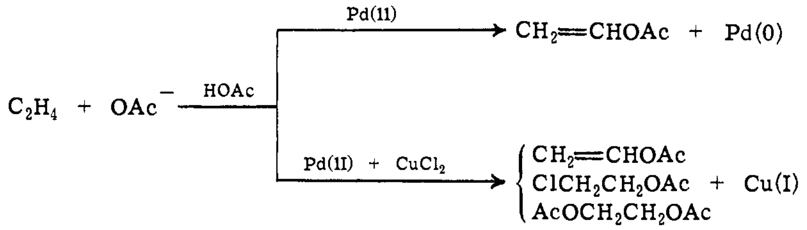
Oxidation of Olefins by Palladium(II). V. Oxidation of Cyclohexene by a Combination of Palladium(II) Chloride and Copper(II) Chloride in Acetic Acid[1,2]

Patrick M. Henry[3]

Contribution No. 1560 from the Research Center, Hercules Incorporated, Wilmington, Delaware 19899. *Received June 21, 1971*

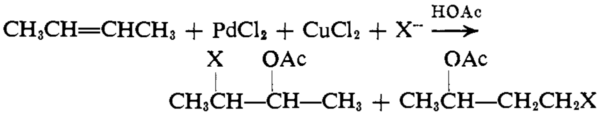
Abstract: The oxidation of cyclohexene by a mixture of Pd(II) and Cu(II) in acetic acid gives, in addition to 2-cyclohexen-1-ol acetate and 3-cyclohexen-1-ol acetate, obtained in the absence of Cu(II), saturated disubstituted cyclohexanes. These saturated esters were either chloro acetates or diacetates. Control experiments demonstrated that the saturated esters were formed only when both $PdCl_2$ and $CuCl_2$ were present in the reaction mixture. The saturated esters were mainly the 1,2 isomers although 1,3 and 1,4 chloro acetates and diacetates were also formed. Only certain isomers of these products were obtained. Thus the diacetates were all of cis stereochemistry. The 1,3 and 1,4 chloro acetates were almost exclusively trans while the 1,2 chloro acetate was an approximately equimolar mixture of cis and trans isomers. Reaction schemes involving π-allyls or Pd(IV) species can be eliminated by the experimental results. Oxidation of cyclohexene-*3,3,6,6-d*$_4$ gave 3-cyclohexen-1-ol acetate and trans-1,3 and -1,4 chloro acetates which retained all four deuteriums. The distributions of deuterium in these products were stereospecific. Based on the present results and related studies, a reaction scheme can be proposed which is consistent with the stereochemical results as well as kinetic and equilibrium studies on other Pd(II) systems. This scheme involves trans acetoxy-palladation followed by stepwise movement of the Pd(II) around the ring by cis palladium(II) hydride eliminations and readditions. The decomposition of the Pd(II) adduct occurs by reaction with Cu(II). This decomposition is believed to involve transfer of electrons from the Pd(II)–carbon bond in the adduct directly to Cu(II).

In a previous paper[2a] of this series the general features of a new olefin oxidation reaction requiring the presence of both Pd(II) and Cu(II) was described. Thus, in acetic acid, whereas Pd(II) alone oxidizes ethylene to vinyl acetate, in the presence of Cu(II), β-chloroethyl acetate and ethylene glycol diacetate are also formed. The yield of saturated esters increases with increasing soluble Cu(II) concentration in the supernatant of the heterogeneous reaction mixtures.



(1)

One particularly interesting aspect of the oxidation is that products, other than those which would arise from simple 1,2 addition to the double bond, are formed. Thus 2-butene gives 1,3- as well as 1,2-disubstituted butanes ($X^- = Cl^-$ or OAc^-).



$$CH_3CH{=}CHCH_3 + PdCl_2 + CuCl_2 + X^- \xrightarrow{HOAc} CH_3\overset{X}{C}H{-}\overset{OAc}{C}H{-}CH_3 + CH_3\overset{OAc}{C}H{-}CH_2CH_2X \qquad (2)$$

This paper reports the results of a study of the product distributions obtained by the oxidation of cyclohexene under several reaction conditions. Cyclohexene was used for this study rather than, for example, *cis*- or *trans*-2-butene for several reasons. The complication of Pd(II)-catalyzed olefin isomerization is avoided. The stereochemistry of the 1,3 and 1,4 products as well as that of the 1,2 products can be determined. The stereochemical results are easier to interpret in terms of mechanism because there cannot be free rotation around the carbon–carbon bonds in any reaction intermediates.

Results

Product distributions were determined at 25, 50, 75, and 100°. Reaction mixtures contained various amounts of $PdCl_2$, $CuCl_2$, either LiOAc or NaOAc, and sometimes LiCl. The reaction mixtures were usually heterogeneous because of the low solubility of many of the salts in acetic acid, the solvent used for all of the runs. Under one set of reaction conditions, the reaction was run on a large scale, and all of the reaction products were separated and positively identified. Control experiments were run to determine which products were the results of the reactions catalyzed by Pd(II) alone and by the Pd(II)-$CuCl_2$ combination. It was found that Pd(II) alone gave 2-cyclohexen-1-ol acetate and 3-cyclohexen-1-ol acetate while Pd(II)-$CuCl_2$ reaction gave, in addition to the unsaturated esters, 1,2-, 1,3-, and 1,4-disubstituted cyclohexanes which were either chloroacetates or diacetates. Other controls indicated these were all primary products.

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[1] Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstract S-78. In addition a preliminary communication on this work has appeared: P. M. Henry and G. A. Ward, *J. Amer. Chem. Soc.*, **93**, 1494 (1971).

[2] (a) Paper III: P. M. Henry, *J. Org. Chem.*, 32, 2575 (1967); (b) paper IV: *J. Amer. Chem. Soc.*, **94**, 4437 (1972).

[3] Address correspondence to author at the Department of Chemistry, University of Guelph, Guelph, Ontario, Canada.

Another product, 1,2-dichlorocyclohexane, was formed by the $CuCl_2$-catalyzed chlorination of cyclohexene.[2,4] Other products, such as 1,4-diacetoxy-2-cyclohexene, were formed by further oxidation of the initial cyclohexenyl acetate products.

Product distributions at three soluble chloride levels, given in Table I, demonstrate the effect of Cu(II) on product distribution. The Cu(II) concentration depends on the soluble chloride. Thus, no. 1 contains sodium acetate so the chloride level is quite low, because NaCl is sparingly soluble in acetic acid,[5] and the Cu(II) concentration is correspondingly low. Number 2 contains LiOAc so the chloride concentration is much higher, since LiCl is quite soluble in acetic acid. Number 3 contains the highest chloride, since, in addition to using LiOAc, it is 2 *M* in LiCl and is homogeneous. Other runs with a high chloride but low Cu(II) concentration demonstrated that [Cu(II)] is the important factor in product distribution rather than soluble chloride. Thus as soluble Cu(II) increases, the percentage of saturated products increases. This is accomplished by increasing the rate of formation of saturated products while leaving the rate of formation of unsaturated products unchanged or decreased. After all the Cu(II) was solubilized, a further increase in soluble chloride actually decreased the rate.

Table I. Product Distributions for the Oxidation of Cyclohexene at 75° for Three Soluble Copper(II) Concentrations[a]

Product	% of product[b] No. 1 [Cu(II)] = 0.07 *M*	No. 2 [Cu(II)] = 0.75 *M*	No. 3 [Cu(II)] = 1.0 *M*
Unsaturated esters			
1-Cyclohexen-1-ol acetate	<0.1	<0.1	<0.1
2-Cyclohexen-1-ol acetate	88	46.5	39.3
3-Cyclohexen-1-ol acetate	3.5	6.9	6.6
1,2 Isomers			
Cis chloro acetate	0.36	12.5	13.9
Trans chloro acetate	0.75	11.8	18.9
Cis diacetate	0.49	12.4	11.1
Trans diacetate	<0.1	<0.1	<0.1
1,3 Isomers[c]			
Cis chloro acetate	<0.1	<0.1	<0.1
Trans chloro acetate[c]	2.7	6.5	6.0
Cis diacetate[c]	0.67	0.9	0.67
Trans diacetate	<0.1	<0.1	<0.1
1,4 Isomers			
Cis chloro acetate	0.25	0.2	0.2
Trans chloro acetate[c]	1.4	2.3	3.0
Cis diacetate[c]	0.34	0.5	0.33
Trans diacetate	<0.1	<0.1	<0.1

[a] All contain 1.0 mol of cupric chloride and 0.01 mol of Pd(II) per liter of solution. No. 1 also contains 1.0 mol of sodium acetate, no. 2 contains 1.0 mol of lithium acetate, and no. 3 contains 1.0 mol of lithium acetate and 2.0 mol of lithium chloride. No. 1 and 2 were heterogeneous; no. 3 was homogeneous. [b] Product distributions are the average of at least three runs with about 10% variation between runs. [c] Trans-1,3 and -1,4 chloro acetates, and cis-1,3 and -1,4 diacetates were not separated by glc. In no. 2 nmr analysis indicated a ratio of 1,3 to 1,4 isomers for both chloro acetates, and that of diacetate was 2 to 1. Product distributions for no. 1 and 3 were calculated assuming the same ratio.

The trends of product distribution of saturated products given in Table I is representative of all the runs. In no case was 1-cyclohexen-1-ol acetate or trans 1,2-, 1,3-, or 1,4-diacetate detected.

As might be expected, increasing the temperature increased the rate of product formation probably both by increasing soluble chloride and by the usual Arrhenius increase in rate with temperature. The product distributions, however, were not greatly changed by changing the temperature.

Several other experiments were performed to test various mechanistic possibilities for the reaction. Thus, π-cyclohexenylpalladium(II) chloride was decomposed under the reaction conditions of no. 2 in Table I. The only product observed was 2-cyclohexen-1-ol acetate in 30% yield. In the absence of $CuCl_2$, no product was observed.

To test the possibility that Pd(IV) salts were involved in the reaction sequence, cyclohexene was oxidized with either K_2PdCl_6 or $(NH_4)_2PdCl_6$. Only 1,2-dichlorocyclohexane and *trans*-2-chloro-1-cyclohexyl acetate were obtained as products in low yields.

trans-2-Acetoxycyclohexyl *p*-toluenesulfonate was solvolyzed under the reaction conditions to see what products would be obtained if 1,2 acetoxonium ions are intermediates in the reaction sequence.[6] Results are given in Table II.

Cyclohexene-*3,3,6,6-d*$_4$ was oxidized under the same reaction conditions of run no. 2 in Table I, and the positions of the deuterium label in the unsaturated esters and the trans-1,3 and -1,4 chloro acetated were determined by nmr.

The use of vicinal coupling constants to determine cis–trans relationships in substituted cyclohexanes has recently been thoroughly reviewed by Booth.[7] 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 III.

From the coupling constant data presented it is apparent that in the 1,3 chloro acetate the H_1 and H_2 protons are trans. In the 1,4 chloro acetate H_1 and H_2 protons 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. Thus they must have the structures given by A to C, respectively. The 1:1 mixture of the 2-allylic esters is indicated by the ratio of areas of the H_1 proton in D and the olefinic protons in D and E.

Discussion

The most significant stereochemical results of this study are: (1) cis- and trans-1,2 chloro acetates are produced while the 1,3 and 1,4 chloro acetates are almost exclusively trans; (2) the 1,2-, 1,3-, and 1,4-diacetates are exclusively the cis isomers; (3) the trans-1,3 and 1,4 chloro acetates and the 3-cyclohexen-1-ol acetate from cyclohexene-*3,3,6,6-d*$_4$ have the structures

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(4) R. J. Arganbright and W. F. Yates, *J. Org. Chem.*, 27, 1205 (1962).

(5) At 75° the solubility of NaCl is 0.22 *M*: H. Stephen and T. Stephen, "Solubilities of Inorganic and Organic Compounds," Vol. 1, Part 1, Pergamon Press, New York, N. Y., 1963, p 655.

(6) S. Winstein, C. Hanson, and E. Grunwald, *J. Amer. Chem. Soc.*, 70, 812 (1948), and other included references.

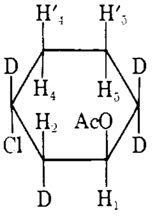
(7) H. Booth, *Progr. Nucl. Magn. Resonance Spectrosc.*, 5, 149 (1969).

Table II. Solvolysis of *trans*-2-Acetoxycyclohexyl *p*-Toluenesulfonate in Acetic Acid at 75° [a]

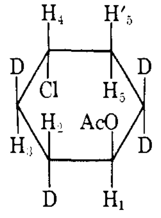
Composition of reaction mixtures, mol/l. of acetic acid					Relative product distribution[b]		
$PdCl_2$	$CuCl_2$	LiOAc	NaOAc	LiCl	*t*-ClA	*c*-DA	*t*-DA
0.01	1.0	1.0		0.01	0.25	1.0	ND
		3.0			ND	1.0	1.45
0.02		3.0		0.02	Trace	1.0	ND
	2.0	3.0			0.2	1.0	ND
			3.0		ND	1.0	3.0
0.01		1.0		2.0	0.2	1.0	ND

[a] Reaction mixtures were run for 24 hr. All reaction mixtures were dried with excess Ac_2O. [b] *t*-ClA = trans-1,2 chloro acetate, *c*-DA = cis-1,2 diacetate, *t*-DA = trans-1,2 diacetate. ND = not detected.

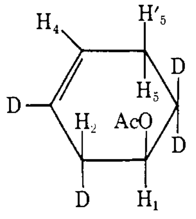
Table III



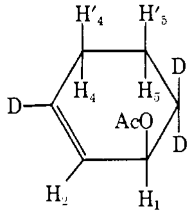
A



B



C



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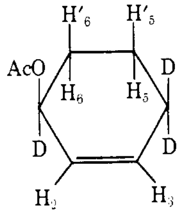

E

Compd	Proton[a]	δ, ppm[b]	J, Hz (±0.2)
A, trans-1,3 chloro acetate	H_1	5.0 d	$J_{1,2} = 7.0$
	H_3	ND	
B, trans-1,4 chloro acetate	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	5.66 t	$J_{4,5} = J_{4,5'} = \sim 3.5$
	H_1	5.2 d	$J_{1,2} = \sim 3.5$
D, 2-cyclohexen-1-ol acetate[c]	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 the two isomers. D and E.

given by A–C, respectively. Also of mechanistic importance were the findings that π-allylcyclohexenylpalladium chloride gave only 2-cyclohexen-1-ol acetate when decomposed in acetic acid,[8] and Pd(IV) did not give the same products from cyclohexene as a combination of Pd(II) and Cu(II).

Possible mechanisms for the formation of saturated esters include: (1) formation of Pd(IV) species which are the actual oxidants, (2) formation of π-allylic intermediates which then react with $CuCl_2$, (3) direct decomposition of π complexes to give saturated esters, and (4) formation of intermediate acetoxypalladation adducts which react with $CuCl_2$ to give saturated esters.

The first two possibilities seem very unlikely because of the experiments with Pd(IV) and π-cylohexenylpalladium chloride, and because it is difficult to visualize how direct decomposition of π complexes could give 1,3- and 1,4-disubstituted cyclohexanes. Thus, as concluded previously,[3] the mechanism which appears to best fit the results is no. 4. The initial acetoxypalladation adduct would, of course, be the 1,2 adduct which would react with $CuCl_2$ to give the 1,2-disubstituted cyclohexanes. The 1,3 and 1,4 products would arise from stepwise movement of the Pd(II) around the ring to give 1,3 and 1,4 acetoxypalladation adducts before reaction with $CuCl_2$.[2a]

In support of this mechanism, oxypalladation adducts have been proposed for other Pd(II)[11–14] oxidations, and there is evidence[2a,12,15] that these adducts can isomerize.

Now the stereochemical results must be considered in relationship to this scheme. The fact that only certain isomers are formed indicates that acetoxypalladation and movement of Pd(II) around the ring must be stereospecific processes. The mechanism for movement of Pd(II) around the ring which is most consistent with routes proposed for other Pd(II)-catalyzed reactions such as isomerization[16] and oxidation[12] is palladium(II) hydride elimination and readdition. Little more can be said about the reaction sequence until the stereochemistry of acetoxypalladation and palladium(II) hydride elimination readdition is known. Fortunately the deuterium labeling results provide strong evidence for the stereochemistry of acetoxypalladation. Thus, the trans arrangement of the hydrogens in A, B, and C requires that acetoxypalladation and palladium(II) hydride elimination readdition have different stereochemistries.[17] Since trans palladium-

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[8] This result is consistent with other studies of the decomposition of π-allyls.[9,10]

[9] W. Kitching, C. F. Fong, and B. F. Hegarty, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, 14 (2), B84 (1969).

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

[11] P. M. Henry, *ibid.*, **86**, 3246 (1964).

[12] W. Kitching, Z. Rappoport, S. Winstein, and W. G. Young, *ibid.*, **88**, 2054 (1966).

[13] I. I. Moiseev and M. N. Vargaftik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 759 (1965).

[14] R. Jira, J. Sedlmeier, and J. Smidt, *Justus Liebigs Ann. Chem.*, **693**, 99 (1966).

[15] M. Green, R. N. Haszeldine, and J. Lindley, *J. Organometal. Chem.*, **6**, 107 (1966).

[16] For recent reviews see (a) N. R. Davies, *Rev. Pure Appl. Chem.*, 17, 83 (1967); (b) E. W. Stern, *Catal. Rev.*, 1, 73 (1967); (c) F. R. Hartley, *Chem. Rev.*, **69**, 799 (1969).

[17] The only other likely mechanism which gives the observed deuterium distribution is cis acetoxypalladation followed by a concerted diaxial–diequatorial-type shift. However, when a reagent almost certain to add cis, namely phenylpalladium, was used, the deuterium distribution was consistent with cis phenylpalladation and cis palladium-

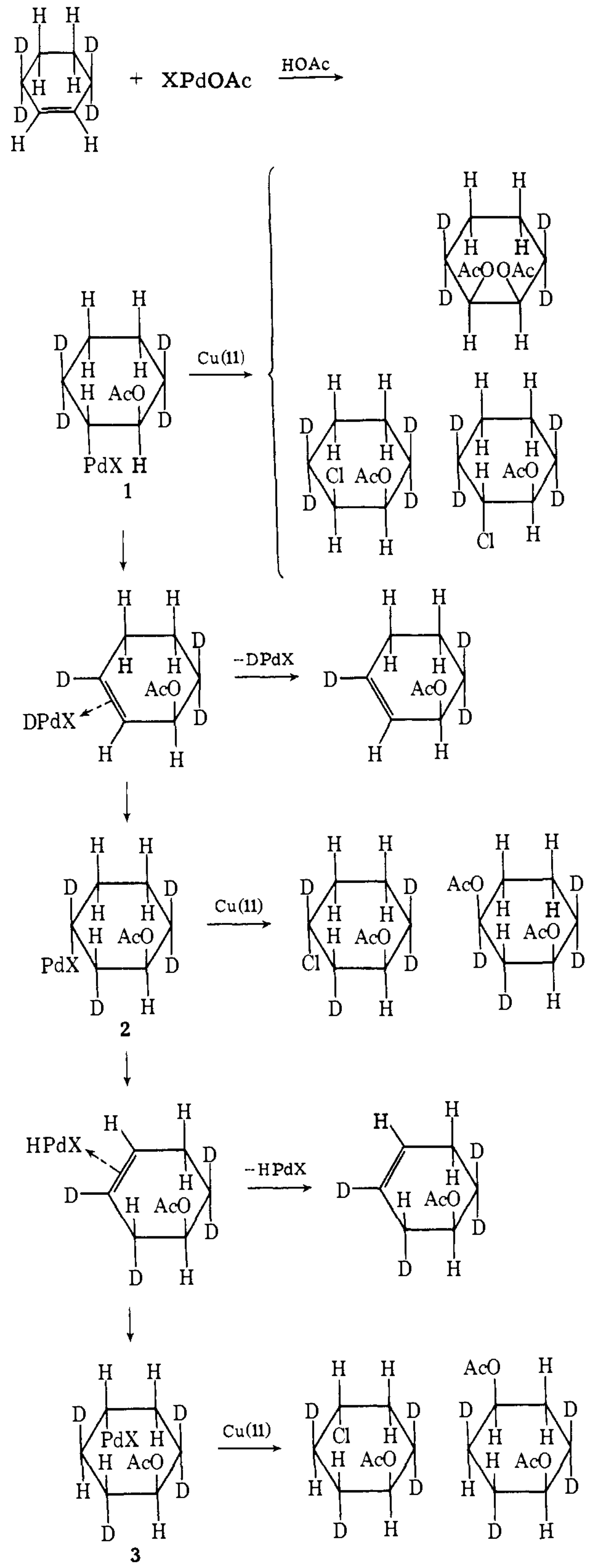
(II) hydride elimination to give free hydride is a very unlikely process in a hydroxylic solvent such as acetic acid, the acetoxypalladation must have trans stereochemistry. The reaction sequence is shown in Scheme I.[19]

Trans acetoxypalladation is consistent with other kinetic and equilibrium studies. Thus OAc^- is not appreciably coordinated to Pd(II) in solutions containing excess chloride[20] and kinetic studies of vinyl ester exchange indicate that OAc^- coordination is not required prior to acetoxypalladation.[21] Finally studies of vinyl chloride exchange with OAc^- indicate acetoxypalladation and chloropalladation have different stereochemistries.[22] Since chloride is complexed to Pd(II) in these systems chloropalladation would be expected to be a cis process.

The stereochemistry of the final products is also consistent with the lack of acetate complexing to Pd(II). The oxidation of norbornene by a mixture of $PdCl_2$ and $CuCl_2$ in acetic acid gives rearranged products,[23] a result best rationalized by acetoxypalladation followed by heterolytic metal–carbon bond splitting to give a norbornyl cation which rearranges before reacting with chloride or acetate. If **2** or **3** decomposed *via* this type of mechanism, the incipient carbonium ion would most likely be neutralized by a chloride complexed to Pd(II) to give a chloro acetate of the same configuration as **2** or **3**. On the other hand, attack of acetate would most likely occur from outside the coordination sphere to give cis diacetates. The appreciable yield of cis chloro acetates in the case of the 1,2 isomer may reflect the inductive inhibition of SN1 solvolysis by neighboring acetate.[24] Thus SN2 attack by chloride could become important in this case.

Since acetate and Pd(II) have a trans configuration in **1**, **2**, and **3**, the possibility of decomposition to give 1,2, 1,3, or 1,4 acetoxonium ions must be considered. The 1,2 acetoxonium ion intermediate is well documented[6] while the 1,3 acetoxonium ion has been suggested as intermediate in some solvolysis reactions.[25] To the author's knowledge, no 1,4 acetoxonium ions have been suggested as intermediates in solvolysis reactions. At first glance, acetoxonium ions would be expected to give trans diacetates.[26] To ensure that this would be the case under the reaction conditions, *trans*-2-acetoxycyclohexyl *p*-toluenesulfonate was solvolyzed under the reaction conditions. This solvolysis is known to proceed *via* 1,2 acetoxonium ions.[6] The products shown in Table II show that, in fact, the acetoxonium ion opens to give cis diacetate under the reaction conditions. This surprising result, interesting in itself, indicates that metal ions such as Pd(II) or Cu(II) can cause the acetoxonium ions to open to give cis diacetates. Thus acetoxonium ions cannot be eliminated as intermediates in the decomposition of the acetoxypalladation adducts. However, this route cannot be the only mode of decomposition because cis-

Scheme I



(II) hydride elimination and readdition. It was inconsistent with cis phenylpalladation and diaxial–diequatorial shifts.[18]

[18] P. M. Henry and G. A. Ward, *J. Amer. Chem. Soc.*, **94**, 673 (1972).

[19] Pd(II)–olefin π complexes are likely intermediates in the oxypalladation[11] step but are not shown for the sake of simplicity. Also, because the actual state of the Pd(II) is not known in these systems, the other two coordination positions of the Pd(II) are not specified.

[20] P. M. Henry and O. Marks, *Inorg. Chem.*, **10**, 373 (1971).

[21] P. M. Henry, *J. Amer. Chem. Soc.*, **93**, 3853 (1971).

[22] A. Sabel, J. Smidt, R. Jira, and H. Prigge, *Chem. Ber.*, **102**, 2939 (1969); E. W. Stern and H. C. Volger, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, 14 (4), F4 (1969).

[23] W. C. Baird, Jr., *J. Org. Chem.*, **31**, 2411 (1966).

[24] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 115.

[25] (a) L. J. Dolby and M. T. Schwarz, *J. Org. Chem.*, **30**, 3581 (1965); (b) O. Kovacs, G. Schneider, and L. K. Lang, *Proc. Chem. Soc., London*, 374 (1963); (c) L. J. Dolby, C. N. Lieske, D. R. Rosencrantz, and M. J. Schwarz, *J. Amer. Chem. Soc.*, **85**, 47 (1963).

[26] P. M. Henry, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14** (4), F5 (1969).

1,2 chloro acetate is not formed in these systems but is found as a product in the Pd(II) plus Cu(II) oxidation of cyclohexene. It also cannot explain the high yields of trans chloro acetates since, even at high chlorides, little trans-1,2 chloro acetate was obtained from the acetoxonium ion intermediate. In any case, whether the cis diacetates are formed *via* acetoxonium ions or by SN2 attack of acetate ions, both involve the attack of acetate from outside the coordination sphere.

The present results do not elucidate the mode of interaction of Pd(II) in **1**, **2**, and **3** with $CuCl_2$ to give saturated products. It is possible that Pd(II) transfers alkyl to Cu(II), the Cu(II) alkyl then decomposing to give the saturated products. However, we believe[26] that the mechanism most likely involves transfer of electrons from the Pd(II)–carbon bond to the $CuCl_2$–Pd(II) polynuclear complex. As has been discussed previously,[27,28] the reason Pd(II) alone does not give saturated products is that, in the transition state for formation of these products, Pd(0) would be formed. However, kinetic measurements[2a,29] have not been able to completely define the reaction, and more work is required before the exact nature of the decomposition will be known.

Three other points deserve brief comment. No enol acetates are found in the reaction mixtures. They would be a predicted product of trans acetoxypalladation and cis hydride elimination. However, the oxidation of 2-butene by $Pd(OAc)_2$ does not give any enol acetate[12] even though 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.

Second, the allylic esters product would be expected to be D rather than a 1:1 mixture of D and E. However, the mechanistic interpretation of this result is uncertain since Pd(II) catalyzes allylic isomerization.[12,30] It is, of course, possible that π-allylic routes are responsible for some or most of the allylic product. As mentioned above, decomposition of π-cyclohexenylpalladium chloride gives 2-cyclohexen-1-ol acetate, and oxidation of cyclohexene-*3,3,6,6*-d_4 by this route would give a 1:1 mixture of D and E.[31]

Third, control experiments indicated the unsaturated esters were not interconverted under the reaction conditions (see Experimental Section). Thus, in Scheme I once the olefin DPX or HPdX π bonds in the intermediate in going from **1** to **2** or **2** to **3** is broken, the hydride must be rapidly decomposed by $CuCl_2$ to give $PdCl_2$ and H^+ or D^+. If this were not the case, the unsaturated esters would be interconverted under the reaction conditions and intermolecular hydride or deuteride transfer would be observed.

Experimental Section

Materials. Aldrich cyclohexene was distilled and stored under N_2. $PdCl_2$ was purchased from Engelhardt Industries. All other salts were of reagent grade. Preparation and analysis of Pd(II) stock solutions in dry acetic acid have been described previously.[2,20] The cyclohexene-*3,3,6,6*-d_4 was purchased from Merck Sharp and Dohme of Canada.

trans-2-Acetoxycyclohexyl *p*-toluenesulfonate was prepared by a literature procedure[32] as was π-cyclohexenylpalladium(II) chloride.[33]

The corresponding acetate ester standards were prepared by acetylation of the following alcohols: 2-cyclohexen-1-ol (Aldrich Chemical Co.), 3-cyclohexen-1-ol (Columbia Chemical), *trans*-2-chlorocyclohexanol (K & K Laboratories), *trans*-1,2-cyclohexanediol (Aldrich), and *cis*-1,2-cyclohexanediol (K & K). A mixture of *cis*- and *trans*-1,4-cyclohexanediol diacetates was separated by crystallization[34] and identified by melting point and nmr spectra. Pure samples of the *cis*- and *trans*-1,3-cyclohexanediol diacetate isomers were collected by preparative gas–liquid chromatography (glc) and identified by nmr spectra.

Pure *trans*-4-chlorocyclohexanol acetate was prepared by reaction of 1,4-epoxycyclohexane with HCl[35,36] followed by acetylation. Pure samples of each isomer of the cis–trans mixture were obtained by preparative glc. The nmr and the glc retention time of one of the isomers of the mixture were identical with those of the trans-1,4 chloro acetate while the nmr of the other was consistent with that of the cis-1,4 chloro acetate. A sample of *cis*-2-chlorocyclohexanol acetate was supplied by the late Professor Winstein. 1-Cyclohexen-1-ol acetate was prepared by reaction of cyclohexanone with acetic anhydride using concentrated H_2SO_4 as a catalyst. 2-Chlorocyclohexane was purchased from K & K while *trans*-1,2-dichlorocyclohexane was purchased from Aldrich.

Analyses. All product analyses were carried out using a 15-ft 10% Ucon 75h column on Gas Chrom Z programmed from 130 to 200° at 2.4°/min. The helium flow rate was 100 ml/min.

These conditions did not separate the trans-1,3 and -1,4 chloro acetates from each other nor the cis-1,3 and -1,4 diacetates from each other. No conditions we tried could effect these separations. Thus, in most reaction mixtures, the ratio of 1,3 to 1,4 isomers was not known for these materials. However, in the large-scale run there were sufficient materials for these ratios to be determined by nmr.

Soluble Cu(II) concentrations were determined by reaction of the supernatant with iodide ion followed by titration of the iodine with thiosulfate.

Experimental Procedure. Runs were usually made on a 250-ml scale in 750-ml soft drink bottles under an N_2 atmosphere. The bottle was capped with a metal cap having holes sealed by a rubber liner through which syringe-needles could be inserted into the bottle. All the ingredients except the cyclohexene were added and the bottle was capped. The bottle was evacuated and pressured to atmospheric with N_2. The bottle was then put in an oil bath at the desired temperature and allowed to come to equilibrium. Then the run was started by adding the cyclohexene using a syringe. After the desired reaction time, the reaction mixture was removed from the bottle and diluted with CH_2Cl_2; the acetic acid and inorganic salts were removed by washing with water. The last traces of acetic acid were removed by washing with saturated aqueous $NaHCO_3$. After drying over $MgSO_4$, the organic phase was concentrated to a known volume and analyzed by glc. The reaction times were usually 0.5 hr at 100°, 2 hr at 75°, 4 hr at 50°, and 6 hr at 25°. During these periods, conversions based on cyclohexene were less than 5%.

Representative product distributions under various reaction conditions are given in Table IV. Results are the average of three runs.

Identification of Products. Preliminary identification was by glc retention time. To obtain enough product for positive identification the reaction was run 12 times on a 2.5-l. scale to about 50% conversion under one set of reaction conditions (no. 2 in Table I). The products from all the reactions were combined and distilled using an 80 theoretical plate column. A total of 35 cuts were obtained, a number of which consisted of pure components. Almost all of the cuts consisted of no more than two components. Pure samples were easily obtained by preparative glc and identified by nmr and ir spectra. In this way, all components of the reaction

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Table IV. Sample Product Distributions under Various Conditions

Reaction mixture[a]	2	3	1	2	3	2	3
Temp, °C	25	25	50	50	50	100	100
Reaction time, hr	6	112	46	4	4	0.5	0.5
			Products ($M \times 10^3$)				
3-Cyclohexen-1-ol acetate	0.18	ND	3.6	0.22	0.25	1.7	0.80
2-Cyclohexen-1-ol acetate	1.02	2.4	41.0	1.4	2.1	4.2	3.75
			1,2 Isomers				
Trans chloro acetate	0.21	ND	1.3	0.35	0.09	1.2	1.65
Cis chloro acetate	0.22	1.58	0.7	0.39	0.26	1.0	1.40
Cis diacetate	0.33	0.96	1.1	0.61	0.13	1.21	0.78
			Other Isomers				
Trans-1,3 and 1,4 chloro acetate	0.13	ND	3.5	0.16	0.72	0.80	0.87
Cis-1,4 chloro acetate	ND	ND	0.7	ND	0.06	0.06	0.07
Cis-1,3 and 1,4 diacetate	ND	ND	0.77	0.03	ND	0.19	0.11

[a] Corresponds to reaction mixtures in Table I.

mixture except the 1,3 chloro acetates were positively identified. The peak with the retention time of both cis-1,3 and -1,4 diacetates was found to consist of two parts of 1,3 to one part of 1,4. One high-boiling component was found to have an nmr consistent with 2-cyclohexene-1,4-diol diacetate. Other unknowns present in trace amounts consisted of materials which were apparently 1,3- or 1,4-dichlorocyclohexanes.

Several cuts contained material which gave one peak on glc analysis. The retention time of this material was identical with that of the trans-1,4 chloro acetate. However, nmr indicated that the material was only *ca.* one-third trans-1,4 chloro acetate, the remainder being either cis-1,4 chloro acetate or trans-1,3 chloro acetate.[37] However, the unknown could not be cis-1,4 chloro acetate, since it is known that an authentic sample has a different retention time. Although several attempts were made to prepare the cis- and trans-1,3 chloro acetates, none were successful, and to our knowledge this material has never been completely characterized.[39] The mixture of acetate esters could be hydrolyzed without decomposition by letting the mixture stand at room temperature overnight in methanol acidified with a little methanesulfonic acid. More vigorous conditions such as use of $LiAlH_4$ give extensive decomposition. The mixture of free alcohols now gave two peaks on glc analysis. The smaller peak, one-half the size of the large peaks, had a retention time identical with that of the trans-1,4 alcohol. The separation of the peaks was not sufficient for effective preparative glc purification so the mixture of alcohols was chromatographed using neutral alumina as support and hexane, CH_2Cl_2, and ether as eluents. Several cuts were obtained which, by glc, were over 90% "trans-1,3 chloro acetate." However, nmr indicated considerable decomposition to bicyclohexyl derivatives had occurred. The phenylurethane derivative of the crude product was prepared and rechromatographed. Several crystalline cuts were obtained, which upon several recrystallizations from hexane had mp of 88.2–88.6°. *Anal.* Calcd for $C_{13}H_{16}NO_2Cl$: C, 61.53; H, 6.35; Cl, 13.9. Found: C, 61.59; H, 6.33; Cl, 13.9. The nmr confirmed the 1,3 structure. The signal due to the CH_2 group between the chloride and urethane groups appears at δ 2.08 while the signal for the other ring protons appears at δ 1.7. In the free alcohol and acetate esters, this difference does not exist.

Control Experiments. A number of controls were run to ensure that the products in Table I were primary products. They were run the same as regular runs except one or more of the products were added to see if they were stable under the reaction conditions. All saturated products were completely stable while the unsaturated products reacted very slowly. Furthermore, the unsaturated products were not isomerized into each other. However, they did not produce any of the saturated products in Table I. Other control experiments were made in the same fashion as regular runs except that Pd(II) was omitted. The only product formed was 1,2-dichlorocyclohexane. Other control experiments were made omitting the $CuCl_2$. In no case were any saturated products formed.

Pd(IV) Runs. Three runs were made. The first, 0.2 *M* in K_2PdCl_6 and 2.0 *M* in LiCl, was run 18 days at 25°. Only traces of 1,2-dichlorocyclohexane and *trans*-2-chlorocyclohexyl acetate were formed. The second, 0.16 *M* in K_2PdCl_6, 2.0 *M* in LiCl, and 1.0 *M* in LiOAc, was run 23 hr at 75°. The reaction mixture was 0.0003 *M* in dichlorocyclohexane and 0.0077 *M* in *trans*-2-chlorocyclohexyl acetate. In the third, the reaction mixture was 0.5 *M* in $(NH_4)_2PdCl_2$ and the reaction was run 6 hr at 75°. The reaction mixture was 0.05 *M* in 1,2-dichlorocyclohexane and 0.011 *M* in *trans*-2-chlorocyclohexyl acetate.

π-Cyclohexenylpalladium(II) Chloride Runs. Reaction conditions remained the same as no. 2 in Table I except a 10-ml scale was used. Instead of cyclohexene, 1 mmol of the π-cyclohexenylpalladium(II) chloride was added. After 2 hr at 75° the reaction mixture was worked up in the usual fashion and analyzed by glc. The yield of 2-cyclohexen-1-ol acetate was 30%. In another run, the $CuCl_2$ was omitted. No product was detected by glc.

Decomposition of 2-Acetoxycyclohexyl *p*-Toluenesulfonate. Reaction mixtures were prepared on a 50-ml scale and put in a constant-temperature bath set at 75° for 2 hr. Then 2 g (*ca.* 6 mmol) of the sulfonate was added. After 24 hr the runs were worked up in the usual fashion and analyzed.

Cyclohexene-*3,3,6,6-d*$_4$ Runs. These runs were made on a 25-ml scale under the same reaction conditions as run no. 2 in Table I. To obtain enough products for analysis the reaction was run for 6 hr. The reaction mixture was worked up in the same fashion as the nondeuterated and samples were collected by preparative glc; *ca.* 20 mg of the allylic ester was obtained but less than 1 mg of A, B, and C was available for nmr analysis. However, using time averaging, satisfactory spectra of all the components were obtained.

Acknowledgments. The author gratefully acknowledges helpful discussions with Dr. H. G. Tennent and Professors M. Kilpatrick, H. Taube, H. Goering, and S. Wolfe, and the late Professor S. Winstein. The author is also grateful to Dr. G. Ward for interpretation of the nmr results and to Mr. M. Centuolo and F. Kriss for their technical assistance.

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(37) This assignment is based on peak width.[38] The unknown had a much narrower peak width than that of the trans-1,4 chloro acetate. This is consistent with the unknown being either cis-1,4 or trans-1,3 chloro acetate.

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