

transition state which has been developed on the basis of the other investigations mentioned above.³⁻⁶ The proposal^{6,12} that relief of steric crowding is an important factor in perester decompositions evidently is not applicable in these cases.¹³

(12) C. Rüchardt and I. Mayer-Rüchardt, *Chem. Ber.*, **104**, 593 (1971).

(13) Professor Ch. Rüchardt has also observed only minimal steric acceleration in decomposition of certain peresters and azo compounds leading to radicals (unpublished results privately communicated).

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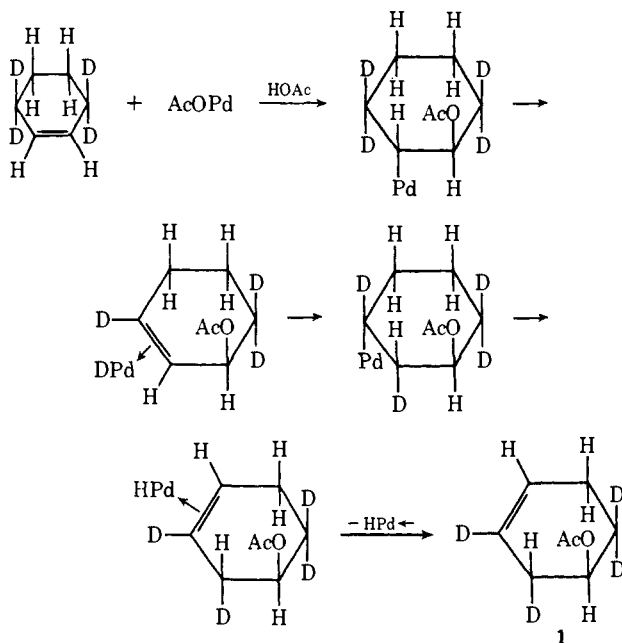
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Stereochemistry of Phenylpalladation of Cyclohexene¹

Sir:

The oxidation of cyclohexene-3,3,6,6-*d*₄ by a mixture of PdCl₂ and CuCl₂ in acetic acid was previously reported² to give products which were consistent with trans acetoxypalladation followed by cis palladium(II) hydride (or deuteride) eliminations and readditions. Thus the structure of the homoallylic acetate formed can be explained by Scheme I. **1** was also formed by

Scheme I



the oxidation of cyclohexene-3,3,6,6-*d*₄ with Pd(OAc)₂ in acetic acid.³

Although Scheme I is believed to be most consistent with known palladium(II) chemistry, there are other mechanistic paths which will give **1** as product. Cis acetoxypalladation and trans palladium(II) hydride (or deuteride) elimination and readdition is one possibility. This route is considered very unlikely because it would require free hydride to exist in a protonic solvent such as acetic acid. Another possibility is cis acetoxypalladation followed by 1,2 shifts of hydrogen

(1) Hercules Research Center Contribution No. 1578.

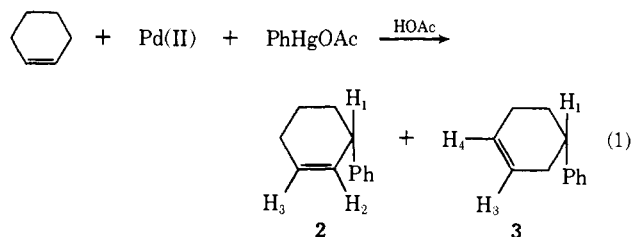
(2) P. M. Henry and G. A. Ward, *J. Amer. Chem. Soc.*, **93**, 1494 (1971).

(3) S. Wolfe and P. G. C. Campell, *ibid.*, **93**, 1497 (1971).

(or deuterium) and Pd(II) by concerted diaxial ⇌ diequatorial type shifts.³

One way to test Scheme I is to use a reagent that will add cis to cyclohexene. If homoallylic product arises from cis palladium hydride (or deuteride) eliminations and readditions as shown in Scheme I, the arrangement of protons in the homoallylic product will be different from that found in **1**. Such a reagent is apparently phenylpalladium. Reaction of olefins with this reagent, formed *in situ* by the exchange of arylmercury(II) compounds with palladium(II) salts, has been studied extensively,⁴ and stereochemical results indicate that phenylpalladation and palladium(II) hydride elimination have the same stereochemistry.⁵ Since the phenyl is covalently bonded to palladium(II), phenylpalladation would be expected to be a cis process. For that reason the oxidation of cyclohexene and its deuterated analog by mixtures of phenylmercuric acetate and Pd(II) salts was studied.

The oxidation with PhHgOAc and either Pd(OAc)₂ or catalytic amounts of PdCl₂ plus CuCl₂ gave two main products by vapor phase chromatography (vpc).⁶ Each peak was collected by preparative vpc and identified by nmr. The spectra indicated both were phenyl-substituted cyclohexenes,⁷ one the allylic isomer and the other the homoallylic isomer. The reaction thus proceeds as shown by eq 1. The first peak to elute,



which was about one-half the area of the second peak, was assigned the structure **2** on the basis of the chemical shifts of the H₁ protons. Thus in **3**, δ₁ is at 2.78 ppm, while in **2** it is shifted to 3.41 ppm. Such a shift is expected when the double bond is moved closer to H₁. Furthermore in **3** the olefinic protons are unresolved at approximately δ 5.76 ppm, using a 60-MHz spectrometer. When the double bond is moved closer to the phenyl, they are resolved with δ₂ ~5.7 ppm and δ₃ ~5.9 ppm. Aromatic protons appear as a sharp singlet at δ 7.25 ppm in both isomers.

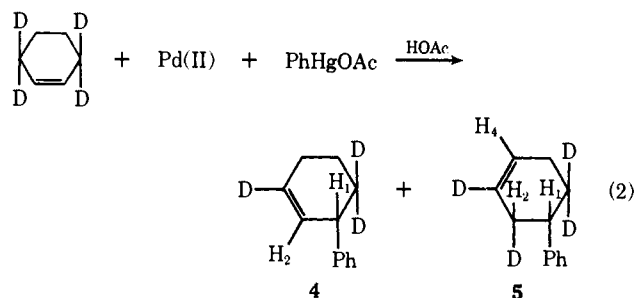
The Pd(OAc)₂ run was repeated using cyclohexene-3,3,6,6-*d*₄, and the products were again collected by preparative vpc and their nmr spectra taken. On the basis of the chemical shifts and area measurements the products were assigned structures **4** and **5**. In **4**, H₁

(4) R. F. Heck, *ibid.*, **90**, 5518 (1968), and following papers.

(5) R. F. Heck, *ibid.*, **91**, 6707 (1969).

(6) All runs were made at 25°. Pd(OAc)₂ reaction mixtures contained 0.2 mol of Pd(OAc)₂, PhHgOAc, and cyclohexene per liter of acetic acid. The PdCl₂ runs contained 0.01 mol of PdCl₂, 0.2 mol of PhHgOAc and cyclohexene, and 0.4 mol of CuCl₂ per liter of acetic acid. All reactants except the Pd(II) salts were mixed and stirring begun. The reaction was then started by adding the Pd(II) salts. Since the salts were sparingly soluble in acetic acid all runs were heterogeneous. Reaction time was 2 hr. Conversion of cyclohexene was about 50%. Reaction mixtures were worked up by diluting with CH₂Cl₂ and washing with water to remove inorganic salts and acetic acid. After drying, the organic phase was concentrated to a known volume and analyzed by vpc. A 20-ft 20% Lac 446 on 60-80 mesh Chromosorb W column was used. Temperature was 200° and helium flow rate was 100 ml/min.

(7) The PdCl₂ plus CuCl₂ reaction mixtures produced little, if any, saturated products. Contrast this with the results in the acetate reaction mixtures.²



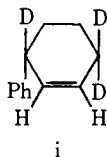
and H_2 appear at approximately 3.4 and 5.7 ppm, respectively.⁸ H_1 in **5** appears at $\delta \sim 2.8$ ppm and H_4 at $\delta \sim 5.8$ ppm.⁹ At 25°, the temperature at which most of the spectra were run, deuterium coupling broadened the H_1 signal in compound **5** to such an extent that $J_{1,2}$ could not be determined. However, upon cooling to -60°, the H-D coupling was reduced due to quadrupolar effects,¹⁰ and the signal became a doublet with $J_{1,2} = 3.0 \pm 0.5$ Hz. This value is clearly in the range of a cis coupling constant,¹¹ indicating H_1 and H_2 have cis stereochemistry.

The structure of **5** is consistent with Scheme I if phenylpalladation has cis stereochemistry. It is inconsistent with trans palladium(II) hydride elimination-readdition or concerted 1,2 shifts unless the rather unreasonable postulate is made that acetoxy-palladation is cis and phenylpalladation is trans. The formation of **4** and **5** would thus proceed as shown in Scheme II.

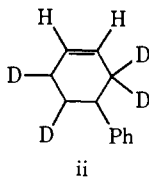
The fact that the allylic product consists entirely of **4** rather than containing some of its allylic isomer⁸ indicates that symmetrical intermediates such as π -allylic complexes are not intermediates. In the $Pd(OAc)_2$ oxidation the allylic acetates consisted of a 1:1 mixture of the two possible allylic isomers indicating the intermediacy of symmetrical intermediates.³ However, the two systems would be expected to have considerable differences since phenylpalladium contains $Pd(II)$ -carbon bonds while the acetate system does not.

In conclusion, no matter what the absolute stereochemistry, the addition of the elements of $Pd(II)$ and acetate across double bonds must have different stereochemistry from that of the addition of phenylpalladium across double bonds. This result supports

(8) All CH_2 and CDH protons in both **4** and **5** have δ 1.3 to 2.4 ppm. Area measurements indicate that less than 10% of the allylic isomer of **4**, i, is present.



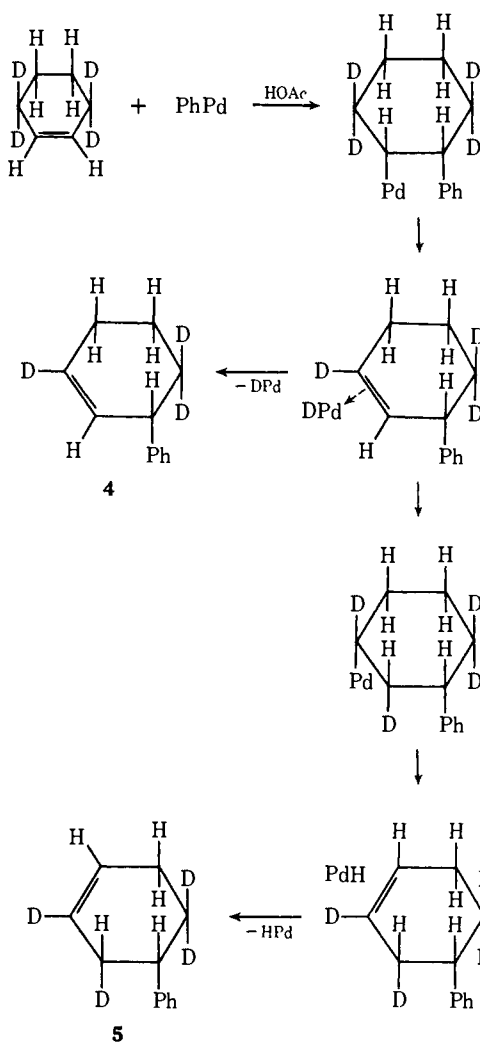
(9) The areas of H_1 and H_4 in **5** were the same to within 10% so large amounts of the other possible homoallylic isomer, ii, cannot be present.



(10) C. Brevard, J. P. Kintzinger, and J. M. Lehn, *Chem. Commun.*, 1193 (1969).

(11) H. Booth, *Progr. Nucl. Magn. Resonance Spectrosc.*, **5**, 149 (1969).

Scheme II



the earlier contention² that addition of nucleophiles and palladium(II) across double bonds can have either cis or trans stereochemistry depending on the nature of the nucleophile. The most important factor is probably the ability of the nucleophile to coordinate to palladium(II) prior to addition.

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On the Structure of Protonated Ethylene

Sir:

In the light of the considerable interest in recent literature in the structure of the ethyl cation, $C_2H_5^+$,¹

(1) R. Sustman, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 5350 (1969); J. E. Williams, V. Buss, L. C. Allen, P. von R. Schleyer, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **92**, 2141 (1970); G. V. Pfeiffer and J. G. Jewett, *ibid.*, **92**, 2143 (1970); W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **93**, 808 (1971).