Palladium(II)-Catalyzed Exchange and Isomerization Reactions. VII. Isomerization and Exchange of Enol Propionates in Acetic Acid Catalyzed by Palladium(II) Chloride[1]

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Abstract: 1-Propen-1-ol and 2-buten-2-ol propionates undergo two Pd(II)-catalyzed reactions in acetic acid. One is exchange of propionate for acetate, a reaction which all enol esters undergo. The rate expression for exchange is as follows: $-d[\text{enol propionate}]/dt = ([\text{Li}_2\text{Pd}_2\text{Cl}_6][\text{enol propionate}]/[\text{LiCl}])(k_1 + k_2[\text{LiOAc}])$. For vinyl propionate it was shown that this rate expression is valid over a wide range of acetate and chloride concentrations. The exchange of *cis*- or *trans*-1-propen-1-ol propionate occurs only with isomerization, evidence that exchange occurs by an acetoxypalladation–depropoxypalladation. The second reaction of *cis*- or *trans*-1-propen-1-ol propionate is isomerization without exchange. The rate expression for this reaction is rate = $k[\text{Li}_2\text{Pd}_2\text{Cl}_6][\text{enol propionate}]/[\text{LiCl}]$. This rate expression is consistent with formation of a π complex followed by isomerization without the intervention of an external reagent. The effect of methyl substitution on the vinylic carbons is quite different for the two reactions. The rate of exchange of 1-propen-1-ol propionate is 1000 times faster than that for 2-buten-2-ol propionate while the factor for isomerization is only 30. Of the two mechanisms, π-allylic and metal hydride, previously suggested for isomerization of olefins, the π-allylic mechanism can be eliminated in the present case since enol esters without allylic hydrogens undergo isomerization without exchange. Other results make hydride mechanisms unlikely. A mechanism involving rearrangement of the π complex to a Pd(II)-substituted carbonium ion is suggested as one possibility.

In the first paper of this series[3] a kinetic study of the exchange of enol acetates with acetic acid using deuterium labels was described. The rate expression is given by eq 1. This kinetic expression is consistent

$$\text{rate} = [\text{Li}_2\text{Pd}_2\text{Cl}_6][\text{enol ester}]/[\text{LiCl}] \times (k' + k''[\text{LiOAc}]) \quad (1)$$

with an acetoxypalladation–deacetoxypalladation mechanism shown in eq 2–4 for exchange of C_2H_3OO-
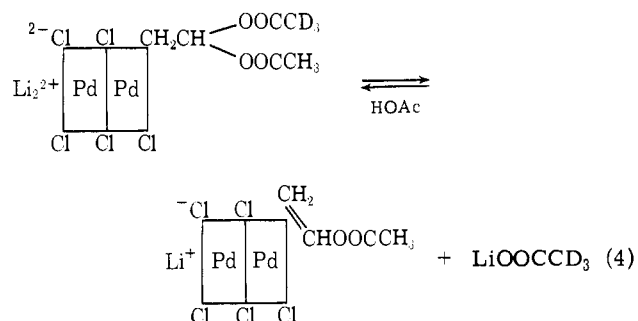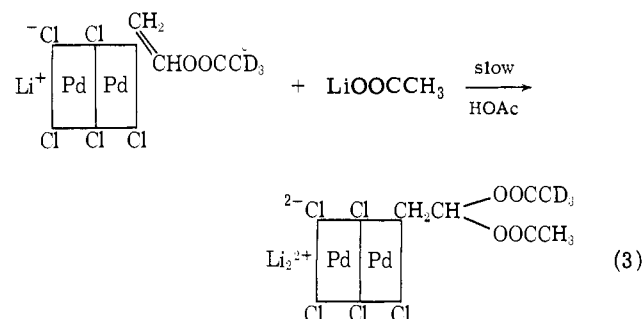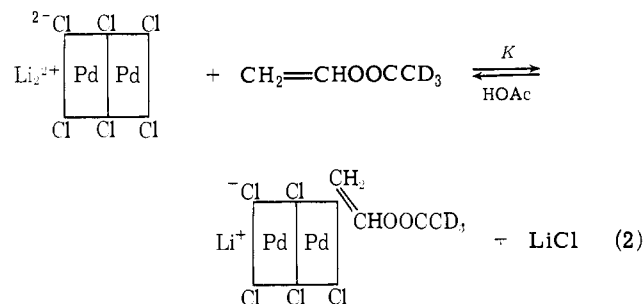
CCD$_3$. Further evidence that this type of mechanism was taking place was provided by the results on the exchange and isomerization of *cis*- and *trans*-propenyl acetates. Thus this mechanism would predict that exchange occurs only with isomerization as shown by eq 5 (X = Cl or OAc). Cis acetoxypalladation is used
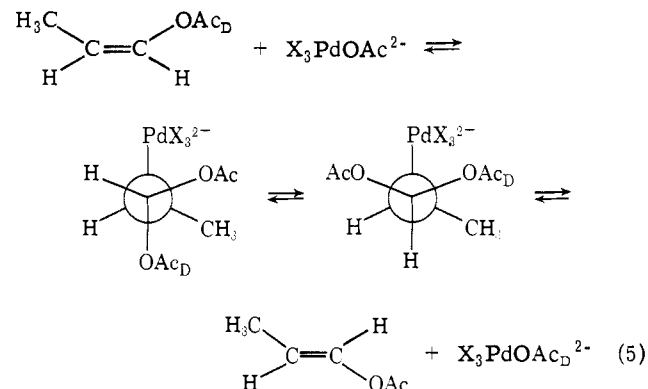
only for the purpose of illustration. Trans acetoxypalladation would give the same final result.

At higher acetate concentrations this was the observed result. However, at lower acetate concentrations there was evidence that another reaction was taking place. This reaction is cis–trans isomeriza-

(1) (a) Paper VI: P. M. Henry, *J. Amer. Chem. Soc.*, **94**, 7311 (1972). (b) A preliminary communication on this work has appeared; see P. M. Henry, *ibid.*, **93**, 3547 (1971).
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(3) P. M. Henry, *J. Amer. Chem. Soc.*, **93**, 3853 (1971).

Table I. Rate Constants for Exchange and Isomerization[a]

[LiOAc]	k_{14}	k_{41}	k_{12}	k_{13}	k_{43}	k_{42}	k_{23}[b]	k_{32}[b]
				Values of various k's (sec^{-1} × 10⁵)				
0.005	2.1	0.95	<0.03	0.2	<0.03	0.1	3.2	1.9
0.1	2.0	0.90	<0.3	2.7	<0.3	1.35	6.5	4.0
0.5	c	c	<1.0	10.6	<0.5	5.4	15.5	9.5
1.0	c	c	<2.2	23.6	<1.2	12.7	31.9	19.5

[a] $[Na_2Pd_2Cl_6] = 0.0177\ M$ and $[NaCl] = 0.013\ M$ for all runs. [b] The values of the equilibrium mixture of **2** and **3** are reported to be 62%
3: Z. Rappoport, P. D. Sleezer, S. Winstein, and W. G. Young, *Tetrahedron Lett.*, 3719 (1965). This value was used in calculating k_{23}
and k_{32} from the kinetic data. [c] k_{13} and k_{42} are too large to permit determination of k_{14} and k_{41}.

tion without exchange of acetate with the solvent. This paper will describe a study of this reaction.

A secondary purpose of the present work was to study the exchange reaction over a wider range of reaction conditions than used in the previous study, using vinyl propionate as substrate. In the previous work there was some indication of a reaction higher order in [LiCl] than represented by eq 1. Vinyl propionate is ideally suited for such a study since its exchange is much simpler to measure than deuterium-labeled acetate.
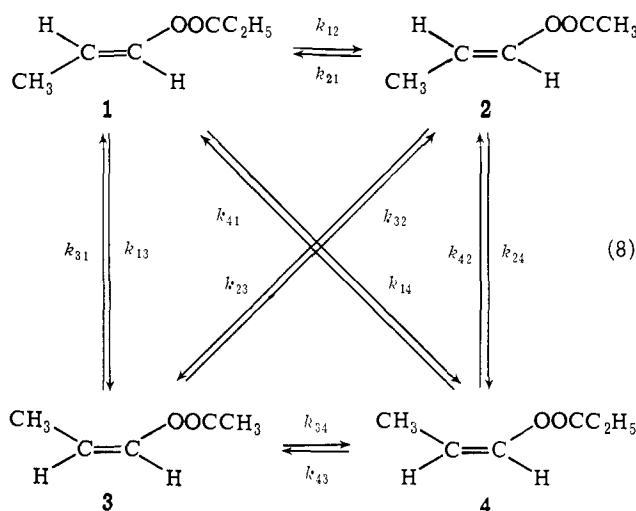
Results

All kinetic runs were made in dry acetic acid at 25°. In defining the kinetic expressions, use was made of the previously determined[4] values of K_1 (0.1 M^{-1}) and K_D (2.6 M^{-1}) to calculate the concentrations of the various species under any set of reaction conditions from the total concentrations of Pd(II) and ($[Pd(II)]_t$),

$$Li_2Pd_2Cl_6 + 2LiCl \overset{K_1}{\rightleftharpoons} 2Li_2PdCl_4 \qquad (6)$$

$$2LiCl \overset{K_D}{\rightleftharpoons} Li_2Cl_2 \qquad (7)$$
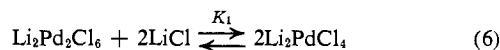
and total chloride concentration, $([Cl]_t)$, obtained by analysis. Runs were usually made with Pd(II) solutions with LiCl as the chloride salt. Some runs, however, were made using NaCl as the chloride salt. These runs were made using acetic acid saturated with NaCl. At 25°, $[NaCl] = 0.013\ M$ and Pd(II) is almost completely in the form of the dimer, $Na_2Pd_2Cl_6$.[4]

Enol Propionate Isomerization. Even at very low LiOAc concentration, exchange was a serious side reaction which complicated the measurement of the rate of isomerization without exchange. The complete reaction sequence is given in eq 8. The two rate constants of present interest are k_{14} and k_{41}. This scheme is very similar to that previously found for allylic ester exchange and isomerization[5] and was treated in the same fashion. The pseudo-first-order rate constants for conversion of acetate to propionate, k_{21}, k_{24}, k_{31}, and k_{34}, are very small since the acetate concentration is very much higher than the propionate concentration at all stages of reaction. k_{32} and k_{23} can be measured independently by equilibrating the acetate esters under identical reaction conditions. The values for the other six rate constants were determined for a given set of reaction conditions using computer calculation of the change in product distribution with time for various values of k's. Thus, for one set of reaction conditions, k_{23} and k_{32} were determined by equilibrating the acetate esters. Then the product distributions with time were

(4) P. M. Henry and O. Marks, *Inorg. Chem.*, **10**, 373 (1971).
(5) P. M. Henry, *J. Amer. Chem. Soc.*, **94**, 5200 (1972).

(8)

determined starting with both **1** and **4**. Then various values of the k's were used to simulate product distributions with time until the product distributions starting with either **1** or **4** were matched within experimental error by the same set of k's. Values of the various rate constants at one set of $[Na_2Pd_2Cl_6]$ and $[NaCl]$ and four different [LiOAc] are shown in Table I. The values of the rate constants, k_{14} and k_{41}, for isomerization without exchange do not increase with increasing [LiOAc]; the values of the exchange rate constants k_{13} and k_{42} do increase as would be predicted from eq 1. Furthermore, the values of k_{12} and k_{43} are zero within experimental error as would be predicted from eq 5.

The isomerization without exchange is thus zero order in [LiOAc] and first order in vinyl ester since the product distributions could be reproduced only if this order is assumed. Next, the order in active Pd(II) species and [LiCl] must be determined. A plot of k_{obsd} (where $k_{obsd} = k_{41} + k_{14}$) $vs.$ $[Li_2Pd_2Cl_6]$ at constant [LiCl], shown in Figure 1, is linear with zero intercept, indicating a reaction first order in $[Li_2Pd_2Cl_6]$. A plot of $k_{obsd}/[Li_2Pd_2Cl_6]$ $vs.$ $1/[LiCl]$, shown in Figure 2, is also linear with zero intercept. This type of plot indicates a first-order LiCl inhibition. The complete rate expression is thus

$$\text{rate} = k[Li_2Pd_2Cl_6][\text{enol propionate}]/[LiCl] \qquad (9)$$

where $k_{cis} = 9.3 \times 10^{-6}$ sec^{-1} and $k_{trans} = 1.97 \times 10^{-5}$ sec^{-1} since the equilibrium mixture contains 68% cis and 32% trans isomers. In no run was any allyl propionate observed.

To determine whether strong acid catalyzes the isomerization, the rate of isomerization without exchange was measured under one set of reaction conditions with and without added CF_3COOH. Results are listed in Table II. Also listed are two control
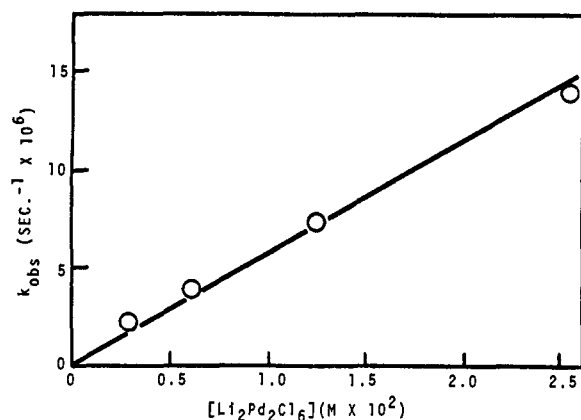
Figure 1. Plot of k_{obsd} vs. [Li₂Pd₂Cl₆]; [LiCl] = 0.049 ± 0.001 M.

Table II. Effect of CF₃COOH on Rate of Isomerization of
1-Propen-1-ol Propionate

[Pd(II)]ₜ, M	[Cl]ₜ, M	[CF₃COOH], M	k_{obsd},[a] sec⁻¹
0.048	0.37	0.0	4.1
0.048	0.37	0.1	4.2
0.048	0.37	1.0	5.9
0.0	0.0	0.0	<10⁻¹ [b]
0.0	0.0	1.0	<10⁻¹ [b]

[a] $k_{obsd} = k_{41} + k_{14}$ under the reaction conditions. [b] No isomerization observed in 48 hr. Lower limit based on the assumption that 2% isomerization would be detectable.

experiments which demonstrate that isomerization does not occur without Pd(II).

The rates of isomerization and exchange of the trans isomer of 2-buten-2-ol propionate and the cis and trans isomers of the enol propionate of phenylacetaldehyde were determined. Results are summarized in Table III along with the rates of exchange of some enol propionates which do not have cis–trans isomers.

Several mechanistic experiments were carried out to test the possibility of palladium(II) hydride species as intermediates. First trans-1-propen-1-ol propionate was isomerized by Pd(II) in CH₃COOD to an equilibrium mixture. The cis-1-propen-1-ol propionate was then analyzed for deuterium content by mass spectrometry. The ester was found to contain 1% deuterium. Next, a sample of trans-1-propen-1-ol propionate was isomerized in the presence of a sixfold excess of ethylene-d₄. No detectable amount of deuterium was incorporated into the cis-1-propen-1-ol propionate formed.

The reactivity of the esters was also tested in the presence of palladium(II) and rhodium(II) hydrides. The palladium(II) hydride was produced in situ by reaction of a palladium(II) chloride solution in acetic acid with diethylmercury. Presumably, palladium(II) ethyl is formed which eliminates ethylene to give palladium(II) hydride.[6] In the presence of this reagent allyl propionate and cis- and trans-1-propen-1-ol propionate disappeared, but during the course of the decomposition reaction, no isomerization of any of the esters into either of the other two was observed. In addition, no acetate esters were formed and propylene was identified as one of the products. An isomerization which

Figure 2. Plot of k_{obsd}/[Li₂Pd₂Cl₆] vs. 1/[LiCl].

Table III. Rates of Exchange and Isomerization of
Various Enol Propionates at 25°

Enol propionate	Isomerization k, sec⁻¹	Exchange[a] k_1, sec⁻¹	k_2, M^{-1} sec⁻¹
CH₂=CHO₂CC₂H₅		1.4×10^{-4}	1.2×10^{-2}
(H)(CH₃)C=C(O₂CC₂H₅)(H)	1.97×10^{-5}	8×10^{-7}	1.65×10^{-4}
(CH₃)(H)C=C(O₂CC₂H₅)(H)	9.3×10^{-6}	5×10^{-7}	8.9×10^{-5}
(H)(C₆H₅)C=C(O₂CC₂H₅)(H)	1.8×10^{-6}	5.8×10^{-7}	5.9×10^{-6}
(C₆H₅)(H)C=C(O₂CC₂H₅)(H)	1.7×10^{-6}	9.5×10^{-7}	6.7×10^{-6}
H₂C=C(CH₃)(O₂CC₂H₅)		2.7×10^{-6}	1.23×10^{-5}
(H)(CH₃)C=C(O₂CC₂H₅)(CH₃)	6×10^{-7}	[b]	1.4×10^{-7}

[a] Values of k_1 and k_2 determined by rate measurements at two or more LiOAc concentrations. [b] Value of k_1 too low to determine.

is known to proceed via a rhodium(III) hydride is the isomerization of olefins by (C₂H₄)₂RhCl plus HCl.[8] When the three propionate esters were treated with this reagent in acetic acid, they were once again decomposed without isomerization. In separate control experiments, it was shown that allyl propionate is stable under the conditions that cis- and trans-1-propen-1-ol

(6) There is little doubt that Hg(II) alkyls exchange with Pd(II) salts[7a] and that Pd(II) alkyls with β-hydrogens eliminate Pd(II) hydride.[7b]
(7) (a) See R. F. Heck, J. Amer. Chem. Soc., 90, 5518 (1968); (b) G. Calvin and G. E. Coates, J. Chem. Soc., 2008 (1960).
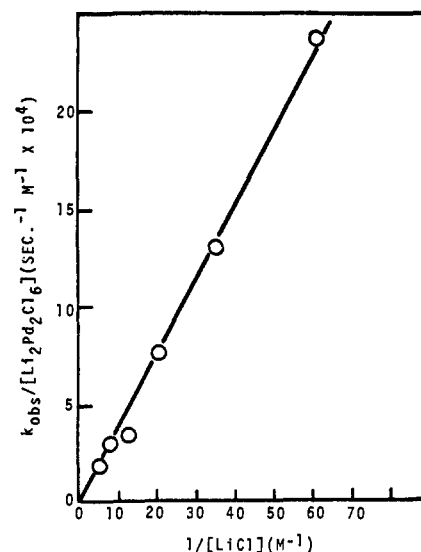
(8) R. Cramer, J. Amer. Chem. Soc., 88, 2272 (1966).

Table IV. Variation of Exchange Rate Constants[a]

[Pd(II)]$_t$, M	[Cl]$_t$, M	[Li$_2$Pd$_2$Cl$_6$], M	[Li$_2$PdCl$_4$], M	[LiCl], M	[Li$_2$Cl$_2$], M	$10^4 k_{obsd}$, sec^{-1}	$k_1 + k_2$[LiOAc], sec^{-1} × 10^3
0.02436	0.0952	0.0118	0.00067	0.0195	0.001	23.1	3.83
0.02436	0.1052	0.0117	0.00094	0.0273	0.0019	7.20	1.68
0.02436	0.1152	0.0116	0.0012	0.0347	0.0031	5.70	1.71
0.02436	0.1252	0.0115	0.0014	0.0418	0.0045	4.93	1.79
0.02436	0.1352	0.0114	0.0016	0.0484	0.0060	3.93	1.67
0.02436	0.1452	0.0113	0.0018	0.0549	0.0077	3.10	1.51
0.02436	0.1952	0.0108	0.0027	0.0836	0.018	1.82	1.41

[a] [LiOAc] = 0.1 M for all runs.

Table V. Variation of Exchange Rate Constants with [LiCl] at Low [LiCl][a]

[Pd(II)]$_t$, M	[Cl]$_t$, M	[Li$_2$Pd$_2$Cl$_6$], M	[Li$_2$PdCl$_4$], M	[LiCl], M	[Li$_2$Cl$_2$], M	$10^4 k_{obsd}$, sec^{-1}	$k_1 + k_2$[LiOAc], sec^{-1} × 10^3
0.00776	0.0362	0.00376	0.00232	0.0120	0.00037	4.95	1.47
0.00776	0.0462	0.00368	0.00392	0.0204	0.0011	2.96	1.64
0.00776	0.0562	0.00361	0.00537	0.0283	0.0021	1.99	1.56
0.00776	0.0662	0.00354	0.00672	0.0357	0.0033	1.44	1.45
0.00776	0.0762	0.00348	0.00798	0.0428	0.0047	1.20	1.47
0.00388	0.0231	0.00187	0.00015	0.0107	0.00029	2.22	1.26
0.00388	0.0331	0.00181	0.00026	0.0193	0.0010	1.27	1.35
0.00388	0.0431	0.00176	0.00036	0.0273	0.0019	0.90	1.40
0.00388	0.0531	0.00171	0.00046	0.0348	0.0031	0.678	1.40
0.00388	0.0631	0.00167	0.00054	0.0419	0.0045	0.564	1.41
0.01552	0.0524	0.00768	0.00015	0.00553	0.000078	11.0	0.78
0.00776	0.0262	0.00385	0.000055	0.00282	0.000020	8.25	0.60
0.00388	0.0131	0.00193	0.00002	0.00143	0.000005	5.3	0.39

[a] [LiOAc] = 0.1 M for all runs.

propionate are isomerized. The only reaction which occurs is the slow conversion of allyl propionate to allyl acetate.[9]

Exchange. The rate expression for exchange, shown in eq 1, was tested over a much wider range of variables, using vinyl propionate as substrate. In all cases linear first-order plots over as many as five half-lives were obtained when the reaction was assumed to be first order in vinyl propionate. As shown in Figure 3 the exchange is strictly first order in [LiOAc] up to [LiOAc] = 2 M.

The anomalous behavior of k' and k''[LiOAc] at low [LiCl] reported earlier[3] is demonstrated by the data in Table IV. This result could be due to another reaction taking place at very low [LiCl] or to inaccuracies in analyzing stock solutions. Thus at low [LiCl] most of the chloride comes from the Pd(II) stock solutions and is the difference between two large numbers as shown by eq 10. Small errors in [Cl]$_t$ or [Pd(II)]$_t$ analysis cause

$$[LiCl] = [Cl]_t - 6[Li_2Pd_2Cl_6] - 4[Li_2PdCl_4] \quad (10)$$

large errors in [LiCl]. To test this possibility, Pd(II) stock solutions were prepared which contained little excess LiCl. Reaction mixtures could be prepared from this Pd(II) stock solution and a 1.0 M LiCl stock solution for which [LiCl] is accurately known even at low [LiCl]. The values of $k' + k''$[LiOAc] obtained using these reaction mixtures now remained constant even at low [LiCl] as shown in Table V. The last three runs in this table indicate that at very low [LiCl] the value of the rate constant actually decreases.

In Table VI are shown the values of the rate constants over a range of [Cl]$_t$ from 0.023 to 3.08 M.
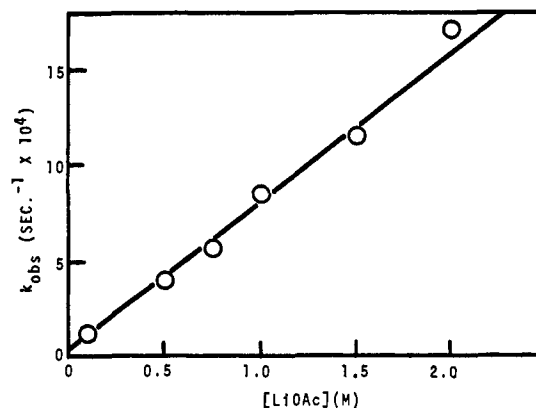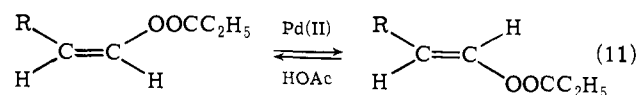
(9) P. M. Henry, J. Amer. Chem. Soc., 94, 1527 (1972).

Figure 3. Plot of k_{obsd} vs. [LiOAc]; [Pd(II)]$_t$ = 0.02668 M; [Cl]$_t$ = 0.2928 M.

Discussion

Enol Propionate Isomerization. The important new result reported in this paper is the observation of a Pd(II)-catalyzed isomerization reaction which the

$$R\!-\!C\!=\!C\!-\!OOCC_2H_5 \xrightleftharpoons[HOAc]{Pd(II)} R\!-\!C\!=\!C\!-\!H \quad (11)$$

author believes does not occur by any of the mechanisms previously proposed for this type of reaction.

There has been many reports of cis–trans isomerization catalyzed by metal salts.[10] Mechanisms suggested for these reactions include intermolecular hydride

(10) 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).

Henry / Pd(II)-Catalyzed Isomerization of Enol Propionates

Table VI. Variation of Exchange Rate Constants with [LiCl] at High [LiCl][a]

[Pd(II)]$_t$, M	[Cl]$_t$, M	[Li$_2$Pd$_3$Cl$_6$], M	[Li$_2$PdCl$_4$], M	[LiCl], M	[Li$_2$Cl$_2$], M	$10^4 k_{obsd}$, sec^{-1}	$k_1 +$ k_2[LiOAc]$_3$, sec$^{-1} \times 10^3$
0.00388	0.0231	0.0187	0.000147	0.0107	0.00029	2.22	1.26
0.02436	0.2952	0.0101	0.00415	0.1306	0.0437	1.14	1.48
0.02436	0.4952	0.0091	0.00614	0.2035	0.106	0.5	1.12
0.02436	0.8952	0.0078	0.0087	0.3125	0.250	0.25	1.0
0.02436	1.199	0.00712	0.0101	0.379	0.368	0.206	1.10
0.02436	1.475	0.00662	0.0111	0.432	0.479	0.191	1.25
0.02436	1.8952	0.0060	0.0124	0.5049	0.653	0.147	1.23
0.02436	2.0952	0.00575	0.0129	0.536	0.737	0.112	1.05
0.02436	2.5868	0.00464	0.0131	0.608	0.949	0.0643	0.84
0.02436	3.0868	0.00425	0.0139	0.674	1.166	0.0603	0.97

[a] [LiOAc] = 0.1 M for all runs.

transfer *via* metal hydrides, intramolecular transfer *via* π-allyl hydrides, and reversible π-allyl complex formation. A series of experiments was performed to determine if any of the mechanisms could be operative. The fact that the enol propionate of phenylacetaldehyde isomerized (*e.g.*, eq 11, R = phenyl) eliminates the two involving π-allyls since these enol propionates cannot form π-allyls.

The hydride mechanism is not as easy to test. The mechanisms usually suggested involve hydride formation: either oxidation addition of H$^+$ to Pd(II) to give palladium(IV) hydride or to Pd(0) to give palladium(II) hydride. The first seems unlikely because of the high potential of Pd(IV). On the other hand the palladium(II) hydride mechanism requires the formation of Pd(0) for the production of palladium(II) hydride by oxidative addition. It is usually postulated that the Pd(0) is formed by oxidation of a small amount of organic substrate. This mode of palladium(II) hydride formation would require induction periods rather than the clean kinetics actually observed.[11] Another piece of evidence against either type of hydride formation by oxidative addition is the lack of appreciable strong acid catalysis. Other Pd(II)-catalyzed reactions believed to occur *via* hydrides formed by oxidative addition have exhibited strong acid catalyses.[12]

However, plausible reaction schemes involving palladium(II) hydrides which fit the kinetics can be written, such as shown in eq 12–14 (X = OOCC$_2$H$_5$ or Cl).

If small equilibrium amounts of palladium(II) hydride are rapidly established *via* eq 12 and 14 and isomerization (eq 13) is very fast compared with decomposition (eq 14), the observed kinetics might be expected.
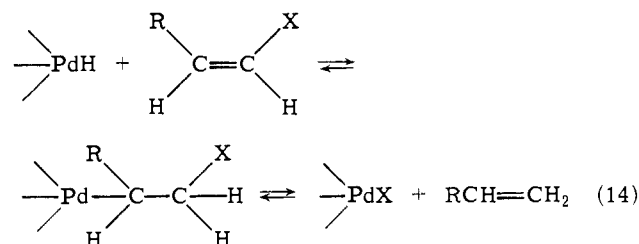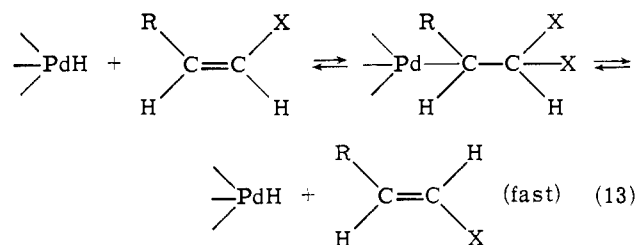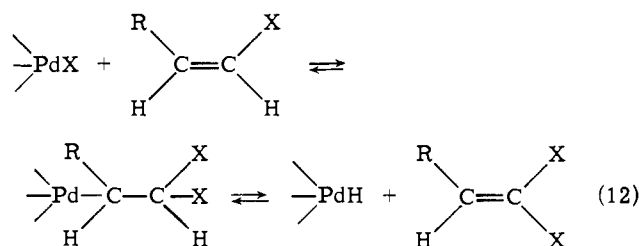
However, the following experimental observations make *any* hydride mechanism unlikely. (1) There is no exchange of olefinic hydrogen with deuterium when CH$_3$COOD is used as solvent.[13] (2) No isomerization of enol and allylic esters into each other was observed. (3) No exchange between C$_2$D$_4$ and the enol ester was observed.[14] (4) Palladium(II) hydride, formed *in situ*

$$\text{—PdX} + \begin{array}{c} R \\ \diagup \\ C=C \\ \diagup \quad \diagdown \\ H \quad\quad H \end{array} \overset{X}{\rightleftarrows}$$

$$\text{—Pd—C—C—X} \rightleftarrows \text{—PdH} + \begin{array}{c} C=C \end{array} \quad (12)$$

$$\text{—PdH} + \begin{array}{c} C=C \end{array} \rightleftarrows \text{—Pd—C—C—X} \rightleftarrows$$

$$\text{—PdH} + \begin{array}{c} C=C \end{array} \quad \text{(fast)} \quad (13)$$

$$\text{—PdH} + \begin{array}{c} C=C \end{array} \rightleftarrows$$

$$\text{—Pd—C—C—H} \rightleftarrows \text{—PdX} + RCH\!=\!CH_2 \quad (14)$$

by reaction with Hg(II) alkyls, did not cause isomerization of enol propionates (eq 13) but only decomposition (eq 14).

If the cis–trans isomerization does not occur by any of the routes previously suggested for double bond isomerizations, then a new type of mechanism must be operative. It is noteworthy that the rate expression (*e.g.*, eq 9) indicates that π complex, formed by eq 15, is

$$\text{Li}_2\text{Pd}_2\text{Cl}_6 + \text{enol ester} \rightleftarrows \text{Li}_2\text{Pd}_2\text{Cl}_5(\text{enol ester}) + \text{LiCl} \quad (15)$$

the reactive species. Three possible mechanisms are listed below.

(1) π–σ Rearrangement to a Diradical. Analogous intermediates have been postulated for metal carbonyl catalyzed photoisomerization of olefins (eq 16).[15]

erized butenes apparently contained deuterium.[12] This reaction is acid catalyzed and most likely proceeds *via* a palladium(II) hydride mechanism. The reason higher deuterium levels were probably not found is that the palladium(II) deuteride can apparently exchange with solvent, and the butene was in sixfold excess. In the mechanism represented in eq 12–14, much higher deuterium levels would be expected because the C$_2$D$_4$ was in sixfold excess over the enol propionate and exchange with solvent is not postulated.

(11) Induction periods have been observed in Pd(II)-catalyzed isomerizations; for instance, see G. C. Bond and M. Hellier, *J. Catal.*, **4**, 1 (1965).

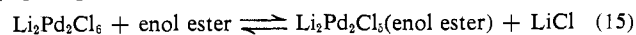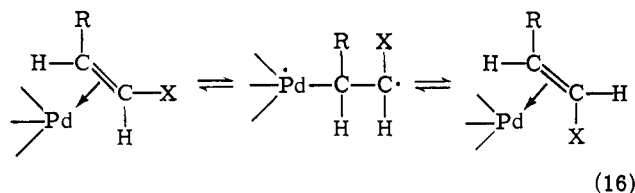(12) R. Cramer and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **88**, 3534 (1966).

(13) Only a small amount of exchange with solvent would be observed if the metal hydride catalyzed many isomerizations before decomposition. However, considerable exchange with solvent would be good evidence for hydride intermediates.

(14) In a similar isomerization experiment, using *cis*-2-butene and C$_2$D$_4$ catalyzed by a CF$_3$COOH–Pd(II) mixture, about 4% of the isom-

(15) M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Amer. Chem. Soc.*, **93**, 3285 (1971).

$$\text{(16)}$$

This same intermediate may also be operative in the metal carbonyl catalyzed thermal isomerization of olefins.[16]

**(2) π–σ Rearrangement to a Carbonium Ion.** This mechanism consists of rearrangement of the π complex to a Pd(II)–carbon bonded carbonium ion. The carbonium ion would be stabilized by the oxygen of the ester group.[17]

$$\text{(17)}$$
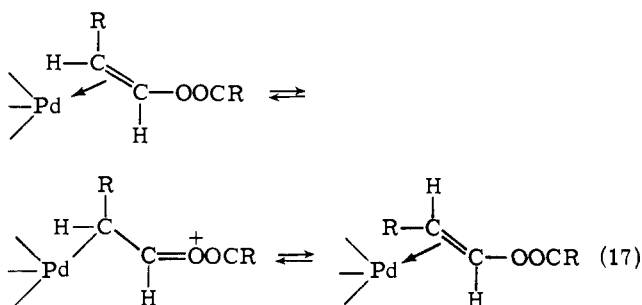
The type of intermediate shown in eq 15 is analogous to the type of intermediate which would be involved in the palladation of aromatics to give unstable phenyl-palladation compounds. These compounds are believed to be intermediates in the Pd(II)-catalyzed cou-

$$\text{(18)}$$
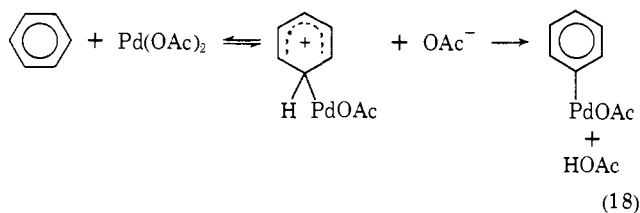
pling of benzene[18] as well as other Pd(II)-catalyzed reactions.[19] Another reaction which may occur *via*

$$\text{(19)}$$
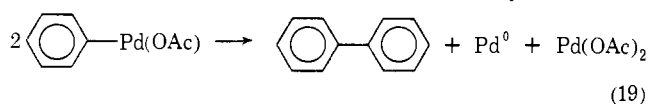
carbonium ion type intermediates is the coupling of certain substituted olefins to give substituted butadienes.[20,21] The reaction scheme is that shown in eq 20 and 21.

Other apparent examples of σ–π rearrangements of metal-bonded cations are the racemization of ferrocenyalkyl cations[22] and the carbon–metal hyperconjugation of α-metalloalkyl groups.[23]

An intermediate analogous to the carbonium ion in eq 18 has recently been detected in the reaction of Hg(II) with norbornene in FSO_3H–SbF_5–SO_2 solutions.[24]

(16) T. A. Manuel, *J. Org. Chem.*, **27**, 3941 (1962).
(17) G. A. Olah, *Chem. Eng. News*, **45** (14), 76 (1967).
(18) J. M. Davidson and C. Triggs, *Chem. Ind. (London)*, 457 (1966); *J. Chem. Soc.*, 1324 (1968)
(19) J. Tsuji, *Accounts Chem. Res.*, **2**, 144 (1969).
(20) C. F. Kohll and R. Van Helden, *Recl. Trav. Chim. Pays-Bas*, **86**, 193 (1967).
(21) H. C. Volger, *ibid.*, **86**, 677 (1967).
(22) D. Marquarding, H. Klusacek, G. Gokel, P. Hoffman, and I. Ugi, *J. Amer. Chem. Soc.*, **92**, 5389 (1970).
(23) W. Hanstein and T. G. Traylor, *Tetrahedron Lett.*, 4451 (1967).

$$\text{(20)}$$

$$\text{(21)}$$
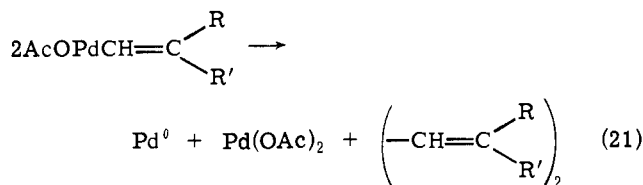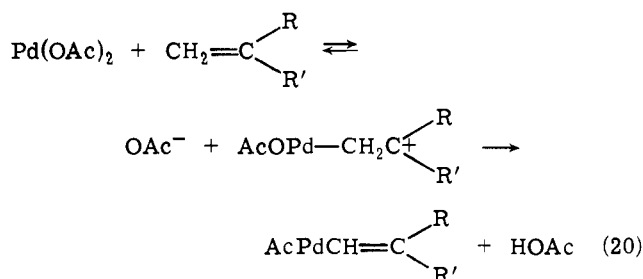
(3) Chloropalladation–Dechloropalladation. A third possibility is nonstereospecific chloropalladation–dechloropalladation (A = addition; E = elimination). It has been shown[25] that chloropalladation is not stereo-

$$\text{(22)}$$
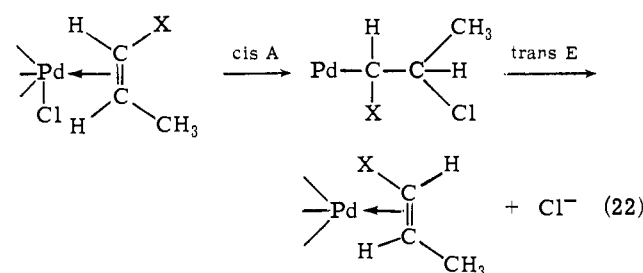
specific so this mechanism is quite reasonable. One argument against this mechanism is that chloropalladation of vinylic chlorides was found to have a different rate expression from that given by eq 9. This argument is far from conclusive since the rate expression for eq 22 may well be different from that for chloropalladation of vinylic chlorides. In any case more mechanistic work is required before a definite mechanism can be proposed.

The author does not mean to imply that hydride mechanisms are completely absent although they appear to be minor reactions. The increase in rate of isomerization when CF_3COOH is added and the small amount of exchange with deuterated solvent most likely result from palladium(II) hydride reactions.

Exchange. The present results with vinyl propionate eliminate the discrepancy in the earlier studies and indicate that eq 1 is valid over a very wide range of LiOAc and chloride concentrations. Only at very low $[Cl]_t$ does the rate expression become invalid. This result is probably due to polymerization of the dimer to give less reactive species. Similar effects have been noted in aqueous solution.[26,27]

The value of the exchange rate constant (Table VI) does show a gradual decrease with increasing [LiCl]. However, the range of $[Cl]_t$ is a factor of 150 from the lowest to the highest value. In a system so compli-

(24) G. A. Olah and P. R. Clifford, *J. Amer. Chem. Soc.*, **93**, 126 (1971).
(25) P. M. Henry, *J. Org. Chem.*, **37**, 2443 (1972).
(26) R. Jira, J. Sedlmeier, and J. Smidt, *Justus Liebigs Ann. Chem.*, **693**, 99 (1966).
(27) P. M. Henry, *J. Amer. Chem. Soc.*, **88**, 1595 (1966).

cated, even small errors in K_D and K_1 (eq 6 and 7) would result in such a drift. Thus at the highest $[Cl]_t$, 3.0868, over 70% of the chloride not complexed with Pd(II) is in the form of the dimer Li_2Cl_2.

The effect of enol propionate structure on rate of exchange, as shown in Table III, closely follows that previously found for exchange of enol acetate esters.[3] The large retardation in rate caused by substitution on the vinylic carbons indicates a large steric requirement for acetoxypalladation. This is not surprising since the elements of Pd(II) dimer and propionate must be added across a double bond which is already substituted with at least an acetate group.

On the other hand, the effect of substitution on rate of isomerization is much less than that for exchange. Thus the rate of exchange of the enol propionate of propionaldehyde is about 1000 times faster than the enol propionate of 2-butanone. For isomerization the factor is only 30. This lower effect of steric factors on isomerization is consistent with mechanisms 1 and 2 since only Pd(II) is added to the double bond but is inconsistent with mechanism 3 since chloropalladation has a steric factor closer to that for acetoxypalladation.[25]

Experimental Section

Materials. Sources of most chemicals and preparation of stock solutions have been described previously.[2] Vinyl propionate was purchased from Aldrich Chemical Co. The enol propionates of propionaldehyde and 2-butanone were prepared by procedures analogous to those used for preparation of the acetates. The corresponding aldehyde or ketone was refluxed with propionic anhydride with potassium propionate as catalyst. Pure samples of the cis and trans enol propionates from propionaldehyde were obtained by preparative vpc (20-ft column packed with 20% Lac 446 on 60–80 mesh Chromosorb W. The temperature was 120° and helium flow 60 ml/min). Their structures were confirmed by nmr analysis.[28] In the case of 2-butanone, two peaks were obtained.

Collection of the two peaks by preparative vpc (the Lac 446 column at 150°) followed by nmr analysis indicated that peak 1 was a mixture of trans-2-buten-2-ol propionate and 1-buten-2-ol propionate in a 2.3/1 ratio while peak 2 was pure cis-2-buten-2-ol propionate.[29] Only the pure cis isomer was used for the kinetic runs. The isopropenyl propionate was prepared by exchange of isopropenyl acetate with propionic acid using $Hg(OAc)_2$–H_2SO_4 as catalyst.[30] The propionate ester was separated from the acetate ester by preparative vpc (6-ft 20% Carbowax 20M on an 70–80 mesh ABS support. Temperature was programmed from 80 to 200° at 7.5°/min; the helium rate was 60 ml/min).

Samples of the enol propionates and acetates of phenylacetaldehyde were kindly supplied by Dr. R. F. Heck.

Samples of all esters used for kinetic runs were purified by preparative vpc. The purity of the cis or trans isomers was over 95%.

The $[(C_2H_4)_2RhCl]_2$ was prepared by a literature procedure.[31]

Kinetic Runs. Vpc analysis was used for all kinetic runs. Conditions were the same as for preparative vpc. The 6-ft Carbowax 20M column programmed from 80 to 200° at 7.5°/min with a helium flow rate of 60 ml/min was used for the analysis in the isobutyraldehyde–enol propionate runs. In all runs but those containing trifluoroacetic acid, samples were injected without work-up. In the run containing the strong acid, the acid was neutralized with LiOAc before injection.

In the equilibrium runs in which little exchange occurred, the kinetics were treated in the usual fashion for first-order runs approaching equilibrium.[32] If $[C]_e$ is the concentration of one

isomer at equilibrium and $[C]_t$ is the concentration of this isomer at a given time, then a plot of $\ln([C]_e - [C]_t)$ vs. time should give a straight line, the slope of which is k_e. Straight lines were obtained, indicating a first-order reaction. If k_e is the rate constant for isomerization of the cis isomer into the trans, and k_t is the corresponding rate constant for the trans isomer, then $k_e = k_c + k_t$. The individual values of k_c and k_t can be calculated from the equilibrium mixture using the relationship: [cis isomer]/[trans isomer] = k_t/k_c.

Runs in which both exchange and isomerization were taking place were treated by means of the computer program previously used for allylic exchange and isomerization.[5]

CH₃COOD Experiments. These runs were made in the same fashion as the others except that CH₃COOD was used as solvent. When the concentration of the enol propionates had almost reached their equilibrium values, the organic product was extracted into methylene chloride; the acetic acid and inorganic salts were removed by washing with water. The cis isomer was then collected separately in 100% collection tubes[3] and analyzed by mass spectroscopy. The deuterium analysis was made using the molecular ion (m/e 114 for undeuterated). In calculating the amount of deuterium present, a correction was made for the presence of ^{13}C.

C₂D₄ Experiment. This run was made in the same fashion as other isomerization runs with the exception that C_2D_4 was present. In a 17-ml tube equipped with a mouth so it could be capped in the same fashion as a soft drink bottle were placed 2 ml of the Pd(II) reaction mixture and 0.1 mmol of cis-1-propen-1-ol propionate. A rubber liner was then placed over the mouth of the tube and the tube capped with a metal cap which contained a small hole. Then, by means of a syringe needle inserted through the hole in the metal cap and through the rubber liner, the tube was evacuated and pressured to about 2 psig with ethylene-d_4. Since the gas volume of the tube was 15 ml and the volume of 1 mmol of gas at 25° is less than 25 ml, the tube contained at least 0.6 mmol of C_2D_4. The solution changed from red to yellow, no doubt because of ethylene π-complex formation via an equilibrium analogous to eq 21. The π-complex formation slowed the rate of isomerization by a factor of about 5, but after a week an equilibrium mixture of the two isomers was reached. The organic products were extracted into methylene chloride and the trans isomer was collected in a 100% collection tube and analyzed for deuterium by mass spectral analysis. None was found with a limit of detection of 0.5%. The limit was this high because of some material which interfered with the analysis.

Palladium(II) Hydride Experiments. To a reaction mixture 1.0 ml in volume and containing 0.06 mmol of Pd(II) and 1.0 mmol of cis-1-propen-1-ol propionate or allyl propionate was added 0.06 mmol of diethylmercury. A black precipitate formed almost immediately. The supernatant was analyzed periodically for the enol and allylic esters. No cis–trans or enol–allylic isomerization was observed but the ester concentration decreased with time. In the case of allyl propionate, only 25% remained after 12 min. Mass spectral analysis of the gas phase indicated propylene was present. The enol ester decomposed much slower, about 25% remaining after standing overnight. A control experiment demonstrated that allyl propionate was stable to the reaction conditions in the absence of diethylmercury. The only reaction observed was exchange to allyl acetate, a reaction which, under the experimental conditions, had a half-life of days.

Rhodium(III) Hydride Experiments. To 1.0 ml of an acetic acid solution, 1.0 M in LiCl, and 1.0 M in CF_3COOH were added 0.18 mmol of $[(C_2H_4)_2RhCl]_2$ and 0.1 mmol of cis-1-propen-1-ol propionate. Results were qualitatively the same as with palladium-(II) hydride although decomposition was slower. It took 67 min for the allyl ester to decompose to one-third of its original concentration while the enol esters had not noticeably decomposed after standing overnight. A control experiment demonstrated that allyl propionate was stable to the reaction conditions if $(C_2H_4)_2$-RhCl is not present.

(28) H. O. House and V. Kramar, *J. Org. Chem.*, **28**, 3362 (1963).

(29) Assignments were made by the same reasoning used previously for the corresponding acetate ester.[3] W. E. Parham and J. F. Dooley, *J. Org. Chem.*, **33**, 1476 (1968).

(30) H. Hopff and M. A. Osman, *Tetrahedron*, **24**, 2205 (1968).

(31) R. Cramer, *Inorg. Chem.*, **1**, 722 (1962).

(32) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1960, p 186.