuCl in aqueous solution at 60 °C and fed in hexa-1,5-diene vapour in a stream of excess of oxygen. Substantial catalytic conversion into acetone was obtained. This result strongly supports the view that a bis(η^3-allyl)Pd^{II} complex is the key intermediate in the catalysed[1] Cope rearrangement. The current theory[4] for the thermal Cope rearrangement is that it proceeds *via* a sigmatropic [3,3] shift starting from the diene in the chair conformation. In the Pd^{II} complexes the bidentate diene ligand also seems to be held in the same conformation and to develop into the bis(η^3-allyl) complex with the orientation shown in equation (2). This explains



(2)

why the catalytic Cope rearrangement of 2,5-disubstituted dienes does not occur,[1] since steric hindrance would then prevent formation of the bis(η^3-allyl) complex in the orientation required. Quite clearly the mechanisms of the thermal and catalysed rearrangements are extremely similar, the interaction of the developing π-orbitals of the allylic ligands with appropriate Pd orbitals being the key to the much lower energy pathway in the latter. Although bis(η^3-allyl)$PdCl_2$ has never been isolated, the formation of this 18-electron Pd^{IV} compound seems feasible on a molecular orbital basis. The two Cl^- ligands and the centres of the two η^3-allyl ligands can be regarded as lying in the *xy* plane in a square planar arrangement. The non-bonding π-orbitals of the allyl ligands then have appropriate symmetry to engage the d_{xz} and d_{yz} orbitals, respectively, of the metal ion.



Scheme. Other ligands have been omitted for the sake of clarity.

The conversion of the η^3-allyl ligands into acetone under oxidizing conditions is of considerable interest, and apparently occurs *via* nucleophilic attack by hydroxide ion at the C-2 position to give the corresponding hydroxymetallacyclobutane derivative (Scheme). The hydride and proton shift reactions involved in converting the $-CH_2CH(OH)-CH_2-$ligand into acetone are obvious. The first reaction in the Scheme has precedent in the observation[5] that an analogous reaction in which H^- or Me^- adds to an η^3-allyl Mo compound to give the corresponding metallacyclobutane complex readily takes place.

When the Wacker oxidation process is carried out with propene or higher alk-1-enes the corresponding ketones rather than aldehydes, as in the case of ethylene, are obtained.[3] The present results and mechanism suggest that the selective conversion into ketones is also due to formation of η^3-allyl intermediates and their reaction with hydroxide ions as in the Scheme. This theory for the Wacker process contrasts with the currently accepted mechanism of addition of hydroxide ion to π-bonded olefin,[3] a reaction which apparently occurs when the olefin in question is ethylene. Furthermore the selective conversion of propene into acetone in oxygen and steam on a heterogeneous MoO_x–SnO_y–Al_2O_3 catalyst[6] may be another example of this novel aspect of the chemistry of η^3-allyl intermediates.

(*Received*, *26th January* 1981; *Com.* 094.)

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