Palladium(II)-Catalyzed Exchange and Isomerization Reactions. III. Allylic Ester Isomerization in Acetic Acid Catalyzed by Palladium(II) Chloride[1,2]

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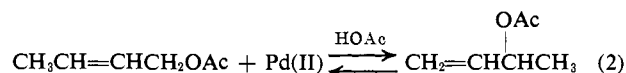
Abstract: The isomerization and exchange of the acetate, propionate, and trifluoroacetate esters of crotyl alcohol and 3-buten-2-ol in acetic acid were found to proceed by two paths: one involving simultaneous exchange and isomerization and the other involving isomerization without exchange. The first reaction has the following rate expression: rate = $([Li_2Pd_2Cl_6][\text{allylic ester}]/[LiCl])(k' + k''[LiOAc])$. This reaction almost certainly proceeds by addition of Pd(II) and acetate across the double bond followed by the elimination of Pd(II) and propionate. The second reaction, isomerization without exchange, has the following rate expression: rate = $([Li_2Pd_2Cl_6][\text{allylic ester}]/[LiCl])(k'/(1 + k''[LiOAc]))$. During isomerization an ^{18}O label was found to transfer from ester oxygen to carbonyl oxygen. The kinetic and labeling results are consistent with a mechanism involving a 1,3-acetoxonium ion type intermediate of the type shown in eq 22. LiOAc inhibition results from capture of the 1,3-acetoxonium ion by LiOAc. When R_3 is CF_3, the rate of isomerization is much slower than when it is CH_3 or C_2H_5. Retardation of rate by an electron-withdrawing group such as CF_3 is consistent with an acetoxonium-type intermediate.

In the previous paper[2] of this series, a kinetic study of the Pd(II)-catalyzed exchange of allylic, propionate, and trifluoroacetate esters with acetic acid was described. The rate expression was found to have the form shown in eq 1. This rate expression is of the

$$\frac{-d[\text{allylic ester}]}{dt} =$$

$$\frac{[Li_2Pd_2Cl_6][\text{allylic ester}]}{[LiCl]}(k' + k''[LiOAc]) \quad (1)$$

same form as that previously found[4] for vinyl ester exchange which was found to occur by an acetoxypalladation–deacetoxypalladation mechanism. This similarity in rate expressions suggested that allylic ester exchange occurred *via* an analogous mechanism. To test this mechanism, the exchange and isomerization of unsymmetrical allylic esters were undertaken. This paper will describe that study.

Pd(II) salts in acetic acid have been reported[5,6] to catalyze the isomerization of one allylic acetate to another, *i.e.*, crotyl acetate to 3-buten-2-ol acetate.

$$CH_3CH{=}CHCH_2OAc + Pd(II) \underset{\xrightarrow{\hspace{0.8cm}}}{\overset{HOAc}{\rightleftarrows}} CH_2{=}CHCHCH_3 \quad (2)$$
(OAc on the central carbon)

One mechanism that has been suggested[5] for this reaction involves an acetoxypalladation–deacetoxypalladation sequence. When crotyl acetate is the starting ester, the scheme shown in eq 3 occurs.

(1) A preliminary report on this work was presented at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, Abstract ORGN-127. In addition, a preliminary communication on this work has appeared: P. M. Henry, *Chem. Commun.*, 328 (1971).
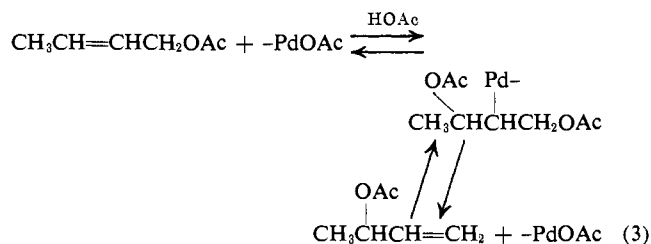
(2) Paper II: P. M. Henry, *J. Amer. Chem. Soc.*, **94**, 1527 (1972).

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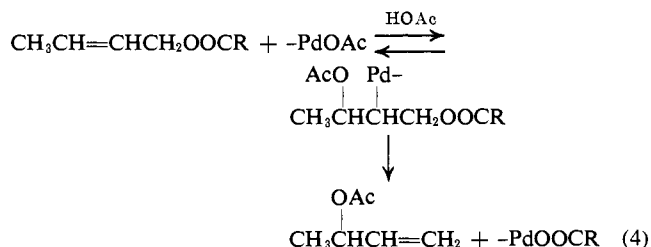
(4) P. M. Henry, *J. Amer. Chem. Soc.*, **93**, 3853 (1971).

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

(6) T. Matsuda, T. Mitsuyasu, and Y. Nakamura, *Kogyo Kagaku Zasshi*, **72**, 1751 (1969).

$$CH_3CH{=}CHCH_2OAc + {-}PdOAc \underset{\xleftarrow{\hspace{0.6cm}}}{\overset{HOAc}{\rightleftharpoons}}$$

$$\begin{array}{c} OAc\ \ Pd{-} \\ | \quad\ | \\ CH_3CHCHCH_2OAc \end{array}$$

$$\begin{array}{c} OAc \\ | \\ CH_3CHCH{=}CH_2 + {-}PdOAc \end{array} \quad (3)$$

This mechanism can be tested by isomerizing esters of other acids in acetic acid. If the mechanism shown in eq 3 is operative, exchange should occur when and only when there is isomerization. For example, when a crotyl ester is the starting material the scheme shown in eq 4 occurs.

$$CH_3CH{=}CHCH_2OOCR + {-}PdOAc \overset{HOAc}{\rightleftarrows}$$

$$\begin{array}{c} AcO\ \ Pd{-} \\ | \quad\ | \\ CH_3CHCHCH_2OOCR \end{array}$$

$$\downarrow$$

$$\begin{array}{c} OAc \\ | \\ CH_3CHCH{=}CH_2 + {-}PdOOCR \end{array} \quad (4)$$

Results

All kinetic runs were made at 25°.

Propionate Esters. The exchange and isomerization reactions of crotyl and 3-buten-2-ol propionates were found to be more complicated than the scheme shown by eq 4. Thus, not only was isomerization with exchange observed but also isomerization without exchange. The entire possible reaction sequence is shown in eq 5. To define this system kinetically requires 12 rate constants. Fortunately, the kinetic treatment can be simplified since k_{21}, k_{24}, k_{34}, and k_{31} are zero because the solvent is acetic acid and k_{32} and k_{23} can be measured independently. The values for the other six rate constants were determined for a given set of reaction conditions using a computer calculation of the change in product distribution with time for various
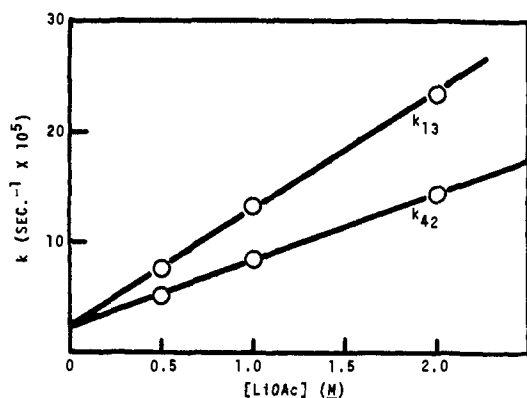
Figure 1. Plot of k_{13} and k_{42} vs. [LiOAc]. [Li$_2$Pd$_2$Cl$_6$] = 0.00287 M and [LiCl] = 0.055 M.
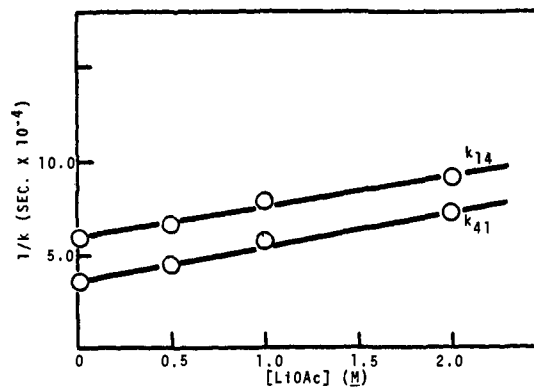
Figure 2. Plot of $1/k_{14}$ and $1/k_{41}$ vs. [LiOAc]. [Li$_2$Pd$_2$Cl$_6$] = 0.00287 M and [LiCl] = 0.055 M.

$$CH_3CH=CHCH_2OOCC_2H_5 \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} CH_3CH=CHCH_2OAc$$

$$\mathbf{1} \qquad\qquad \mathbf{2}$$

(5)

$$\underset{CH_2=CHCHCH_3}{\overset{OAc}{|}} \underset{k_{43}}{\overset{k_{34}}{\rightleftarrows}} \underset{CH_2=CHCHCH_3}{\overset{OOCC_2H_5}{|}}$$

$$\mathbf{3} \qquad\qquad \mathbf{4}$$
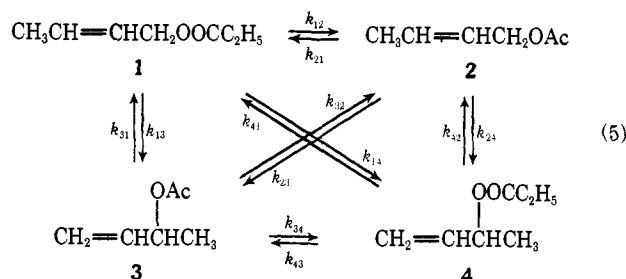
values of k's. Thus, for one set of reaction conditions, k_{23} and k_{32} were determined by equilibrating the acetate esters. Then the product distributions with time were determined starting with both **1** and **4**. Then various values of the k's were used to simulate product distributions with time until the product distributions starting with either **1** or **4** were matched within experimental error by the same set of k's.

Next, the rate expression for the various processes involved was determined by finding how each of the six experimental rate constants varied with [Pd(II)]$_t$, [Cl]$_t$, [LiOAc], and allyl ester concentration. For any given allyl ester concentration, the reaction was found to be first order in allyl ester since the data could be fitted only if this assumption was made. However, it is known from the previous work on the exchange reaction[2] that allyl ester actually inhibits the reaction. Since this inhibition is not important at low allyl ester concentration, the rate expressions were first defined at low ester concentration before the inhibition was studied.

Within experimental error the values of k_{12} and k_{43} were found to be negligible for all reaction conditions. Although they may have low positive values, these values are less than 10% of the lowest value of the other four rate constants. Of the other four rate constants, k_{13} and k_{42} were found to increase with increasing [LiOAc] while k_{14} and k_{41} actually decrease. A plot of k_{13} and k_{42} vs. [LiOAc] is shown in Figure 1.

The positive intercepts for k_{13} and k_{42} indicate a reaction zero order in [LiOAc].

The decrease of k_{14} and k_{41} caused by [LiOAc] would most likely result from capture of an intermediate in the isomerization reaction by [LiOAc]. If this is the case, we have the following relationship ($k' = k_{obsd}$ at [LiOAc] = 0; see Experimental Section).
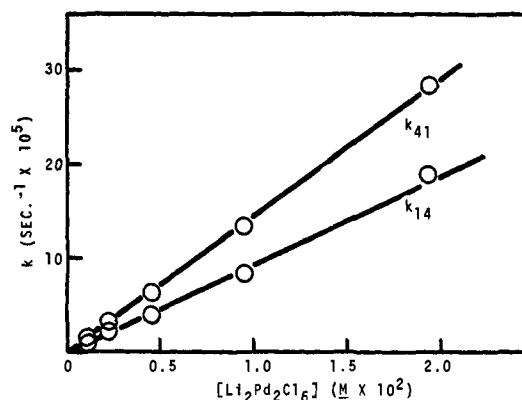
$$k_{obsd} = k'/(1 + k''[LiOAc]) \qquad (6)$$

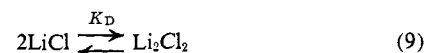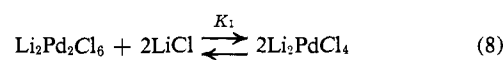Figure 3. Plot of k_{14} and k_{41} vs. [Li$_2$Pd$_2$Cl$_6$]. [LiCl] = 0.0057 M and [LiOAc] = 0.01 M.

Inverting we have

$$1/k_{obsd} = 1/k' + (k''/k')[LiOAc] \qquad (7)$$

A plot of $1/k_{obsd}$ vs. [LiOAc] should be linear with an intercept of $1/k'$ and a slope of k''/k'. As Figure 2 shows, this relationship is obeyed.

The values of the rate constants were such that at a lithium acetate concentration of less than 0.1 M, exchange was very slow compared with isomerization without exchange. Thus the remainder of the rate expression was defined by making runs at [LiOAc] = 0.01 M. A number of runs were also made at higher acetate concentrations to confirm that the exchange reaction followed the same kinetics found earlier.[2]

Next, the reactive Pd(II) species and the order in the species as well as the order in [LiCl] must be defined. This requires a knowledge of the equilibria involving Pd(II) and LiCl in acetic acid. A recent study[7] indicated that the following equilibria must be considered.

$$Li_2Pd_2Cl_6 + 2LiCl \underset{}{\overset{K_1}{\rightleftarrows}} 2Li_2PdCl_4 \qquad (8)$$

$$2LiCl \overset{K_D}{\rightleftarrows} Li_2Cl_2 \qquad (9)$$

K_1 was found to have an value of 0.1 M^{-1} and K_D a value of 2.56 M^{-1}.

To determine whether the reaction is first order in dimer, runs were made at various values of [Li$_2$Pd$_2$Cl$_6$] but constant [LiCl]. Plots of k_{14} and k_{41} vs. [Li$_2$Pd$_2$Cl$_6$] are shown in Figure 3. [Li$_2$Pd$_2$Cl$_6$] was calculated cor-

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

Table I. Values of Exchange and Isomerization Rate Constants for Various Allylic Esters

Ester	Exchange		Isomerization	
	k', sec^{-1} × 10^5	k'', M^{-1} sec^{-1} × 10^4	k', sec^{-1} × 10^5	k'', M^{-1}
$CH_3CH=CHCH_2OOCC_2H_5$	5.4	2.5	5.3	0.25
$CH_2=CHC(OOCC_2H_5)HCH_3$	4.7	1.6	8.6	0.32
$CH_3CH=CHCH_2OAc$	5.3^a	2.5^a	4.1	
$CH_2=CHC(OAc)HCH_3$	7.0^a	2.3^a	6.2^a	
$CH_3CH=CHCH_2OOCCF_3$	0.23	5.5	~0.01^b	
$CH_2=CHC(OOCCF_3)HCH_3$	0.54	16.2	~0.018^b	
$C_2H_5CH_2=CC(OOCC_2H_5)HCH_3$	1.0	0.5	1.0	
$CH_2=C(CH_3)C(OOCC_2H_5)CH_3$	1.0 × 10^{-3}	3.2 × 10^{-4}	9.2 × 10^{-4}	0.81

^{a} Calculated assuming (1) at [LiOAc] = 0.01 M only reaction taking place is isomerization without exchange, (2) for isomerization, k'' to k' is the same as for corresponding propionate esters, and (3) ratio of k' to k'' for exchange is same as for propionate esters. ^{b} These values are inaccurate because of side reactions.
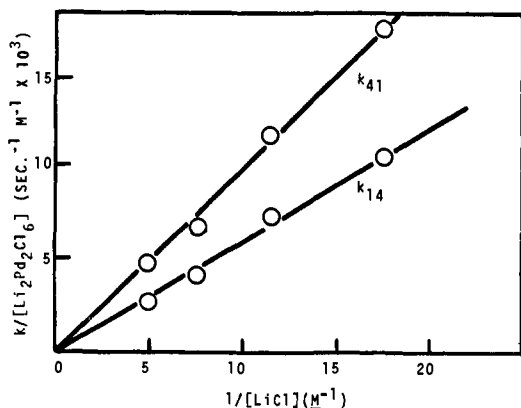
Figure 4. Plot of $k_{14}/[Li_2Pd_2Cl_6]$ and $k_{41}/[Li_2Pd_2Cl_6]$ vs. $1/[LiCl]$.

recting for the removal of dimer by LiCl via eq 8. The plots indicate the reaction is first order in dimer.

Values of k_{13} and k_{42} were determined at two different levels of $[Li_2Pd_2Cl_6]$. In these runs [LiCl] = 0.056 ± 0.01 M and [LiOAc] = 1.0 M. At $[Li_2Pd_2Cl_6]$ = 0.028 M, k_{13} was 1.92 × 10^{-5} sec^{-1} while k_{42} was 1.45 × 10^{-6} sec^{-1}. At $[Li_2Pd_2Cl_6]$ = 0.00939 M k_{13} was 5.85 × 10^{-5} sec^{-1} while k_{42} was 5.1 × 10^{-5} sec^{-1}. These values indicate a first-order dependence on $[Li_2Pd_2Cl_6]$.

The order in [LiCl] can now be determined by plotting $k/[Li_2Pd_2Cl_6]$ vs. $1/[LiCl]$. The linear plots of k_{14} and k_{41} with zero intercept shown in Figure 4 are indicative of a first-order LiCl inhibition. The free [LiCl] calculated from eq 8 and 9 was the value used in these plots. Similar plots were obtained with k_{13} and k_{42}.

The complete rate expression for the isomerization reaction is shown in eq 10 while the rate expression for

$$k_{14 \text{ (or 41)}} = \frac{[Li_2Pd_2Cl_6][\text{allylic ester}]}{[LiCl]} \left(\frac{k'_{14 \text{ (or 41)}}}{1 + k_{14 \text{ (or 41)}}[LiOAc]} \right) \quad (10)$$

the exchange reaction is shown in eq 11.

$$k_{13 \text{ (or 42)}} = \frac{[Li_2Pd_2Cl_6][\text{allylic ester}]}{[LiCl]} \times (k'_{13 \text{ (or 42)}} + k''_{13 \text{ (or 42)}}[LiOAc]) \quad (11)$$

Values of the rate constants are given in Table I. Also included are the values for two other allylic propionates which contain methyl substitution on the vinylic carbons.
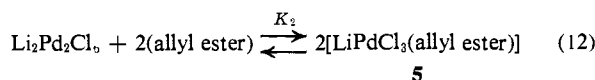
Acetate Esters. If the isomerization of the acetate esters follows a rate expression of the form given in eq

10 and 11, approximate values of the exchange and isomerization components of k_{23} and k_{32} may be obtained by runs at various LiOAc concentrations. These values are given in Table I.

To determine whether other than simple allylic isomerization took place, 1-penten-3-ol acetate was isomerized. The only product was 2-penten-1-ol acetate. No 3-penten-2-ol acetate was detected.

Trifluoroacetate Esters. Runs were made with crotyl and 3-buten-2-ol trifluoroacetates at 0.01 and 2.0 M [LiOAc]. Even at the lower [LiOAc], exchange is faster than isomerization, and at the higher [LiOAc], isomerization without exchange could not be detected. Thus the exchange rate constants could be determined quite accurately. However, the isomerization rates are only estimates because of the slow rates and the complication of exchange to give the acetate esters. Another complication which did not occur with the other esters was exchange with chloride to give the corresponding chlorides. This reaction was the fastest reaction at the lower [LiOAc]. Rate constants are given in Table I.

Inhibition by Allylic Ester. In the previous paper it was reported that the allylic esters themselves inhibited the reaction by the formation of an unreactive π complex 5 in an equilibrium represented by eq 12.

$$Li_2Pd_2Cl_6 + 2(\text{allyl ester}) \overset{K_2}{\underset{\longleftarrow}{\longrightarrow}} 2[LiPdCl_3(\text{allyl ester})] \quad (12)$$

5

In the present work 5 also cannot be a reactive species for if it were, at low allyl ester concentration the reaction would be one-half order in $[Li_2Pd_2Cl_6]$ rather than first order as observed.

The effect of allylic ester on rate was determined using acetate esters to simplify the kinetic scheme. As shown in Table II, the crotyl acetate concentration has

Table II. Effect of Crotyl Acetate Ester Concentration on Rate^a

$\begin{bmatrix} \text{Crotyl} \\ \text{acetate} \end{bmatrix}$	k_{23}, sec^{-1} × 10^5	k_{32}, sec^{-1} × 10^5
0.02	11.7	18.9
0.1	11.1	18.5
0.25	10.9	17.7
0.5	10.5	17.3

^{a} [Pd(II)]$_t$ = 0.02668 M; [Cl]$_t$ = 0.1428 M; [LiOAc] = 0.01 M.

little effect on rate. If the small inhibition results from

Table III. Values of Isomerization Rate Constants k_{32} Obtained by Correcting for 3-Buten-2-ol Acetate Inhibition[a]

[Pd(II)]$_t$	[Cl]$_t$	Allyl ester (ol)	[Li$_2$Pd$_2$Cl$_6$]	[Li$_2$PdCl$_4$]	[LiPd$_2$Clol]	Obsd k_{32}, sec^{-1} × 10^5	k',[b] M^{-1} sec^{-1} × 10^4
0.02668	0.1428[c]	0.02	0.0122	0.00170	0.00060	15.2	6.09
0.02668	0.1428[c]	0.1	0.0111	0.00163	0.0029	13.2	5.82
0.02668	0.1428[c]	0.25	0.00928	0.00149	0.00663	10.0	5.28
0.02668	0.1428[c]	0.50	0.00694	0.00129	0.0115	8.7	6.15

[a] [LiOAc] = 0.01 M; product distribution calculated assuming K_2 in eq 12 is 0.08 M^{-1}. [b] $k'' = k_{32}$[LiCl]/[Li$_2$Pd$_2$Cl$_6$]. [c] [LiCl] = 0.049 M.

the equilibrium shown in eq 12, the value of K_2 is about 0.005 M^{-1}.

3-Buten-2-ol acetate did, however, have an appreciable inhibitory effect on rate. The inhibition would decrease as the reaction proceeded because crotyl acetate, which is a weak inhibitor, is formed during the course of the run. For that reason, rates are initial rates. The value of K_2 which best fits the data is 0.08 M^{-1}. As shown in Table III the value of k'' remains constant when inhibition via the mechanism in eq 12 is assumed and this value of K_2 is used.

^{18}O Labeling Experiment. To determine the mode of transfer of the propionate group in the exchange reaction, a sample of crotyl propionate labeled in the ester oxygen was prepared and isomerized by Pd(II). At several times during the course of the run, both the crotyl propionate and 3-buten-2-ol propionate were isolated and analyzed by mass spectrometry to determine the ^{18}O content of the carbonyl oxygens. The results given in Table IV indicate that when isomerization

Table IV. Mass Spectrometer Analysis of Carbonyl Groups during Course of Exchange Reaction Starting with Crotyl Propionate (1) Labeled in Ester Oxygen[a,b]
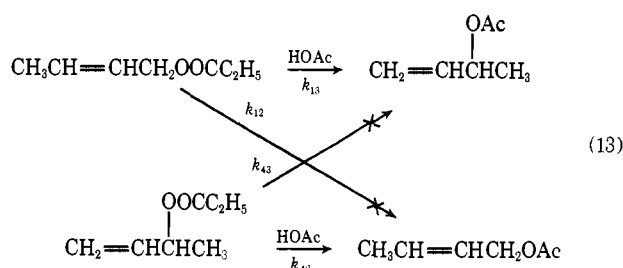
Time, min	% 1[c]	% ^{18}O in carbonyl oxygen 1	% ^{18}O in carbonyl oxygen 4
20	87.5	0.52	2.1
50	79.5	0.51	1.91
111	66.7	0.48	2.03
234	59.8	0.41	2.04

[a] Ca. 2.1% ^{18}O. [b] [Pd(II)]$_t$ = 0.0244 M; [Cl]$_t$ = 0.1436 M; [LiOAc] = 0.01 M. [c] At equilibrium per cent of 1 = ca. 60%.

occurs, the ester oxygen of the crotyl propionate becomes the carbonyl oxygen of the 3-buten-2-ol propionate.

Discussion

The results are consistent with two separate reactions taking place, one first order in [LiOAc] and the other zero order in [LiOAc]. The [LiOAc] dependent reaction is concurrent exchange and isomerization (eq 13).

$$CH_3CH=CHCH_2OOCC_2H_5 \xrightarrow[k_{13}]{HOAc} CH_2=CHCHCH_3 \quad (OAc)$$

$$CH_2=CHCHCH_3 \quad (OOCC_2H_5) \xrightarrow[k_{42}]{HOAc} CH_3CH=CHCH_2OAc$$

with k_{12}, k_{43} (13)

The rate expression is identical with that previously found for exchange of symmetrical allylic esters[2] and,

as discussed in the introduction, the fact that exchange only occurs with isomerization (i.e., k_{12} and k_{43} are zero) is good evidence for the acetoxypalladation–deacyloxypalladation mechanism (eq 3). This type of mechanism is also expected on the basis of other Pd(II) catalytic chemistry.[8–10]

The rate expressions for the two exchange reactions studied to date, allylic[2] and vinyl ester exchange,[4,11] both have identical rate expressions and both almost certainly proceed via acetoxypalladation–deacyloxypalladation mechanisms. As discussed previously,[2,4] the LiCl inhibition in eq 11 is consistent with the first step (eq 14) being the formation of a π complex by dis-

$$Li_2Pd_2Cl_6 + R_1CH=CHCHOOCCR_3 \rightleftharpoons$$

6
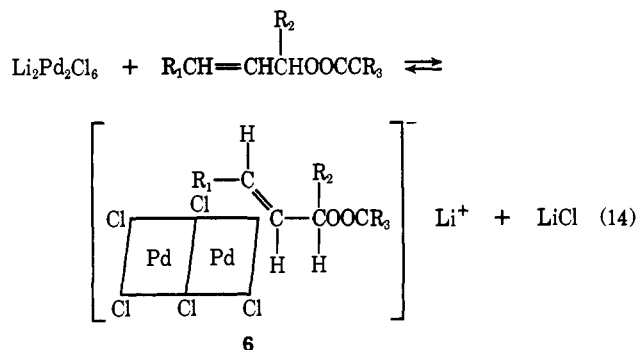
placement of LiCl from Li$_2$Pd$_2$Cl$_6$ in a rapid equilibrium (R_1, R_2 = H or CH$_3$, R_3 = CH$_3$). The next step (eq 15)

$$6 + LiOAc \xrightarrow{slow}$$
(or HOAc)

7
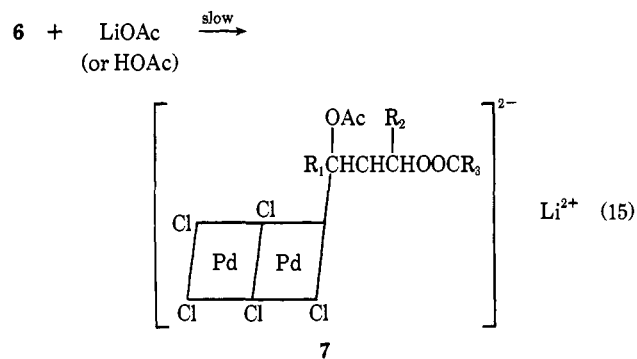
must involve the attack of HOAc or LiOAc on the π complex to give the acetoxypalladation adduct. The exact mode of this step is not obvious from the kinetics, but other evidence suggests that attack is from outside the Pd(II) coordination sphere.[2,4] The last step (eq 16) is deacyloxypalladation to give exchange. Of course, deacetoxypalladation from 7 must occur some of the time but this would result in no net change and would lessen the rate of exchange. Acetate and propionate

(8) E. W. Stern, Catal. Rev., 1, 73 (1967).
(9) A. Aguilo, Advan. Organometal. Chem., 5, 327 (1967).
(10) F. R. Hartley, Chem. Rev., 69, 799 (1969).
(11) P. M. Henry, Amer. Chem. Soc., Div. Petrol. Chem., Prepr., 14 (2), B15 (1969), but also see 14 (4), F3 (1969).

$$7 \longrightarrow \text{LiOOCR}_3 + \left[\begin{array}{c} \text{OAc} \\ | \\ R_1-\text{CH} \\ | \\ H-C \\ Cl \quad | \quad Cl \\ \boxed{\begin{array}{cc} Pd & Pd \end{array}} \quad C-R_2 \\ Cl \quad Cl \quad Cl \quad H \end{array}\right] \text{Li}^+ \quad (16)$$
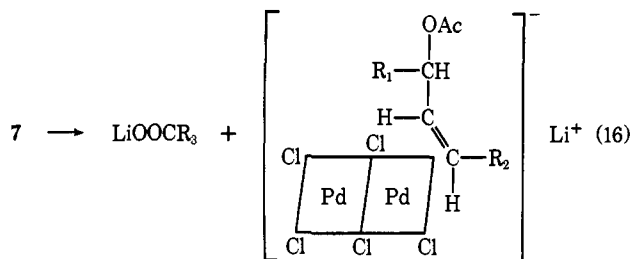
esters would be expected to have similar rates for eq 14, 15, and 16 and the similarity in exchange rate constants in Table 1 indicates that they do. However, the trifluoroacetate esters exchange appreciably faster than the other two esters. As discussed previously,[2] this result most likely reflects the activation of the olefin by electron-withdrawing groups for nucleophilic attack.

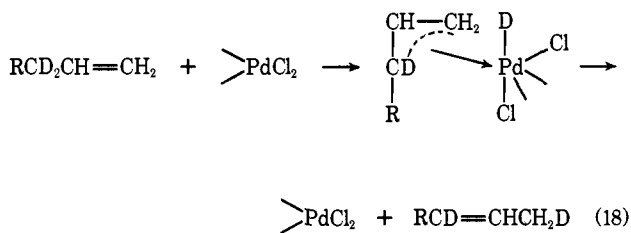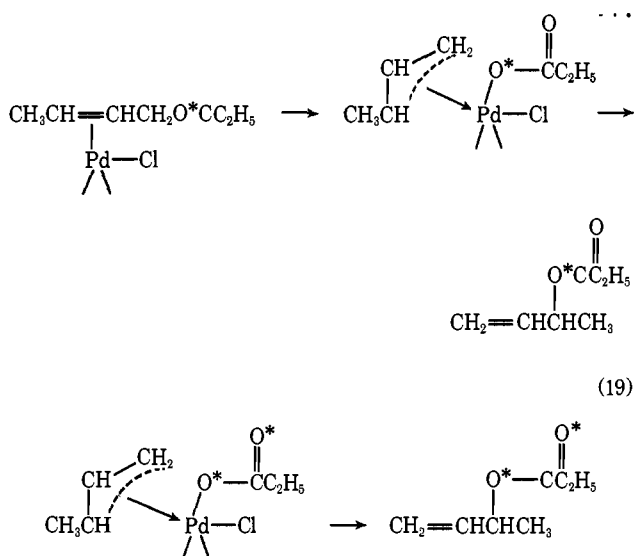The second reaction is isomerization without exchange. This reaction was unexpected and has no clear analogy to other Pd(II)-catalyzed reactions. Formally, it has similarity to the 1,3-deuterium shift found for Pd(II)-catalyzed isomerization of olefins (eq 17).[12]

$$\text{RCD}_2\text{CH}=\text{CH}_2 \xrightarrow{\text{Pd(II)}} \text{RCD}=\text{CHCH}_2\text{D} \quad (17)$$

This shift has been postulated to proceed via a π-allyl palladium(IV) hydride (eq 18). However, the ^{18}O

$$\text{RCD}_2\text{CH}=\text{CH}_2 + \text{>PdCl}_2 \longrightarrow \begin{array}{c} \text{CH}-\text{CH}_2 \quad D \\ | \quad \diagup \quad | \\ \text{CD} \quad \text{Pd} \diagdown \text{Cl} \\ | \quad \diagup \diagdown \\ R \quad Cl \end{array} \longrightarrow$$

$$\text{>PdCl}_2 + \text{RCD}=\text{CHCH}_2\text{D} \quad (18)$$

experiments rule out similar mechanisms for the ester isomerization. If ester ^{18}O-labeled crotyl propionate is isomerized via a π-allyl Pd(II) acetate formed by breaking the C–O ester bond, as shown in eq 19, there
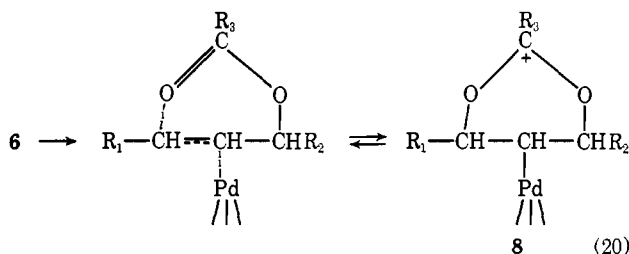
$$\text{CH}_3\text{CH}=\text{CHCH}_2\text{O}^*\text{CC}_2\text{H}_5 \longrightarrow \begin{array}{c} \text{CH}-\text{CH}_2 \quad O \\ | \quad \diagup \quad \| \\ \text{CH}_3\text{CH} \quad O^*-\text{CC}_2\text{H}_5 \\ \diagup \quad \text{Pd}-\text{Cl} \\ \diagup \diagdown \end{array} \longrightarrow$$

$$\begin{array}{c} O \\ \| \\ O^*\text{CC}_2\text{H}_5 \\ | \\ \text{CH}_2=\text{CHCHCH}_3 \end{array}$$

(19)

$$\begin{array}{c} \text{CH}-\text{CH}_2 \quad O^* \\ | \quad \diagup \quad \| \\ \text{CH}_3\text{CH} \quad O^*-\text{CC}_2\text{H}_5 \\ \diagup \quad \text{Pd}-\text{Cl} \\ \diagup \diagdown \end{array} \longrightarrow \begin{array}{c} O^* \\ \| \\ O^*-\text{CC}_2\text{H}_5 \\ | \\ \text{CH}_2=\text{CHCHCH}_3 \end{array}$$

are two limiting possibilities for the ^{18}O distribution. First, if there is no ^{18}O scrambling in the π-allyl intermediate, the principle of microscopic reversibility requires that all the ^{18}O remain in the ester oxygen. On
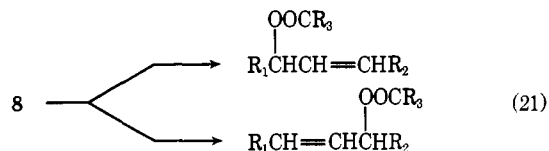
(12) A. J. Chalk and J. F. Harrod, J. Amer. Chem. Soc., **88**, 3491 (1966).

the other hand, if there is complete scrambling, the ^{18}O will be equally divided between ester and carbonyl oxygen. Neither limiting case nor degree between the two extremes is consistent with the experimental results. Of course, other less likely modes of ^{18}O scrambling are possible for the π-allyl mechanism but none are consistent with the experimental results.
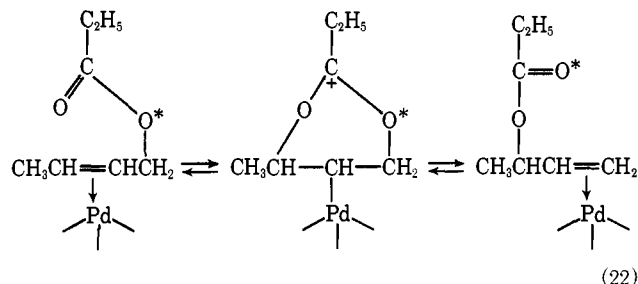
A mechanism consistent with the kinetic scheme, ^{18}O-labeling experiment and results with the trifluoroacetate esters, involves neighboring carboxylate participation. The first step would be the same as for exchange, reversible formation of a π complex (eq 14). However, rather than attack by LiOAc, the next step would be internal attack of the carbonyl group of the ester. The kinetics suggest that this attack also occurs from outside the coordination sphere of the Pd(II) (eq 20).

$$6 \longrightarrow \begin{array}{c} R_3 \\ | \\ C \\ \diagup \quad \diagdown \\ O \quad\quad O \\ | \quad\quad | \\ R_1-\text{CH}\cdots\text{CH}-\text{CHR}_2 \\ | \\ Pd \\ /|\backslash \end{array} \rightleftharpoons \begin{array}{c} R_3 \\ | \\ C^+ \\ \diagup \quad \diagdown \\ O \quad\quad O \\ | \quad\quad | \\ R_1-\text{CH}-\text{CH}-\text{CHR}_2 \\ | \\ Pd \\ /|\backslash \end{array}$$

8   (20)

The intermediate **8** can then reverse itself to give back the starting allylic ester or the isomerized allylic ester (eq 21). The ^{18}O-labeling result is consistent with this
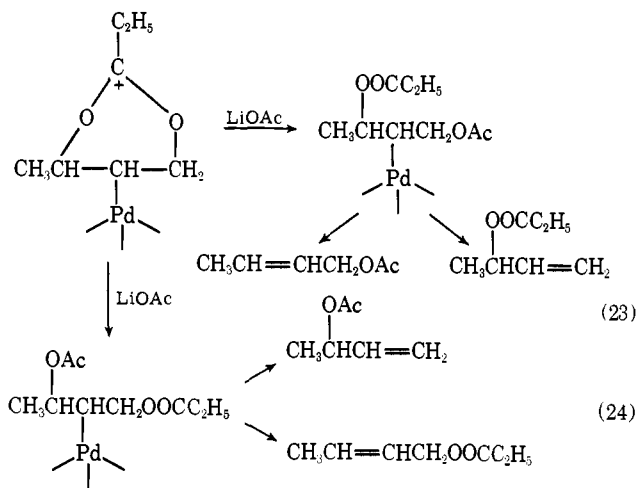
$$\mathbf{8} \longrightarrow \begin{cases} \begin{array}{c} \text{OOCR}_3 \\ | \\ R_1\text{CHCH}=\text{CHR}_2 \end{array} \\ \begin{array}{c} \text{OOCR}_3 \\ | \\ R_1\text{CH}=\text{CHCHR}_2 \end{array} \end{cases} \quad (21)$$

mechanism as shown in eq 22.

$$\begin{array}{c} C_2H_5 \\ | \\ C \\ \diagup \quad \diagdown \\ O \quad\quad O^* \\ \diagdown \quad \diagup \\ \text{CH}_3\text{CH}=\text{CHCH}_2 \\ \downarrow \\ \diagup\text{Pd}\diagdown \\ | \end{array} \rightleftharpoons \begin{array}{c} C_2H_5 \\ | \\ C^+ \\ \diagup \quad \diagdown \\ O \quad\quad O^* \\ \diagdown \quad \diagup \\ \text{CH}_3\text{CH}-\text{CH}-\text{CH}_2 \\ | \\ \diagup\text{Pd}\diagdown \\ | \end{array} \rightleftharpoons \begin{array}{c} C_2H_5 \\ | \\ C=O^* \\ | \\ O \\ | \\ \text{CH}_3\text{CHCH}=\text{CH}_2 \\ \downarrow \\ \diagup\text{Pd}\diagdown \\ | \end{array}$$
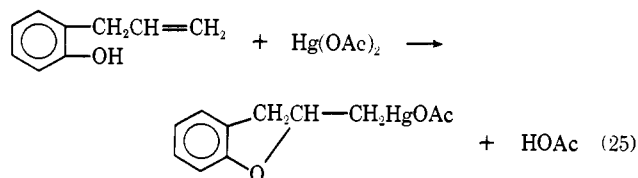
(22)

The 500-fold rate decrease when R_3 is changed from $-C_2H_5$ to $-CF_3$ is also consistent with this mechanism since electron-withdrawing groups would destabilize **8**. If ester carbon–oxygen bond cleavage to give an allylic carbonium ion–carboxylate anion type of intermediate were occurring, the opposite result would be expected.[13]

The decrease in k_{14} and k_{41} with increasing [LiOAc] (eq 10) is also understandable on the basis of this mechanism. Thus, the intermediate **8** would be susceptible to attack by acetate. All four products would result from each allylic ester as shown in eq 23 and 24. The net result in the case of the propionate esters would be to lower k_{14} and k_{41} and give k_{12} and k_{43} finite values. Unfortunately the kinetics were not sensitive enough to detect the changes in k_{13}, k_{42}, k_{12}, and k_{13}.

(13) E. S. Lewis, J. T. Hall, and E. R. Newman, ibid., **90**, 662 (1968).

C₂H₅
|
C
/+\
O   O
| |
CH₃CH—CH—CH₂   —LiOAc→   OOCC₂H₅
| |
Pd   CH₃CHCHCH₂OAc
/ | \ |
                                  Pd
                                 / | \
|LiOAc
↓   ↙   ↘
                CH₃CH=CHCH₂OAc   CH₃CHCH=CH₂
OAc   OOCC₂H₅
|
CH₃CHCHCH₂OOCC₂H₅
/ | \
Pd   OAc   (23)
                      |
                      CH₃CHCH=CH₂
                     ↗

OAc
|
CH₃CHCHCH₂OOCC₂H₅
|
Pd   (24)
/ | \
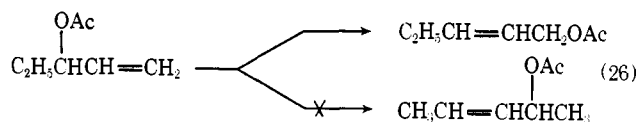   ↘ CH₃CH=CHCH₂OOCC₂H₅

The intermediate **8** is very similar to the 1,3-acet-oxonium ion proposed previously as intermediates in solvolysis reactions.[14-17] However, there is, to our knowledge, no previous report of their being formed by a metal ion addition to an olefin. A related reaction is the very facile hydroxymercuration[18-20] and hydroxy-thallation[21] reactions which occur with olefins containing hydroxy groups to give cyclic ether structures. An example is *o*-allylphenol.[18,19]

[benzene ring]—CH₂CH=CH₂
              —OH   + Hg(OAc)₂ ⟶

[benzene ring with O]—CH₂CH—CH₂HgOAc   + HOAc   (25)

This new example of neighboring group participation in metal ion reactions is likely to be a very general reaction, occurring with other metal ions than Pd(II) and with other neighboring groups than acetate.

The isomerization of 1-penten-3-ol acetate was run because isomerization of similar structure by Pd(OAc)₂ was reported[6] to give products such as 3-penten-2ol acetate which would result from other than simple allylic isomerization. This type of isomerization would be difficult to explain on the basis of the present mechanism. Under our reaction conditions, 3-penten-1-ol acetate was formed by isomerization of 1-penten-3-ol acetate but no 3-penten-2-ol acetate was found.

OAc
|
C₂H₅CHCH=CH₂ ⟨   ⟶ C₂H₅CH=CHCH₂OAc
                                    OAc   (26)
                                    |
              ✗⟶ CH₃CH=CHCHCH₃

The effect of methyl substitution on rate of exchange, demonstrated by the results for the last two allylic esters in Table I, is in agreement with that previously found for exchange of symmetrical esters. In the pres-

(14) L. J. Dolby and M. J. Schwartz, *J. Org. Chem.*, **30**, 358 (1965).
(15) O. Kovacs, G. Schneider, and L. K. Lang, *Proc. Chem. Soc.*, 374 (1963).
(16) L. J. Dolby, C. N. Lieske, D. R. Rosencrantz, and M. J. Schwartz, *J. Amer. Chem. Soc.*, **85**, 47 (1963).
(17) R. J. Ouellette and R. D. Robins, *Tetrahedron Lett.*, 397 (1968).
(18) R. Adams, F. L. Roman, and W. N. Sperry, *J. Amer. Chem. Soc.*, **44**, 1781 (1922).
(19) L. E. Mills and R. Adams, *ibid.*, **45**, 1842 (1923).
(20) J. Halpern and H. B. Tinker, *ibid.*, **89**, 6427 (1967).
(21) H. J. Kabbe, *Justus Liebigs Ann. Chem.*, **656**, 204 (1962).

ent study the rate of isomerization without exchange can also be measured for the unsymmetrical esters. The effect of methyl substitution on the latter reaction is within a factor of 2 of that found for exchange. This result is not surprising since both most likely involve the trans attack of acetate on the π complex.

Experimental Section

Materials. Sources of most chemicals and preparation of stock solutions have been described previously.[2,4] Allylic esters were prepared by reaction of alcohols with corresponding anhydride using pyridine as catalyst. The alcohols were treated with tri-fluoroacetic anhydride without catalyst. After about 15 min, they were diluted with methylene chloride followed by washing with water to remove the acid formed. Esters were then isolated by distillation. If this procedure was not followed, the acid isomerized them to a mixture of crotyl and 3-buten-2-ol trifluoroacetates. The boiling point of the crotyl ester was 106–107° and that of the 3-buten-2-ol ester was 88–89°.

Kinetic Runs. The runs were made on either a 1.0- or 5-ml scale. Usually 5 ml of reaction mixture was prepared by adding measured amounts of LiPdCl₃, LiCl, and LiOAc stock solutions followed by diluting to 5 ml with dry HOAc. Portions (1 ml) were used for runs with crotyl ester and with 3-buten-2-ol ester. Another 1-ml portion was used for a run with either crotyl or 3-buten-2-ol acetate to obtain k_{23} and k_{32} necessary for the calculation of the other rate constants. The runs were thermostated in a 25° bath for about 1 hr before being started by adding the desired amount of ester. Usually runs were made at 0.2 M ester but in some runs the concentration was varied to determine order in ester. Samples (usually 0.01 ml) were removed periodically and analyzed by vapor-phase chromatography using a 6 ft, 20% Carbowax 20M on ABS (70–80 mesh) programmed from 80 to 200° at 7.5°/min. Flow rate was 60 ml/min. The relative responses of the various allylic esters were determined by use of standards. Concentrations of all materials could then be determined since the total concentration of allylic ester was known.

From initial changes in product distribution, estimates of the various rate constants could be made. They were refined by use of a computer program which reproduced product distributions with time for a given set of rate constants.[22] Of course, the same set of rate constants had to reproduce the product distribution under a given set of conditions for runs started with either crotyl ester or 3-buten-2-ol ester. By running at low LiOAc, the position of equilibrium was found to be ca. 60% crotyl ester. The per cent crotyl acetate is reported[23] to be 62%. Thus the ratios of k_{14}/k_{41} and k_{23}/k_{32} are known. This eliminates one unknown. The crotyl and 3-buten-2-ol trifluoroacetates at equilibrium could not be obtained in acetic acid because of the slow rates of isomerization, but the mixtures were assumed to contain about 60% of the crotyl isomer.

The LiOAc inhibition equation is derived as follows. The π complex **6** (eq 15) reacts to form **8** (eq 20) which can either reverse itself to **6**, isomerize to the other ester (A), or react with acetate to form other products (call these products B).

$$6 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 8 \overset{k_2}{\underset{k_3}{\diagup\diagdown}} \begin{matrix} A \\ B \end{matrix} \qquad (27)$$
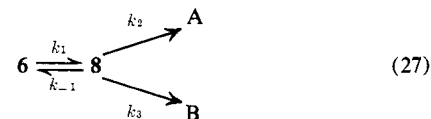
Under one set of reaction conditions [LiOAc] is a constant, and thus k_3 is a pseudo-first-order rate constant equal to k_3'[LiOAc]. Thus we have

$$d[8]/dt = k_1[6] - [k_{-1} + k_2 + k_3][8] \qquad (28)$$

and using the steady-state approximation

$$d[8]/dt = 0 = k_1[6] - [k_{-1} + k_2 + k_3][8] \qquad (29)$$

and

$$8 = k_1[6]/[k_{-1} + k_2 + k_3] \qquad (30)$$

(22) This program was written by Dr. W. B. Nichols of the Chemical Engineering Division, Hercules Research Center.
(23) Z. Rappoport, P. D. Sleezer, S. Winstein, and W. G. Young, *Tetrahedron Lett.*, No. 42, 3719 (1965).

$$\mathrm{d}[A]/\mathrm{d}t = k_2[8] - k_1 k_2[6]/(k_{-1} + k_2 + k_3) \quad (31)$$

If $k_3 = 0$

$$\mathrm{d}[A]/\mathrm{d}t = k_1 k_2[6]/(k_{-1} + k_2) \quad (32)$$

Dividing eq 31 by $k_{-1} + k_2$ and setting $k_3 = k_3'[\mathrm{LiOAc}]$, we have

$$\frac{\mathrm{d}[A]}{\mathrm{d}t} = \frac{\dfrac{k_1 k_2}{k_{-1} + k_2}[6]}{\left(1 + \dfrac{k'_3[\mathrm{LiOAc}]}{k_{-1} + k_2}\right)} = k_{\mathrm{obsd}}[6] \quad (33)$$

which is of the same form as eq 6.

Labeling Experiments. ^{18}O-Labeled crotonaldehyde was prepared by equilibration. Freshly distilled crotonaldehyde (5 ml) was stirred for 3 days with 1.15 ml of H_2O containing 9% ^{18}O and a trace of p-toluenesulfonic acid. The mixture was diluted with ether and the water removed by magnesium sulfate. The crotonaldehyde was isolated by distillation and analyzed for ^{18}O content by mass spectral analysis. The ^{18}O content was 2.93%. The crotonaldehyde was reduced to the alcohol by $NaBH_4$ in aqueous NaOH. The alcohol was esterified with propionic anhydride and the ester isolated and analyzed by mass spectral analysis. The most accurate analysis of ^{18}O content of the crotyl propionate was the carbonyl oxygen using the CH_3CHCO^+ fragment (m/e 57).[24] The

(24) There is little doubt that m/e 57 represents this fragment. No other simple fragmentation pattern will give this peak and the corresponding fragment is found in the spectra of all esters. See, for instance, R. M. Silverstein and G. C. Bossler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1963, p 14.

analysis of the ^{18}O content of the ester oxygen is somewhat less accurate. The carbonyl oxygen of the crotyl propionate contained 0.65% ^{18}O and the ester oxygen 2.1 ± 0.2%. Thus, some scrambling occurred on esterification.

The isomerization run was carried out on a 5-ml scale. It was started by adding 0.2 ml of the labeled crotyl propionate. At various times samples (2 ml for first sample, 1 ml for remaining samples) were withdrawn; 0.01 ml was analyzed by vpc and the remainder diluted with methylene chloride and the acetic acid, and inorganic salts were removed by washing with water. The organic phase was concentrated and the entire sample injected on vpc. The crotyl propionate and 3-buten-2-ol propionate were collected from the vpc eluent in capillary tubes which were analyzed by mass spectral analysis. For the 3-buten-2-ol propionate the most accurate analysis was also the carbonyl oxygen so this is the analysis given in Table IV.

Positional Dependence of Substituent Effects on Long-Range Couplings in Propane Derivatives[1]

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Abstract: The effect of substituents on $^4J_{HH}$ in propane and neopentane derivatives depends on the point of attachment of the substituent to the atom chain linking the coupled nuclei, suggesting that orbitals of different symmetry types are being perturbed. The results are discussed in light of recent theoretical treatments, and it is suggested that long-range coupling constants are sensitive probes into interaction between substituents and electronic systems.

Recent studies[2-4] of substituent effects on $^4J_{\mathrm{Me,Me}}$ in molecules of the types **1a** and **2a** indicated that

1a, R = CH₃   2a, R = CH₃
 b, R = H   b, R = H
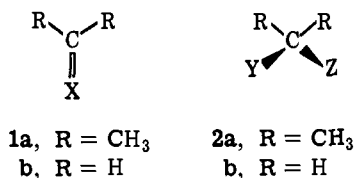
the behavior of $^4J_{\mathrm{Me,Me}}$ parallels that of $^2J_{HH}$ in the series **1b** and **2b** and that the observed trends can be rationalized in terms of a simple, qualitative molecular orbital model proposed independently by us[3] and Barfield and Chakrabarti.[5] According to this model, removal of electrons *via* a σ acceptor or back-donation

(1) Presented at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972.
(2) D. J. Sardella, *Chem. Commun.*, 1613 (1968).
(3) D. J. Sardella, *J. Mol. Spectrosc.*, **31**, 70 (1969).
(4) E. R. Curry and D. J. Sardella, *Proc. Int. Congr. Pure Appl. Chem.*, **23**, 342 (1971).
(5) M. Barfield and B. Chakrabarti, *Chem. Rev.*, **69**, 757 (1969).

of electrons by a suitably oriented π type orbital will cause an algebraic increase in $^4J_{HH}$, whereas electron withdrawal *via* a π orbital will cause $^4J_{HH}$ to decrease. Substituent effects on coupling constants therefore appear to be sensitive probes into electronic effects of substituents.

This paper presents data which indicate the effect of a substituent to depend, not only on whether it releases or withdraws electrons, but also on its point of attachment to the atom chain linking the coupled protons. The trends exhibited by our data agree with the predictions of the crude, qualitative model[3,5] and, with one exception, with the results of recent INDO calculations.[6] Support for our interpretation also stems from an empirical parallelism between two-bond and four-bond couplings which we have observed.[2-4]

Results

Our attention was first attracted by the observation that the methyl–methylene couplings in neopentyl

(6) M. Barfield, *J. Amer. Chem. Soc.*, **93**, 1066 (1971).