Homogeneous Catalysis. III. Isomerization of Deuterio Olefins by Group VIII Metal Complexes

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Abstract: Vinyl- and allyl-deuterated 1-olefins were isomerized by homogeneous metal-complex catalysts, both alone and in the presence of unlabeled olefin. Movement of deuterium in the pure deuterio olefins, and between deuterio olefin and unlabeled olefin, was followed as the isomerization proceeded. Isomerization of deuterio olefins by rhodium trichloride was found to be accompanied by a redistribution of deuterium onto all of the carbon atoms of the allylic system. Also, with this catalyst a facile intermolecular exchange of deuterium was demonstrated, the exchanging deuterium appearing on all of the carbon atoms of the allylic system of the initially unlabeled olefin. These results are rationalized in terms of a reaction mechanism involving a rapid, reversible addition of hydride to coordinated olefin. Results obtained with a bis(benzonitrile)dichloropalladium catalyst differed significantly from those obtained with the rhodium catalyst. In the palladium-catalyzed reaction the double-bond shift seemed to occur by a shift of deuterium, or hydrogen, from C_3 to C_1. Although intermolecular deuterium exchange occurred, the extent was only about half that observed with the other catalyst, and very little of the exchanging deuterium became attached to doubly bonded carbon atoms. A modified π-allyl mechanism is proposed to explain these results.

In the first part of this series[1] we described some qualitative observations on the isomerization of 1-olefins by a variety of metal complexes. Both before and since[2-7] the publication of part I of this series, the accumulation of such qualitative information has been considerable, but no mechanism has yet been proposed for these reactions that may be unequivocally substantiated by the available experimental evidence.

The migration of a double bond in an olefin involves the net movement of a hydrogen atom, or hydrogen atoms, from one carbon atom to another. However, the various plausible mechanistic routes available for such a net movement of hydrogen predict quite different relocations of hydrogen atoms, either within an olefin molecule, or between olefin molecules. In order to trace the fate of specific hydrogen atoms during metal ion catalyzed olefin isomerization, we have made studies on the isomerization of olefins substituted with deuterium at specific points in the molecule. The present paper describes the results of these experiments and their application to interpreting the mechanism of the catalyzed isomerization of olefins.

Experimental Section

Preparation of Deuterio Olefins. (i) **1-Pentene-1,2-d_2.** 1-Pentene was deuterated using the hydrogenation catalyst described by Lindlar.[8] After the theoretical amount of deuterium had been consumed the reaction vessel was attached to a vacuum transfer line; the product was distilled through a column of activated alumina and condensed in liquid nitrogen. This technique allowed the separation of quite small quantities of deuterio olefin from the quinoline solvent, an important factor since a minute quantity of quinoline is an effective inhibitor of the isomerization reactions under investigation.

The deuteriopentene produced in this reaction was found to contain more than two deuterium atoms per molecule by H/D mass spectroscopic analysis. Analysis by nmr showed the surplus deuterium to be present at the terminal vinyl methylene group, usually to the extent of 0.2 to 0.3 atom of deuterium. No other exchange occurs during this hydrogenation. The lack of exchange at the allylic methylene, a critical factor in the interpretation of the isomerization results, was established in the preparation of 1-heptene-3-d_2.

(ii) **1-Heptene-3-d_2.** This olefin was prepared in a four-step synthesis, each step giving a yield in excess of 90%. The steps were as follows.

$$C_4H_9COOCH_3 \xrightarrow{LiAlD_4} C_4H_9CD_2OH \qquad (i)$$

$$C_4H_9CD_2OH + TsCl \xrightarrow{pyridine} C_4H_9CD_2OTs \qquad (ii)$$

$$C_4H_9CD_2OTs + enLiC{\equiv}CH \xrightarrow{(CH_3)_2SO} C_4H_9CD_2C{\equiv}CH^{9} \qquad (iii)$$

$$C_4H_9CD_2C{\equiv}CH + H_2 \longrightarrow C_4H_9CD_2CH{=}CH_2 \qquad (iv)$$

en = ethylenediamine, Ts = *p*-toluenesulfonyl

The final hydrogenation was carried out by the same technique as described above for the deuteration of 1-pentyne. The olefin product was found to contain less than 0.10% (based on total protons) of protons in the allylic methylene position, thus confirming that negligible exchange occurs at this position during the hydrogenation, or during the preceding synthetic steps.[10] The remaining protons were also found to be present in the correct stoichiometry.

Isomerization Reactions. A typical procedure in the case of the rhodium trichloride catalyzed reactions was to place a sample of olefin (0.5 ml) in a standard nmr sample tube and run a high-resolution spectrum with a Varian HR-60 spectrometer. The rhodium trichloride was then added as an isopropyl alcohol solution (5 μl, 0.1 *M*), and with the spectrometer tuned for low resolution, spectra were scanned at suitable time intervals. The lower resolution was used to facilitate planimetric integration of the spectra.

In practice it was found that the vinyl and allylic methylene protons could be consistently measured to within *ca.* 0.02 proton of the true value for the pure starting materials. However, after the onset of isomerization the broadening of the spectrum, resulting from the new species, led to a progressive deterioration in resolution so that after about 80% reaction the estimated error in the measured values of vinyl and allylic methylene protons was *ca.* ±0.05 and ±0.1 proton, respectively.

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[3] D. W. Aubrey, A. Barnatt, and W. Gerrard, *Polymer Letters*, **3**, 357 (1965).

[4] G. C. Bond and M. Hellier, *J. Catalysis*, **4**, 1 (1965).

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[6] G. C. Bond and M. Hellier, *Chem. Ind.* (London), 35 (1965).

[7] R. E. Rinehart and J. S. Lasky, *J. Am. Chem. Soc.*, **86**, 2516 (1964).

[8] H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

[9] R. E. A. Dear and F. L. M. Pattison, *J. Am. Chem. Soc.*, **85**, 622 (1963).

[10] A similar conclusion was deduced for the gas phase deuteration of 1-butyne by E. F. Meyer and R. L. Burwell, *ibid.*, **85**, 2881 (1963).

Table I. Isomerization of $CH_3CH_2CH_2CD{=}CD_{1.2}H_{0.8}$ by $RhCl_3 \cdot 3H_2O$[a]

t,	Number of protons per average molecule					
min	H(a)	H(b)	H(c)	H(d)	H(e)	H(total)
0	3.02 ± 0.1	2.00 ± 0.1	2.00 ± 0.1	0.00 ± 0.05	0.80 ± 0.05	7.82
5	2.95	1.90	1.89	0.56	0.50	7.80
7	2.98	1.82	1.87	0.70	0.42	7.79
12	3.09	1.85	1.82	0.91	0.19	7.86
16	3.01	1.80	1.87	1.03	0.17	7.88
25	3.00	1.78	1.85	1.14	0.12	7.89

[a] [Rh] = 0.005 *M*, 38°.

Table II. Isomerization of $CH_3CH_2CH_2CD{=}CD_{1.15}H_{0.85}$ by $(C_6H_5CN)_2PdCl_2$[a]

t,	Number of protons per average molecule					
min	H(a)	H(b)	H(c)	H(d)	H(e)	H(total)
0	3.00 ± 0.1	2.00 ± 0.1	2.0 ± 0.1	0 ± 0.05	0.85 ± 0.05	7.85
5	3.00	2.06	1.84	0.27	0.64	7.81
10	2.80	2.14	1.80	0.58	0.52	7.84
15	2.60	2.21	1.75	0.86	0.38	7.80
25	2.46	2.42	1.43	1.38	0.11	7.80

[a] [Pd] = 0.005 *M*, 55°. Nomenclature as for Table I.

Table III. Isomerization of $C_4H_9CD_2CH{=}CH_2$ by $RhCl_3 \cdot 3H_2O$[a]

t,	Number of protons per average molecule				
min	H(f)	H(g)	H(i)	H(j)	H(total)
0	8.97 ± 0.1	0.00 ± 0.1	1.02 ± 0.05	2.06 ± 0.05	12.05
32	9.20	0.49	0.86	1.56	12.11
65	9.30	0.75	0.74	1.19	11.98
81	9.50	0.92	0.65	0.90	11.97
180	9.50	1.65	0.53	0.29	11.97

[a] [Rh] = 0.001 *M*, 38°.

A slight modification of the above technique was used in the case of bis(benzonitrile)dichloropalladium(II)-catalyzed reactions. The palladium catalyst was first dissolved in perdeuteriobenzene (0.5 ml.), and this solution was then added to the olefin (0.5 ml) in an nmr sample tube. After the first spectrum had been recorded the sample was removed from the spectrometer and placed in a constant temperature bath at 55°. The sample was periodically replaced in the spectrometer for recording the spectrum. The latter procedure was necessary since the rate of the palladium-catalyzed reaction was very slow at the spectrometer cavity temperature (38°), in the range of catalyst concentration (0.01 to 0.001 *M*) of interest.

Exchange Reactions. In the exchange reactions, the reaction mixtures were the same as described in the previous section except that instead of 0.5 ml of olefin, a mixture of 1-pentene (0.5 ml) and 1-heptene-3-d_2 (0.5 ml) was used and the palladium was run in ordinary benzene. After completion of the reaction the mixed olefins were fractionated chromatographically into pentenes and heptenes on a 20-in. β,β'-oxydipropionitrile column. Infrared spectra were measured on a Perkin-Elmer Model 337 grating spectrometer. Deuterium analyses were performed mass spectrometrically by J. Nemeth, University of Illinois, Urbana, Ill.

Materials. All olefins were Phillips Research Grade and were always passed over activated alumina before use. The latter was important because of severe peroxide inhibition of rhodium-catalyzed isomerizations.

Lithium acetylide–ethylenediamine was a product of Foote Mineral Co.

Rhodium trichloride was the commercial trihydrate. Solutions were analyzed by reduction with hydrogen and weighing the precipitated metal. The benzonitrile–palladium complex was the same as used previously.[1]

Results

Isomerization of Vinyl-Deuterated Pentene. The results of an isomerization of 1-pentene-1-$d_{1.2}$,2d_1 by $RhCl_3 \cdot 3H_2O$ are shown in Table I. The results show the changes in the numbers of various protons as the double bond moves from the terminal to the internal position. The protons, as measured by nmr, are labeled as follows: aliphatic CH_3, H(a); aliphatic CH_2 + allylic CH_3, H(b); allylic CH_2, H(c); nonterminal vinyl, H(d); terminal vinyl, H(e). The numbers for specific protons are an average value for the various components of the isomerizing mixture.

The results of a similar experiment, using a $(C_6H_5CN)_2PdCl_2$ catalyst, are listed in Table II. These data were derived from spectra such as those shown in Figure 1. The change in 1-pentene concentration, calculated on the assumption that it is proportional to the number of terminal vinyl protons, is compared to the concentration calculated from infrared measurements of the terminal $>C{=}C<$ stretching absorption in Figure 2. The two measurements correspond reasonably well up to about 70% reaction, but beyond this there is a significant deviation between the two sets of measurements. In the case of the palladium-catalyzed reaction no deviation between the two types of measurements was observed.

Isomerization of Allyl-Deuterated 5-Heptene. The results of some isomerizations of 1-heptene-3-d_2 by rhodium and palladium catalysts are shown in Tables III and IV. The protons are labeled thus: aliphatic and allylic CH_3 and aliphatic CH_2, H(f); allylic CH_2, H(g); nonterminal vinyl, H(i); terminal vinyl, H(j).

A comparison between 1-heptene concentrations calculated from nmr and from infrared data is shown in Figure 3 for the rhodium-catalyzed reaction. Again there appears to be a deviation at high conversion, but in the opposite direction from that observed with the pentene isomerization. Similar measurements on the palladium-catalyzed reaction showed no deviation.

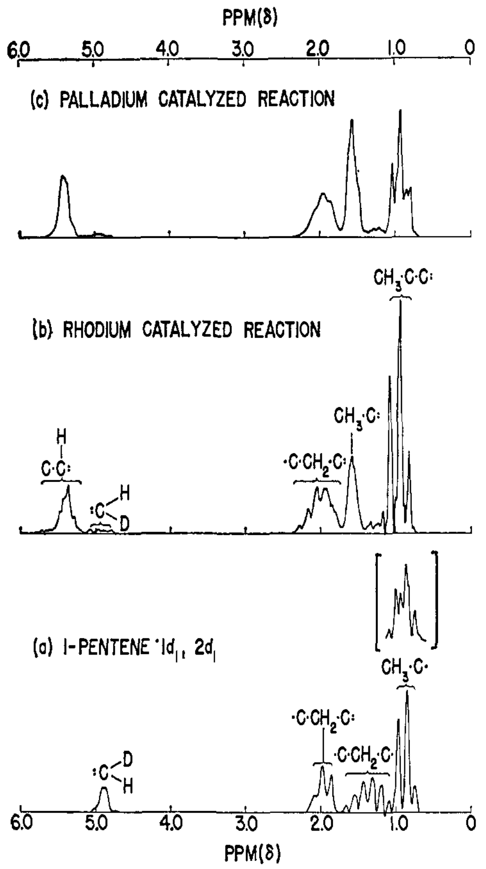


Figure 1. Nmr spectra of deuterated pentenes: (a) 1-pentene-1-$d_{1,2}$,2-d_1 (inset: methyl resonance of rhodium-catalyzed pentenes at *ca.* 50% reaction); (b) pentene-$d_{2,2}$, after *ca.* 80% reaction, catalyzed by $RhCl_3 \cdot 3H_2O$; (c) pentene-$d_{2,2}$, after *ca.* 80% reaction, catalyzed by $(C_6H_5CN)_2PdCl_2$.

Table IV. Isomerization of $C_4H_9CD_2CH{=}CH_2$ by $(C_6H_5CN)_2Pd^a$

t, min	Number of protons per average molecule H(f)	H(g)	H(i)	H(j)	H(total)
0	9.00	0	0.9	2.04	11.94
14	8.70	0.67	1.14	1.39	11.90
28	8.72	1.20	1.11	0.95	11.98
48	8.60	1.92	1.05	0.32	11.89

[a] [Pd] = 0.001 *M*, 55°.

Exchange between Labeled and Unlabeled Olefins. Two experiments were performed in which a mixture of equal volumes of 1-pentene and 1-heptene-3-d_2 was isomerized in the presence of (i) $RhCl_3 \cdot 3H_2O$ and (ii) $(C_6H_5CN)_2PdCl_2$. The isomerizations were allowed to proceed until about 90% of the 1-olefin had been consumed and then the pentenes and heptenes were separated chromatographically. Examination of the pentenes by infrared spectroscopy showed that they had acquired considerable amounts of deuterium, in both the rhodium- and palladium-catalyzed reactions.

A more careful examination of the infrared spectra revealed significant differences between the products of the rhodium- and the palladium-catalyzed reactions. The spectra of these products are shown in Figure 4. It is quite clear from these spectra that there is significantly less deuterium in the pentene product of the palladium-catalyzed reaction and also that the distribution of deuterium is quite different in the products of the two reactions. In the case of the rhodium-catalyzed reaction, both the C_5 and C_7 fractions have bands at 2150 (methyl ?), 2210 (vinyl), and 2230 cm^{-1} (sh) (vinyl). In the product of the palladium-catalyzed reaction, the C_7 fraction shows a definite strong band at 2200 cm^{-1} attributable to vinyl deuterium, but the C_5 fraction shows very little, if any, vinyl deuterium. The principal bands of the C_5 and C_7 fractions (2160 and 2140 cm^{-1}, respectively) may be due to aliphatic, or allylic, methyl, or methylene deuterium. An attempt

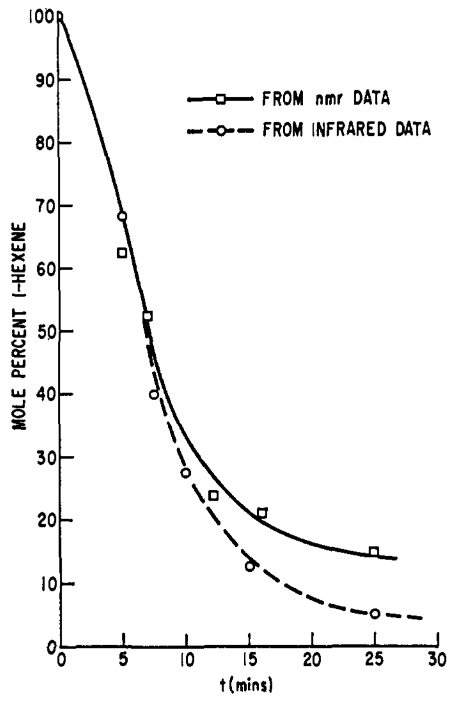


Figure 2. Comparison between nmr and infrared determination of 1-pentene-$d_{2,2}$ concentration ($RhCl_3 \cdot 3H_2O$ catalyst).

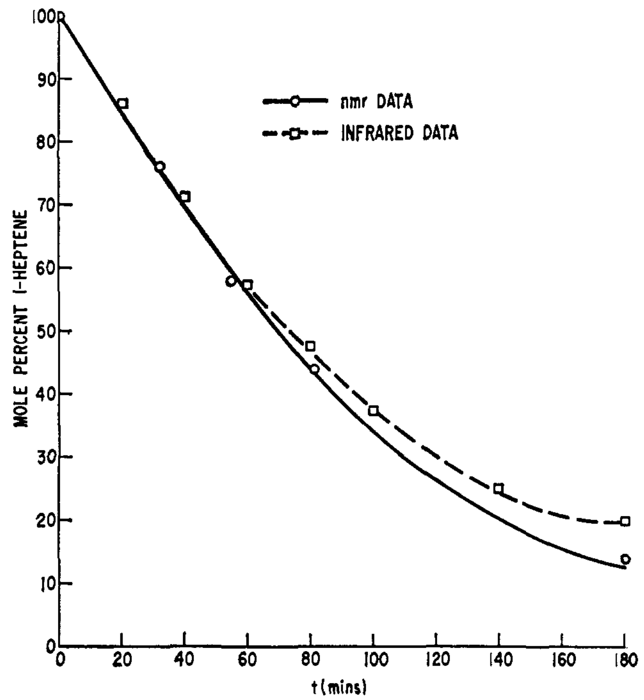


Figure 3. Comparison between nmr and infrared determination of 1-heptene-d_2 concentration ($RhCl_3 \cdot 3H_2O$ catalyst).

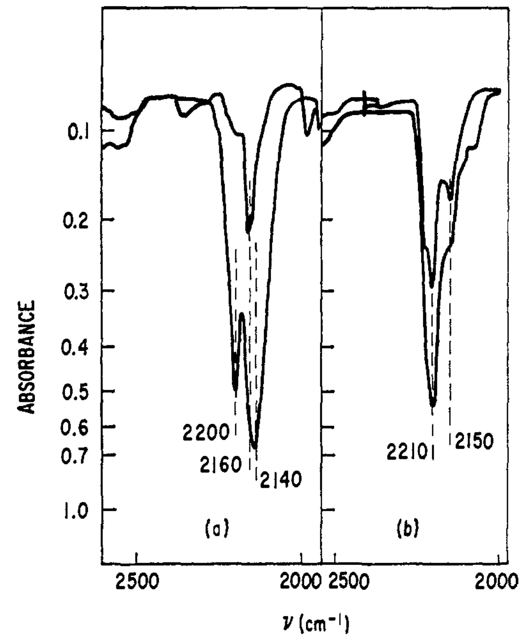


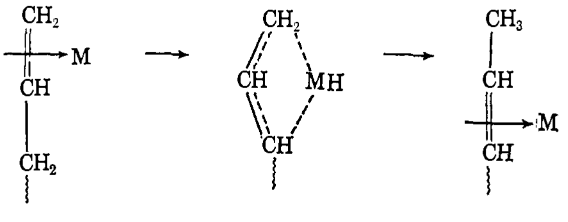
Figure 4. Infrared spectra of isomerized C_5 and C_7 olefins in the C–D stretching region: (a) palladium catalyzed, (b) rhodium catalyzed (upper spectra C_5, lower C_7).

to locate the deuterium on the C_5 fraction by nmr proton counts was inconclusive.

Mass spectrometric analysis showed the C_5 fractions to have the compositions $C_5H_{9.47}D_{0.53}$ (rhodium catalyzed) and $C_5H_{9.75}D_{0.25}$ (palladium catalyzed). The C_7 fractions were found to be, $C_7H_{12.6}D_{1.40}$ (rhodium catalyzed) and $C_7H_{12.2}D_{1.8}$.

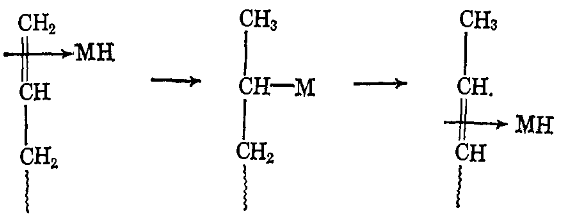
Discussion

Two plausible types of mechanism have been previously discussed in attempts to explain the metal ion catalyzed isomerization of olefins. The essential difference between these two mechanisms is that one invokes a catalytic intermediate in which the olefinic residue has assumed a π-allylic character,[2,7] and the other an intermediate in which the olefin has assumed the character of an alkyl group.[1] The essence of these two mechanisms may be represented schematically thus



(1)

π-allyl mechanism



(2)

The possible origin of the initiating hydride has been discussed previously.[1]

The Rhodium-Catalyzed Reaction. In a previous publication[11] we described some preliminary results obtained with vinyl-deuterated hexene. The present, more detailed study indicates that two of the observations made earlier were in fact misleading. In the first place, we have now established that the origin of the large difference in rate between deuterated and nondeuterated hexenes was largely due to inhibiting impurities in the nondeuterated hexene. Immediate use of the same olefins after vacuum distillation through an alumina column resulted in very similar rates of reaction for both deuterated and nondeuterated hexenes. Also, competititive isomerizations using 1-pentene-1,2-d_2 and 1-heptene in one reaction and 1-pentene and 1-heptene in another, showed that deuterium had very little effect on the rate of isomerization.

Secondly, the present study shows that our previous conclusion (concerning vinyl-deuterated hexene) that "no detectable movement of deuterium occurs during isomerization" was wrong. This erroneous conclusion was based on the use of a single analysis experiment, where the isomerization was taken to virtual completion and the proton distribution determined in the final reaction product. The continued monitoring method used in the present study shows that there is in fact an appreciable replacement of deuterium at C_2 during the isomerization of vinyl-deuterated 1-pentene.

We have previously observed, using 1-hexenes and 1-heptenes and gpc analysis, the distinctly stepwise nature of the rhodium-catalyzed reaction, a phenomenon presumably associated with a large difference between the reactivity of terminal and internal olefins. The stepwise nature of the reaction is further illustrated by the nmr results obtained with 1-pentene-1,2-d_2. In the course of reaction the initial aliphatic methyl (adjacent to aliphatic methylene) resonance disappears and is replaced by a slightly lower field methyl (adjacent to allylic methylene) resonance. The sharp methyl triplet in the product indicates that there is a negligible amount of deuterium present in, or adjacent to, the methyl group (see Figure 1b), since interaction of methyl protons with deuterium would produce a more complex splitting pattern. The observation that the methyl proton count does not deviate significantly from a value of 3 (Table I) is also a consequence of the fact that a second shift of the double bond occurs to a negligible extent up to 80% consumption of 1-olefin.

Given the facts that only a single shift of the double bond occurs, and that, at least initially, the terminal vinyl proton count is proportional to the concentration of 1-pentene, it is apparent from Table I that partial exchange of deuterium is occurring at the internal vinyl carbon atom. A single shift of the double bond without exchange would produce a reaction product with a single nonterminal proton. Complete exchange would produce a reaction product with two nonterminal vinyl protons, thus

$$CH_3CH_2CH_2CD{=}CDH \xrightarrow{k_3} CH_3CH_2CH{=}CDCH_2D \quad (3)$$

$$CH_3CH_2CH_2CD{=}CDH \xrightarrow{k_4} CH_3CH_2CH{=}CHCD_2H \quad (4)$$

The products of reactions 3 and 4 represent an average composition, dictated by the necessity to conserve

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[11] J. F. Harrod and A. J. Chalk, *Nature*, 205, 280 (1965).

deuterium and hydrogen. The nature of the exchange process and composition of products will be discussed in more detail below.

Using the above information, one may calculate the expected proton distributions for various values of k_3/k_4. The results of such a calculation are shown in Table V for the nonterminal vinyl protons. From the table it is apparent that a value for $k_3/k_4 \approx 1$ fits the data very well in the initial stages of reaction.

Table V. Effect of k_1/k_2 on the Proton Distribution in Isomerized Pentene

Terminal vinyl (exptl)	Nonterminal vinyl (calcd) k_3/k_4 0	1	2	Nonterminal vinyl (exptl)
0.80	0.00	0.00	0.00	0.00
0.50	0.75	0.56	0.50	0.56
0.42	0.95	0.71	0.64	0.70
0.19	1.53	1.15	1.02	0.91
0.17	1.60	1.20	1.07	1.03
0.12	1.70	1.28	1.13	1.14

The data from the heptene-3-d_2 reaction (Table III) may be treated similarly, using eq 5 and 6. The calculated values for the nonterminal vinyl protons are shown in Table VI. Again, the data agree reasonably well with a value for $k_5/k_6 \approx 1$.

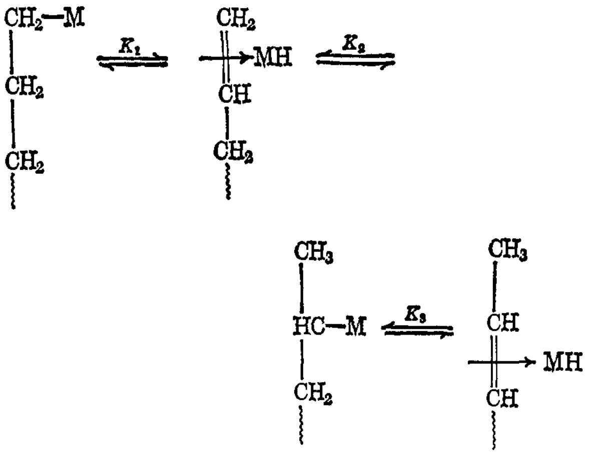
$$C_4H_9CD_2CH{=}CH_2 \xrightarrow{k_5} C_4H_9CD{=}CHCDH_2 \qquad (5)$$

$$C_4H_9CD_2CH{=}CH_2 \xrightarrow{k_6} C_4H_9CD{=}CDCH_3 \qquad (6)$$

Table VI. Effect of k_3/k_4 on the Proton Distribution in Isomerized Heptene

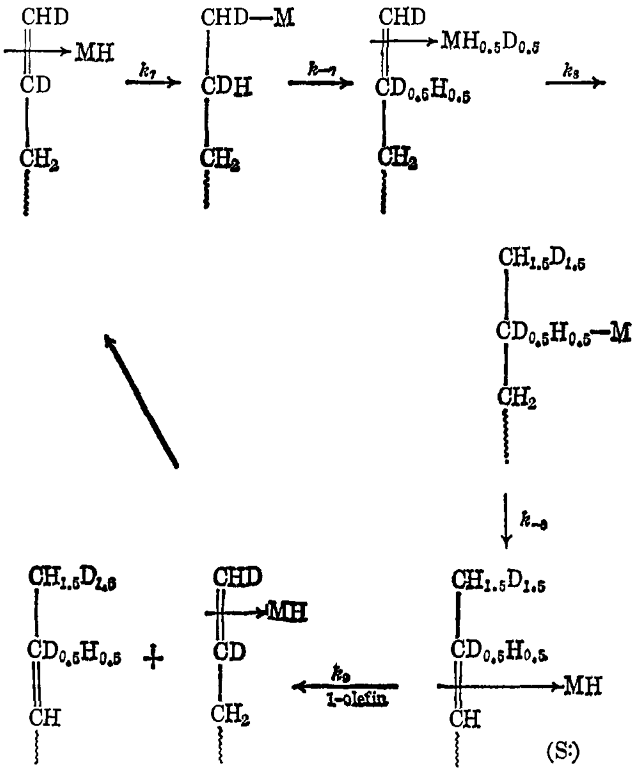
Terminal vinyl (exptl)	Nonterminal vinyl (calcd) k_5/k_6 0	1	2	Nonterminal vinyl (exptl)
2.06	1.00	1.00	1.00	1.02
1.56	0.76	0.88	0.92	0.86
1.19	0.58	0.79	0.86	0.74
0.90	0.44	0.72	0.81	0.65
0.29	0.14	0.58	0.71	0.53

All of the results discussed above may be rationalized on the assumption of an alkyl mechanism (eq 2) for the isomerization step, but it is also necessary to consider other hydride addition and removal steps which do not lead to isomerization. These steps may be schematically summarized by the series of equilibria shown in eq 7. Whereas, the equilibrium K_3 is the only one that results in movement of the double bond, the equilibria K_1 and K_2 can allow exchange at C_2 and C_1. In addition to the equilibria shown in (7), there will be further equilibria between free and complexed olefin. The stepwise double-bond shift observed experimentally suggests that 2-olefin formed in the early stages of reaction is displaced completely by 1-olefin, before a second bond shift can occur.

 (7)

On the basis of eq 7, we may write a mechanism for the isomerization of deuterio olefins reasonably consistent with the experimental results (see Scheme I).

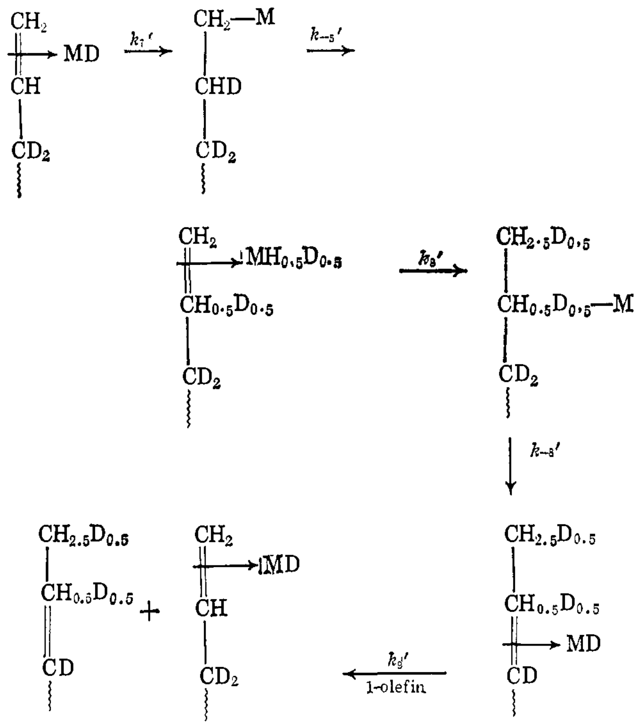
Scheme I. Vinyl-Deuterated Olefins



Since catalyst and solvent are present in negligible amounts, the olefin is the only effective source of hydrogen in this catalytic cycle and the average stoichiometry of the olefin must be preserved. The steps k_7 and k_{-7} provide a mechanism for exchange at C_2, but since the total amount of MH is negligible, this exchange can only proceed if there is a replenishing source of protium. In our scheme, the source of protium is the isomerization step k_{-8}, and there are two possible schemes that will give rise to the experimentally observed 50% exchange at C_2. The first possibility is that $k_7 \approx k_8$ and secondary alkyl rarely reverts to 1-olefin. The second possibility is that $k_7 > k_8$, but displacement of 1-olefin is slow compared to k_8 and k_{-8}. A distinction between these two alternatives is not possible from the present study. Theoretically this question could be resolved by periodic analysis of the 1-pentene for exchange at

C_1 and C_2 during the reaction, but we were unable to do this with the small quantities of material and the equipment available to us. With allyl-deuterated olefin (Scheme II), the isomerization step (k_{-8}') provides a supply of deuterium, which may then exchange at C_2 through reactions k_7' and k_{-7}'.

Scheme II. Allyl-Deuterated Olefins



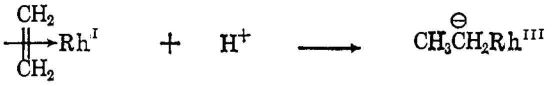
Further evidence in favor of this mechanism is provided by the magnitude of the allylic methyl peak in the isomerized pentenes (Figure 1b). Owing to coincidence between the allylic methyl and aliphatic methylene peaks, an accurate measurement of the former is not possible. However, the value is undoubtedly quite close to 1.5 protons, as would be expected from roughly equal contributions from the products of reactions 3 and 4.

Finally, the infrared evidence (Figure 4b) that intermolecular exchange leads to the appearance of deuterium on all the carbon atoms of the allylic system, and in an amount corresponding to equilibration of one deuterium atom between the labeled and unlabeled olefins, may also be taken as supporting evidence for the proposed mechanism.

In the catalytic cycle, as written above, we have made no allowance for reversion of secondary alkyl to primary olefin. Such a process would permit exchange at the terminal carbon atom, and the fact that such exchange was not observed as a major reaction suggests that the forward reaction of equilibrium K_3 is faster than the back reaction of equilibrium K_2. A small amount of this type of exchange could explain the deviations between nmr and infrared determinations of 1-olefin concentration, shown in Figures 2 and 3.

The proposed mechanism does not provide a simple explanation for the apparent decrease in allylic methylene protons (Table I). If this decrease is real there must be exchange processes occurring other than those accounted for in the proposed mechanism. However, we are inclined to believe that the decrease may in fact be due to a progressive underestimation of the overlap between the allylic methylene and allylic methyl peaks of the nmr spectra; *i.e.*, our estimate of the error in this measurement may be too small.

In a recent paper,[12,12a] Cramer has presented detailed evidence that the reversible addition of a proton to a Rh(I)–olefin complex occurs thus



$$(CH_2{=}CH_2)\rightarrow Rh^{I} + H^{+} \longrightarrow CH_3CH_2\overset{\ominus}{R}h^{III}$$

This author also mentioned unpublished results which indicated that isomerization proceeds *via* the same type of process.

The Palladium-Catalyzed Reaction. It has been observed both by ourselves and by several other workers[2,4] that the isomerization of 1-olefins by palladium complexes results in the simultaneous appearance of all possible internal isomers at roughly comparable rates. This behavior is quite different from isomerizations with rhodium trichloride, with which double-bond migration occurs in a distinctly stepwise fashion. With the deuteriopentene used in our experiment, the possibility exists for producing four distinct 2-pentene isomers by single and double shifts of the double bond, thus

$$CH_3CH_2CH_2CD{=}CDH \begin{cases} \nearrow CH_3CH_2CH{=}CDCDH_2 \ \text{(a)} \\ \searrow CH_3CH{=}CHCDHCDH_2 \ \text{(b)} \end{cases} \qquad (8)$$

and

$$CH_3CH_2CH_2CD{=}CDH \begin{cases} \nearrow CH_3CH_2CH{=}CHCD_2H \ \text{(a)} \\ \searrow CH_3CH{=}CHCH_2CD_2H \ \text{(b)} \end{cases} \qquad (9)$$

We have been unable to fit the experimental results to any model which assumes significant contributions from (9a) or (9b). Proton distributions calculated on the assumption that the reaction product contains equal contributions from (8a) and (8b), and none from (9), give reasonable agreement with experiment. The calculated values are listed in Table VII. The different behavior of H(a), (b), and (c) protons in the rhodium- and palladium-catalyzed reactions are readily explained by the assumption of eq 8a and 8b for the latter. Also, in Figure 1c, the large allylic methyl peak and the more complex splitting of the aliphatic methyl group should be noted. Although an accurate estimate of the former

Table VII. Calculated Proton Distributions for Palladium-Catalyzed Pentene Isomerization

H(e),	Calculated values			
exptl	H(a)	H(b)	H(c)	H(d)
0.85	3.00	2.00	2.00	0
0.64	2.88	2.13	1.87	0.37
0.52	2.80	2.20	1.82	0.59
0.38	2.73	2.28	1.73	0.83
0.11	2.57	2.44	1.53	1.30

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(12) R. Cramer, *J. Am. Chem. Soc.*, 87, 4717 (1965).

(12a) Note Added in Proof. In a more recent paper (R. Cramer, *ibid.*, 88, 2273 (1966)) convincing evidence is presented in support of a mechanism involving protonation of a Rh(I) olefin complex for the isomerization reaction.

is not possible, it is fairly certain that there is a minimum of two allylic methyl protons, a significantly larger value than that obtained with the rhodium catalyst. The complex splitting of the aliphatic methyl peak may be due to the presence of at least two types of methyl, one with deuterium and one without, as expected from eq 8. The methyl resonance in Figure 1c may be compared with the methyl resonance of the rhodium-catalyzed mixture after about 50% reaction (inset, Figure 1a). The latter also shows two types of methyl groups, attributable to methyl adjacent to aliphatic and allylic methylene. Although the major methyl resonance in the palladium-catalyzed mixture corresponds to methyl adjacent to allylic methylene, the underlying second methyl resonance has a slightly different chemical shift from that of the 1-olefin.

The results of the palladium-catalyzed 1-heptene-3-d_2 isomerization are also consistent with a mechanism involving $C_3 \rightarrow C_1$ hydrogen shifts. It may be noted that in the case of allyl deuteration even two shifts of the double bond still result in only a single nonterminal vinyl proton by a $C_3 \rightarrow C_1$ mechanism; thus

$$C_3H_7CH_2CD_2CH{=}CH_2 \longrightarrow C_3H_7CH_2CD{=}CHCH_2D \longrightarrow C_3H_7CH{=}CDCH_2CH_2D$$

Nevertheless, we expect the double bond to move farther along the chain, and the fact that the number of nonterminal vinyl protons does not increase significantly above one is rather puzzling. This observation may indicate significant movement of deuterium along the chain as the reaction progresses, or alternatively there may be some feature of kinetic origin which limits migration of the double bond to the 3 position.

The appearance of the 3-heptene is reflected in a decrease in the H(f) (aliphatic methyl and methylene and allylic methyl) protons and an excess of H(g) (allylic methylene) protons over that expected for a single migration of the double bond. Also, although the various protons grouped together as H(f) cannot be resolved accurately in the nmr spectrum of the mixed heptenes, they are well enough resolved to clearly show that there are more aliphatic methyl than aliphatic methylene protons in the palladium-catalyzed reaction product. This is only possible if the 3 isomer is present.

Since there is a simultaneous appearance of products in which the double bond has moved through one and more positions in the palladium-catalyzed reaction, the results are less easy to interpret than in the case of the rhodium-catalyzed reaction. Nevertheless, there is little doubt that the isomerization proceeds predominantly *via* a $C_3 \rightarrow C_1$ shift of hydrogen, and that there is significantly less intermolecular hydrogen transfer than in the case of the rhodium-catalyzed reaction.

By far the simplest explanation of the $C_3 \rightarrow C_1$ shift is the π-allyl reaction (1), since this mechanism does not require the breaking of the C–H bond at C_2, even when the double bond moves from the 2 to 3 position. Based on the fact that π-allyl complexes of palladium were not catalytically active, we have previously rejected the possibility of a π-allyl mechanism.[11] This rejection is not necessarily valid, however, since the intermediate species in eq 1 contains a proton which is not available in complexes such as bis(π-allyl)-μ-dichlorodipalladium (II). Cramer has shown[12] that rhodium(I)–olefin complexes, which we found inactive as isomerization catalysts,[1] are active in the presence of acid. We do not find this to be the case with allylpalladium complexes, and consequently the simple reversible protonation of a π-allyl complex still does not seem to provide an adequate mechanism for the isomerization reaction. On the basis of the present evidence, we are inclined to believe that the inherent stability of the palladium–π-allyl system may play a role in assisting a $C_3 \rightarrow C_1$ proton shift, but the details of how the $C_3 \rightarrow C_1$ shift and the intermolecular hydrogen transfer occur must await the results of further experiments.

The infrared evidence, from the intermolecular deuterium exchange experiment (Figure 4), also suggests different mechanisms for the reactions catalyzed by rhodium and palladium complexes, both with regard to quantity and location of exchanged deuterium. Whereas most of the exchanged deuterium appears on the vinyl position with the rhodium catalyst, there is very little vinyl deuterium in the pentene product of the palladium-catalyzed reaction, although the heptene still contains a considerable amount of vinyl deuterium. This result can only be explained on the assumption that exchanging deuterium is being transferred almost exclusively to the terminal vinyl carbon atom of the 1-pentene.

In fact, the results of the palladium-catalyzed reactions could be explained by a reversible alkyl hydride, provided addition of palladium hydride to terminal olefin led almost exclusively to the formation of a secondary alkyl. Although such a possibility is not completely without precedent,[13] we do feel that it is sufficiently improbable to be regarded with considerable scepticism.

In conclusion we would like to emphasize that the present study indicates that different catalyst systems may utilize different mechanistic routes to effect the isomerization of 1-olefins, but it must also be borne in mind that different *substrates*, or different *reaction media*, may cause changes in mechanism for the same metal-ion catalyst. Thus, certain olefinic compounds such as allylbenzene,[14] or cyclooctadienes,[7] may prefer a π-allylic mechanism, by virture of their forming a particularly stable π-allylic ligand system. Also, the use of a basic, hydride-donor solvent such as an alcohol[1] may promote a quite different mechanism from a relatively inert hydrocarbon solvent, or an acidic solvent,[2] that can inhibit the proton abstraction necessary for π-allylic ligand formation.

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(13) M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.*, **1**, 58 (1963).

(14) L. Roos and M. Orchin, *J. Am. Chem. Soc.*, **87**, 5502 (1965).