

Acknowledgment. The authors are grateful for helpful discussions and exchange of unpublished data with Professor S. Wolfe and Dr. P. G. C. Campbell.

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Received December 8, 1970

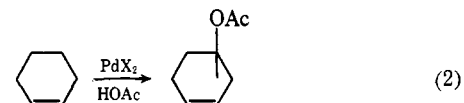
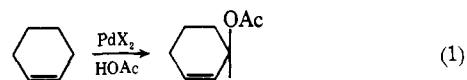
Allylic and Homoallylic Oxidation of Cyclohexene and Cyclohexene-3,3,6,6-*d*₄ by Palladium(II) Salts. Evidence for Competing "Symmetrical" and Oxypalladation Intermediates

Sir:

The reaction of an olefin with a Pd^{II} salt¹ may lead, depending upon the nature of the substrate and the experimental conditions, to a carbonyl compound,² a vinyl ester,³ allylic oxidation,⁴ or homoallylic oxidation.⁵ The first two processes have been studied in considerable detail in recent years, and it is generally accepted that a (cis) oxypalladation adduct is a necessary intermediate in each case. The mechanisms of the allylic and homoallylic oxidations afforded by Pd^{II} salts in acetic acid solvent are less clear, but it has been proposed^{4c,5} that the observations made so far are also compatible with oxypalladation followed, in the case of allylic oxidation, by elimination of [HPdX] (*i.e.*, addition-elimination) and, in the case of homoallylic oxidation, by a 1,2 shift of palladium prior to the elimination of [HPdX] (*i.e.*, addition-rearrangement-elimination).

In the course of our continuing investigation of mechanisms of allylic oxidation,⁶ we have studied the allylic (eq 1) and homoallylic (eq 2) oxidations of cyclohexene and cyclohexene-3,3,6,6-*d*₄ (1) by Pd^{II} salts. In this and the following communication⁷ we present evidence that the two oxidation paths are the result of two competing processes, *only one of which* involves an oxypalladation adduct.

Initial attempts to observe oxidation of cyclohexene with PdCl₂ or with Pd(OAc)₂⁸ in neutral or buffered



acetic acid solutions were unsuccessful because of the superposition of a much more rapid Pd⁰-catalyzed disproportionation of cyclohexene which led to the disappearance of both the substrate and the oxidizing agent.^{9,11} To avoid this problem it was necessary to perform the reaction in the presence of a reoxidant and/or disproportionation inhibitor.¹² Inclusion of small amounts of HNO₃, HNO₂, or Hg(OAc)₂¹⁴ in the reaction mixtures led to the required inhibition, and over 90% conversions of cyclohexene to the desired oxidation products were then obtained. Table I summarizes some of the relevant results.

The *allylic* acetate from 1 was found in all cases to be a 1:1 mixture of 2 and 3.¹⁷ This mixture was

(8) T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 3632 (1965).

(9) The reaction is autocatalytic; Pd⁰, formed in the initial oxidation-reduction step, aromatizes cyclohexene, and the available hydrogens thus produced reduce Pd^{II} to Pd⁰ to continue the process.¹⁰

(10) P. G. C. Campbell and S. Wolfe, to be published.

(11) R. G. Brown, J. M. Davidson, and C. Triggs, 157th National Meeting of the American Chemical Society, Symposium on Homogeneous Catalytic Reactions Involving Palladium, Minneapolis, Minn., April 1969, Preprints, p B23.

(12) This approach has also been found necessary by Davidson,¹¹ in whose work precipitation of Pd⁰ is avoided by performing oxidations under a pressure of 50 atm of oxygen. It should be noted that a similar approach was inadvertently used by Anderson and Winstein.^{4b} Their "palladous acetate" was prepared by the exchange reaction of silver acetate with palladium(II) chloride.¹³ In our hands this material did indeed effect the oxidation of cyclohexene without concomitant disproportionation. However, on investigation the material was found to be an impure palladium acetate containing bound acetic acid and an unidentified silver-containing component (AgOAc?). Clearly this impurity is acting as an efficient disproportionation inhibitor, allowing the oxidation of cyclohexene to proceed; in the absence of this impurity (*i.e.*, with pure palladium(II) acetate), disproportionation completely masks the desired oxidation.

(13) C. B. Anderson, Ph.D. Thesis, UCLA, 1963.

(14) Use of Hg(OAc)₂ in the mixture was prompted by some observations by Moiseev and Vargaftig,¹⁵ and with the expectation that reversible oxymercuration of the olefin^{6b} would protect it from Pd⁰-catalyzed disproportionation. That the free olefin, not the oxymercuration adduct, is the reactive species in these oxidations is suggested by the following observations: (i) the product composition is the same, and disproportionation is inhibited, for cyclohexene-adduct ratios varying from 0.06 to 9.0; (ii) 3- and 4-acetoxycyclohexene are formed, but not cyclohexanone, cyclohexenone, or cyclohexenol, when 2-hydroxycyclohexylmercuric acetate is allowed to react in acetic acid with the PdCl₂-NaOAc system; (iii) similarly, only 3- and 4-acetoxycyclohexene are obtained when Hg(OAc)₂ is included in the aqueous acetic acid runs 7 and 8 (Table I). Had the hydroxymercurial reacted, cyclohexanone would have been formed. These observations may be contrasted with those reported in ref 16.

(15) I. I. Moiseev and M. N. Vargaftig, *Dokl. Akad. Nauk SSSR*, 166, 370 (1966).

(16) (a) R. Heck, *J. Amer. Chem. Soc.*, 90, 5546 (1968), and the immediately preceding papers in this series; (b) P. M. Henry, *Tetrahedron Lett.*, 2285 (1968).

(17) The basis for this analysis has been given previously.^{6b} Assignment of structure 2 is based on the presence of an AB quartet for the vinyl protons at τ 4.05, 4.27 ($J \approx 10$ Hz). The structure of 3 has been established rigorously by deuterium decoupling experiments.¹⁸ Under these conditions the proton geminal to acetate appears as a quartet at τ 4.9 ($^3J \approx 3.5$, $^2J \approx 2.0$ and 0 Hz¹⁹). See also ref 20.

(18) We thank Dr. Alan Maritz, Defence Standards Laboratories, Melbourne, Australia, for the deuterium decoupling experiments.

(19) See R. J. Abraham, H. Gottschalk, H. Paulsen, and W. A. Thomas (*J. Chem. Soc.*, 6268 (1965)) for examples of long-range proton-proton coupling in substituted cyclohexenes.

(20) Acetate 4 shows no allylic absorption at τ 4.9; the vinyl protons appear at τ 4.05 (H_A, two triplets, $J \approx 2$, 12 Hz) and 4.3 (H_B, doublet, $J = 12$ Hz). Equilibration of 4 with 5 is accompanied by appearance

(1) For recent reviews of synthetic capabilities of Pd^{II} salts and Pd^{II} complexes, see (a) R. Hüttel, *Synthesis*, 2, 225 (1970); (b) J. Tsuji, *Accounts Chem. Res.*, 2, 144 (1969).

(2) (a) J. Smidt, W. Hafner, R. Jira, R. Sieber, J. Sedlmeier, and A. Sabel, *Angew. Chem., Int. Ed. Engl.*, 1, 80 (1962); (b) P. M. Henry, *J. Amer. Chem. Soc.*, 86, 3246 (1964); 88, 1595 (1966); (c) R. Jira, J. Sedlmeier, and J. Smidt, *Justus Liebigs Ann. Chem.*, 693, 99 (1966); (d) E. W. Stern, *Catal. Rev.*, 1, 73 (1967); (e) P. M. Henry, *Advan. Chem. Ser.*, No. 70, 126 (1968).

(3) (a) I. I. Moiseev, M. N. Vargaftig, and Y. K. Syrkin, *Dokl. Akad. Nauk SSSR*, 133, 377 (1960); (b) I. I. Moiseev, A. P. Belov, and Y. K. Syrkin, *Izv. Akad. Nauk SSSR*, 1527 (1963); (c) I. I. Moiseev and M. N. Vargaftig, *ibid.*, 759 (1965); (d) A. P. Belov, I. I. Moiseev, and N. G. Uvarova, *ibid.*, 1642 (1966); (e) E. W. Stern and M. L. Spector, *Proc. Chem. Soc.*, 370 (1961); (f) E. W. Stern, *ibid.*, 111 (1963); (g) R. Van Helden, C. F. Kohll, D. Medena, G. Verberg, and T. Jonkhoff, *Recl. Trav. Chim. Pays-Bas*, 87, 961 (1968).

(4) (a) M. N. Vargaftig, I. I. Moiseev, and Y. K. Syrkin, *Izv. Akad. Nauk SSSR*, 930 (1962); (b) S. Winstein and C. B. Anderson, *J. Org. Chem.*, 28, 605 (1963); (c) W. Kitching, Z. Rappoport, S. Winstein, and W. G. Young, *J. Amer. Chem. Soc.*, 88, 2054 (1966).

(5) (a) M. Green, R. N. Haszeldine, and J. Lindley, *J. Organometal. Chem.*, 6, 107 (1966); (b) P. M. Henry, *J. Org. Chem.*, 32, 2575 (1967).

(6) (a) S. Wolfe and P. G. C. Campbell, *Can. J. Chem.*, 43, 1184 (1965); (b) S. Wolfe, P. G. C. Campbell, and G. E. Palmer, *Tetrahedron Lett.*, 4203 (1966); (c) S. Wolfe and D. V. C. Awang, *J. Amer. Chem. Soc.*, 89, 5287 (1967); (d) S. Wolfe and P. G. C. Campbell, Proceedings of the XIIth International Conference on Coordination Chemistry, Sydney, Australia, 1969, pp 54-56; (e) S. Wolfe and D. V. C. Awang, *Can. J. Chem.*, in press.

(7) S. Wolfe and P. G. C. Campbell, *J. Amer. Chem. Soc.*, 93, 1499 (1971).

Table I. Oxidation of Cyclohexene and Cyclohexene-3,3,6,6-*d*₄ by Palladium(II) Oxidants in Acetic Acid at 25°^a

Run	Oxidant	mmol	Cyclohexene (mmol)	Time, hr	Coreactant (mmol)					Product composition ^{b,c}	
					HNO ₃	HNO ₂	NaOAc	Hg(OAc) ₂	H ₂ O	Allylic acetate	Homoallylic acetate
1	[Pd(OAc) ₂] ₃ ·NO ₂ ^d	0.49	1.7	18	0.33					92-100	0-8
2	[Pd(OAc) ₂] ₃ ·NO ₂ ^d	0.38	0.42 ^f	4.5	0.13					92-100	0-8
3	[Pd(OAc) ₂] ₃ ·NO ₂ ^d	0.31	0.79	3.0						92-100	0-8
4	[Pd(OAc) ₂] ₃ ·NO ₂ ^d	0.36	0.32 ^f	5.0						92-100	0-8
5	PdCl ₂	1.05	1.13	65			2.2	1.01		~92	~8
6	PdCl ₂	1.04	1.08 ^f	48			2.2	1.04		70	30
7	[Pd(OAc) ₂] ₃ ·NO ₂ ^e	0.66	0.96	3.0		0-0.45	0.84-1.07		55	85	15
8	[Pd(OAc) ₂] ₃ ·NO ₂ ^e	0.68	0.99 ^f	1.0		0-0.45	0.84-1.07		55	45	55

^a Glacial acetic acid containing 3-5% acetic anhydride was used for all runs except no. 7 and 8; a standard reaction volume of 3 ml was employed. ^b The product composition was determined by ir, nmr, and glc analysis; less than 8% of the homoallylic acetate could not be detected in the presence of the allylic acetate. ^c The following possible products were searched for, but not detected: cyclohexyl acetate, Δ¹-cyclohexenyl acetate (enol acetate), cyclohexanone, Δ²-cyclohexenol, Δ²-cyclohexenone, cyclohexane, benzene. ^d This material, "oxidant-C," was prepared⁸ by oxidation of metallic palladium with excess HNO₃ in glacial acetic acid followed by lyophilization; microanalytical data, molecular weight determinations, and ir and nmr spectral measurements on oxidant-C suggest the formulation indicated, [Pd(OAc)₂]₃·NO₂.¹⁰ ^e This oxidant was prepared as in footnote *d*, followed by buffering with excess NaOAc instead of lyophilization to give oxidant-C *in situ*. ^f Cyclohexene-3,3,6,6-*d*₄ was employed in this run.

observed for both short and long reaction times, and indicates that allylic oxidation proceeds *via* a symmetrical intermediate, possibly a π-allylic complex. To check this conclusion the stability of the monodeuterated

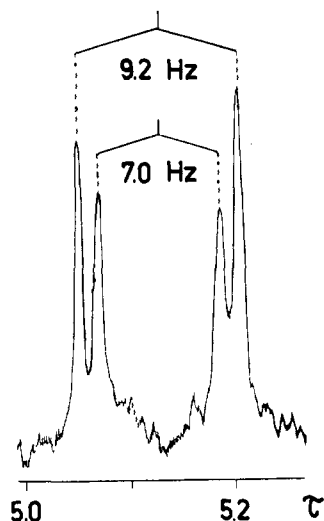


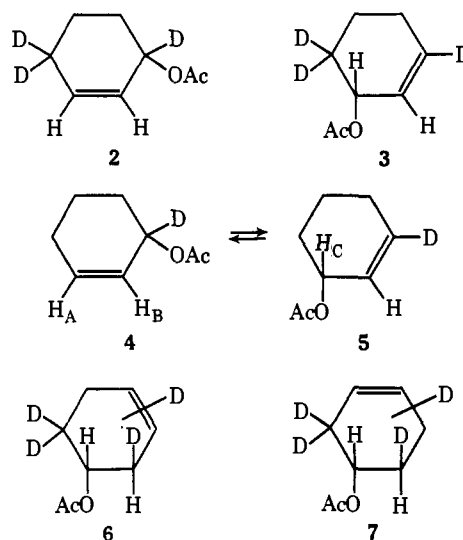
Figure 1. Deuterium-decoupled spectrum showing the proton geminal to the acetoxy group in the mixture of 13 and 14.

acetate 4 to the reaction conditions was investigated. Under all conditions examined, *i.e.*, conditions simulating those of runs 1-6, allylic rearrangement (4 → 5) could be detected, but this reaction was much too slow to account for the observed 1:1 mixture of 2 and 3 from the oxidation of the olefin.²⁰

The homoallylic acetate from 1 was identified as a mixture of 6 and 7 on the basis of the nmr pattern for the proton geminal to acetate. With deuterium decoupling,¹⁸ the signal for this proton is observed (Figure 1) at τ 5.13 as two doublets, ³J_{HH} = 9.2 and 7.0 Hz, of unequal intensity. Since the inner peaks of this quartet have lower intensity than the outer peaks, the observed pattern is compatible only with the presence of two compounds, each of which contains a low field proton vicinal and trans to only one other proton.²¹ Consequently, in both of the

of a peak at τ 4.9 (H_C of 5), a decrease in the absorption at τ 4.05, and no change in the intensity of the τ 4.3 peak.

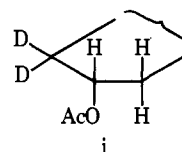
(21) An alternate interpretation in terms of part structure i can be ruled out because the observed intensities are inconsistent with a



homoallylic acetates, the acetoxy group must be attached to one end of the original double bond, and at least one stereospecific deuterium migration has occurred. This result seems to require that the homoallylic acetate is formed by an addition-rearrangement-elimination sequence. Such a sequence must necessarily operate independently of any sequence which affords a symmetrical intermediate.

The isotope effects noted between runs 5 and 6 and runs 7 and 8 also demonstrate that allylic and homoallylic oxidation proceed *via* different intermediate stages. If the formation of a π-allylic complex²⁴ and an oxypalladation adduct were the rate-determining steps leading to allylic and homoallylic oxidation, respectively, a primary isotope effect would be ob-

description in terms of the X portion of an ABX pattern,²² and because the separation of lines 1,2 and 3,4 (1.2 Hz) is too small for a *cis* coupling constant.²³



(22) (a) L. M. Jackman and S. Sternhell, "Applications of NMR Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, London, 1969, pp 132-134; (b) E. W. Garbisch, *J. Chem. Educ.*, **45**, 402 (1968).

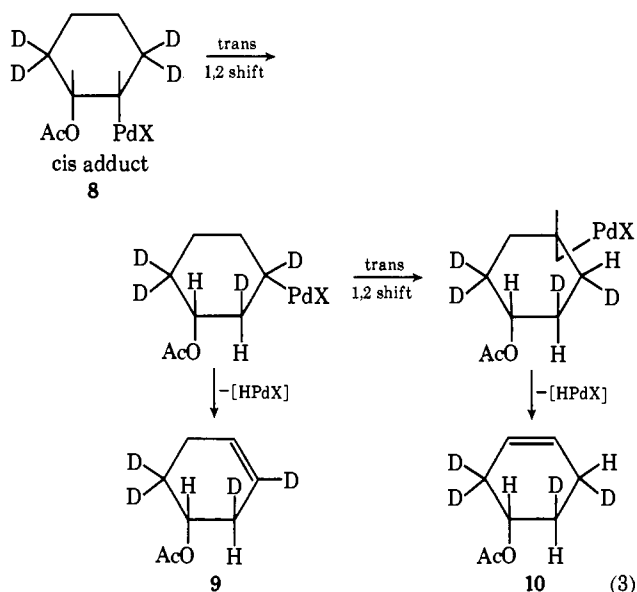
(23) S. Wolfe and J. R. Campbell, *Chem. Commun.*, 877 (1967).

(24) M. L. H. Green and P. L. I. Nagy, *Adv. Organometal. Chem.*, **2**, 325 (1964).

served only in the case of allylic oxidation on changing the substrate from cyclohexene to cyclohexene-3,3,6,6- d_4 . This follows because the formation of a π -allylic or related complex would involve the breaking of an allylic C-H (C-D) bond.²⁵

A study of the solvolytic behavior of some π and π -allylic palladium(II) complexes derived from cyclohexene has suggested⁷ that the latter are plausible intermediates in allylic oxidation,^{11,26} and are, therefore, suitable representations of the symmetrical species required by the present work. We suggest that, with our oxidizing agents, cyclohexene reacts principally *via* a monomeric π -allylic²⁷ or "switching" σ -allylic palladium complex²⁸ which is solvolyzed to allylic acetate. Under our conditions oxypalladation is a competing, less important, reaction leading mainly if not exclusively to homoallylic acetate. Regarding this latter pathway, structures **9** and **10** for the homoallylic acetate are consistent with either mechanism I (eq 3)

Mechanism I



or mechanism II (eq 4).

Mechanism I involves *cis*-acetoxypalladation (**8**), a series of 1,2 shifts of *trans*-palladium and H(D) atoms (*cf.* the diaxial \rightleftharpoons diequatorial rearrangement²⁹), and eventual elimination of [HPdX]. This scheme is consistent with current views of olefin insertion into a Pd-X bond,^{1,30} with the finding that water is not incorporated into the products when X = OAc (Table I, runs 7,8), and with the absence of 1,2-diacetates from the reaction products.³¹ It contains the novel (for palladium chemistry) postulate of a trans 1,2 shift. Mechanism II involves *trans*-acetoxypalladation (**11**), a

(25) Comparison of runs 5 *vs.* 6 and 7 *vs.* 8 provides a measure of the cumulative (kinetic + product) isotope effects (*ca.* 5) operating in the system; direct measurement of the reaction rates of deuterated and nondeuterated olefins would be required to provide the kinetic isotope effect alone.

(26) R. Van Helden, quoted (ref 3) in H. C. Volger, *Recl. Trav. Chim. Pays-Bas*, **86**, 677 (1967).

(27) K. Vrieze, C. MacLean, P. Cossee, and C. W. Hilbers, *ibid.*, **85**, 1077 (1966).

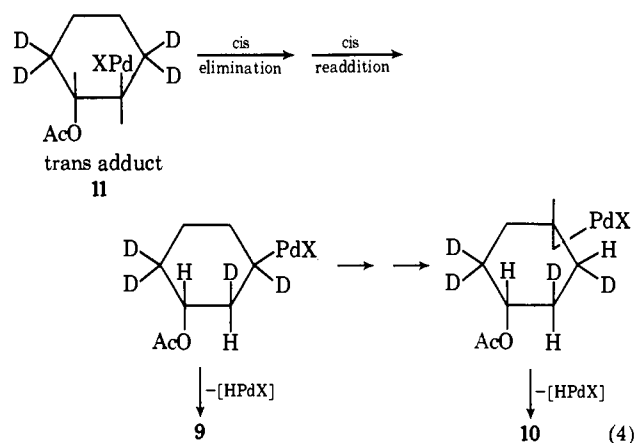
(28) F. A. Cotton, J. W. Faller, and A. Musco, *Inorg. Chem.*, **6**, 179 (1967).

(29) J. F. King, K. A. Kar, D. M. Deaken, and R. J. Pews, *Can J. Chem.*, **46**, 1 (1968), and references cited therein.

(30) B. L. Shaw, *Chem. Commun.*, 464 (1968).

(31) P. M. Henry, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstract S-78.

Mechanism II



series of *cis* elimination-readdition steps, and eventual elimination of [HPdX]. This scheme, favored by Henry and Ward³² for the *addition* reactions of cyclohexene with a $\text{Li}_2\text{PdCl}_4\text{-CuCl}_2$ reagent, is supported by their kinetic evidence that acetate anion does not coordinate to palladium prior to the rate-determining step, and is consistent with current descriptions of metal-hydride-promoted olefin isomerizations.^{33,34}

Acknowledgments. We thank the National Research Council of Canada for support of this work and for the award of a Studentship, and Drs. P. M. Henry and G. A. Ward for helpful discussion and the exchange of unpublished data.

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

(33) N. R. Davies, *Rev. Pure Appl. Chem.*, **17**, 83 (1967).

(34) A referee has suggested that "some choice between mechanisms I and II in favor of I might be made based on lack of exchange with solvent." In this connection, the unreacted olefin recovered from run 4 (Table I) was found to be identical with the starting material, cyclohexene-3,3,6,6- d_4 , and showed no evidence of hydrogen-deuterium exchange. Although this result seems to provide support for mechanism I, it is not decisive because of our present lack of information concerning the possible reversibility of the initial steps of mechanism II.

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Received December 9, 1970

Allylic and Homoallylic Oxidation of Cyclohexene by Palladium(II) Salts. Solvolytic Behavior of Possible Organopalladium Intermediates

Sir:

A number of divalent organopalladium complexes may be postulated to intervene in the oxidation of an olefin by a Pd^{II} salt. With cyclohexene as the substrate these include the π -complex **1**,¹ the π -allylic complex **2**,² the σ -allylic complex **3**,³ the *cis* oxypalladation adduct **4**,^{4a,b,f} and the *trans* oxypalladation ad-

(1) (a) M. S. Kharasch, R. C. Seyler, and F. R. Mayo, *J. Amer. Chem. Soc.*, **60**, 882 (1938); (b) J. R. Holden and N. C. Baenziger, *ibid.*, **77**, 4987 (1955); (c) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(2) B. L. Shaw and S. D. Robinson, *ibid.*, 5002 (1964); B. L. Shaw and N. Sheppard, *Chem. Ind. (London)*, 517 (1961). For a review, see M. L. H. Green and P. L. I. Nagy, *Advan. Organometal. Chem.*, **2**, 325 (1964).

(3) F. A. Cotton, J. W. Faller, and A. Musco, *Inorg. Chem.*, **6**, 179 (1967).

(4) (a) E. W. Stern, *Catal. Rev.*, **1**, 73 (1967); (b) B. L. Shaw, *Chem. Commun.*, 464 (1968); (c) C. B. Anderson and B. J. Burreson, *Chem. Ind. (London)*, 620 (1967); (d) J. K. Stille and R. A. Morgan, *J. Amer.*