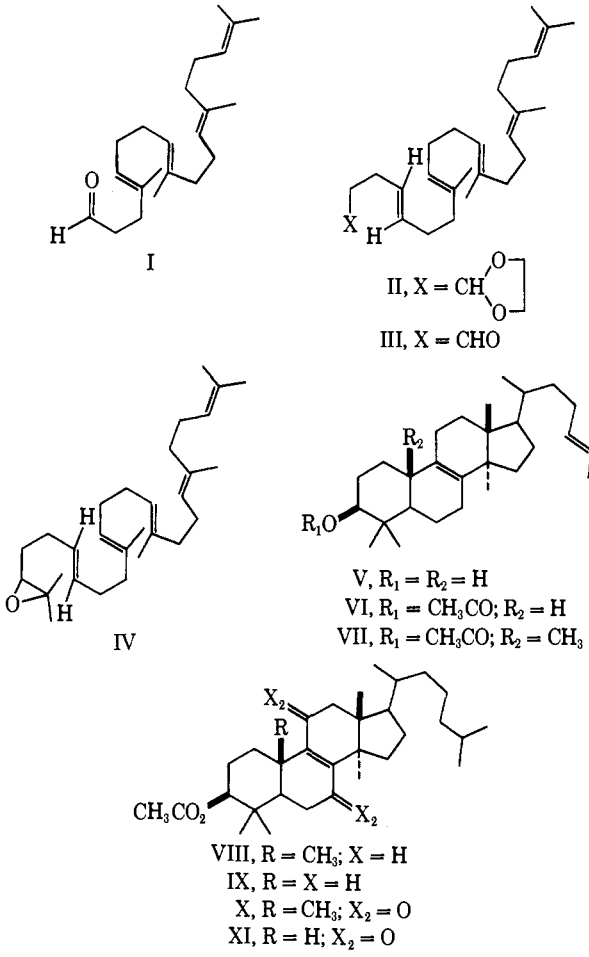

matographically indistinguishable from lanosterol (*e.g.*, R_f 0.21 with silica gel and chloroform for development), afforded an acetyl derivative VI with excess acetic anhydride–pyridine, giving essentially identical R_f values as lanosteryl acetate using silica gel or silica gel impregnated with silver nitrate as adsorbent (evidence for monoacetylation).

The mass spectrum of the acetate VI (purified by tlc) was obtained using a mass spectrometer (LKB Instrument Co.) coupled to a vapor-phase chromatographic (vpc) apparatus fitted with an OV-1 column,[12] and that of lanosteryl acetate (VII) was measured under the same conditions for comparison. In agreement with structure VI for the enzymically derived acetate, the molecular ion was observed at *m/e* 454 (M^+ for VII, 468). Further, major fragments from VI (in the range *m/e* >180) occurred at *m/e* 439, 379, 325, 283, 241, and 189, and those from VII were found at 453, 393, 325, 283, 255, and 189, that is, either displaced by *m/e* 14 or of the same value. Catalytic reduction of the acetate VI using a platinum catalyst in ethyl acetate with 1 atm of hydrogen, conditions which afford 24,25-dihydrolanosteryl acetate (VIII) from VII, led to selective formation of the dihydro derivative IX. The R_f values observed for VIII, IX, and VII using silver nitrate impregnated silica gel with chloroform–hexane, 3:7, for development were 0.36, 0.36, and 0.30, respectively. Oxidation of dihydrolanosteryl acetate (VIII) and the labeled acetate IX using dipyridine–chromium trioxide complex in methylene chloride at 25° for 9 hr led (*ca.* 50% yield) to the enedione derivatives X and XI, respectively. The mass spectra (LKB instrument as above) of these enediones fully support the assigned structures; for XI found (*m/e*): 484 (M^+), 469, 424, 381, 329, 302, 269, 241, 187; and for X found (*m/e*): 498, 483, 438, 395, 343, 302, 283, 255, 187. The major fragments found for X and XI differ, as expected, by either 14 or 0 *m/e* units.

The dihydro acetates VIII and IX also exhibited parallel behavior toward ruthenium tetroxide, both undergoing conversion to seco-diketo acetates.

Anaerobic incubation of labeled IV with the sterol cyclase in the presence of a 200-fold *M* amount of unlabeled 2,3-oxidosqualene results in only a 2.4% conversion of IV to the sterol V under the same conditions which lead to a 60% conversion in the absence of 2,3-oxidosqualene. This experiment indicates that the sterol cyclase is responsible for the transformation of IV to V.[13]

From the structural information outlined above, we conclude that des-6-methyl-2,3-oxidosqualene (IV) is an excellent substrate for the sterol cyclase enzyme and undergoes conversion to 19-norlanosterol (V).

In view of the findings of the dispensability with regard to enzymic cyclization of each of the methyl groups in 2,3-oxidosqualene which become angular methyl substituents on the sterol nucleus, it would be interesting to see whether the 2,3-oxidosqualene analog lacking methyl groups at C-6, C-10, *and* C-15 would be converted to a sterol which is completely devoid of angular methyl groups, and such an experiment is planned.

Acknowledgment. This work was assisted financially by grants from the National Institutes of Health and the National Science Foundation and a CNRS (France) fellowship to A. K.

(12) We are indebted to Dr. James Orr, Massachusetts General Hospital, for the use of this apparatus.

(13) Thermally (70°, 4 min) denatured sterol cyclase is ineffective for the generation of V from IV.

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Stereochemistry of Acetoxypalladation of Cyclohexene[1]

Sir:

The addition of the elements of Pd(II) or Pt(II) and nucleophiles across the double bonds of diolefins to give stable adducts has been found to have trans stereochemistry.[2] In contrast, the stereochemistry of the addition to monoolefins is usually considered to be cis[3] because the kinetics of the oxidation of olefins to aldehydes and ketones suggest the initial step is the cis addition of Pd(II)–OH to the double bond.[4,5]

(1) Hercules Research Center Contribution No. 1545.

(2) (a) L. F. Dahl and W. Oberhansli, *Inorg. Chem.*, **4**, 629 (1965); (b) W. A. Witla, H. M. Powell, and L. M. Venanzi, *Chem. Commun.*, 310 (1966); (c) J. K. Stille and R. A. Morgan, *J. Amer. Chem. Soc.*, **88**, 5135 (1966); (d) M. Green and R. I. Hancock, *J. Chem. Soc. A*, 2054 (1967); (e) C. Panattoni, G. Bombieri, E. Forsellini, and B. Crociani, *Chem. Commun.*, 187 (1969).

(3) (a) B. L. Shaw, *ibid.*, 464 (1968); (b) F. R. Hartley, *Nature (London)*, **223**, 615 (1969).

(4) P. M. Henry, *J. Amer. Chem. Soc.*, **86**, 3246 (1964); **88**, 1595 (1966).

However, this generalization may not be valid for all nucleophiles or reaction conditions, since results of studies of Pd(II)-catalyzed exchange reactions indicate that acetoxypalladation and chloropalladation have opposite stereochemistries[6] and it has recently been reported[7] that amines add trans to Pt(II)–monoolefin complexes. In this communication we report results which are best interpreted in terms of trans acetoxypalladation.

The oxidation of olefins by a mixture of Pd(II) and $CuCl_2$ in acetic acid gives diacetates and chloroacetates in addition to the unsaturated acetates found in the absence of $CuCl_2$.[8] One particularly interesting aspect of this reaction is that oxidation of higher olefins gives 1,3- and 1,4-disubstituted alkanes in addition to the 1,2 products expected from simple addition across the double bond. To obtain information about the stereochemistry of these processes, we have studied the oxidation of cyclohexene in this system. A typical product distribution is given in Table I.

Table I. Product Distribution from the Oxidation of Cyclohexene at 75° [a]

Product	% of total product		
Unsaturated Esters			
2-Cyclohexen-1-ol acetate		46.0	
3-Cyclohexen-1-ol acetate		6.9	
Saturated Products	1,2 isomers[b]	1,3 isomers	1,4 isomers
cis-Chloroacetate	12.5	<0.1	0.2
trans-Chloroacetate	11.8	6.3	2.5
cis-Diacetate	12.4	0.9	0.5
trans-Diacetate	<0.1	<0.1	<0.1

[a] The reaction mixture contains 0.01 mol of Pd(II), 1.0 mol of $CuCl_2$, 0.5 mol of cyclohexene, and 1.5 mol of LiOAc per liter of acetic acid. At 75°, $CuCl_2$ solubility is 0.75 *M*; the reaction was run for 2 hr. Conversion was about 5% of cyclohexene. The reaction was run in capped soft drink bottles under nitrogen. [b] Traces of 1,2-dichlorocyclohexane formed but these products were shown to result from the $CuCl_2$-catalyzed chlorination.[8]

The main points of interest are: (1) only *cis*-diacetates are obtained for all three positional isomers and (2) the 1,2-chloroacetates are approximately a 1:1 mixture of the cis and trans isomers while the 1,3- and 1,4-chloroacetates are almost exclusively trans.

Cyclohexene-*3,3,6,6-d*$_4$ was oxidized under the same conditions and the positions of the deuterium label in the unsaturated esters and the *trans*-1,3- and 1,4-chloroacetates were determined by nmr.

The use of vicinal proton–proton coupling constants to determine cis–trans relationships in substituted cyclohexanes has recently been thoroughly reviewed by Booth.[9] In general, cis protons in rapidly interconverting mixtures of conformers give vicinal coupling constants in the 3.5–4.0-Hz range. Trans coupling constants are much larger, usually at least 6.5–7.0 Hz. A summary of the values obtained for the various products in this study are given in Table II.

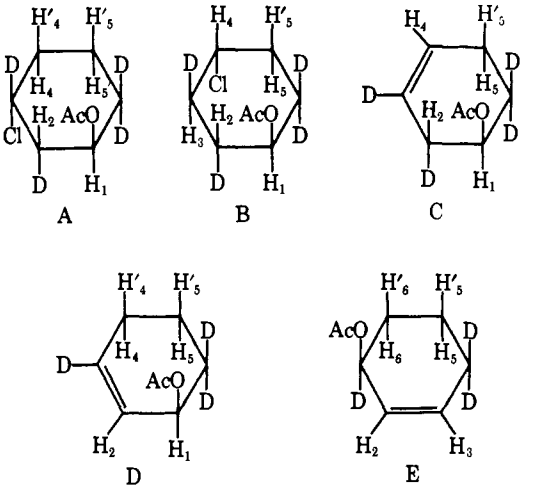


Table II

Compd	Proton[a]	δ, ppm[b]	*J*, Hz ± 0.2 Hz
A, *trans*-1,3-chloroacetate	H_1	5.0 d	$J_{1,2}$ = 7.0
	H_3	ND	
B, *trans*-1,4-chloroacetate	H_1	4.7 d	$J_{1,2}$ = 6.5
	H_4	4.0	$J_{3,4}$ = 7.2
			$J_{4,5'}$ = 3.5
			$J_{4,5}$ = 7.2
C, 3-cyclohexen-1-ol acetate	H_1	5.1 d	$J_{1,2}$ = 7.1
	H_4	5.66t	$J_{4,5} = J_{4,5'}$ = *ca.* 3.5
D, 2-cyclohexen-1-ol acetate[c]	H_1	5.2 d	$J_{1,2}$ = *ca.* 3.5
	H_2	5.7	
	H_3	ND	
E, 2-cyclohexen-1-ol acetate[c]	H_1	ND	$J_{2,3}$ = 10.0
	H_2	5.7 d	
	H_3	5.9 d	

[a] All CH_2 and >CHD protons occur in the δ 1.5–2.2 region. [b] ND = not detected, d = doublet, t = triplet, m = multiplet. [c] This product consisted of a 1:1 mixture of these two isomers.

From the coupling constant data presented it is apparent that in the 1,3-chloroacetate the H_1 and H_2 protons are trans. In the 1,4-chloroacetate H_1 and H_2, and H_3 and H_4 are trans. In addition, since the Cl and OAc are trans, the H_2 and H_3 protons must also be trans. In the 3-cyclohexen-1-ol acetate the H_1 and H_2 protons are again trans. In all three compounds all four deuteriums are retained. The 1:1 mixture of the 2-allylic esters was previously reported for the Hg(II) oxidation of the deuterated cyclohexene[10] and for the Pd(II) oxidation in the accompanying communication.[11]

The deuterium distributions of the first three products in Table II are consistent with their being formed *via* an initial acetoxypalladation followed by stepwise movement of the Pd(II) around the ring. Although several reasonable mechanisms can be written for these 1,2 shifts of hydrogen (or deuterium), including the concerted diaxial ⇄ diequatorial type shift suggested as one possibility by Wolfe and Campbell,[11] we believe the mechanism most consistent with known Pd(II) chemistry is Pd(II)–hydride (or deuteride) elimination and readdition. Decomposition to final product would occur either by Pd(II)–hydride elimation to give unsaturated ester or by reaction with $CuCl_2$ to give sat-

(5) The kinetics do not absolutely require cis attack of Pd(II)–OH. See P. M. Henry, *Adv. Chem. Ser.*, **No. 70**, 136 (1968).

(6) (a) E. W. Stern, *Catal. Rev.*, **1**, 125 (1967); (b) A. Sabel, J. Smidt, R. Jira, and H. Prigge, *Chem. Ber.*, **102**, 2939 (1969); (c) E. W. Stern and H. C. Volger, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14** (4), F 4 (1969).

(7) A. Panunzi, A. De Renzi, and G. Paiaro, *J. Amer. Chem. Soc.*, **92**, 3488 (1970).

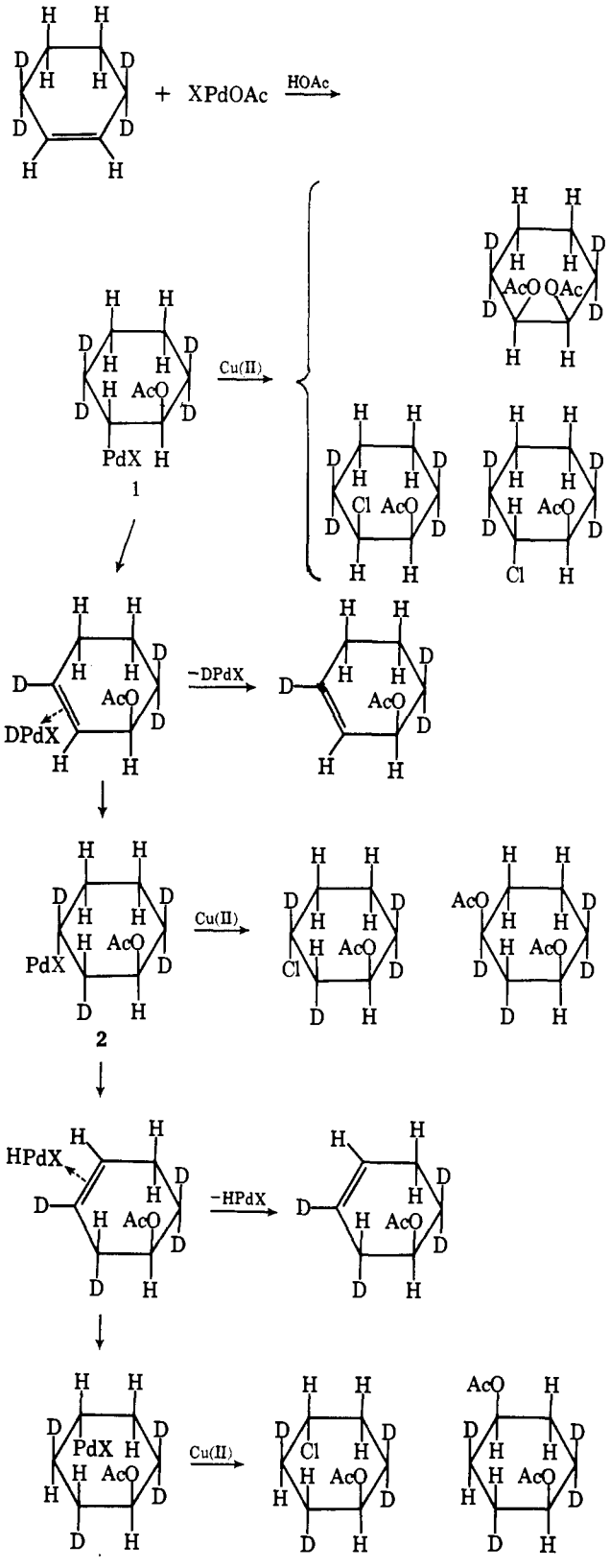
(8) P. M. Henry, *J. Org. Chem.*, **32**, 2575 (1967).

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

(10) S. Wolfe, P. G. C. Campbell, and G. E. Palmer, *Tetrahedron Lett.*, 4203 (1966).

(11) S. Wolfe and P. G. C. Campbell, *J. Amer. Chem. Soc.*, **93**, 1497 (1971).

Scheme I



urated products. *However, the trans arrangements of the hydrogens in these compounds requires that acetoxypalladation and Pd(II)–hydride elimination readdition have different stereochemistries.* Since trans Pd(II)–hydride elimination to give free hydride is a very unlikely process in a hydroxylic solvent such as acetic acid the acetoxypalladation must have trans stereochemistry. The reaction sequence is shown in Scheme I.

Kinetic and equilibrium studies are consistent with the scheme. Thus OAc^- is not appreciably coordinated to Pd(II) in solutions containing excess chloride[12] and kinetic studies of vinyl acetate exchange[12b,13] indicate that OAc^- coordination prior to acetoxypalladation is not required. The stereochemistry of the final saturated products is also consistent with the relative affinities of Cl^- and OAc^- for Pd(II). Thus, if the decomposition of **2** or **3** is occurring *via* an SN1 mechanism the incipient carbonium ion would most likely be neutralized by a chloride complexed to Pd(II) to give a chloroacetate of the same configuration as **2** or **3**. On the other hand, attack of acetate would most likely occur from outside the coordination sphere in an SN2 fashion to give cis diacetates. The appreciable yield of cis chloroacetates and higher ratios of diacetate to chloroacetate product in the case of the 1,2 isomers may reflect the inductive inhibition of SN1 solvolysis by neighboring acetate. Thus SN2 attack by chloride or acetate could become more important in this case. It is also possible that acetoxonium ions could be involved in some of the decompositions.

The present work does not elucidate the mode of interaction of Pd(II) in **1**, **2**, **3**, and $CuCl_2$ to give saturated products. We believe[14] it most likely involves transfer of electrons from the Pd(II)–carbon bond to a $CuCl_2$–Pd(II) polynuclear complex.

Several other results of this work deserve comment. First, the allylic ester product from this scheme would not be expected to be the 1:1 mixture. However, the mechanistic interpretation of this result is uncertain since Pd(II) catalyzes allylic isomerization.[15] It is, of course, possible that π-allylic routes are responsible for some of the allylic ester product.[11] Second, enol acetate would be a predicted product by cis elimination of HPdX from **1**, but is absent. However, the oxidation of 2-butene by $Pd(OAc)_2$ does not give enol acetate[15a] although there is no stereochemical reason why it should not be a product. Thus, with some olefins enol acetates are not favored even though stereochemically possible. Third, the HPdX formed in going from **1** to **2** must not exchange with solvent. It is quite reasonable that elimination–readdition be faster than exchange and, in fact, in olefin isomerizations postulated to proceed *via* HPdX little or no exchange with solvent is observed.[16]

In conclusion, it appears that coordination of the nucleophile to palladium is not nceessarily required prior to attack on coordinated olefin. In cases where there is nucleophile coordination, it may result from secondary factors. Thus, chloride may give cis chloropalladation because it is strongly coordinated to Pd(II), and in the Wacker reaction OH may be coordinated to Pd(II) before attack on the olefin because this species could not exist to any appreciable extent free in solution under the acid conditions of the reaction.[4]

(12) (a) P. M. Henry and O. Marks, *Inorg. Chem.*, **10**, 373 (1971); (b) P. M. Henry, *J. Amer. Chem. Soc.*, in press.
(13) P. M. Henry, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14** (2), B15 (1969); see also **14** (4), F3 (1969).
(14) P. M. Henry, *ibid.*, **14** (4), F5 (1969).
(15) (a) W. Kitching, Z. Rappoport, S. Winstein, and W. G. Young, *J. Amer. Chem. Soc.*, **88**, 2054 (1966); (b) T. Masuda, T. Mitsuyasu, and Y. Nakamura, *Kogyo Kagaku Zasshi*, **72**, 1751 (1969); (c) P. M. Henry, submitted for publication.
(16) R. Cramer and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **88**, 3534 (1966).

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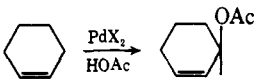
Allylic and Homoallylic Oxidation of Cyclohexene and Cyclohexene-*3,3,6,6-d*$_4$ by Palladium(II) Salts. Evidence for Competing "Symmetrical" and Oxypalladation Intermediates

Sir:

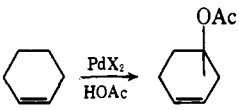
The reaction of an olefin with a Pd^{II} salt[1] may lead, depending upon the nature of the substrate and the experimental conditions, to a carbonyl compound,[2] a vinyl ester,[3] allylic oxidation,[4] or homoallylic oxidation.[5] The first two processes have been studied in considerable detail in recent 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 communication[7] 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 $PdCl_2$ or with $Pd(OAc)_2$[8] in neutral or buffered



(1)



(2)

acetic acid solutions were unsuccessful because of the superposition of a much more rapid Pd^0-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 HNO_3, HNO_2, or $Hg(OAc)_2$[14] 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

(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).

(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; Pd^0, formed in the initial oxidation–reduction step, aromatizes cyclohexene, and the available hydrogens thus produced reduce Pd^{II} to Pd^0 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 Pd^0 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 Pd^0-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 $PdCl_2$–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 ($J \simeq 10$ 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 ($^3J \simeq 3.5$, $^5J \simeq 2.0$ and 0 Hz[19]). 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, $J \sim 2$, 12 Hz) and 4.3 (H_B, doublet, $J = 12$ Hz). Equilibration of **4** with **5** is accompanied by appearance