Iron Carbonyl Catalyzed Isomerization of 3-Ethyl-1-pentene. Multiple Olefin Isomerizations *via* a π-Allyl Metal Hydride Intermediate

Charles P. Casey* and Clifford R. Cyr

Contribution from the Department of Chemistry,
University of Wisconsin, Madison, Wisconsin 53706.

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Abstract: The $Fe_3(CO)_{12}$ catalyzed isomerization of 3-ethyl-1-pentene-*3-d*$_1$ (**1**-*d*) gives 3-ethyl-2-pentene (**2**). The deuterium label in **2** was shown to be randomly scrambled among the three methyl groups of **2** by nmr and by ozonolysis of **2** which gave acetaldehyde and 3-pentanone with deuterium in the methyl groups only. Nmr analysis of recovered **1**-*d* indicated that scrambling of deuterium onto the methyl groups and the terminal vinyl carbon of 3-ethyl-1-pentene (**1**) occurs 1.8 ± 0.2 times more rapidly than isomerization of **1**-*d* to **2**. The absence of crossover products from the isomerization of a mixture of **1**-*d* and 3-methyl-1-butene (**3**) demonstrated that the olefin isomerization reaction occurs *via* intramolecular hydrogen shifts. No primary deuterium isotope effect was observed when a mixture of **1** and **1**-*d* was isomerized. The isomerization of a mixture of **1** and of 3-ethyl-2-pentene-*1-d*$_3$ (**2**-*d*$_3$) indicated that the isomerization of **1** to **2** is 3.6 ± 1.5 times faster than the degenerate isomerization of **2**. An olefin isomerization mechanism involving a π-allyl metal hydride intermediate is invoked to explain the observed intramolecular 1,3 hydrogen shifts which accompany the isomerization of **1**-*d*. The scrambling of deuterium in **2** and in recovered **1**-*d* requires that the rate of isomerization of a complexed alkene be rapid in comparison with the rate of decomplexation of the alkene.

The isomerization of olefins catalyzed by transition metal complexes constitutes one of the most important types of reaction in organometallic chemistry.[1] Depending upon the particular catalyst involved, the isomerization can occur by either a metal hydride addition–elimination mechanism or by a mechanism involving a π-allyl metal hydride intermediate. One of the fundamental differences between the two mechanisms is that the metal hydride addition–elimination mechanism constitutes a 1,2 hydrogen migration while the π-allyl metal hydride mechanism results in a 1,3 hydrogen shift.

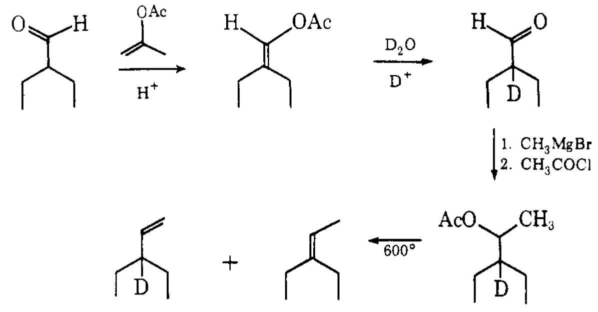
During a study of the mechanism of formation of 3-ethylhexanal in the dicobalt octacarbonyl catalyzed hydroformylation of 3-methyl-1-hexene-*3-d*$_1$,[2] we found that olefin isomerization proceeded *via* a metal hydride addition–elimination mechanism involving 1,2 hydrogen shifts and that these additions and eliminations were rapid in comparison with the rate of decomplexation of the alkene from the metal catalyst. We were interested in determining whether such rapid multiple olefin isomerizations might also occur in olefin isomerization reactions proceeding *via* the π-allyl metal hydride mechanism. The iron carbonyl catalyzed isomerization of 3-ethyl-1-pentene (**1**) was chosen for study since a π-allyl metal hydride mechanism for the isomerization of monoolefins by iron carbonyls had been proposed[3] and since analysis of the alkene mixture is simplified because 3-ethyl-2-pentene (**2**) is the only other alkene with the same carbon framework as **1**.

Here we present results which indicate that the iron catalyzed isomerization of **1** occurs by intramolecular 1,3 hydrogen shifts probably *via* a π-allyl metal hydride intermediate and that isomerization of the complexed alkenes is rapid compared with decomplexation of the alkene.

Results

Synthesis. To determine whether the isomerization of **1** was inter- or intramolecular and to determine whether isomerization occurred *via* 1,2 or 1,3 hydrogen shifts, it was necessary to synthesize 3-ethyl-1-pentene-*3-d*$_1$ (**1**-*d*) (Scheme I). Deuterium was introduced into the α position of 2-ethylbutanal by converting the aldehyde to its enol acetate and then hydrolyzing the enol acetate with deuterium oxide to give 2-ethylbutanal-*2-d*$_1$ in 50% yield. Reaction of the deuterated aldehyde with methylmagnesium bromide, followed by acetylation of the resulting alcohol, gave 3-ethyl-2-pentyl-*3-d*$_1$ acetate in 70% yield. Pyrolysis of the acetate at 600° gave a quantitative yield of a 3 : 1 mixture of **1**-*d* : **2** which was separated by spinning band distillation. Mass spectral analysis of **1**-*d* indicated that it contained 94.5% d_1 and 5.5% d_0 material.

Scheme I. Synthesis of 3-Ethyl-1-pentene-*3-d*$_1$ (**1**-*d*)



1-*d*   **2**

3-Ethyl-2-pentene-*1-d*$_3$ (**2**-*d*$_3$) for use in competitive isomerizations with **1** (*vide infra*) was synthesized by

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(1) For reviews of transition metal catalysis of olefin isomerization, see (a) N. R. Davies, *Rev. Pure Appl. Chem.*, **17**, 83 (1967); (b) C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Academic Press, New York, N. Y., 1967, p 67; (c) M. Orchin, *Advan. Catal. Relat. Subj.*, **16**, 1 (1966); C. A. Tolman in "Transition Metal Hydrides," Vol. 1, E. L. Muetterties, Ed., Marcel Dekker, New York, N. Y., 1971, Chapter 6.

(2) C. P. Casey and C. R. Cyr, *J. Amer. Chem. Soc.*, **93**, 1280 (1971); C. P. Casey and C. R. Cyr, *ibid.*, **95**, 2240 (1973).

(3) (a) T. A. Manuel, *J. Org. Chem.*, **27**, 3941 (1962); (b) H. Alper and P. C. LePort, *J. Amer. Chem. Soc.*, **91**, 7553 (1969); (c) F. G. Cowherd and J. L. von Rosenberg, *ibid.*, **91**, 2157 (1969).

reaction of (ethylidene-*2*-d_3)triphenylphosphorane with 3-pentanone. Mass spectral analysis indicated that **2**-d_3 contained 1.6% d_0, 5.4% d_2, and 93.0% d_3 material.

Isomerization of 3-Ethyl-1-pentene-*3*-d_1 (1-*d*). 3-Ethyl-1-pentene (**1**) is isomerized to 3-ethyl-2-pentene (**2**) upon heating to 80° in *n*-octane solution in the presence of 0.5–2.0 mol % triiron dodecacarbonyl. In a typical experiment, 16% isomerization of **1** to **2** occurred within 40 min at 80° using 1.7 mol % $Fe_3(CO)_{12}$. Upon equilibration, a mixture of 3 ± 1% **1** and 97 ± 1% **2** is obtained starting from either pure **1** or pure **2**.

1 and **1**-*d* isomerize at approximately the same rate as demonstrated by an experiment in which a 1.00:0.98 mixture of **1**:**1**-*d* was isomerized to 7% conversion. Mass spectra of the isomerized olefin indicated that it was a 1.00:0.89 mixture of d_0 and d_1 **2**. This indicates that there is no appreciable primary deuterium isotope effect on the isomerization.

The isomerization of **1**-*d* in the presence of a fivefold excess of 3-methyl-1-butene (**3**) was studied to determine whether the isomerization processes are intra- or intermolecular. Isomerization of the mixture was carried to 55% conversion of **1**-*d* to **2** and 89% conversion of **3** to isomeric products. Very little, if any, deuterium was incorporated into 2-methyl-2-butene (**5**), the major isomerization product of **3**. Mass spectral analysis indicated that **5** was a mixture of 99.3% d_0 and 0.7% d_1 material. Mass spectral analysis of **2** (9.6% d_0, 89.2% d_1, and 1.2% d_2) indicated an increase of about 5% in the combined amounts of d_0 and d_2 material. In a similar reaction carried to 93% conversion of **1**-*d* to **2** and 99% conversion of **3** to isomeric products, more extensive scrambling of deuterium in **2** was observed (17.7% d_0, 80.2% d_1, and 2.2% d_2), but **5** still showed little incorporation of deuterium (98.9% d_0 and 1.1% d_1). These results indicate that the isomerization process occurs intramolecularly in the initial portion of the isomerization.

To determine whether isomerization occurs *via* a net 1,2 or 1,3 hydrogen shift, the isomerization of **1**-*d* was carried to 84% conversion and the products were examined. The olefin mixture was separated from the catalyst by bulb-to-bulb distillation under high vacuum. Pure samples of isomerized **2** and recovered **1** were isolated by preparative gas chromatography.

The position of the deuterium label in **2** was determined by spectral methods and by chemical degradation. The mass spectrum of **2** obtained upon 84% conversion of **1**-*d* indicated predominant retention of the single deuterium atom (7.4% d_0, 89.1% d_1, and 3.5% d_2). Integration of the nmr spectrum of this sample of **2** gave the ratio 0.98:4.00:2.68:5.34 for the vinyl, methylene, allylic methyl, and methyl protons, respectively, indicating that the deuterium label was approximately equally distributed among the three methyl groups.

The location of the deuterium in all of the methyl groups of **2** was confirmed by ozonolysis followed by dimethyl sulfide work-up which cleaved the molecule to give acetaldehyde and 3-pentanone. The deuterium content of the acetaldehyde could not be determined by mass spectral analysis due to a large M − 1 peak. However, the presence of a substantial amount of deuterium in the methyl group of acetaldehyde was shown by integration of the nmr spectrum which indicated a 1.00:2.79 ratio of aldehyde:methyl protons. The 3-pentanone obtained from ozonolysis was shown to be a mixture of 38.5% d_0, 60.1% d_1, and 1.4% d_2 material by mass spectral analysis. Integration of the nmr spectrum indicated a ratio of 4.00:5.48 for the methylene to methyl protons. Treatment of the 3-pentanone ozonolysis product with aqueous potassium carbonate for 3 days at 100° led to no loss of deuterium as shown by mass spectrometry (37.8% d_0, 61.6% d_1, and 0.5% d_2). In a control experiment, these reaction conditions were shown to exchange deuterium in the methylene positions of 3-pentanone. Consequently, the deuterium label in **2** is randomly distributed among the three methyl groups but is absent from the methylene and vinyl carbon atoms.

Samples of **2** isolated from isomerization reactions carried to 5 and 20% conversion also indicated nearly complete scrambling of deuterium among all three methyl groups. Ozonolysis of a sample of **2** obtained from 20% conversion of **1**-*d* gave 3 pentanone with a ratio of methylene:methyl protons of 4.00:5.42; a ratio of 4.00:5.35 is calculated for complete scrambling of deuterium among the three methyl groups. The nmr spectrum of a sample of **2** obtained from 5% conversion of **1**-*d* showed a ratio of methylene to terminal methyl protons of 4.00:5.40 ± 0.05; a ratio of 4.0:6.0 is expected for no scrambling and a ratio of 4.0:5.33 is expected for complete scrambling. The observed ratio indicated that, in the sample of **2** isolated from 5% conversion of **1**-*d*, approximately 90% of the material has deuterium scrambled among the three methyl groups, while only 10% of the material results from a single specific deuterium migration to the vinylic methyl group. The scrambling of deuterium label in **2** recovered from low conversion of **1**-*d* cannot be due to prior scrambling of label in **1**-*d* since at 5% conversion to **1**-*d*, only about 8% scrambling of **1**-*d* would be expected (*vide infra*).

Examination of a sample of **1**-*d* recovered from an isomerization reaction carried to 20% conversion to **2** indicated that deuterium was retained in the molecule, but that extensive scrambling of deuterium within the molecule had occurred. The mass spectrum of recovered **1**-*d* (5.2% d_0, 94.2% d_1, and 0.7% d_2) was substantially the same as that of the starting material. However, integration of the nmr spectrum of recovered **1**-*d* revealed that the ratio of the tertiary allylic proton to the methylene protons of the ethyl groups had risen to 0.42 ± 0.05:4.00 from 0.10 ± 0.05:4.00 in the starting material.[4] To accommodate the labeling results found for **2**, the label in recovered **1**-*d* can only be on the terminal vinyl carbon, the allylic carbon, and the methyl carbons. Complete scrambling of deuterium between these positions of **1**-*d* would have led to an nmr integral ratio of 0.89:4.00. Therefore, the degenerate isomerization of **1** is 1.8 ± 0.2 times faster than the isomerization of **1** to **2**.

Competitive Isomerization of 1 and 3-Ethyl-2-pentene-*1*-d_3 (2-d_3). To determine the rate of the isomerization of **1** to **2** relative to the degenerate isomerization of **2**, the isomerization of equimolar mixtures of undeuterated **1** and 3-ethyl-2-pentene-*1*-d_3 (**2**-d_3) was examined. After partial conversion of **1** to **2**, 3-ethyl-2-pentene was separated from the reaction mixture by gas chromatography and analyzed by nmr and mass spectrometry. The per cent isomerization of **1** and **2** was determined by

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[4] The ratio for a sample of recovered **1**-*d* from an isomerization carried to 5% conversion was 0.13 ± 0.05:4.00.

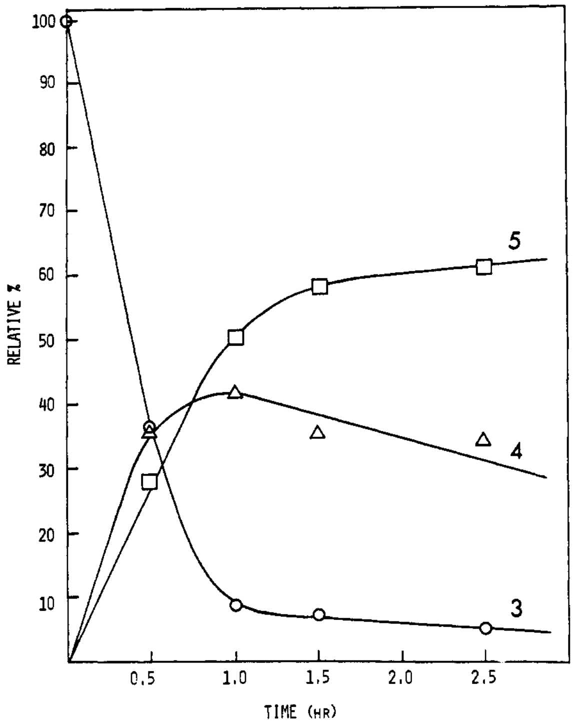


Figure 1. Isomerization of 3-methyl-1-butene (**3**): (○) relative % 3-methyl-1-butene (**3**); (△) relative % 2-methyl-1-butene (**4**); (□) relative % 2-methyl-2-butene (**5**).

mass spectral measurements of **2** using the assumption that the additional d_0 material in the sample resulted from the isomerization of **1**. The extent of isomerization of **2**-d_3 to give **2** with the deuterium label scrambled over all three methyl group was determined by nmr. The ratio V/E of the number of vinyl methyl protons to the number of ethyl methyl protons in **2** is readily obtained from nmr integration and is a sensitive function of the extent and position of deuterium labeling in **2**. Equation 1 indicates how the V/E ratio of the product

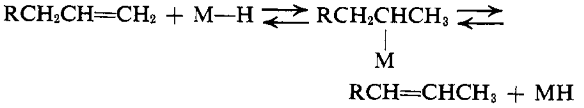
$$(V/E)_{\text{product}} = [(1 - D)(V/E)_{\text{initial}} + D(V/E)_{\text{random}} + P(V/E)_{d_0}]/(1 + P) \quad (1)$$

can be expressed as a function of the initial V/E ratio of the **2**-d_3 starting material (0.021), of the V/E ratio expected for random placement of the deuterium label in any of the three methyl groups of **2** (0.50), of the V/E ratio expected for d_0 **2** obtained from the isomerization of undeuterated **1** (0.50). P is the extent of isomerization of **1** to **2** and D is the fraction of **2**-d_3 which has undergone isomerization to scramble the deuterium label over the three methyl groups. The various V/E ratios obtained by careful integration of 100-MHz nmr spectra and P (determined previously by mass spectrometry) were substituted into eq 1 to yield a value for D. For $P = 0.28 \pm 0.02$ and $(V/E)_{\text{product}} = 0.155 \pm 0.006$, the calculated value of D was 0.077 ± 0.031 and the ratio of P/D was 3.6 ± 1.5.[5] Consequently, the rate of scrambling of label in **2**-d_3 is 3.6 ± 1.5 slower than the rate of isomerization of **1** to **2** which in turn is 1.8 ± 0.2 times slower than the rate of scrambling of label in **1**-*d*.

Isomerization of 3-Methyl-1-butene (3). The isomerization of 3-methyl-1-butene (**3**) was studied for comparison with the isomerization of **1**-*d* and to gain further insight into the mechanism of the olefin isomerization process. **3** isomerizes upon heating to 80° in *n*-octane solution in the presence of 0.1 mol % triiron dodecacarbonyl. In the initial stages of isomerization, the major product is 2-methyl-1-butene (**4**). But as time progresses, the thermodynamically more stable isomer 2-methyl-2-butene (**5**) gradually accumulates at the expense of **4** (see Figure 1). In separate experiments, **4** was shown to isomerize to **5** while **5** was unchanged under the reaction conditions. These results are similar to those obtained in the isomerization of **1**-*d* where the production of isomerized terminal olefin (deuterium scrambled **1**) was faster than the production of the more substituted olefin **2**.

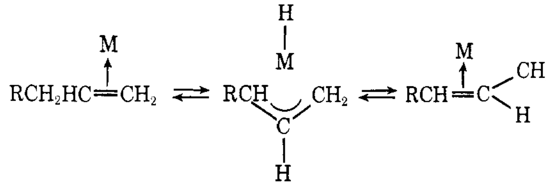
Discussion

Olefin isomerization catalyzed by transition metal complexes normally occurs either by a metal hydride addition–elimination mechanism or by a π-allyl metal hydride mechanism.[1,6] The reaction sequence involved in the metal hydride addition–elimination mechanism (eq 2) leads to a net 1,2 hydrogen shift. For isomerization to occur *via* this mechanism, a cocatalyst such as hydrogen or an acid is often necessary, presumably because the cocatalyst reacts with the metal complex to produce an intermediate metal hydride. For catalyst systems in which the intermediacy of a metal hydride is well known or can confidently be assumed, considerable evidence establishing the importance of the 1,2-addition–elimination mechanism has been presented. Some representative catalyst systems that isomerize olefins *via* the metal hydride addition–elimination mechanism are $HCo(CO)_4$,[8] $[(C_2H_4)_2RhCl]_2$,[9a] and $Ni[P(OEt)_3]_4$,[9b] which require an acid as a cocatalyst, and $PtCl_2(Ph_3P)_2$–$SnCl_2$, which requires H_2 as a cocatalyst.[10]



$$\mathrm{RCH_2CH{=}CH_2 + M{-}H \rightleftarrows \underset{\underset{M}{|}}{RCH_2CHCH_3} \rightleftarrows RCH{=}CHCH_3 + MH} \quad (2)$$

The π-allyl metal hydride mechanism for olefin isomerization is shown in reaction sequence 3 and involves an overall 1,3 hydrogen shift. The π-allyl metal hydride mechanism is much less common than the metal



(3)

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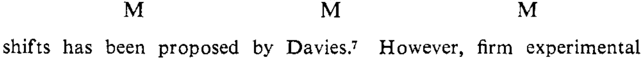
(5) In another run in which less isomerization had occurred, P was 0.168 ± 0.020 and (V/E) product was 0.087 ± 0.006. The calculated value of D was slightly negative, -0.006 ± 0.026; the 95% confidence limits for the value of P/D include all values greater than 3.7.

(6) An additional mechanism for olefin isomerization involving an intermediate metal–carbene complex and successive 1,2 hydrogen



$$\mathrm{RCH_2{-}\underset{\overset{\downarrow}{M}}{CH}{=}CH_2 \rightleftarrows RCH_2{-}\underset{\overset{\|}{M}}{C}{-}CH_3 \rightleftarrows RCH{=}\underset{\overset{\downarrow}{M}}{CH}{-}CH_3}$$

shifts has been proposed by Davies.[7] However, firm experimental evidence for such a metal–carbene mechanism has not been found for any transition metal-catalyzed olefin isomerization.

(7) N. R. Davies, *Aust. J. Chem.*, **17**, 212 (1964).

(8) P. Taylor and M. Orchin, *J. Amer. Chem. Soc.*, **93**, 6504 (1971).

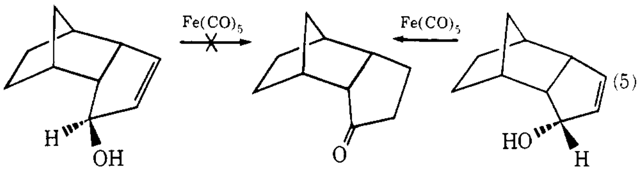
(9) (a) R. Cramer, *ibid.*, **88**, 2272 (1966); (b) C. A. Tolman, *ibid.*, **94**, 2994 (1972).

(10) R. W. Adams, G. E. Batley, and J. C. Bailar, Jr., *ibid.*, **90**, 6051 (1968).

hydride addition–elimination mechanism. Although the π-allyl metal hydride mechanism has often been suggested to account for olefin isomerization by transition metal complexes not containing hydride ligands, there are few well-documented cases in which this mechanism has been established. Harrod and Chalk[11] were able to explain the 1,3 hydrogen shifts which occurred in the isomerization of 1-heptene-*3*-d_2 catalyzed by bis(benzonitrile)dichloropalladium(II) only by invoking a π-allyl palladium hydride intermediate.

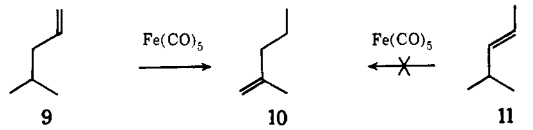
The isomerization of allyl alcohol to propionaldehyde catalyzed by iron pentacarbonyl is probably the best documented example of an isomerization which proceeds by a π-allyl metal hydride mechanism.[12] The deuterium labeling studies of Hendrix, *et al.*, demonstrated a net 1,3 hydrogen shift in the conversion of allyl alcohol to propionaldehyde. The labeling results could also have been accounted for by a metal hydride addition–elimination mechanism if the iron atom of an iron hydride species added exclusively to the more substituted carbon atom of allyl alcohol; however, this possibility was discounted since metal hydrides such as $HCo(CO)_4$ normally add the metal atom preferentially to the least substituted carbon atom. The possibility of isomerization of allyl alcohols to carbonyl compounds *via* a 1,3 sigmatropic hydrogen shift from the side opposite the metal in an iron–olefin complex was ruled out by Cowherd and von Rosenberg since the endo alcohol **6** but not the exo alcohol **7** could be isomerized to the ketone **8** by $Fe(CO)_5$.[3c]

$$CH_2{=}CHCD_2OH \xrightarrow{Fe(CO)_5} [DH_2CCH{=}CDOH] \longrightarrow DCH_2CH_2CDO \quad (4)$$



7 **8** **6** (5)

Manuel has suggested a π-allyl metal hydride mechanism for the iron carbonyl catalyzed isomerization of terminal olefins.[3a] He has also suggested that multiple isomerizations of the complexed alkene must be occurring to account for the isomerization of 4-methyl-1-pentene (**9**) to 2-methyl-1-pentene (**10**) under conditions where 4-methyl-2-pentene (**11**) does not isomerize. However, since an intramolecular 1,3 hydrogen shift[13] was not demonstrated, a metal hydride addition–elimination mechanism is also consistent with Manuel's results. The $HFe(CO)_4^-$ catalyzed olefin isomerization occurs *via* a metal hydride addition–elimination mechanism, and the possibility that this or a related iron hydride species is responsible for the olefin isomerization in the presence of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ cannot be discounted. However, Asinger has observed that very different product ratios of isomerized olefins are obtained from iron pentacarbonyl and $NaHFe(CO)_4$ catalyzed isomerizations.[14]



9 **10** **11** (6)

The results presented here establish a π-allyl metal hydride mechanism for the $Fe_3(CO)_{12}$ catalyzed isomerization of alkenes. The isomerization of a mixture of **1**-*d* and **3** essentially constitutes a double labeling experiment. The absence of crossover products in this experiment demonstrates the intramolecularity of the hydrogen shifts involved in the olefin isomerization reaction. Since deuterium was found only in the three methyl groups of **2** obtained from isomerization of **1**-*d*, the isomerization of **1**-*d* to **2** is accompanied exclusively by 1,3 hydrogen shifts. Only a π-allyl metal hydride mechanism is consistent with the observed intramolecular 1,3 hydrogen shifts.

The scrambling of the label in **1**-*d* starting material was 1.8 ± 0.2 times faster than isomerization of **1**-*d* to **2** and could have resulted *a priori* either from multiple isomerization of an iron complex of **1**-*d* or from isomerization of **1**-*d* to **2** followed by rapid isomerization of **2** to scrambled **1**. However, since the rate of scrambling of label in **2**-d_3 was found to be substantially slower than isomerization of **1**-*d* to **2**, only multiple isomerizations of an iron complex of **1**-*d* can explain the scrambling of label in **1**-*d*. Similarly, samples of **2** isolated from low conversion of **1**-*d* showed deuterium label scrambled among all three methyl groups of **2**. This result taken together with the more rapid isomerization of **1**-*d* to **2** compared with scrambling of the label of **2**-d_3 can be explained only by multiple isomerizations of an iron complex of **1**-*d*. The results obtained from the isomerization of 3-methyl-1-butene in which 2-methyl-1-butene was the major product early in the reaction and 2-methyl-2-butene was the major equilibrium product also are understandable in terms of multiple isomerization of an olefin–iron complex. Consequently, olefin isomerization of a complexed alkene is faster than the rate of decomplexation of the alkene.

The mechanism shown in Scheme II best explains the observations on the $Fe_3(CO)_{12}$-catalyzed isomerization of alkenes. The rate-determining step in the isomerization process cannot involve the breaking of a carbon–hydrogen bond to give a π-allyl metal hydride intermediate since no primary deuterium isotope effect on the reaction was observed. Olefin isomerization can proceed by an internal oxidative addition of an allylic carbon–hydrogen bond of a complexed alkene to the four coordinate d^8 Fe(0) complex, $Fe(CO)_3$(alkene), to give a six coordinate d^6 Fe(II) complex, $Fe(CO)_3H(\pi\text{-allyl})$.[15]

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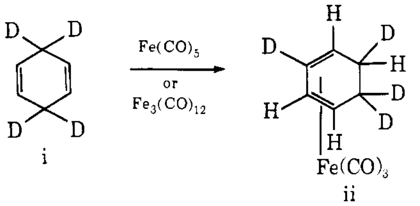
[11] J. F. Harrod and A. J. Chalk, *J. Amer. Chem. Soc.*, **88**, 3491 (1966).

[12] (a) G. F. Emerson and R. Pettit, *ibid.*, **84**, 4591 (1962); (b) W. T. Hendrix, F. G. Cowherd, and J. L. von Rosenberg, *Chem. Commun.*, 97 (1968).

[13] Similarly, while Alper's study of the conversion of the deuterated 1,4-cyclohexadiene i to 1,3-cyclohexadieneiron tricarbonyl ii indicated a net 1,3 hydrogen shift, the intramolecularity of the process was not studied, and consequently the results are also compatible with a metal hydride addition–elimination mechanism.[3b]

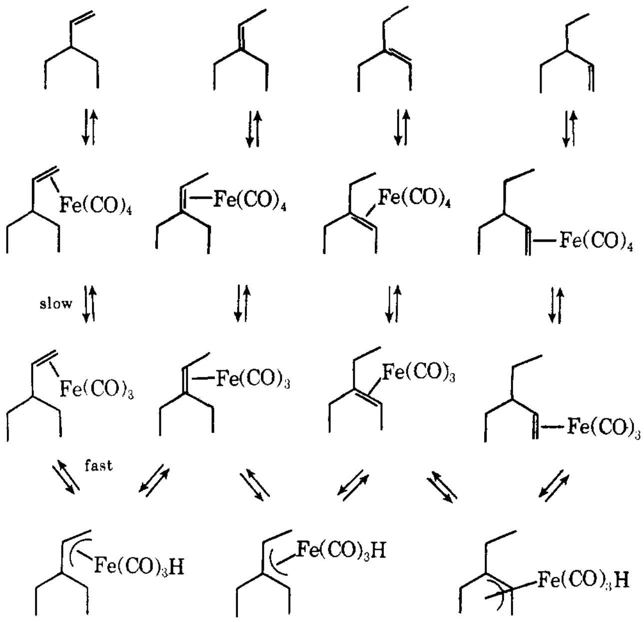


i ii

[14] F. Asinger, B. Fell, and G. Collin, *Chem. Ber.*, **96**, 716 (1963).

[15] For a review of oxidative addition, see J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, **7**, 53 (1969). This may be viewed as a simple example of insertion into C—H bonds; for a review, see G. W. Parshall, *Accounts Chem. Res.*, **3**, 139 (1970).

Scheme II



The reversible oxidative addition and reductive elimination reactions must be fast compared with the rate of alkene decomplexation to explain the observed multiple olefin isomerizations. The rate-determining step in these isomerizations must be either the formation of the Fe(CO)$_4$(alkene) or, more likely, the formation of the coordinately unsaturated Fe(CO)$_3$(alkene).

Multiple isomerizations of a complexed alkene *via* a π-allyl metal hydride mechanism can explain the iron carbonyl catalyzed reaction of 4-methyl-1-pentene which gives 2-methyl-1-pentene as the major initial product under conditions where the isomerization of 4-methyl-2-pentene is slow.[3a] Examples of multiple olefin isomerizations proceeding *via* a metal hydride addition–elimination mechanism include our demonstration of multiple isomerization preceding aldehyde formation in the hydroformylation reaction[2] and the isomerization of an initial isopropyliridium compound to an *n*-propyliridium compound.[16]

Stepwise olefin isomerization proceeding *via* a metal hydride addition–elimination mechanism is also known. Cramer has shown that the isomerization of *cis*-2-butene catalyzed by [(C$_2$H$_4$)$_2$RhCl]$_2$ gives only *trans*-2-butene-*2-d*$_1$ by a stereospecific addition of a rhodium deuteride followed by a stereospecific elimination of a rhodium hydride.[9a] Johnson has shown a stepwise isomerization of 4-methyl-1-pentene (**9**) to 4-methyl-2-pentene (**11**) to 2-methyl-2-pentene (**12**) accompanying a HCo(CO)$_4$ catalyzed hydroformylation.[17] Lyons has observed that catalyst systems with bulky phosphines such as RuCl$_2$(PPh$_3$)$_3$ and PtCl$_2$(PPh$_3$)$_2$–SnCl$_2$ are selective stepwise olefin isomerization catalysts.[18]

Both multiple and stepwise metal-catalyzed olefin isomerizations are now well documented and can occur either by a metal hydride addition–elimination mechanism or by a π-allyl metal hydride mechanism. The factors which determine whether multiple or stepwise isomerization will occur for a given catalyst stystem, however, remain undefined.

Experimental Section

Nmr spectra were determined using Varian A-60A, T-60, and XL-100 spectrometers. Infrared spectra were recorded on a Beckman IR-8 spectrophotometer. Mass spectra were determined using an AEI-902 mass spectrometer. Gas chromatographic analyses were performed using a Hewlett-Packard Model 5750 research chromatograph; preparative gas chromatography was accomplished with a Varian 90-P gas chromatograph. A Nester-Faust Model 65TB annular Teflon spinning-band distillation column was employed for distillation of the olefins. The 3-methyl-1-butene was Phillips pure grade. Triiron dodecacarbonyl was prepared according to the procedure of King.[19]

1-Acetoxy-2-ethyl-1-butene. The method of House and Kramar was modified to prepare the enol acetate of 2-ethylbutyraldehyde.[20] Isopropenyl acetate (400 g, 4.0 mol), 2-ethylbutyraldehyde (200 g, 2.0 mol), and *p*-toluenesulfonic acid (2.0 g) were heated under nitrogen to 110°. Acetone was slowly distilled from the mixture through a 30-in. column of glass helices over 4 days. The enol acetate was isolated from the reaction mixture by distillation under reduced pressure. Redistillation gave 199.8 g (70%) of 1-acetoxy-2-ethyl-1-butene: bp 98–101° (90 mm); ir $\nu_{\max}^{\text{neat}}$ 1750, 1670 cm^{-1}; nmr $\delta_{\text{TMS}}^{\text{CCl}_4}$ 1.00 and 1.06 (overlapping triplets, 6 H, 2 C*H*$_3$CH$_2$), 1.80–2.40 (m, 4 H, CH$_2$), 2.08 (s, 3 H, CH$_3$CO$_2$), and 6.85 (broad s, 1 H, *H*C-(OAc)=C).

2-Ethylbutanal-*2-d*$_1$ was obtained by the method of Hine, *et al.*[21] Deuterium oxide (33.8 g, 1.69 mol), 1-acetoxy-2-ethyl-1-butene (199 g, 1.41 mol), and 4 drops of concentrated sulfuric acid were refluxed under nitrogen for 4 days. Ether (500 ml) was added to the reaction mixture. The ether layer was washed successively with saturated Na$_2$CO$_3$ solution, saturated NaHCO$_3$ solution, and saturated NaCl solution, and dried (MgSO$_4$). Distillation under nitrogen gave 98.4 g (70%) of 2-ethylbutanal-*2-d*$_1$: bp 115–118°; ir $\nu_{\max}^{\text{neat}}$ 2700 (m), 2120 (w), and 1725 (s) cm^{-1}; nmr $\delta_{\text{TMS}}^{\text{CCl}_4}$ 9.25 (overlapping triplets, 6 H, 2 C*H*$_3$CH$_2$), 1.3–1.9 (m, 4 H, CH$_3$C*H*$_2$CD), and 9.55 (s, 1 H, CHO).

3-Ethyl-2-pentanol-*3-d*$_1$. A solution of 2-ethylbutanal-*2-d*$_1$ (99 g, 0.98 mol) in an equal volume of dry ether was added dropwise over 6 hr to methylmagnesium bromide in ether (400 ml, 1.05 mol). The mixture was refluxed overnight, cooled to 0°, and hydrolyzed by successive addition of 200 ml of 10% HCl and 300 ml of saturated NH$_4$Cl solution. The ether layer was washed with saturated NaHCO$_3$ solution and saturated NaCl solution and dried (MgSO$_4$). Distillation gave 97 g (85%) of 3-ethyl-2-pentanol-*3-d*$_1$: bp 147–149°; ir $\nu_{\max}^{\text{neat}}$ 3170 (br), 2100 (w) cm^{-1}; nmr $\delta_{\text{TMS}}^{\text{CCl}_4}$ 0.7–1.8 (m, 13 H), 2.10 (broad s, 1 H, OH), and 3.75 (q, 1 H, C*H*(OH)CH$_3$).

3-Ethyl-2-pentyl-*3-d*$_1$ Acetate. Dry ether (150 ml), *N,N*-dimethylaniline (145 g, 1.20 mol), and 3-ethyl-2-pentanol-*3-d*$_1$ (0.96 g, 0.82 mol) were heated to reflux. Then without additional heating, acetyl chloride (84 g, 1.07 mol) was added dropwise at a rate to maintain reflux. The mixture was refluxed an additional 16 hr after the completion of the addition. Water was then added. The ether layer was washed four times with 10% H$_2$SO$_4$, two times with saturated NaHCO$_3$ solution, and once with 100 ml of saturated NaCl solution, dried (MgSO$_4$), and distilled to give 106.5 g (82%) of the acetate: bp 163–168°; ir $\nu_{\max}^{\text{neat}}$ 2100 (w), 1730 (s) cm^{-1}; nmr $\delta_{\text{TMX}}^{\text{CCl}_4}$ 0.7–1.7 (m, 13 H), 1.95 (s, 3 H, O$_2$CCH$_3$), and 4.85 (q, 1 H, C*H*(OAc)-CH$_3$).

3-Ethyl-1-pentene-*3-d*$_1$ (1-*d*). 3-Ethyl-2-pentyl-*3-d*$_1$ acetate (104 g, 0.654 mol) was passed dropwise under a slow stream of nitrogen through a 20-cm column packed with glass beads heated to 600 ± 10°. The olefin and acetic acid were collected in a series of −78° traps. The column was washed with pentane after completion of the pyrolysis. The pentane solutions from the traps were washed with NaHCO$_3$ solution and dried (MgSO$_4$). Analysis of the mixture by glpc indicated quantitative conversion of the acetate to a 3:1 mixture of 3-ethyl-1-pentene and 3-ethyl-2-pentene. The mixture was separated by spinning band distillation and redistilled from sodium to give 11.2 g of **1**-*d*: >99% purity by gc; ir $\nu_{\max}^{\text{neat}}$ 2120 (w), 1635 (w), 990 (m), and 908 (s) cm^{-1}; nmr $\delta_{\text{TMS}}^{\text{CCl}_4}$ 0.85 (overlapping triplets, 6 H, C*H*$_3$CH$_2$), 1.30 (m, 4 H, CDC*H*$_2$CH$_3$), 4.70–5.15 (m, 2 H, CH=C*H*$_2$), and 5.20–5.85 (m, 1 H, C*H*=CH$_2$). The spinning band distillation also gave 2.7 g (4.2%) of 3-ethyl-2-pentene, >99% purity by gc.

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3-Ethyl-1-pentene (1) was prepared by the same method as the deuterated olefin: ir $\nu_{\max}^{\text{neat}}$ 1635 (w), 992 (m), and 909 (s) cm^{-1}; nmr $\delta_{\text{TMS}}^{\text{CCl}_4}$ 0.82 (2 overlapping triplets, 6 H, $\mathrm{C}\mathit{H}_3\mathrm{CH}_2$), 1.0–1.6 (m, 4 H, $\mathrm{CH_3C}\mathit{H}_2\mathrm{CH}$), 1.5–2.0 (m, 1 H, $(\mathrm{CH_2})_2\mathrm{C}\mathit{H}\mathrm{C{=}C}$), 4.70–5.15 (m, 2 H, $\mathrm{CH{=}C}\mathit{H}_2$), and 5.20–5.90 (m, 1 H, $\mathrm{C}\mathit{H}\mathrm{{=}CH_2}$).

3-Ethyl-2-pentene (2) was prepared in 84% yield by the iodine-catalyzed dehydration of 3-ethyl-2-pentanol following the procedure of Marker:[22] bp 91–92°; ir $\nu_{\max}^{\text{neat}}$ 822 (w), 1640 (w) cm^{-1}; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 0.95 (t, 6 H, $\mathrm{C}\mathit{H}_3\mathrm{CH}_2$), 1.75 (d, 3 H, $\mathrm{C}\mathit{H}_3\mathrm{CH{=}C}$), 2.03 (2 overlapping quartets, 4 H, $\mathrm{CH_3C}\mathit{H}_2$), and 5.10 (q, 1 H, $\mathrm{CH_3C}\mathit{H}\mathrm{{=}C}$).

3-Ethyl-2-pentene-*1*-d_3 (2-d_3). The procedure of Shiner[23] was modified to prepare bromoethane-*2*-d_3. Acetic acid-d_4 (10.0 g, 0.156 mol) in 100 ml of diethylene glycol diethyl ether (freshly distilled from lithium aluminum hydride) was added dropwise to a slurry of lithium aluminum hydride (8.0 g, 0.210 mol) in 200 ml of diethylene glycol diethyl ether at 0°. The mixture was stirred at 25° for 6 hr, heated at 90° for 16 hr, and cooled to 0°. Diethylene glycol mono-*n*-butyl ether (100 ml, dried over $\mathrm{CaSO_4}$ and distilled) was then added. Distillation under aspirator vacuum into a −78° trap gave 7.2 g (94%) of ethanol-*2*-d_3: ir $\nu_{\max}^{\text{neat}}$ 3330 (broad) and 2220 (m) cm^{-1}. The deuterated ethanol was cooled to *ca.* −5 and −10° with an ice-salt bath, and phosphorus tribromide (16.4 g, 0.06 mol) was added slowly so that the temperature remained below 5°. After completion of the addition, the mixture was stirred for 2 hr at 0°. Distillation of the reaction mixture gave 12.3 g (75%) of bromoethane-*2*-d_3 which was dried ($\mathrm{K_2CO_3}$): nmr $\delta_{\text{TMS}}^{\text{CCl}_4}$ 3.34 (singlet).

The procedure of Atkinson, *et al.*,[24] was followed to prepare (ethyl-*2*-d_3)triphenylphosphonium bromide. Triphenylphosphine (30.2 g, 0.116 mol) and bromoethane-*2*-d_3 (12.3 g, 0.110 mol) were mixed with 275 ml of acetonitrile, and the mixture was refluxed for 2 days. The acetonitrile was evaporated. The solid residue was washed with a little ether and dried under vacuum to give 36.8 g (89%) of (ethyl-*2*-d_3)triphenylphosphonium bromide. The method of Corey, *et al.*, was followed in preparing 3-ethyl-2-pentene-*1*-d_3 (**2**-d_3).[25] To a solution of sodium hydride (5.0 g of a 50% dispersion, 0.10 mol) in 150 ml of dry dimethyl sulfoxide was added (ethyl-*2*-d_3)triphenylphosphine bromide (36.8 g, 0.088 mol). After the mixture was stirred for 1 hr at 25°, 3-pentanone (8.6 g, 0.10 mol) was added in one portion. The mixture was stirred at 25° for 16 hr. The olefin was removed from the reaction mixture by distillation under reduced pressure and redistilled to give 6.0 g (60%) of 3-ethyl-2-pentene-*1*-d_3 (**2**-d_3). Benzene (6% by nmr) and a trace of unreacted ketone were removed by preparative glpc (20% UCON 50 HB 280X polar on Chromosorb P, 20 ft × 0.25 in., 95°): nmr $\delta_{\text{TMS}}^{\text{CCl}_4}$ 0.93 (overlapping triplets, 6 H, $\mathrm{C}\mathit{H}_3\mathrm{CH}_2$), 2.0 (overlapping quartets, 4 H, $\mathrm{CH_3C}\mathit{H}_2\mathrm{C{=}C}$), and 5.1 (broad s, 1 H, $\mathrm{CC}\mathit{H}(\mathrm{CD_3})$).

Isomerization Procedure. Triiron dodecacarbonyl (dried under vacuum for several hours immediately before use), the olefin under study, and a gas chromatography internal standard (*n*-hexane for C_5-alkenes and *n*-octane for C_7-alkenes) were weighed into a nitrogen-flushed test tube. The mixture was degassed by three freeze–thaw cycles. The tube was sealed under vacuum and heated to 80 ± 1° to effect olefin isomerization.

Analysis of 3-Ethyl-1-pentene-*3*-d_1 (1-d) Isomerization Reaction Mixture. The hydrocarbons were separated from the catalyst by bulb-to-bulb distillation under vacuum. The extent of isomerization was determined by gas chromatographic measurement (20% UCON 50 HB 280X polar on Chromosorb P, 20 ft × 1/8 in., 100°) of the amounts of 3-ethyl-1-pentene-d_1 and 3-ethyl-2-pentene-d_1 in the reaction mixture. The 3-ethyl-1-pentene-d_1 and 3-ethyl-2-pentene-d_1 were separated by preparative gas chromatography (20% UCON 50 HB 280X polar on Chromosorb P, 20 ft × 0.25 in., 80°). The deuterium content of the pure olefins was determined from mass spectral analysis of the parent ion region obtained using slow scans at 12 eV. Careful integration of 60- and 100-MHz nmr spectra of the olefins indicated the distribution of the deuterium (see Results).

Ozonolysis of 3-Ethyl-2-pentene-d_1. One equivalent of ozone (generated with a Welsbach Ozonizer) was slowly bubbled through a solution of 3-ethyl-2-pentene-d_1 in 10 ml of dichloromethane at −30°. The ozonide was reduced to 3-pentanone and acetaldehyde with dimethyl sulfide (1.1 equiv) according to the procedure of Pappas.[26] The reaction mixture was distilled to give three fractions. The first fraction contained dichloromethane and acetaldehyde, which were separated by preparative gas chromatography (Poropak Q, 50–80 mesh, 5 ft × 0.25 in., 125°). The acetaldehyde was analyzed for deuterium by nmr analysis (see Results). The other two fractions contained dichloromethane and 3-pentanone, which were separated by preparative gas chromatography (25% Carbowax 20M on Chromosorb W, 10 ft × 3/8 in., 100°). The 3-pentanone was analyzed for deuterium by mass spectrometry and nmr analysis (see Results). Confirmation of the absence of deuterium at the methylene positions was obtained by heating the deuterated 3-pentanone in aqueous $\mathrm{K_2CO_3}$ in a sealed ampoule at 100° for 3 days (conditions which were independently demonstrated to exchange deuterium in α-deuterated 3-pentanone).

Analysis of the parent ion region of the mass spectrum (obtained using slow scans at 12 eV) of the 3-pentanone, repurified by preparative gas chromatography, indicated no loss of deuterium.

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