Palladium(II)-Catalyzed Exchange and Isomerization Reactions. X. The Acid-Catalyzed Exchange of 2-Cyclohexen-1-yl Esters with Acetic Acid[1]

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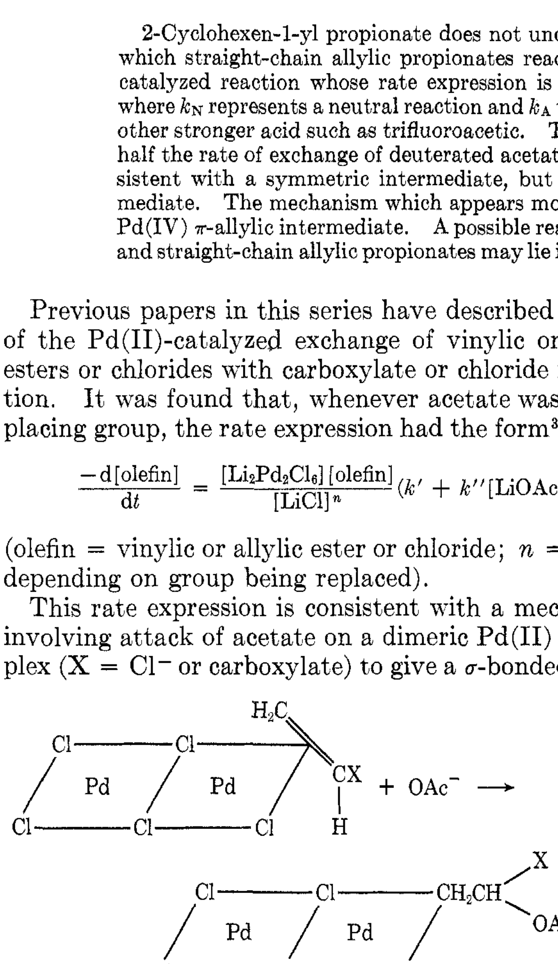
2-Cyclohexen-1-yl propionate does not undergo the acetate ion catalyzed exchange with solvent, the path by which straight-chain allylic propionates react. Instead, this cyclic allylic ester exchanges mainly by an acid-catalyzed reaction whose rate expression is rate = $[Li_2Pd_2Cl_6]$[2-cyclohexen-1-yl propionate]$(k_N + k_A[\text{acid}])$ where k_N represents a neutral reaction and k_A the acid-catalyzed reaction. The acid can be acetic acid itself or another stronger acid such as trifluoroacetic. The allylic isomerization of 2-cyclohexen-1-d_1-1-yl acetate-d_3 was one half the rate of exchange of deuterated acetate ester with CH_3COOH solvent. This stereochemical result is consistent with a symmetric intermediate, but not with an acetoxypalladation–deacetoxypalladation type intermediate. The mechanism which appears most consistent with the kinetic and stereochemical results involves a Pd(IV) π-allylic intermediate. A possible reason for the difference in reactivity between 2-cyclohexen-1-yl esters and straight-chain allylic propionates may lie in the conformational energies of the cyclohexene system.

Previous papers in this series have described studies of the Pd(II)-catalyzed exchange of vinylic or allylic esters or chlorides with carboxylate or chloride in solution. It was found that, whenever acetate was the replacing group, the rate expression had the form[3] of eq 1

$$\frac{-d[\text{olefin}]}{dt} = \frac{[Li_2Pd_2Cl_6][\text{olefin}]}{[LiCl]^n}(k' + k''[LiOAc]) \qquad (1)$$

(olefin = vinylic or allylic ester or chloride; n = 1 or 2 depending on group being replaced).

This rate expression is consistent with a mechanism involving attack of acetate on a dimeric Pd(II) π complex (X = Cl⁻ or carboxylate) to give a σ-bonded intermediate (1) followed by elimination of X to give exchange.



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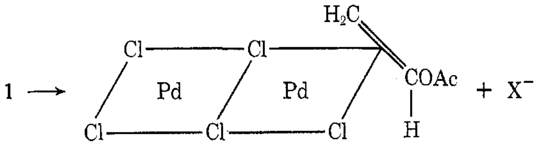

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In a study of the exchange of allylic esters with acetate,[3b] an attempt was made to determine the rate of exchange of 2-cyclohexen-1-yl propionate with acetate. At 1 *M* LiOAc the rate of exchange was much slower than would be expected on the basis of steric effects. Furthermore, the rate of exchange was much faster at 0.01 *M* LiOAc. This effect is opposite to that expected on the basis of equation 1 and suggests that 2-cyclohexen-1-yl propionate has a mechanism for exchange which is different from the other allylic esters. This paper will describe a study of this exchange.

Results

All runs were made at 25°. As in previous studies, the concentrations of the various species present in the reaction mixtures were calculated from total Pd(II) ($[Pd(II)]_t$), and chloride ($[Cl]_t$) concentrations using the previously determined[4] values of K_1 (0.1 M^{-1}) and K_D (2.56 M^{-1}) in eq 4 and 5.

$$Li_2Pd_2Cl_6 + 2LiCl \overset{K_1}{\rightleftharpoons} 2Li_2PdCl_4 \qquad (4)$$

$$2LiCl \overset{K_D}{\rightleftharpoons} Li_2Cl_2 \qquad (5)$$

The earlier qualitative observation[3b] that LiOAc inhibited the rate of exchange was checked by measuring the rate of exchange at constant $[Pd(II)]_t$ and $[Cl]_t$ and various [LiOAc]. The rate did, in fact, decrease with increasing [LiOAc]. This result would be expected if the reaction is acid catalyzed. Thus, since $K_A = [H^+][OAc^-]$, the acid concentration is given by eq 6.[5]

$$[H^+] = K_A/[OAc^-] \qquad (6)$$

In turn the acid dependence of rate is given by eq 7.

$$\text{rate} = k[H^+] = kK_A/[OAc^-] \qquad (7)$$

Equation 7 predicts that a plot of rate *vs.* $1/[OAc^-]$ should give a straight line if the reaction is acid catalyzed. As shown in Figure 1, such a plot is linear with a positive intercept, indicating a reaction independent of $[H^+]$ as well as a reaction with a first order dependence on $[H^+]$.

To test further the postulate of acid catalysis, runs were made at several CF_3COOH concentrations. As Figure 2 shows, there is a linear increase in rate with increase in $[CF_3COOH]$, confirming the acid catalysis. The positive intercept is the rate at $[CF_3COOH] = 0$ and [LiOAc] = 0 or when 1/[LiOAc] = ∞. According to Figure 1, the rate should become infinitely rapid at 1/[LiOAc] = ∞, but of course this is not true since at

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(1) Paper IX: P. M. Henry, *J. Org. Chem.*, **38**, 2766 (1973).

(2) (a) University of Guelph. (b) Work by this author carried out at the Hercules Research Center. Address correspondence to this author at the University of Guelph.

(3) (a) P. M. Henry, *J. Amer. Chem. Soc.*, **93**, 3853 (1971); (b) *ibid.*, **94**, 1527 (1972); (c) *ibid.*, **94**, 7311 (1972); (d) *ibid.*, **94**, 7316 (1972).

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

(5) Equation 6 is, of course, a gross oversimplification in that it does not consider ion pairs and the facts that $[H^+]$ exists as H_2OAc^+ and the acetate ion as the biacetate ion $H(OAc)_2^-$. For a discussion of equilibria in acetic acid see ref 6.

(6) A. I. Popov in "The Chemistry of Nonaqueous Solvents, III," J. J. Lagowski, Ed., Academic Press, New York, N. Y., 1970, Chapter 5.

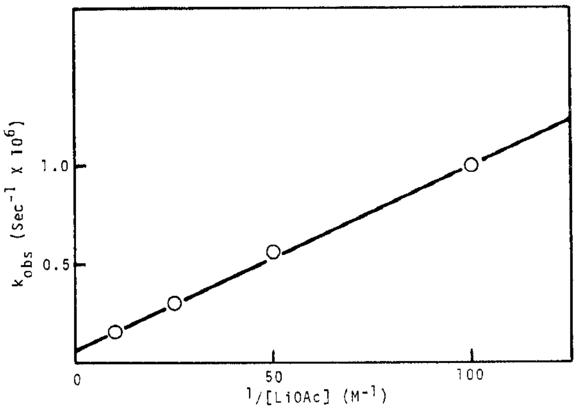

Figure 1.—Plot of k_{obsd} vs. 1/[LiOAc]; $[Pd(II)]_t = 0.024\ M$; $[Cl]_t = 0.088\ M$.

very low added [LiOAc] the concentration of OAc^- is mainly determined by the self-ionization of acetic acid. Next the orders in reactive Pd(II) species and [LiCl] must be determined. Previously it was found that allylic ester exchange[3b] and isomerization[7] were inhibited by the allylic esters themselves because of the following equilibrium to form an unreactive monomeric π complex **2**.

$$Li_2Pd_2Cl_6 + \text{allylic ester} \overset{K_2}{\rightleftharpoons} \underset{\mathbf{2}}{2LiPdCl_3(\text{allylic ester})} \quad (8)$$

The magnitude of this inhibition must be determined, since it will complicate the determination of the order in reactive Pd(II) species. In Table I is shown the effect of allylic ester concentration on rate.

TABLE I

EFFECT OF 2-CYCLOHEXEN-1-YL PROPIONATE CONCENTRATION ON RATE[a]

[2-Cyclohexen-1-yl propionate], M	k_{obsd}, sec^{-1} × 10^6
0.02	3.79
0.10	1.83
0.25	1.60
0.50	0.97

[a] $[Pd(II)]_t = 0.02\ M$ and $[Cl]_t = 0.135\ M$ for all runs.

The dependence of k_{obsd} on allylic ester concentration indicates a value of K_2 in eq 8 of 0.3 M^{-1}. At an allylic ester concentration of 0.02 M or less, the inhibition is negligible. Thus, the Pd(II) dependence was determined using 1-cyclohexen-1-yl propionate concentrations of 0.02 M. As shown in Figure 3, the reaction is strictly first order in $[Li_2Pd_2Cl_6]$.

Finally the order in [LiCl] must be determined. In Table II are listed the values of k_{obsd} for several LiCl concentrations. The value of the ratio in the last column does not change within experimental error; so the reaction is zero order in [LiCl].

The rate expression for the acid region in which LiOAc is added is given by eq 9, in which $[H^+] =$

$$\frac{-d[\text{allyl ester}]}{dt} = [Li_2Pd_2Cl_6][\text{allyl ester}](k_1 + k_2[H^+]) \quad (9)$$

K_A/[LiOAc]. Using a value of 3.5 × 10^{-15} for K_A,[8] a value of k_2 of 2.6 × 10^6 M^{-2} sec^{-1} can be calculated.

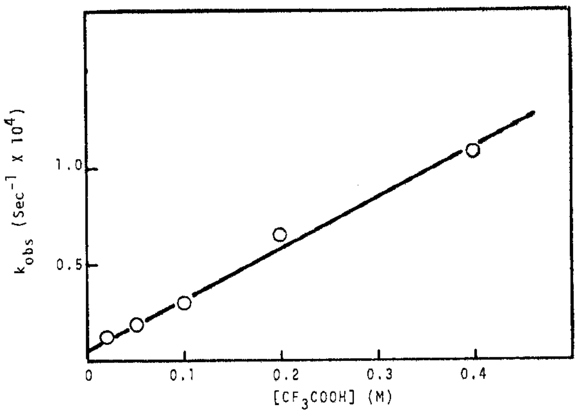

Figure 2.—Plot of k_{obsd} vs. $[CF_3COOH]$; $(Pd(II))_t = 0.024\ M$; $[Cl]_t = 0.088\ M$.

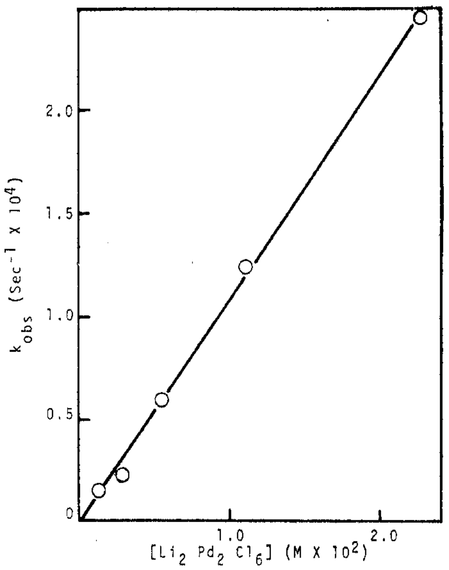

Figure 3.—Plot of k_{obsd} vs. $[Li_2Pd_2Cl_6]$; $[CF_3COOH_3] = 0.4\ M$; [2-cyclohexen-1-yl propionate] = 0.02 M; [LiCl] = 0.04–0.06 M.

TABLE II

EFFECT OF LITHIUM CHLORIDE CONCENTRATION ON RATE[a,b]

$[Cl]_t$, M	$[Li_2Pd_2Cl_6]^-$, M × 10^2	[LiCl], M	k_{obsd}, sec^{-1} × 10^5	$\frac{k_{obsd}}{[Li_2Pd_2Cl_6]}$, sec^{-1} M^{-1} × 10^3
0.135	1.120	0.049	1.83	1.63
0.182	1.074	0.077	1.83	1.68
0.276	1.005	0.123	1.51	1.50
0.464	0.908	0.194	1.54	1.70

[a] For all runs $[Pd(II)]_t = 0.024\ M$, $[H^+] = 0.1\ M$, and [allylic ester] = 0.1 M. [b] Values of $[Li_2PdCl_4]$ and $[Li_2Cl_2]$ can readily be calculated from the quantities given in the table.

From the intercept of Figure 1, a value of 4.6 × 10^{-6} M^{-1} sec^{-1} for k_1 can be calculated.

The rate expression for the region in which CF_3COOH is added is given by eq 10.

$$\frac{-d[\text{allyl ester}]}{dt} = [Li_2Pd_2Cl_6][\text{allyl ester}](k_1' + k_2'[CF_3COOH]) \quad (10)$$

The value of k_1' from Figure 2 is 5.8 × 10^{-4} M^{-1} sec^{-1} and the value of k_2' is 2.13 × 10^{-2} M^{-2} sec^{-1}.

The ratio of exchange to allylic isomerization was determined using 2-cyclohexen-d_1-1-yl acetate-d_3. The

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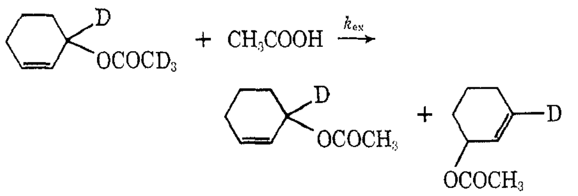
(7) P. M. Henry, *J. Amer. Chem. Soc.*, **94**, 5200 (1972).

(8) S. Bruckenstein and I. M. Kolthoff, *J. Amer. Chem. Soc.*, **78**, 2974 (1956).

rate of exchange of deuterated acetate was measured by mass spectroscopy. Under one set of reaction conditions, $[Pd(II)]_t = 0.0218\ M$, $[Cl]_t = 0.0911\ M$, and $[CF_3COOH] = 0.4\ M$, the value of k_{ex} was found to be 1.02×10^{-4} sec^{-1}. The value of exchange for the propionate ester under these conditions is 1.09×10^{-4} sec^{-1}. The rate of allylic isomerization (eq 12, R = CH_3 or CD_3) was determined by nmr. Under the same reaction conditions the value of k_i was found to be 5.0×10^{-5} sec^{-1}.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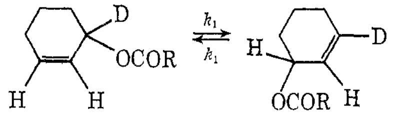
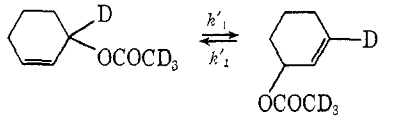

(12)

Pd(II) also catalyzes allylic isomerization without exchange[7] (eq 13). If this isomerization were taking place it would complicate the interpretation of the stereochemical results for exchange. Now since the value of k_i' does not increase with increasing [LiOAc], the rate of exchange and isomerization at [LiOAc] = 0.02 M was measured. Under these conditions the rate of exchange was 4.5×10^{-7} sec^{-1}, which is about the value expected from the kinetic results with propionate ester. The rate of isomerization was 8.1×10^{-7} sec^{-1} under the same conditions. Since the rate of isomerization is faster than exchange, isomerization without exchange may be important under these conditions. These results are subject to some uncertainty however, because a precipitate of Pd metal was observed after about 2 weeks. The Pd metal may have catalyzed allylic isomerization of the ester. Another possibility is thermal isomerization which is not catalyzed by Pd(II). In any case, at $[CF_3COOH] =$ 0.4 M, the rate of isomerization without exchange would make less than a 2% contribution to the total rate of isomerization.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To determine if straight-chain allylic propionates would undergo the acid-catalyzed exchange, crotyl and 3-buten-2-yl propionate were allowed to react at $[Pd(II)]_t = 0.024\ M$ and $[CF_3COOH] = 0.4\ M$. Exchange was very slow compared with the cyclohexenyl propionates. In fact the esters had isomerized without exchange into an equilibrium mixture before an appreciable exchange occurred.

To establish that the double bond is necessary for exchange, cyclohexyl propionate was exposed to the reaction conditions described above for the crotyl and 3-buten-2-yl propionate. No exchange occurred in several days. Its rate of exchange would be less than $^1/_{1000}$ of the rate for 2-cyclohexen-1-yl propionate.

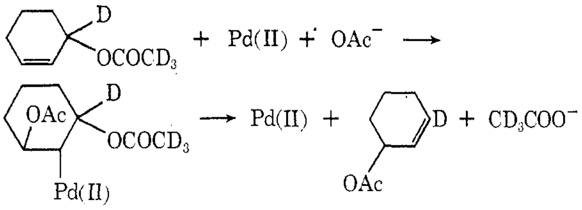
Discussion

Equations 9 and 10 can be summarized in a general rate expression shown in eq 14, where k_N represents the

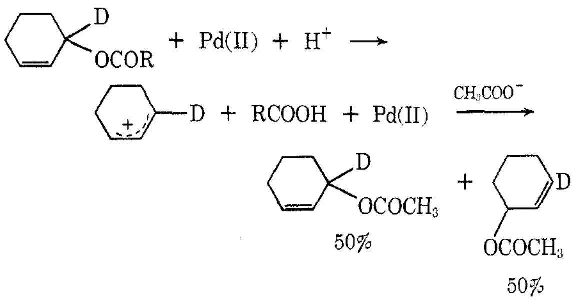
$$\frac{-d[\text{allyl ester}]}{dt} = ([Li_2Pd_2Cl_6][\text{allyl ester}])(k_N + k_A[\text{acid}]) \quad (14)$$

neutral term which equals k_1 in eq 9 and k_A[acid] is represented by $k_2[H^+]$, k_1', and $k_2'[CF_3COOH]$. Of course the value of k_A depends on the specific acid used.

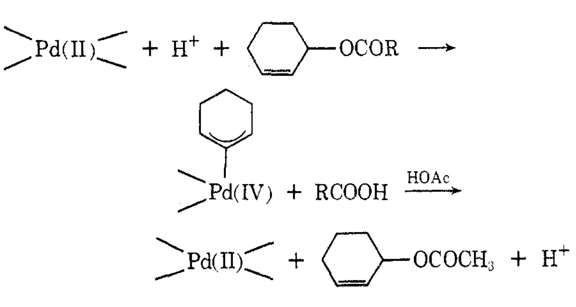
The stereochemical results are not consistent with an acetoxypalladation–deactoxypalladation mechanism proposed for exchange of straight-chain esters[3b,7] because this type of mechanism requires exchange and allylic isomerization to have equal rates. This, of course, is not surprising, since the rate expression for this type of mechanism is quite different from that for acid-catalyzed exchange.


(15)

The stereochemical results are, however, consistent with a symmetrical type of intermediate such as an allylic carbonium ion. Since in this case only $^1/_2$ of the material is isomerized every time there is exchange, the rate of isomerization is $^1/_2$ the rate of exchange. Although this route is analogous to the postulated mechanism of acid-catalyzed allylic rearrangements carried out in the absence of Pd(II),[9] allylic carbonium ion mechanisms do not have any analogy in other Pd(II) chemistry and the role of the Pd(II) is uncertain.


(16)

A mechanism involving a symmetrical intermediate which is more consistent with Pd(II) chemistry involves oxidative addition to Pd(II) to give a Pd(IV) π-allyl. Reversal of this process completes exchange.


(17)

The ability of d^8 noble metal complexes to form stable d^6 complexes is well known and the role of oxidative

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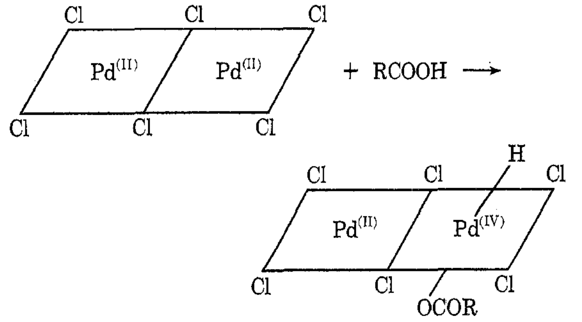
[9] W. G. Young, *J. Chem. Educ.*, **39**, 455 (1962).

addition in catalysis has been discussed.[10-13] Although no stable Pd(IV) π-allyls are known, they have been suggested as intermediates in the Pd(II)-catalyzed double-bond isomerizations.[14,15] Thus there is precedent for proposing Pd(IV) π-allyls as intermediates in Pd(II)-catalyzed reactions.

Presuming a Pd(IV) π-allyl intermediate, the exact mode of formation of this intermediate is uncertain. One path consistent with the rate expression involves oxidative addition of acid (R = CF_3 or CH_3) (eq 18) followed by attack on the allylic ester (eq 19).



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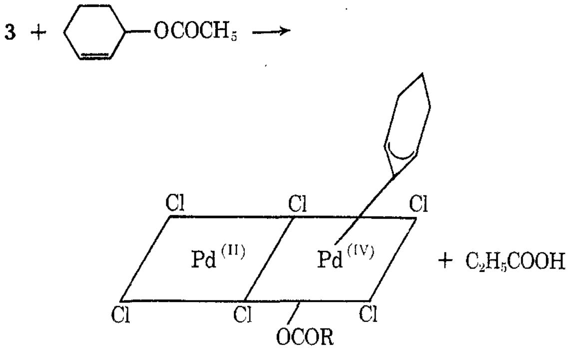

(19)

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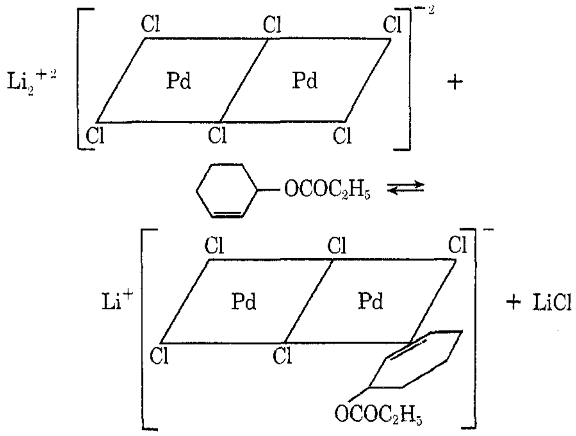
Another route which seems more consistent with Pd(II) chemistry involves initial formation of a dimeric π complex in an initial equilibrium step. Now this step requires an [LiCl] inhibition term in the denominator of the rate expression which must be cancelled by a term in the numerator to give eq 10. The rate expression would thus be eq 21. Rate expressions in which [LiCl] terms cancelled were proposed for two previous exchanges,[16,17] and, in one case,[16] this assumption was substantiated by further studies.[3c]



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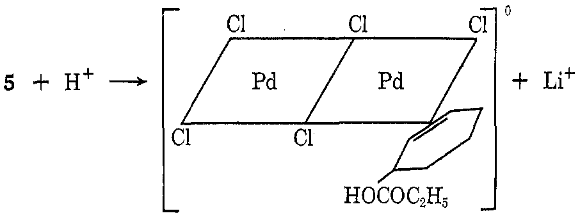
$$\frac{-d[\text{allyl ester}]}{dt} = \frac{[Li_2Pd_2Cl_6][\text{allyl ester}][LiCl]}{[LiCl]}(k_N + k_A[\text{acid}]) \quad (21)$$

The acid catalysis in this path would arise from protonation of the alkyl oxygen of the ester, thus weakening the carbon–oxygen bond. The next step would be oxidative addition to give the Pd(IV) π-allyl. The additional [LiCl] term in the numerator would then be required in this step to fill the sixth coordinative position on the octahedral d^6 Pd(IV).[10,18]



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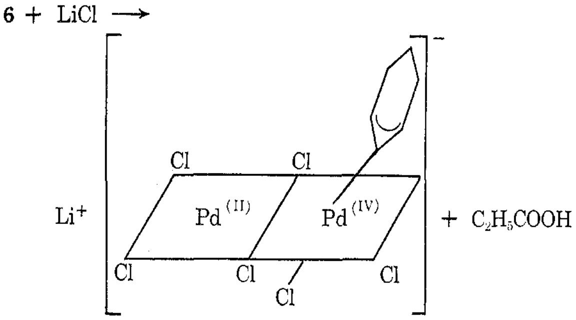

(23)

Certainly more work is required to define the exact mechanism with certainty. However, the important point is that a symmetrical intermediate such as a π-allyl complex is required by the stereochemical results.

The present work raises two questions about the special nature of the cyclohexenyl system. First, why does it undergo acid-catalyzed exchange while the straight-chain allylic esters apparently do not? The authors have no explicit answer to the first question but this behavior is consistent with other Pd(II) chemistry of the cyclohexenyl system. Thus, the kinetics of the aqueous oxidation of cyclohexene to cyclohexanone is different from the kinetics of oxidation of straight-chain olefins.[19] This difference may result from a π-allylic type mechanism rather than a hydroxypalladation type mechanism generally accepted for straight-chain olefins.[20] More recently, it has been reported[21,22] that oxidations of cyclohexene in acetic acid apparently occur to a large extent through π-allyl intermediates. Once again, straight-chain olefins are

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[10] J. Halpern, *Accounts Chem. Res.*, **3**, 386 (1970).

[11] J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).

[12] R. Cramer, *Accounts Chem. Res.*, **1**, 186 (1968).

[13] L. Vaska, *Accounts Chem. Res.*, **1**, 335 (1968).

[14] J. F. Harrod and A. J. Chalk, *J. Amer. Chem. Soc.*, **88**, 3491 (1966).

[15] N. R. Davies, *Rev. Pure Appl. Chem.*, **17**, 83 (1967).

[16] P. M. Henry, *J. Org. Chem.*, **37**, 2443 (1972).

[17] P. M. Henry, *Inorg. Chem.*, **11**, 1876 (1972).

[18] The π-allyl group is known to occupy two coordination positions.

[19] M. N. Vargaftik, I. I. Moiseev, and Y. K. Sirkin, *Dokl. Akad. Nauk SSSR*, **139**, 1396 (1961).

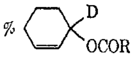
[20] P. M. Henry, *J. Amer. Chem. Soc.*, **86**, 3246 (1964).

[21] S. Wolfe and P. G. C. Campbell, *J. Amer. Chem. Soc.*, **93**, 1497, 1499 (1971).

[22] R. G. Brown and J. M. Davidson, *J. Chem. Soc. A*, 1321 (1971).

TABLE III

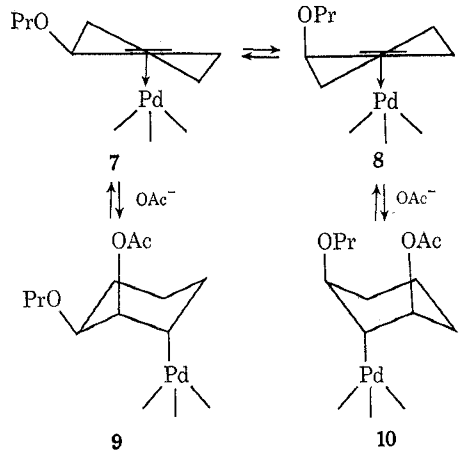
EXCHANGE AND ISOMERIZATION OF 2-CYCLOHEXEN-1-d_1-1-YL ACETATE-d_3[a]

	Exchange		Isomerization	
Time, sec	$\frac{m/e\ 141}{m/e\ 144}$	% acetate-d_3	$\frac{\text{Area HCOCOR}}{\text{area olefinic H}}$	% 
		$[CF_3COOH] = 0.4\ M$		
1,500	0.21	83	0.08	85
3,000	0.35	74	0.11	80
6,000	0.86	54	0.16	72
12,000	2.33	30	0.23	62.5
18,000	5.55	15	0.29	55
		$[LiOAc] = 0.02\ M$		
3.24×10^4	0.07	93.5	0	100
5.62×10^5	0.43	70.0	0.20	67
1.29×10^6	0.92	52.0	0.27	58
2.55×10^7	2.04	32.0	0.32	52

[a] $[Pd(II)]_t = 0.0218\ M$; $[Cl]_t = 0.0911\ M$.

apparently oxidized by an acetoxypalladation type mechanism.[23]

The second question concerns the low reactivity of the cyclohexenyl propionate to the acetate-catalyzed reaction; the answer may lie in the conformational properties of the cyclohexene system. According to the Fürst–Plattner rule,[24] trans attack on cyclohexene oxides[25] and bromonium ions[26] gives diaxially oriented products. The author has recently provided evidence that acetoxypalladation proceeds by a trans attack of acetate on the Pd(II)–cyclohexene π complex.[27] Thus, acetoxypalladation of cyclohexene might also be expected to obey the Fürst–Plattner rule. The scheme for exchange of $C_2H_5COO(PrO)$ with $CH_3COO(OAc)$ is presented in eq 24, where 7 and 8 are the two possible



(24)

conformers of the trans half-chair form π complex. The half-chair is shown because it is much more stable than the half-boat form.[28] The two cis half-chair forms of the π complex are not shown because trans attack on this π complex would not put the OAc⁻ and Pd(II) in position for the trans elimination required by the principle of microscopic reversibility.

If 7, which has the propionate in a pseudoequatorial position, is more stable than 8, the addition of OAc⁻ to give 9 would be more favorable than addition to give 10. However, 9 cannot exchange. It can only eliminate OAc⁻. If the energy difference between 7 and 8 is large enough, exchange would not be expected by the acetoxypalladation mechanism. Little data is available on the relative stability of 3-substituted cyclohexene derivatives. The pseudoaxial 3-chlorocyclohexene (ΔH = 0.64 kcal/mol) and 3-bromocyclohexene (ΔH = 0.70 kcal/mol) have been reported to be the favored conformers in the pure liquids.[29] Of course, a different order of stabilities could exist for the π complexes 7 and 8.

Two comments should be made about the rate expressions given by eq 9 and 10. First, in eq 10 the $[CF_3COOH]$ term is to the first power. According to the usual equations for ionization of acids in the absence of buffer, if H^+ (or $H_2{}^+OOCCH_3$) were the catalyst, this term should appear as a $^1/_2$ power term in the rate expression. Since it does not, molecular CF_3COOH must be the catalyst.

Second, if the simple equilibrium shown in eq 6 completely defines the self-ionization of acetic acid, then the value of k_2 in eq 9 can be used to define the value of k_1' in eq 10. According to eq 6, when [LiOAc] = 0, $[H^+] = K_A{}^{1/2}$. Using a value of 3.5×10^{-15} for K_A, we have $[H^+] = 5.9 \times 10^{-8}\ M$. The value of k_1' in eq 10 is then simply $k_2[H^+]$ or $(2.6 \times 10^6\ M^{-2}\ \text{sec}^{-1}) \cdot (5.9 \times 10^{-8}\ M)$ or $1.5 \times 10^{-1}\ M^{-1}\ \text{sec}^{-1}$. This value for k_1' is considerably higher than the experimental value of $5.8 \times 10^{-4}\ M^{-1}\ \text{sec}^{-1}$. The difference reflects the fact that different ion pairs and thus different ion pair dissociation constants are involved in the two systems.[5]

Experimental Section

Materials.—Sources of most chemicals and preparation of stock solutions have been described previously.[3,4] The propionate and acetate esters of 2-cyclohexen-1-ol were prepared by esterification of the alcohol (Aldrich Chemical Co.) using the corresponding anhydride and pyridine as catalyst. Acid catalysts give decomposition of the alcohol. The 2-cyclohexen-1-d_1-1-yl acetate-d_3 was prepared by the reduction of 2-cyclohexenone with $LiAlD_4$ followed by acetylation with $(CD_3CO)_2O$

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

[24] A. Fürst and P. A. Plattner, Abstracts of Papers, 12th International Congress of Pure and Applied Chem., New York, N. Y., 1951, p 409.

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[26] Reference 25, p 294.

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

[28] Reference 25, p 109.

[29] K. Sakashita, *Nippon Kaguki Zasshi*, **81**, 49 (1960); *Chem. Abstr.*, **54**, 12015*b* (1960).

(Isotopic Products) using the procedure of Campbell.[30] The trifluoroacetic acid was purchased from the Aldrich Chemical Co. It was distilled before use.

Kinetic Runs.—Procedures have been described previously. Runs were usually on a 5-ml scale but runs with 0.02 *M* allyl ester were on a 25-ml scale. Samples were analyzed by vpc using a 6-ft 20% Carbowax 20M on ABS (70–80 mesh) column programmed from 80° to 200° at 7.5°/min. Helium flow rate was 60 ml/min. Runs not containing CF_3COOH were injected without work-up. The runs containing CF_3COOH were neutralized by a 10% excess of 1 *M* LiOAc in HOAc and diluted to a known volume pefore injection. Aliquots (1 or 2 ml) of the 25-ml scale runs were worked up by diluting with CH_2Cl_2 and washing with water to remove HOAc, CF_3COOH, and inorganic salts. After drying over $MgSO_4$, the organic phase was concentrated to a known volume and analyzed by vpc. In one run, the 2-cyclohexen-1-yl acetate was collected by preparative vpc and positively identified by nmr.

2-Cyclohexen-1-d_1-1-yl Acetate-d_3 Run.—A 75-ml reaction mixture which was 0.0218 *M* in Pd(II) and 0.4 *M* in CF_3COOH was prepared and the run was started by adding 1.5 g of the deuterated cyclohexenyl acetate. Samples (12 ml) were worked up by extracting in $CDCl_3$ described above. The samples were analyzed by nmr and mass spectral analysis. The rate of exchange of deuterated ester (eq 11) was determined by the ratio of the parent peaks of the deuterated (*m/e* 144) and undeuterated (*m/e* 141) esters. Data were plotted as a first-order reaction to give k_{ex}. The isomerization rate (eq 12) was determined by nmr using the relative areas of the proton on the carbon containing the acetate[31] and the olefinic protons. Initially this ratio is zero. At equilibrium, when a 50:50 mixture of the two allylic isomers are present, it is 0.33. The data was plotted in the usual fashion for reactions approaching equilibrium. Data[32] are given in Table III.

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Registry No.—Acetic acid, 64-19-7; 2-cyclohexen-1-yl propionate, 34745-78-3; lithium chloride, 7447-41-8; 2-cyclohexen-1-d_1-1-yl acetate-d_3, 40893-39-8.

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[30] P. G. C. Campbell, Ph.D. Thesis, Queen's University, Kingston, Ontario, Canada, 1968, p 256.

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[32] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 86.

Homogeneous Olefin Hydrogenation Catalyzed by Dichlorodicarbonylbis(triphenylphosphine)ruthenium(II)[1]

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The relative hydrogenation rates for a variety of alkenes and alkadienes catalyzed by $RuCl_2(CO)_2(PPh_3)_2$ have been measured in the presence of added PPh_3. Rates decrease in the order conjugated dienes > nonconjugated dienes > terminal alkenes > internal alkenes. In general, polyenes are selectively hydrogenated to monoenes. Double bond isomerization and migration reactions and transannular ring closures (in cyclic dienes) can be important competing reactions. The lower hydrogenation rate for alkenes is attributed to an equilibrium between $RuCl(alkyl)(CO)_2$ and $RuCl(alkyl)(CO)_2PPh_3$ intermediates, which, in the presence of added PPh_3, favors the sterically crowded PPh_3 complexed intermediate. Sterically congested intermediates suffer rapid RuH elimination, while the uncongested complexes survive long enough to undergo hydrogenolysis. This equilibrium is not so important for dienes, since the fifth coordination site on ruthenium is already occupied by chelation of the alkenyl ligand.

Numerous catalysts are known that are capable of performing selective homogeneous hydrogenations,[2] but the stabilities and productivities of most of these catalysts have not been well publicized. Thus, despite the alluring appeal many of these catalysts seem to offer in certain applications, their practical value is uncertain. Recently, the selective hydrogenation of 1,5,9-cyclododecatriene to cyclododecene catalyzed by $RuCl_2(CO)_2(PPh_3)_2$ was described.[3] In this case, the catalyst is exceptionally stable under the reaction conditions and is highly productive.[3] Thus, further elaboration of its behavior seems desirable. Herein are provided relative rate data for a variety of unsaturated hydrocarbons that allow a deeper insight into the hydrogenation process.

Results

Selective Hydrogenation of Polyenes.—The presence of added PPh_3 was previously shown to be necessary in order to achieve selective hydrogenations of 1,5,9-cyclododecatriene.[3] Since most of the interest in this catalyst is anticipated to be in its use as a selective hydrogenation catalyst, olefin hydrogenations were routinely performed with added PPh_3. Under these conditions the $RuCl_2(CO)_2(PPh_3)_2$ catalyzed hydrogenations of several diolefins were carried to greater than 99% conversion to yield the product mixtures given in Table I. The data indicate that the selective hydrogenation of polyunsaturated hydrocarbons to monounsaturated hydrocarbons is a fairly general reaction. For 1,5-cyclooctadiene, double bond migration is so rapid that complete isomerization to the 1,3 isomer occurs before significant amounts of cyclooctene appear. Thus, selective hydrogenation of 1,3-cyclooctadiene rather than 1,5-cyclooctadiene was actually observed. Accompanying the double bond migration reaction in 1,5-cyclooctadiene is a cyclization to bicyclo[3.3.0]oct-2-ene. This by-product was formed in 0.4% yield as 1,5-cyclooctadiene was undergoing

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[1] Presented in part at the 19th Oklahoma American Chemical Society Tetrasectional Meeting, Bartlesville, Okla., Mar 10, 1973.

[2] For recent comprehensive reviews, see: (a) J. E. Lyons, L. E. Rennick, and J. L. Burmeister, *Ind. Eng. Chem. Prod. Res. Develop.*, **9**, 2 (1970); (b) A. Andreeta, F. Conti, and G. F. Ferrari in "Aspects of Homogeneous Catalysis," Vol. I, R. Ugo, Ed., Carlo Manfredi Editore, Milano, 1970, Chapter 4.

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