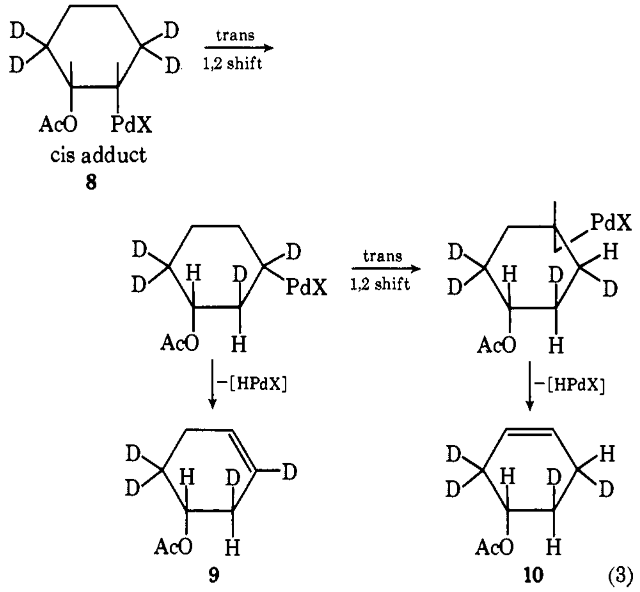
served only in the case of allylic oxidation on changing the substrate from cyclohexene to cyclohexene-*3,3,6,6-d_4*. This follows because the formation of a π-allylic or related complex would involve the breaking of an allylic C–H (C–D) bond.[25]

A study of the solvolytic behavior of some π and π-allylic palladium(II) complexes derived from cyclohexene has suggested[7] 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-allylic[27] or "switching" σ-allylic palladium complex[28] 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)

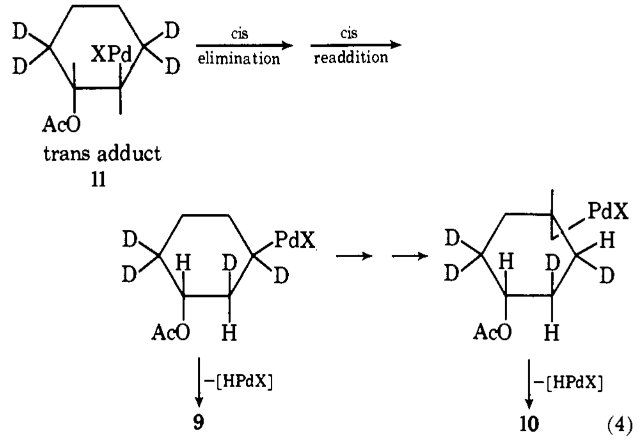
Mechanism I



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 rearrangement[29]), 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 series of cis elimination–readdition steps, and eventual elimination of [HPdX]. This scheme, favored by Henry and Ward[32] for the *addition* reactions of cyclohexene with a Li_2PdCl_4–$CuCl_2$ 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]

Mechanism II



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.

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[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.

[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-

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[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).

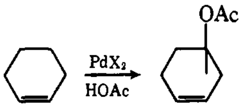
[4] (a) E. W. Stern, *Catal. Rev.*, **1**, 73 (1967); (b) B. L. Shaw, *Chem. Commun.*, 464 (1968); (c) C. B. Anderson and B. J. Burreson, *Chem. Ind.* (*London*), 620 (1967); (d) J. K. Stille and R. A. Morgan, *J. Amer.*

Table I. Solvolysis Studies in Acetic Acid at 25° [a]

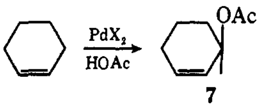
			Added reagents (mmol)						Product composition[b–d]							
Run	Substrate	mmol	NaOAc	Hg(OAc)$_2$	HNO$_2$	NaNO$_2$[e]	H$_2$O	Misc	7	6	Δ^2-Cyclohexenol	Δ^2-Cyclohexenone	Cyclohexyl acetate	Cyclohexane	Cyclohexene	Benzene
1	**8**	1.48	2.72						5	19				Trace	36	40
2[f]	**8**	1.2	2.4	1.2					Trace						100[g]	
3[h]	**8**	1.2	2.4	1.2					~92	~8						
4	**9**	0.2	1.7			1.8			88	12						
5	**10**	2.7	3.6				4.7							33		67
6	**10**	0.7	1.0	1.6				*i*	92–100	0–8					*j*	
7[k]	**11**	0.9			1.3				92–100	0–8						Trace
8[l]	**11**	1.5			1.8				58–63	0–5						34
9	**11**	0.45	0.6			1.7		*m*	92–100	0–8						Trace
10	**11**	0.3				1.8	83		18–20	0–2	55	25				Trace
11	**14**	2.0					167	*n*	50–70		30–50					
12	**13**	0.4							29–32	0–3				24		48
13	**11**	1.0							<1	1			3	22		73

[a] A standard reaction volume of 3 ml was employed. [b] Relative proportions (ξ products = 100%). [c] Volatile products were separated from nonvolatile products and all fractions were subjected to quantitative ir, nmr, and glc analysis; less than 8% of **6** could not be detected in the presence of **7**. [d] All spaces left blank indicate that the compound was searched for, but not detected. [e] Added NaNO$_2$ generates HNO$_2$ *in situ.* [f] 3-hr reaction time. [g] Cyclohexene plus acetoxymercuric acetate adduct. [h] 21-hr reaction time. [i] 0.7 mmol of cyclohexene was included in the reaction mixture. [j] Not determined because of the inclusion of cyclohexene in the mixture. [k] 10-min reaction time. [l] 47-hr reaction time. [m] 0.2 mmol of Pd(OAc)$_2$ was included in the reaction mixture. [n] 2.02 mmol of AgOAc was included in the reaction mixture.

duct **5**.[4b–f,5] Because, *a priori*, each of these may form reversibly, elucidation of the electron-transfer (oxidation–reduction) step of an oxidation requires that those complexes which are necessary intermediates be distinguished from those that are not. Although most of the data on olefin oxidation, including the homoallylic oxidation of cyclohexene (eq 1), are best interpreted in terms of an oxypalladation adduct as the principal product-determining intermediate,[5] we have recently presented evidence[5,6] that the concurrent allylic oxidation of cyclohexene (eq 2) requires a symmetrical intermediate. The present study was undertaken to determine whether the solvolytic behavior of some cyclohexene complexes, under conditions similar to those employed for allylic and homoallylic oxidation, is compatible with this view.

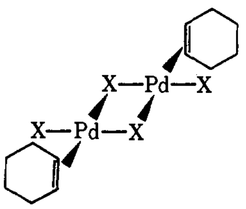


6 (1)

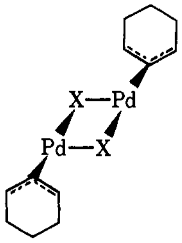


7 (2)

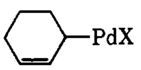
The π-complex **8**[1a] and the π-allylic complex **10**[2] were synthesized by the literature procedures. Conversion of **8** to **9** was achieved with AgOAc in benzene. The ir spectrum of **9** showed two absorptions in both the symmetric and antisymmetric carboxylate regions, indicative of two kinds of acetate groups.[7] This suggests that **9** has a dimeric structure; however, the compound was insufficiently stable to permit a molecular weight determination. Conversion of **10** to **11** was performed with AgOAc in anhydrous acetone[8] or acetic acid. Comparison of the nmr spectrum of **11** (in HOAc) with that of **10** (in CDCl$_3$) revealed the expected similarity, indicating that **11** retained the π-allylic structure.[9] Reaction of **10** in chloroform with 1 equiv of pyridine afforded **12** (τ 4.35, 1 H, t, J = 6.5 Hz; τ 4.91, 2 H, m). Conversion to **13** was achieved upon addition of a slight excess of AgOAc to a suspension of **12** in acetic acid.



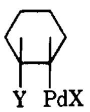
1
8, X = Cl
9, X = OAc



2
10, X = Cl
11, X = OAc



3



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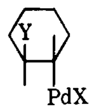

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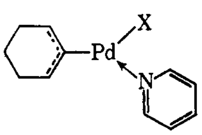

12, X = Cl
13, X = OAc

Solvolyses of complexes **8**, **9**, **10**, **11**, **13**, and of 3-bromocyclohexene (**14**) were performed in acetic acid at 25°; the results are summarized in Table I. The ratio **6**/**7** from run 1 agrees well with that reported

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Chem. Soc., **88**, 5135 (1966); (e) A. C. Cope, J. M. Kliegman, and E. C. Fredrich, *ibid.*, **89**, 2817 (1967); (f) the monomeric forms of **4** and **5** are depicted for simplicity.

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

(6) Our observations on the oxidation of cyclohexene may be summarized as follows: (i) in the presence of an appropriate reoxidant or disproportionation inhibitor, the product of oxidation by PdCl$_2$ or Pd(OAc)$_2$ does not contain cyclohexane, benzene, or cyclohexyl acetate; (ii) with both oxidizing systems *allylic* oxidation predominates over *homoallylic* oxidation; (iii) with the [Pd(OAc)$_2$]$_3$·NO$_2$–NaOAc system, water in the reaction medium is not incorporated into the products.

(7) (a) Y. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, pp 197–206; (b) T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 3632 (1965); (c) T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **29**, 2122 (1967).

(8) (a) S. B. Robinson and B. L. Shaw, *J. Organometal. Chem.*, **3**, 367 (1965); (b) H. C. Volger, 157th National Meeting of the American Chemical Society, Symposium on Homogeneous Catalytic Reactions Involving Palladium, Minneapolis, Minn., April 1969, Preprints, p B73.

(9) **10** shows a one-proton triplet at τ 4.40 and a two-proton multiplet at τ 4.90; **11** has a one-proton triplet at τ 4.45 and a two-proton multiplet at τ 4.82.

by Green *et al.*;[10] however, the direction of this ratio is opposite to that observed upon oxidation of the olefin.[5,6,10] This result argues against the π-complex **8** as a significant product-determining intermediate in the allylic oxidation of cyclohexene, but does suggest its consideration as an intermediate in the competing[5,6] homoallylic oxidation. Attempts to investigate the reactivity of the π-complex **8** in a system containing $Hg(OAc)_2$ were inconclusive; as shown in runs 2 and 3, **8** rapidly reverts to cyclohexene in the presence of $Hg(OAc)_2$ and the olefin then is slowly oxidized in the resulting $PdCl_2$–$Hg(OAc)_2$ system.[5,6] A similar result was obtained with the π-complex **9** in buffered acetic acid (run 4). The presence of cyclohexene in the reaction mixture (*ca.* 4% during the initial stages of reaction), and the high proportion of allylic acetate **7** in the products (*cf.* run 1), indicate that **9** also undergoes at least some reversion to cyclohexene and that this then is oxidized by a route (leading to **7**) which does not involve **9**.

Turning to the π-allylic complexes, we have found that **10** is stable in both neutral and buffered acetic acid;[10] addition of water to the latter solution (run 5) causes complete decomposition[11] *via* a disproportionation rather than substitution pathway. However, in the presence of $Hg(OAc)_2$ (run 6) the substitution pathway predominates, and **10** undergoes rapid solvolysis to give the allylic acetate **7**.[12] Consequently, the π-allylic palladium *chloride* complex **10** is a plausible intermediate in the allylic oxidation of cyclohexene by the $PdCl_2$–$Hg(OAc)_2$ oxidant.[6]

In contrast, the π-allylic palladium *acetate* complex **11** cannot be an intermediate in allylic oxidation by $Pd(OAc)_2$. Thus, in acidic or buffered acetic acids (runs 7–9) the solvolysis of **11** leads not only to allylic acetate **7** but also to benzene;[14] this result should be contrasted with the complete absence of benzene among the products of cyclohexene oxidation by $Pd(OAc)_2$ in similar systems.[5,6] Furthermore, reaction of **11** in aqueous acetic acid (run 10) leads to the incorporation of water in the solvolysis products, whereas the oxidation of cyclohexene in a comparable medium gives only the cyclohexenyl acetates **6** and **7**.[6] A rationalization of these observations that can be reconciled with the required symmetrical intermediate in the oxidation of cyclohexene by $Pd(OAc)_2$ is that the reactions of **11** are those of a dimeric complex,[8] but those of the olefin proceed *via* a monomeric complex[15] or a "switching" σ-allylic complex.[3,16] Runs **10** and **11** demonstrate that the cyclohexenylcarbonium ion is a possible intermediate in the solvolysis of **11** in aqueous acetic acid and, incidentally, rule out the intervention of a carbonium ion in allylic oxidation of cyclohexene by $[Pd(OAc)_2]_3 \cdot NO_2$–NaOAc–HNO_2 in an aqueous medium.[5,6,16,19] The observations of runs **12** and **13** provide support for a monomeric allylic organopalladium intermediate in allylic oxidation. The conversion to **7** upon solvolysis of the monomeric π-allylic complex **13** in neutral acetic acid is an order of magnitude greater than that from **11** under similar reaction conditions (run 13). Formation of benzene in the reaction of **13** is attributed to a competing dissociation–dimerization, followed by disproportionation of the resulting dimeric complex **11**.[14]

In summary, these solvolysis studies do appear to provide support for the view[5,6,20,21] that π-allylic palladium complexes intervene in certain allylic oxidation processes. However, it is also clear that with olefinic substrates other than cyclohexene (*e.g.*, the 2-butenes[13,22]) π-allylic complexes are not involved. The reaction course is evidently very sensitive to small changes in the reaction conditions, the nature of the ligands on palladium, and the structure of the olefin.[8b,22]

Acknowledgments. We thank the National Research Council of Canada for support of this work and for the award of a Studentship, and Dr. P. M. Henry for helpful discussion.

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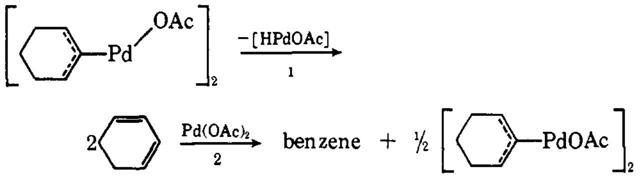
[10] M. Green, R. N. Haszeldine, and J. Lindley, *J. Organometal. Chem.*, **6**, 107 (1966).

[11] *Cf.* R. Hüttel and H. Christ, *Chem. Ber.*, **97**, 1439 (1964), who found that **10** is reasonably stable in aqueous acetic acid in the *absence* of sodium acetate.

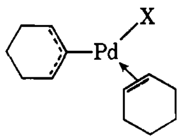
[12] A similar mercuric acetate promoted solvolysis of π-crotylpalladium acetate has been reported by Kitching[13] to give butenyl acetates in a 26:74 primary–secondary ratio. This product distribution was suggested to be consistent with the intervention of the crotylcarbonium ion, perhaps formed by metal acetate attack at palladium; it was concluded that crotylmercuric acetate was not involved in the solvolysis.

[13] W. Kitching, C. F. Fong, and B. F. Hegarty, 157th National Meeting of the American Chemical Society, Symposium on Homogeneous Catalytic Reactions Involving Palladium, Minneapolis, Minn., April 1969, Preprints, p B84.

[14] Benzene was formed *despite* the reoxidants present in the system and the consequent absence of metallic palladium. Therefore, benzene cannot be an artifact arising from the Pd^0-catalyzed disproportionation of cyclohexene. A possible source of the benzene is the sequence shown below; step 2 was demonstrable in the laboratory.

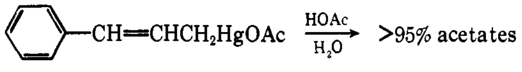


[15] The olefin-complexed monomeric structure i is an intriguing possibility.



i

[16] In aqueous acetic acid *no* alcohol is formed upon allylic oxidation of cyclohexene with $[Pd(OAc)_2]_3 \cdot NO_2$–NaOAc–HNO_2. Similarly, allylic oxidation of allylbenzene by mercuric acetate in aqueous acetic acid, reported to proceed *via* the σ-allyl organomercurial ii,[17] affords less than 5% of allylic *alcohol*. An SNi′ demetalation[18] may thus be characteristic of a σ-allyl organometallic complex.



ii

[17] Z. Rappoport, L. K. Dyall, S. Winstein, and W. G. Young, *Tetrahedron Lett.*, 3483 (1970).

[18] Z. Rappoport, P. D. Sleezer, S. Winstein, and W. G. Young, *ibid.*, 3719 (1965).

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

[20] (a) 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; (b) R. Van Helden, quoted (ref 3) in H. C. Volger, *Recl. Trav. Chim. Pays-Bas*, **86**, 677 (1967).

[21] M. N. Vargaftig, I. I. Moiseev, and Y. K. Syrkin, *Izv. Akad. Nauk SSSR*, 930 (1962).

[22] W. Kitching, Z. Rappoport, S. Winstein, and W. G. Young, *J. Amer. Chem. Soc.*, **88**, 2054 (1966).

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Received December 9, 1970