

NATURE OF THE INTERMEDIATES IN THE REACTION OF
PALLADIUM CHLORIDE WITH OLEFINS

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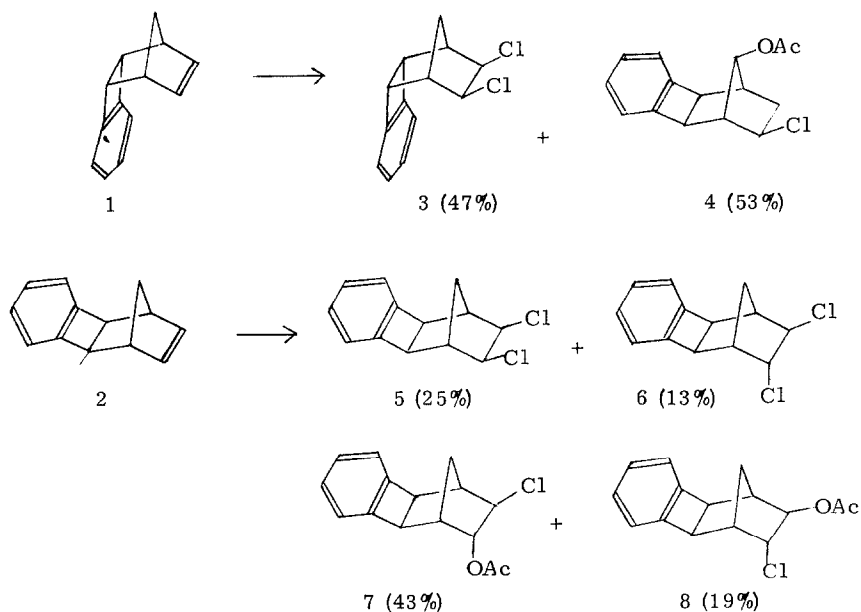
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The nature of the intermediates in the reactions of palladium chloride with olefins has been in question for some time. A number of pathways have been suggested for decomposition of the initially formed π -complex. From deuterium labelling and kinetic studies, hydride shifts, occurring synchronously with nucleophilic attack on the metal-olefin π -complex, have been proposed¹⁻³. Rearrangement of the π -complex to a σ -complex with subsequent hydride shift¹ or ionisation of the σ -complex to form a carbonium ion have also been suggested³. Evidence in favour of the carbonium ion mechanism has been published by Baird in that the reaction of norbornene in the presence of $\text{PdCl}_2\text{-CuCl}_2/\text{AcONa-AcOH}$ yields exo-2-chloro-syn-7-acetoxynorbornane⁴. We report evidence that the nature of the intermediate formed in the reaction of the π -complex produced from (1) differs markedly from that in other carbonium ion reactions of the same system.

The reaction (1) with $\text{PdCl}_2\text{-CuCl}_2/\text{AcONa-AcOH}$ yielded two predominant products (3) and (4), whereas with (2) the four products, (5), (6), (7) and (8) were formed^{5,6}.

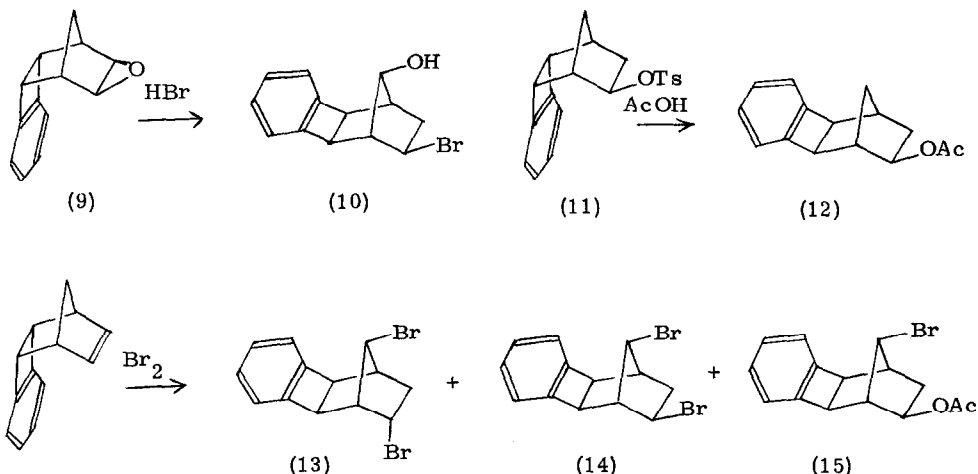
Structures of the products were assigned predominantly by a detailed analysis of the mass spectral and NMR data⁷. (3), mass spectrum, molecular ion 238 and the characteristic pattern for dichloride, $M : M + 2 : M + 4 = 9 : 6 : 1$; NMR (CCl_4), τ 2.77 (4, s, aromatic), 6.27 (4, m, benzylic and $\alpha\text{-Cl}$), 7.24 (2, m, bridgehead), 7.47 and 8.27 (2, AB, $J = 11$ Hz, bridge, lower field syn to $-\text{Cl}$). A spectrum consistent with a symmetrical structure,



benzylic protons at τ 6.27, lower than the equivalent protons in (5)⁸, together with the α -Cl protons also at τ 6.27 provide confirmation for the endo-configuration of the benzene ring and the cis-exo-arrangement of the chlorine substituents. Formation of (4) in this reaction has already been reported⁹.

(5), mass spectrum, molecular ion 238; M : M + 2 : M + 4 = 9 : 6 : 1; NMR (CCl₄), τ 2.94 (4, m, aromatic), 6.07 (2, d, α -Cl), 6.75 (2, s, benzylic), 7.44 (2, s, bridgehead), 8.1 and 9.06 (2, AB, J = 11 Hz). Again a symmetrical structure is apparent with the α -chloro protons less shielded than the corresponding protons in (3). The endo-benzylic protons appear at higher field in this case compared with the exo-benzylic protons of (3)⁸. (6), mass spectrum 238, M : M + 2 : M + 4 = 9 : 6 : 1; NMR (CCl₄), τ 2.90 (4, m, aromatic), 5.66 (1, m, exo-proton, α -Cl), 6.04 (1, d, benzylic), 6.32 (1, m, endo-proton, α -Cl), 6.64 (1, d, benzylic), 7.39 (1, m, bridgehead), 7.46 (1, s, bridgehead), 8.29 and 8.33 (2, AB, J = 11 Hz). The endo-chlorine substituent engenders a difference between the two endo-benzylic protons. Structures (7) and (8) were assigned by similar considerations⁷.

Formation of (3) from the PdCl₂ reaction contrasts sharply with the reaction of the



epoxide (9) with HBr. In this case the exclusive product is the rearranged bromohydrin (10) which had a similar NMR to (4) and yielded the 7-hydroxy olefin on treatment with Bu^tOK/DMSO. This product was expected since we have previously shown that formation of the carbonium ion at C₂, by the solvolysis of the *exo*-2-*p*-toluenesulphonate (11), results in exclusive formation of the *exo*-acetate (12)^{8,10}. A Wagner-Weerwein shift of the C₁-C₆ bond can be seen to occur readily in this system. This has also been demonstrated recently in the addition of bromine to (1) which yields (13, (14) and (15)¹¹.

An explanation for the sharp distinction between the transition metal-catalysed reaction and the other carbonium ion processes lies in the nature of the intermediate of the PdCl₂ reaction. Decomposition of the π-complex by nucleophilic attack is considered to result in the formation of a -C-Pd σ bond, followed by ionisation and further nucleophilic attack^{4,12}. Decomposition of the π-complex derived from (1) by chloride or acetate eventually leads to an intermediate with ionic character and trapping by chloride ion obviously occurs extremely readily to form the *cis*-dichloride (3). This occurs in competition with migration of the C₁-C₆ bond leading to the rearranged product (4). It is suggested that the second chloride for the formation of (3) originates from a tight or intimate ion-pair¹³ formed on decomposition of the π-complex together with Pd⁰. Thus, trapping of the inter-

mediate occurs before extensive rearrangement takes place.

For (2), no rearrangement occurs and all the products arise by nucleophilic attack on the π -complex followed by further nucleophilic attack on the C-atom then associated with the palladium. With this system, a nucleophile can approach from the endo-side in contrast to the intermediate formed from (1) where endo-attack is completely excluded due to marked steric interactions¹⁰. The larger number of products from (2) can therefore be rationalised since the PdCl_2 - π -complex can be initially attacked by either Cl^- or CH_3COO^- followed by attack by either of these nucleophiles. Although trans-addition products predominate, the formation of cis-dichloride (5) probably occurs in a similar manner to (3). In contrast, bromination of (2) has been shown to lead to exclusive formation of the trans-2,3-dibromide¹¹.

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