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Rhodium(I) Catalysis in Olefin Photoreactions

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Abstract: The photorearrangement (254 nm) of 1,5-cyclooctadiene (**1**) in the presence of rhodium(I) chloride to give 1,4-cyclooctadiene (**4**) is shown by deuterium labeling to involve an intramolecular [1,3] shift of hydrogen. A rate-determining cleavage of an allylic C–H bond is indicated by a deuterium isotope effect, $k_H/k_D = 1.55 \pm 0.03$ for the $\mathbf{1} \rightarrow \mathbf{4}$ rearrangement. The acyclic 1,5-diene, 3,3-dimethyl-1,5-hexadiene (**8**), rearranges in the presence of rhodium(I) chloride upon uv irradiation (254 nm) to give *cis*-3,3-dimethyl-1,4-hexadiene (**10**) and the trans isomer **11** in a 1:4 ratio, respectively. This observation supports a mechanism for the photorearrangement of olefins catalyzed by rhodium(I) involving a initial photodissociation of one of two rhodium(I) coordinated carbon–carbon double bonds. This results in an increase in the coordinative unsaturation of rhodium(I) and enhances the proclivity of this d_8 metal atom toward oxidative addition of an allylic C–H bond. A η^3-allylrhodium hydride intermediate then gives rearranged olefin by reductive elimination. Lastly, a novel photochemical, rhodium(I) catalyzed hydrogen transfer is reported which gives cyclooctene (**7**) from cyclooctadienes under unprecedentedly mild conditions.

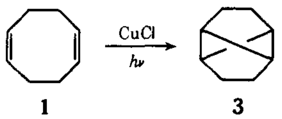
The effort directed toward discovering and understanding organic photochemical reactions which require transition metals as catalysts[2a] has been meager compared with the extensive work on catalyzed thermal reactions.[2b-f] Metal carbonyl complexes are often active catalysts for photoreactions of olefins.[2a,3] The primary process in such reactions appears generally to be photodissociation of a carbonyl ligand to generate coordinatively unsaturated intermediates which catalyze transformations of the olefin substrates in subsequent dark reactions.[4] Metal carbonyl catalysis is thus dominated by the photochemistry of the M–CO bond. It has been suggested that photochemical pathways are operative in olefin rearrangements in olefin–metal carbonyl systems.[3] However, nothing is known about the mechanisms involved since studies of these pathways are beclouded by the dominant thermal pathways.

$$M(CO)_n \xrightarrow{h\nu} M(CO)_{n-1} + CO$$

Some transition metal complexes which do not contain carbonyl groups are also known to catalyze olefin photorearrangement.[2] Even simple salts of copper(I) and rhodium(I) catalyze olefin photoreactions.[6-8] These reactions are especially interesting since the salts form isolable olefin complexes, and since the olefin–metal interaction almost certainly plays a key role in the photochemical process. Thermal pathways are not expected to be important, and these reactions should be relatively simple and especially well suited for mechanistic study.

Recent studies[5] have elucidated the mechanism of olefin photodimerization catalyzed by copper salts.[6] Photodimerization of olefins such as norbornene and *endo*-dicyclopentadiene in the presence of copper(I) trifluoromethanesulfate (CuOTf) were shown to involve photoexcitation of a 2:1 olefin–CuOTf complex. It was also demonstrated that both C=C bonds must be coordinated to the same Cu(I) to effect photodimerization.[5]

We now report a study of olefin photoreactions which are catalyzed by rhodium(I) chloride. The photorearrangement of 1,5-cyclooctadiene (**1**) in the presence of the corresponding rhodium(I) chloride complex **2** has been known for some time.[7] In contrast to the copper(I) chloride catalyzed intramolecular photocycloaddition[7,8] of **1** to give a cyclobutane **3**, irradiation of **1** in the presence of RhCl gives **4** and **5**. We now find that additional products **6** and **7** are also obtained under certain conditions. Moreover, the acyclic 1,5-diene **8** is also photoisomerized in the presence of RhCl. In the present study, we have examined the mechanisms of these interesting rhodium(I) catalyzed photochemical reactions.



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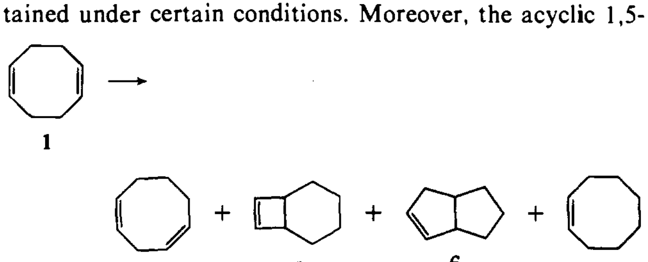

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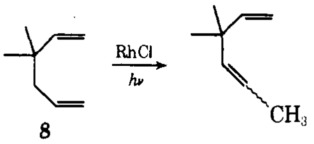

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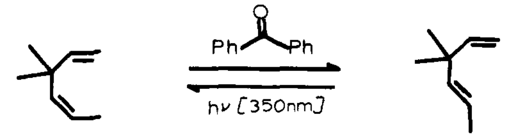
Results

A. Syntheses of Photorearrangement Substrates, Products, and Catalysts. 1,5-Cyclooctadiene-*3,3,4,4,7,7,8,8-d*$_8$ (1-*d*$_8$). Octadeuterio-1,5-cyclooctadiene (**1**-*d*$_8$) was prepared by dimerization of butadiene-*1,1,4,4-d*$_4$ in the presence of Ni[P(OPh)$_3$]$_4$ as catalyst.[9] We preferred this procedure over the previously reported dimerization of butadiene-*d*$_4$ in the presence of diethylbis(dipyridyl)iron.[10] The latter complex is air sensitive and gives 1,5-cyclooctadiene and 4-vinylcyclohexene in a 3:1 ratio. The nickel catalyst is less air sensitive and favors 1,5-cyclooctadiene over 4-vinylcyclohexene by 6:1.

***cis*- and *trans*-3,3-Dimethyl-1,4-hexadiene.** Reaction of 2,2-dimethyl-3-butenal (**9**) with ethylidenetriphenylphosphorane yields exclusively *cis*-3,3-dimethyl-1,4-hexadiene (**10**). The tendency for such Wittig reactions to preferentially yield cis olefin is well documented.[11] The trans isomer **11** was obtained from the benzophenone sensitized isomerization[12] of **10**. The cis and trans isomeric dienes were readily distinguishable and characterized on the basis of their infrared spectra. The cis diene exhibits a strong infrared absorption at 714 cm^{-1} which is absent in the infrared spectrum of the trans diene. The trans diene exhibits a strong infrared absorption at 971 cm^{-1} which is absent in the infrared spectrum of the cis isomer. These absorptions are characteristic of the out-of-plane vinyl hydrogen deformation for cis and trans disubstituted olefins, respectively.[13]

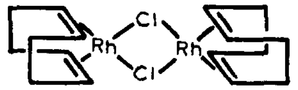
9 10



10 11

μ-Dichloro-bis[η^4-3,3-dimethyl-1,5-hexadiene]dirhodium(I) Chloride (12). The complex **12** was prepared by reaction of excess 3,3-dimethyl-1,5-hexadiene (**8**) with rhodium trichloride in aqueous ethanol.[14] Washing with fresh aqueous ethanol and drying under a stream of nitrogen gave analytically pure complex which could not be recrystallized due to its generally high solubility in organic solvents. In sharp contrast with all other known olefin–rhodium chloride complexes, including μ-dichloro-bis[η^4-1,5-hexadiene]dirhodium(I) chloride (**13**),[7,14] **8** is extremely soluble in pentane.

B. Photolyses. Cyclooctadienes. Rhodium chloride forms a dimeric 1:1 complex **2** with 1,5-cyclooctadiene (**1**).[7b] A structure involving square planar coordination about rhodium was established by X-ray crystallography.[7c,d] The complex exhibits an intense ultraviolet absorption maximum, λ_{max} 233 nm (ϵ 13,500; calculated for the monomer), in diethyl ether solution. The carbon-13 magnetic resonance spectrum of **2** is very different from that of the free ligand **1**. The vinylic carbon resonance of **2** is shifted upfield by 1258 ppm and split into a doublet by coordination with rhodium, while the allylic carbon resonance is shifted slightly downfield. Significantly the carbon resonances due to free ligand **1** are totally absent from the spectrum of the complex **2** in solution, though the spectrum of a mixture of **1** and **2** is identical with a superposition of the spectra of **1** and **2**. Thus, ligand exchange is slow on the NMR time scale and *the complex is undissociated.*



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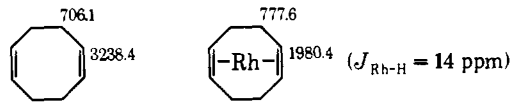

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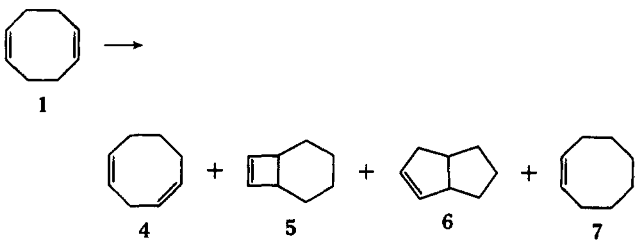
Srinivasan reported[7a] that irradiation (254 nm) of an ether solution of 1,5-cyclooctadiene (**1**) (2.3 × 10^{-2} *M*) saturated with μ-dichloro-bis[η^4-1,5-cyclooctadiene]dirhodium(I) chloride (**2**) gives, before 20% conversion, bicyclo[4.1.0]octene-7 (**5**) (20%) and 1,4-cyclooctadiene (**4**) (23%). We reexamined this reaction and monitored starting diene and product concentrations by gas-liquid phase chromatography (see Figure 1). Besides the previously reported products, we isolated cyclooctene (**7**) from the photolysis reaction mixture. Furthermore, careful scrutiny of the NMR spectrum of the sample of **5** isolated from a photoly-



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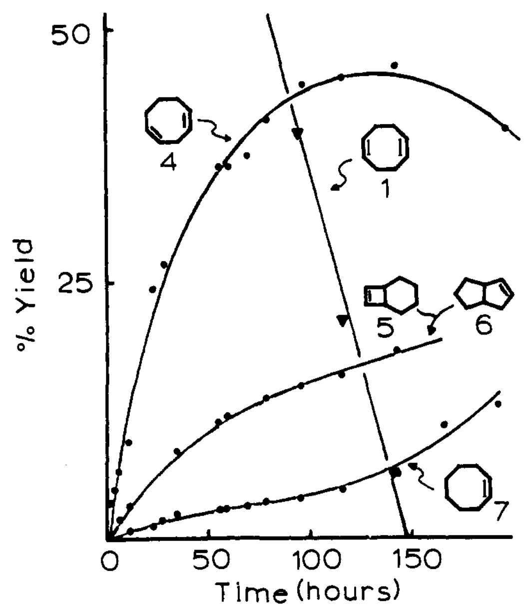
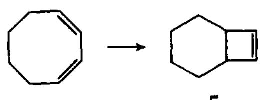


Figure 1. Photolysis of 1,5-cyclooctadiene in the presence of rhodium(I).

sis reaction mixture after about 50% conversion revealed the presence of 15% of bicyclo[3.3.0]octene-2 (**6**). This ratio was confirmed by gas-liquid phase chromatography. The bicyclic olefins **5** and **6** were readily separated with a GLC column containing a saturated solution of silver nitrate in glycerol,[15] while all other columns tried failed to separate these olefins.

Disappearance of 1,5-cyclooctadiene (**1**) during photolysis in the presence of rhodium(I) depends linearly on the time of irradiation (see Figure 1) and does not exhibit an induction period (see Figure 4 below). The initial rate of appearance of the 1,4-diene **4** equals the rate of disappearance of the 1,5-diene **1**. The rate of cyclooctene formation is initially small but increases rapidly *after* all of the 1,5-diene **1** has been consumed.

Photorearrangement of 1,3-cyclooctadiene (**14**) in the presence of rhodium gives exclusively **5** as predicted.[7] Photorearrangement of the 1,4-diene (**4**) to 25% conversion in the presence of rhodium gives cyclooctene (**7**) (40%) and bicyclooctenes **5** and **6** (60%) in a 5:1 ratio, respectively.



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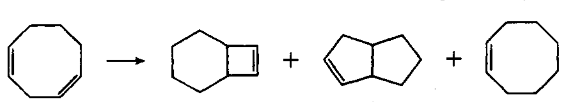

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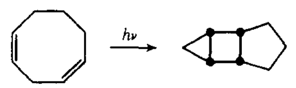
Since the 1,4-diene **4** rearranges to *cis,syn,cis*-tricyclo[5.1.0.0^{2,6}]octane (**15**) under ultraviolet irradiation[16] in the absence of rhodium, the stability of **15** toward the rhodium catalyst **2** was examined. As expected,[17] the rhodium(I) complex **2** induces the rearrangement of **15** to give **6** *without* ultraviolet irradiation. The reaction is pseudo-first-order (see Figure 2) since a plot of log [**15**] vs. time gives a straight line.



4 15

Octadeuterio-1,5-cyclooctadiene (1-d_8). Irradiation (254 nm) of an ether solution of **1**-d_8 in the presence of 4.3 mol percent of RhCl (as **2**-d_8, see Experimental Section), after 50% conversion, gave a mixture consisting of four major volatile products (see Table I). It is noteworthy that the relative yields of **6** and **7** are substantially greater from **1**-d_8 than from **1**-d_0. The starting diene (**1**-d_8) and 1,4-diene (**4**-d_8) were isolated from the reaction mixture. By NMR, the deuterium labeling pattern in recovered unreacted **1**-d_8 is not scrambled. The proton magnetic resonance spectrum of **4**-d_8 is consistent with that expected for the product of a [1,3] shift of deuterium (see Figure 3), 2,3,3,6,6,7,7,8-octadeuterio-1,4-cyclooctadiene. Three different types of protons are present in a ratio of 1:2:1 at δ 5.7, 5.4, and 2.3. The chemical shifts of these protons indicate that they are located at C-2, C-1(5), and C-6, respectively.

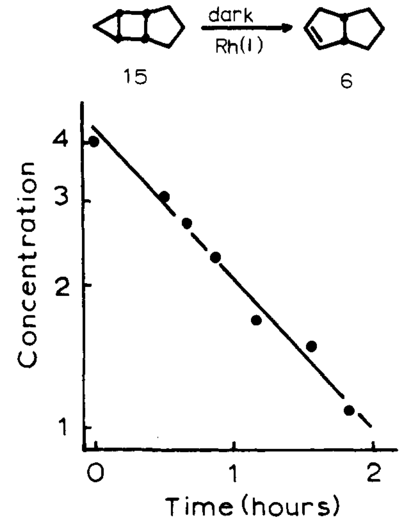
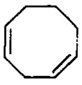
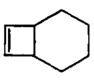
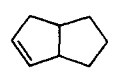
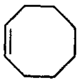


Figure 2. Rearrangement of *cis,syn,cis*-tricyclo[5.1.0.0^{2,6}]octane in the presence of rhodium(I).

Table I. Composition of Photolysis Reaction Product Mixtures from 1,5-Cyclooctadiene-d_0 and -d_8 after 50% Conversion

Starting 1,5-cyclooctadiene	Mole percent of product mixture  **4**	  **5**	  **6**	  **7**
1-d_0	69	21	4	6
1-d_8	57	14	16	14

Photorearrangement of a mixture of **1**-d_0 (50%) and **1**-d_8 (50%)[18] gives **4**-d_0 (49%), **4**-d_1 (1%), **4**-d_7 (7%), and **4**-d_8 (43%). The results are complicated by a slight net loss of deuterium label. Nevertheless, crossover is not detectable within the limit of ±1% for the precision of the isotope ratio determination.

A plot of percent reaction in the photolysis of 1,5-cyclooctadiene-d_8 and of 1,5-cyclooctadiene-d_0 as a function of time is given in Figure 4. The reaction in each case is zero order in olefin. The percent reaction depends only upon the time of irradiation and extrapolates cleanly to time = 0 *without any induction period.*

This linear dependence of the rate of reaction of **1** upon irradiation time can be readily understood if it is assumed that the reaction mixture solution is optically opaque with respect to absorption by the complex **2**. If it is further assumed that allylic deuterium substitution will have a negligible effect on the stability of the diene-rhodium complex then, for a solution containing both **1**-d_0 and **1**-d_8, the concentration of **2**-d_0 will be proportional to the mole fraction

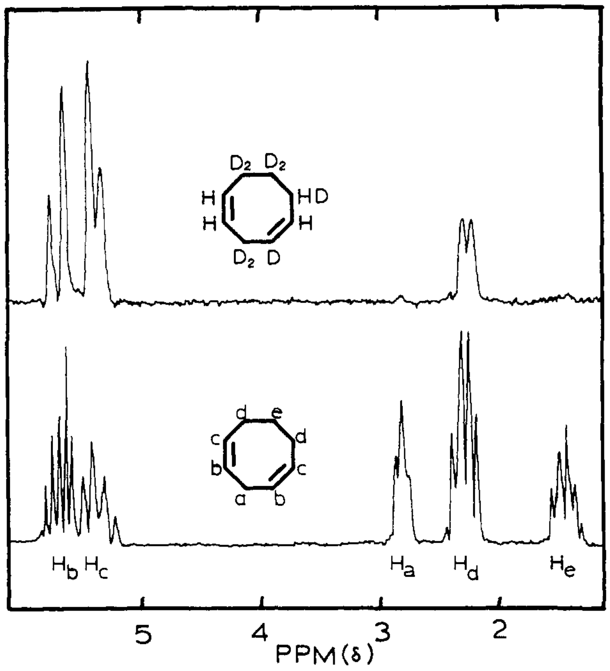


Figure 3. Proton magnetic resonance spectra of 1,4-cyclooctadienes: (upper) octadeuterio; (lower) perhydro.

of **1**-d_0 in the solution. The rate of disappearance of **1**-d_0 will obey eq 1. A similar equation applies to the rate of dis-

$$\mathrm{d}[d_0]/\mathrm{d}t = k_{\mathrm{H}}[d_0]/([d_0] + [d_8]) \qquad (1)$$

appearance of **1**-d_8. These equations lead to eq 2. Rear-

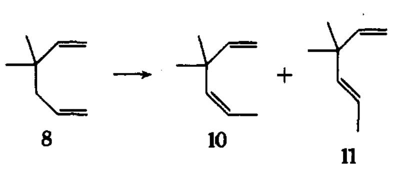
$$\frac{\mathrm{d}[d_0]}{\mathrm{d}[d_8]} = \frac{k_{\mathrm{H}}}{k_{\mathrm{D}}}\frac{[d_0]}{[d_8]} \qquad (2)$$

rangement and integration of equation 2 leads to eq 3 for the deuterium isotope effect of the photorearrangement.

The isotope effect $k_{\mathrm{H}}/k_{\mathrm{D}} = 1.55 \pm 0.03$ was calculated from the $[d_8]$ and $[d_0]$ after five different times of irradiation using eq 3.

$$\frac{k_{\mathrm{H}}}{k_{\mathrm{D}}} = \frac{\ln [d_0] - \ln [d_0]^{\circ}}{\ln [d_8] - \ln [d_8]^{\circ}} \qquad (3)$$

3,3-Dimethyl-1,5-hexadiene (8). Irradiation (254 nm) of the acyclic 1,5-diene **8** in the presence of the corresponding rhodium chloride complex (**12**) in ether solution gives 18% of *cis*-3,3-dimethyl-1,4-hexadiene (**10**) and 82% of *trans*-3,3-dimethyl-1,4-hexadiene (**11**). The cis isomer **10** is stable under the reaction conditions. Thus, photolysis of an ether solution of **10** in the presence of **12** gives only traces of **11**, derived no doubt from decomposition of **12** under conditions which give predominantly **11** from **8**.



Discussion

Primary Photoproduct from 1,5-Cyclooctadiene (1). The 1,4-diene **4** is the exclusive primary photoproduct from the 1,5-diene **1** since the *initial* rate of appearance of the 1,4-diene **4** equals the rate of disappearance of the 1,5-diene. Furthermore, **5**, **6**, and **7**, the other major products of photoreactions of **1**, are observed to arise from further rearrangement of **4** (Scheme I).[19]

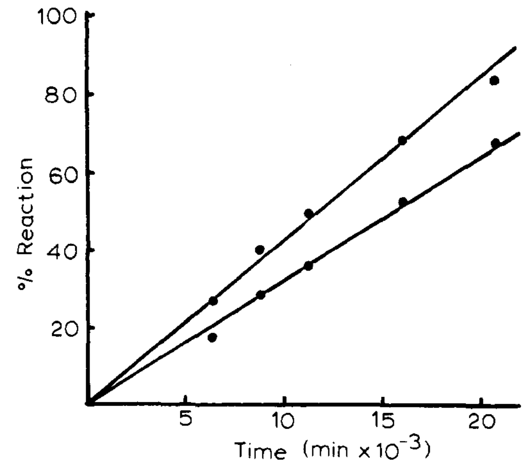
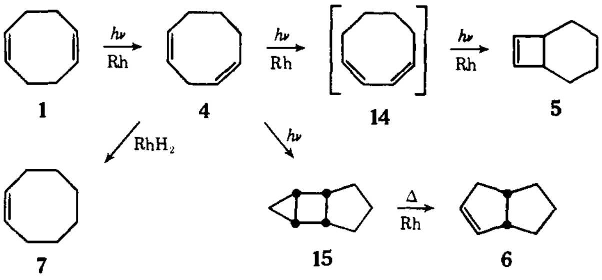


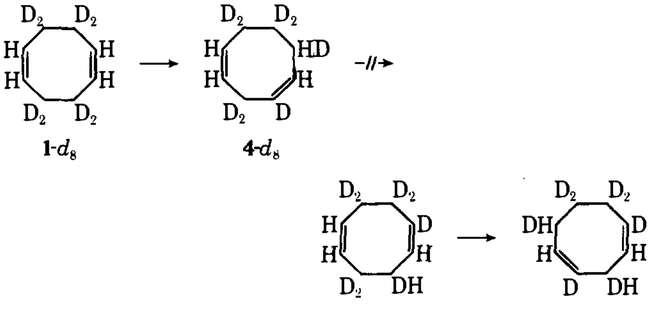
Figure 4. Percent reaction as a function of time of irradiation: (upper line) perhydro; (lower line) octadeuterio-1,5-cyclooctadiene.

Scheme I



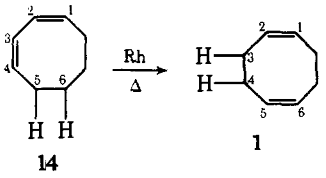
Bicyclooctene **5** arises from rhodium catalyzed photocyclization of 1,3-cycloctadiene (**14**). We confirmed the ready photocyclization of **14** upon irradiation (254 nm) in the presence of rhodium chloride. Formation of **14** undoubtedly involves rhodium assisted allylic rearrangement of 1,4-cyclooctadiene (**4**). Finally, production of bicyclo[3.3.0]oct-2-ene (**6**) is an artifact. In the absence of rhodium(I), the 1,4-diene **4** gives **15** which, we have confirmed, gives **6** in the presence of rhodium(I) in a dark reaction. The observation that the relative yield of **6** vs. **5** is greatly increased from **4**-d_8 vs. **4**-d_0 (see Table I) is readily accommodated by the mechanism of Scheme I. Rearrangement of **4**-d_8 to deuterated **5** involves cleavage of a C–D bond in a [1,3] hydride shift which yields the intermediate **14**. Formation of **5** in the deuterated series is therefore retarded by a deuterium isotope effect while rearrangement to deuterated **15**, which does not involve C–D cleavage, is not retarded. The formation of **7** will be discussed in a later section.

Intramolecular Rhodium(I) Catalyzed 1,3 Hydride Shift. The NMR spectrum of **4**-d_8 from rearrangement of **1**-d_8 is in accord with the spectrum expected for the product of a [1,3] shift of deuterium. The observed deuterium isotope effect ($k_{\mathrm{H}}/k_{\mathrm{D}} = 1.55$) for the rate of disappearance of **1** also supports a mechanism involving the rate-determining cleavage of an allylic C–H bond in **1**. Importantly, the reverse rearrangement **4** → **1** would result in scrambling of the deuterium label in **1**-d_8 and eventually in **4**-d_8. The ob-

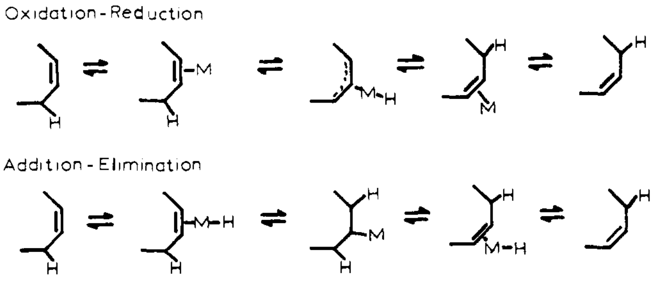


served absence of scrambling in recovered 1-d_8 establishes the irreversibility of the 1 → 4 rearrangement. This irreversibility undoubtedly reflects the greater ease of the competing 4 → 14 conversion which involves cleavage of a doubly allylic C-H bond.

Several groups have noted the possibility that the shift of C=C bonds in metal promoted photochemical isomerizations of 1,5-cyclooctadiene may occur by a skeletal reorganization involving cleavage of C—C bonds and not by hydrogen shifts.[7,20] The present study excludes the operation of such a mechanism in the rhodium catalyzed photorearrangement of 1,5-cyclooctadiene. A mechanism not involving 1,4-cyclooctadiene (4) as an intermediate was proposed for the *thermal* rearrangement of 1,3-cyclooctadiene (**14**) to 1,5-cyclooctadiene (**1**) which is catalyzed by rhodium salts. Thus, the **14** to **1** rearrangement was postulated to occur via a *hydrogen transfer* from the 5,6-position to the 3,4-position of 1,3-cyclooctadiene.[21] Such a mechanism is also excluded by the above results for the photorearrangement of 1,5-cyclooctadiene catalyzed by rhodium(I).



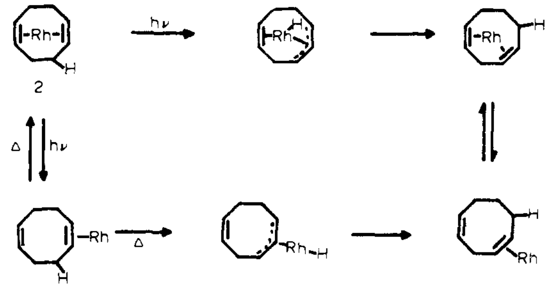
There remain two different types of mechanisms which must be considered for the 1 → 4 conversion (Scheme II).



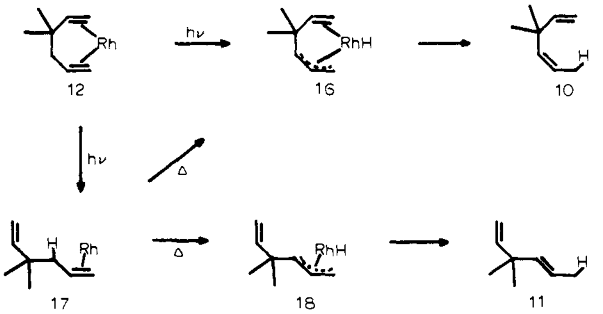
The reaction might be an *intramolecular* [1,3] hydrogen shift, possibly involving an allylrhodium(III) hydride intermediate. Alternatively an *intermolecular* mechanism, for example, involving addition-elimination of rhodium hydrides to C=C bonds, might be operative. These two mechanisms have been proposed for *thermal* interconversions of cyclooctadienes catalyzed by rhodium salts.[22] However, because of a lack of appropriate experimental information, neither mechanism has been established for these reactions. The results of a crossover experiment for photorearrangement of **1** in the presence of rhodium(I) are complicated by a slight net loss of deuterium label. Nevertheless, crossover is not observed, and the main if not exclusive pathway for the 1 → 4 rearrangement is an intramolecular [1,3] shift of hydride.

Photodissociative Activation of the Olefin-Catalyst Complex. The observed linear dependence of the rate of reaction of **1** upon time of irradiation (Figure 1) and the absence of any induction period (Figure 4) both demonstrate that the catalyst is not produced photochemically. The catalyst is present from the start and is undoubtedly the 1,5-diene-rhodium(I) complex **2** itself. The zero-order dependence of reaction rate on 1,5-diene concentration and the dependence of the relative reaction rates of 1-d_0 and 1-d_8 on their relative concentrations, both can be readily understood if rearrangement occurs only upon absorption of light by a diene rhodium complex **2** of constant concentration equal to the total rhodium(I) concentration.

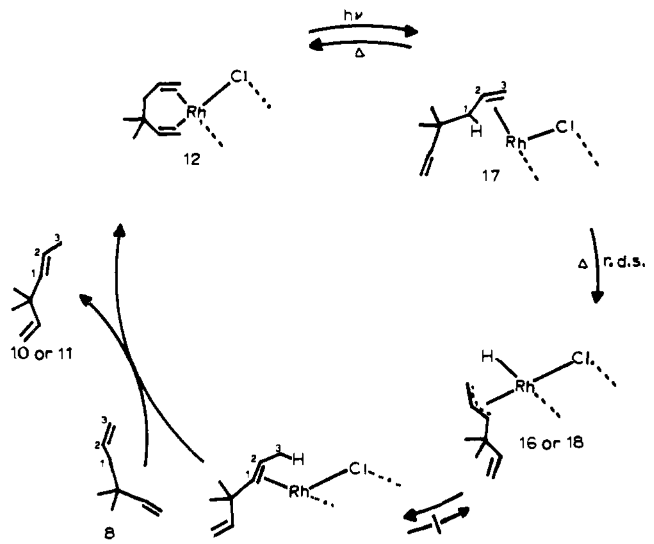
The above experiments do not define the precise role of ultraviolet light in the rearrangement reaction mechanism. Thus, at least two different mechanisms (outlined in Scheme III) could account for the observed rearrangement. In one mechanism, photoexcitation of the diene-rhodium complex **2** leads to oxidative addition of an allylic carbon-hydrogen bond to rhodium producing directly an allylrhodium hydride intermediate which gives a rhodium complex of 1,4-cyclooctadiene by reductive elimination. Alternatively photoexcitation of a diene-rhodium complex leads to photodissociation of one of the olefin ligands to give a coordinatively unsaturated monoolefin-rhodium complex. The complex undergoes a subsequent dark reaction in which an allylic carbon-hydrogen bond oxidatively adds to rhodium to afford an allylrhodium hydride intermediate. Reductive elimination then gives rhodium complex of 1,4-cyclooctadiene. Both mechanisms give the same product and are therefore indistinguishable.



In order to distinguish between these two possible reaction mechanisms, we examined the photorearrangement of 3,3-dimethyl-1,5-hexadiene (**8**) in the presence of the corresponding rhodium chloride complex (**12**) (Scheme IV). Direct oxidative addition of an allylic carbon-hydrogen bond in a photoexcited diene complex would produce a cisoid allylrhodium hydride intermediate (**16**). Reductive elimination would then lead to *cis*-3,3-dimethyl-1,4-hexadiene (**10**). An alternative photodissociation of the diene-rhodium chloride complex would produce a coordinatively unsaturated rhodium-olefin complex (**17**). Oxidative addition of an allylic carbon-hydrogen bond to rhodium in a subsequent reaction, which may involve either an excited or ground state of **17**, could produce either a cisoid (**16**) or a transoid (**18**) allylrhodium hydride intermediate. These intermediates would in turn lead to *cis*- or *trans*-3,3-dimethyl-1,4-hexadiene, respectively. The *gem*-dimethyl substitution was employed to prevent further complicating rearrangements of **10** or **11**.

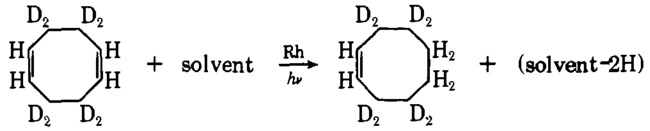


The products of the rhodium catalyzed photoisomerization (254 nm) of 3,3-dimethyl-1,5-hexadiene (**8**) are 18% *cis*-3,3-dimethyl-1,4-hexadiene (**10**) and 82% *trans*-3,3-dimethyl-1,4-hexadiene (**11**). This result is best explained by a mechanism involving an initial photodissociation step (Scheme V). Photodissociation of one of two rhodium(I) coordinated carbon-carbon double bonds results in an increase in the coordinative unsaturation of rhodium(I) and enhances the proclivity of this d_8 metal atom toward oxidative addition. Then, in a subsequent dark reaction, an allylic



carbon–hydrogen bond oxidatively adds to coordinatively unsaturated rhodium in a rate-determining competition with reformation of the diene–rhodium complex. The resulting allylrhodium hydride intermediate undergoes reductive elimination to give a rhodium complex of the corresponding 1,4-diene. The 1,4-diene ligand is then displaced by another molecule of 1,5-diene to give the initial 1,5-diene rhodium complex **12** and a molecule of rearranged olefin. The driving force for the last step is the greater thermodynamic stability of the rhodium complex of the 1,5-diene vs. the rhodium complex of the 1,4-diene.[23]

Photolytic Rhodium Catalyzed Hydrogen Transfer. Production of cyclooctene (**7**) during rhodium catalyzed photorearrangement of cyclooctadienes is especially interesting. Preliminary evidence suggests that the ether solvent is the source of hydrogen in this reaction. Mass spectral analysis showed that the cyclooctene from cyclooctadiene-d_8 contains little or no d_9 or d_{10} product. Hence cyclooctene arises by the addition of two hydrogen atoms to cyclooctadiene-d_8. Further work is necessary to establish the detailed mechanism of this reaction.



Hydrogen transfer from ethers to olefins catalyzed by rhodium(I) is known. However, thermally induced hydrogen transfer catalyzed by tris(triphenylphosphine)rhodium(I) chloride is negligible at temperatures below 120°.[24] The transfer hydrogenation which we observe occurs below 20°, unprecedentedly mild conditions of temperature. The reaction is inhibited by 1,5-cyclooctadiene (see Figure 1). This behavior parallels the inhibition by 1,5-cyclooctadiene of thermally induced hydrogen transfer from ethers to olefins catalyzed by rhodium(I).[25] Also, there is twice as much hydrogen transfer yielding cyclooctene (**7**), relative to rearrangement which gives **4** and **5** from **1**-d_8 compared with **1**-d_0 (see Table I). The formation of **4** and **5** involves cleavage of C–D bonds and is therefore retarded by an isotope effect. The formation of cyclooctene (**7**) involves transfer of hydrogen from solvent. The rate of this competing reaction is not affected by deuterium substitution in the cyclooctadienes. Thus, the rate of transfer hydrogenation relative to rearrangement is expected to be greater for **1**-d_8 compared with **1**-d_0. This results in the observed relatively greater amount of transfer hydrogenation vs. rearrangement for **1**-d_8 compared with **1**-d_0.

It is reasonable to assume that the photochemical rhodium catalyzed transfer hydrogenation which we observe is mechanistically similar to the previously observed thermal reaction. In particular, oxidative addition to rhodium of the α-C–H bond of the ether solvent is a likely rate-determining step. Hydrogenation of the olefin occurs by reaction with a rhodium(III) dihydride intermediate which is generated by β-elimination from the initially formed alkylrhodium(III) hydride. The role of ultraviolet light in the hydrogen transfer is most likely the same as in rhodium(I) catalyzed allylic photorearrangements. Thus, light-induced dissociation of a rhodium coordinated ligand increases the coordinative unsaturation of rhodium(I), enhancing its proclivity toward the rate-determining oxidative addition.

Conclusions

Rhodium(I)–olefin complexes under ultraviolet irradiation catalyze allylic rearrangement of olefins by an intramolecular hydride shift. A key step in the reaction is the photodissociation of one of two rhodium(I)-coordinated carbon–carbon double bonds. The resulting coordinatively unsaturated rhodium(I)-monoolefin complex rearranges to an allylrhodium(III) hydride intermediate in a subsequent dark reaction. Rearranged olefin is formed from this intermediate by reductive elimination of rhodium.

Cyclooctene is produced from cyclooctadienes as a side product during rhodium catalyzed photorearrangement. Photogenerated, coordinatively unsaturated rhodium(I) species are likely catalysts of this reduction. As expected for a rhodium catalyzed hydrogen transfer, the reduction is inhibited by 1,5-cyclooctadiene due to the proclivity of this diene to act as a chelating tetrahapto ligand.

Experimental Section

General. All photolyses were conducted in cylindrical quartz vessels which were cooled with an internal water-cooled cold finger. The reaction mixtures were stirred magnetically and irradiated externally with a Rayonette photochemical reactor (Southern New England Ultraviolet Co. Model RPR-100). All rhodium catalyzed photorearrangements were conducted with 254-nm lamps. Preparative gas–liquid phase chromatography was performed with a Varian Model 202B instrument. Analytical gas–liquid phase chromatography was performed with a Varian Model 1400 instrument. Proton magnetic resonance spectra were recorded with a Varian A60A or HA100FT spectrometer with tetramethylsilane as an internal standard and CCl_4 as solvent unless otherwise indicated. Carbon magnetic resonance spectra were recorded with a Varian XL100 spectrometer with tetramethylsilane as internal standard and $CDCl_3$ as solvent. Mass spectra were recorded with a Varian M66 instrument or directly from a gas chromatograph using a Varian-Mat MS9 instrument. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

Materials. Cycloocta-1,5-diene and 1,3-cyclooctadiene were freshly distilled before use. Diethyl ether for photolyses was freshly distilled from lithium aluminum hydride under dry nitrogen immediately before use. Bicyclo[4.2.0]oct-7-ene,[26] buta-1,3-diene-*1,1,4,4*-d_4,[27] tetrakis[triphenyl phosphite]nickel(0),[28] 2,2-dimethyl-3-butenal,[29] 2,2-dimethyl-4-pentenal,[30] μ-dichloro-bis[η^4-1,5-cyclooctadiene]dirhodium(I) chloride,[7b] 1,4-cyclooctadiene,[31] and *cis,syn,cis*-tricyclo[5.1.0.0^{2,6}]octane[16] were prepared by known procedures.

Cycloocta-1,5-diene-*3,3,4,4,7,7,8,8*-d_8 (1-d_8). The title compound was prepared by dimerization of butadiene-*1,1,4,4*-d_4 in the presence of $Ni[P(OPh)_3]_4$ as catalyst.[9] The desired product was separated from octadeuterio-4-vinylcyclohexene by distillation with a 24 ft Perkin-Elmer spinning band distillation apparatus.

μ-Dichloro-bis[η^4-1,5-cyclooctadiene-*3,3,4,4,7,7,8,8*-d_8]dirhodium(I) Chloride (2-d_8). The title compound was prepared by the procedure of Chatt and Venanzi[7b] for the preparation of the rhodium chloride complex of the unlabeled diene but using 1,5-cyclooctadiene-d_8 (**1**-d_8) in place of the unlabeled diene. The ^1H NMR spectrum of **2**-d_8 indicated a slight loss of allylic deuterium (incorporation of hydrogen into the allylic positions): **2**-d_0 [($CDCl_3$) δ 1.5–2.0 (4 H, m, allyl), 2.3–2.8 (4 H, m, allyl), 4.1–4.4 (4 H, m, vinyl] and **2**-d_8 [($CDCl_3$) δ 1.5–2.0 (0.8 H), 2.3–2.8 (0.8 H), 4.24 (4, H, d, J = 2.5 Hz, vinyl)].

3,3-Dimethyl-1,5-hexadiene (8). A suspension of $MeP(Ph)_3Br$ (0.1 mol) in tetrahydrofuran (250 ml, freshly distilled from sodium benzophenone ketyl) was treated with MeLi (0.1 mol) in ether at 0–10° with magnetic stirring. The resulting mixture was stirred at 10–20° for 2 hr. After cooling to 0°, 2,2-dimethyl-4-pentenal (0.08 mol) was added dropwise, and the resulting mixture was stirred for 10 hr at room temperature. It was then poured into a mixture of water (200 ml) and pentane (200 ml). The pentane extract was washed with water (5 × 200 ml) and dried ($MgSO_4$), and solvent was removed by distillation through a 10-cm Vigreux column. The residue was distilled under reduced pressure to yield **8** (67%), bp 54–56° (110 mm). Further purification was accomplished by preparative gas chromatography as described previously:[32] NMR ($CDCl_3$, 60 MHz) δ 0.98 (6 H, s, methyl), 2.4 (2 H, d, J = 7 Hz, methylene), 4.7–5.2 (4 H, C-1, 6), 5.4–6.1 (2 H, C-2, 5).

μ-Dichloro-bis[η^4-3,3-dimethyl-1,5-hexadiene]dirhodium(I) Chloride (12). Rhodium trichloride hydrate (Englehard) (250 mg) was stirred with 3,3-dimethyl-1,5-hexadiene in ethanol–water 5:1 (4 ml) at room temperature for 2 days. Analytically pure complex **12** was obtained (133 mg) by filtration under a positive pressure of nitrogen and washing with ethanol–water 5:1 (1 ml). The complex was dried under a stream of dry nitrogen to give yellow needles: mp 126–127°; NMR ($CDCl_3$, 60 MHz) δ 0.98 (1 H, dd, J = 9 Hz, J = 13 Hz, C-4), 1.02 (3 H, s, methyl), 1.5–2.1 (2 H, C-4 and vinyl), 2.02 (3 H, s, methyl), 2.78 (1 H, dd, J = 2.5 Hz, J = 6 Hz, vinyl), 2.95 (1 H, t, J = 2.5 Hz, vinyl), 3.81 (1 H, broad d, J = 7 Hz, vinyl), 3.9–4.8 (2 H, vinyl). Anal. Calcd for $C_8H_{14}ClRh$: C, 38.66; H, 5.68. Found: C, 38.69; H, 5.58.

***cis*-3,3-Dimethyl-1,4-hexadiene (10).** A suspension of $EtP(Ph)_3Br$ (26 g, 70 mmol) in tetrahydrofuran (200 ml, freshly distilled from sodium benzophenone ketyl) was treated with MeLi (66 mmol) in ether (39 ml) at 0–10° with magnetic stirring. The resulting mixture was stirred at 10–20° for 2 hr. After cooling to 0°, 2,2-dimethyl-3-butenal (4.9 g, 50 mmol) was added dropwise at 5–10°. The resulting mixture was stirred for 10 hr at 20–25° and then worked up as for **8** above: NMR (CCl_4, 100 MHz) δ 1.15 (6 H, s, C-3-methyl), 1.62 (3 H, d, J = 5 Hz, C-6-methyl), 4.87 (1 H, d, J = 10 Hz, *cis*-C-1-vinyl), 4.94 (1 H, d, J = 17 Hz, *trans*-C-1-vinyl), 5.2–5.4 (2 H, C-4,5-vinyl), 5.90 (1 H, dd, J = 10, J = 17 Hz, C-2-vinyl); ir 685, 714, 733, 910, 955, 1000, 1038, 1157, 1355, 1630, 2960, 3090 cm^{-1}.

***trans*-3,3-Dimethyl-1,4-hexadiene (11).** A solution of the cis isomer **10** (2 g) and benzophenone (2 g) in pentane (150 ml) was irradiated in a quartz cylindrical vessel, fitted with a reflux condenser and a head of nitrogen, in a Rayonette photochemical reactor with 350-nm lamps for 20 hr. The solution was decanted from crystals (oxetane ?) which had deposited on the walls of the reaction vessel. Pentane was removed by distillation through a 20-cm Vigreux column. The residue was distilled through a short-path distillation head under slightly reduced pressure (200 mm) to give 1.2 g of a 1:1 mixture of **10** and **11**. The isomers were separated preparatively by gas–liquid phase chromatography with a 10 ft × 0.25 in. column packed with 40% of a saturated solution of $AgNO_3$ in glycerol on 30–60 Chromosorb P at 55°.[15] Relative retention times were for trans isomer **11** (1.0) and cis isomer **10** (1.7): NMR (CCl_4) δ 1.06 (6 H, s, C-3-methyl), 1.65 (3 H, d, J = 3 Hz, C-6-methyl), 4.83 (1 H, d, J = 11 Hz, *cis*-C-1-vinyl), 4.86 (1 H, d, J = 17 Hz, *trans*-C-1-vinyl), 5.34 (2 H, C-4,5-vinyl), 5.73 (1 H, dd, J = 11, J = 17 Hz, C-2-vinyl); ir 681, 743, 913, 971, 999, 1039, 1157, 1375, 1448, 1635, 2960, 3100 cm^{-1}.

Rhodium(I) Catalyzed Thermal Rearrangement of Tricyclo[5.1.0.0^{2,6}]octane (15). A solution containing *cis,syn,cis*-tricyclo[5.1.0.0^{2,6}]octane (20 mg) and the rhodium(I) complex **2**-d_0 (2 mg) in $CDCl_3$ (0.3 ml) was kept at 35° in the probe of a Varian A60A NMR spectrometer. The rearrangement into bicyclo[3.3.0]oct-2-ene was followed by monitoring the absorption at δ 5.5 due to the vinyl hydrogens of the product **6** (see Figure 2).

Rhodium(I) Catalyzed Photorearrangement of 1,5-Cyclooctadiene (1-d_0). A mixture containing 1,5-cyclooctadiene (**1**-d_0) (80 mg) and the rhodium(I) complex **2**-d_0 (8 mg) in ether (20 ml) was irradiated with 254 nm light. The products were analyzed periodically during the reaction by gas-liquid phase chromatography on a 20 ft × ⅛ in. column packed with 20% FFAP on 60–80 Chromosorb P at 75°. It was determined that no product has a retention time near that of *n*-butylcyclohexane. Therefore, this alkane was used as an internal standard for determination of yields. The relative retention times of **1**-d_0 and the major products are: 1,5-cyclooctadiene (1.67), 1,4-cyclooctadiene (1.22), *n*-butylcyclohexane (1.00), cyclooctene (0.83), and bicyclooctenes **5** and **6** (0.64). After completion of the irradiation, the resulting solution was washed to remove rhodium salts with a mixture of ice (20 g) and ammonium hydroxide (10 ml) and then with water (20 ml), and then was dried (Na_2SO_4). Ether was removed by distillation through a 20-cm Vigreux column. The reaction products were isolated by preparative gas–liquid phase chromatography on a 10 ft × 0.25 in. column packed with 20% FFAP on 60–80 Chromosorb P at 60°. The bicyclooctenes **5** and **6** were obtained as a mixture which was separated by rechromatography on a 10 ft × 0.25 in. column packed with 40% of a saturated solution of $AgNO_3$ in glycerol on 30–60 Chromosorb P at 50°.[15] Relative retention times are **5** (1.00) and **6** (1.38). The reaction products were identified by spectral comparison with authentic samples.

Rhodium(I) Catalyzed Photorearrangement of 1,5-Cyclooctadiene-d_8 (1-d_8). The deuterated diene **1**-d_8 was irradiated (254 nm) in the presence of the rhodium(I) complex **2**-d_8 in ether solution by the same procedure as outlined above for **1**-d_0. Unreacted **1**-d_8 isolated from the reaction product mixture after 50% conversion was identical with starting diene according to proton magnetic resonance and mass spectral analysis. The rearranged 1,4-diene **4**-d_8 was isolated as for **4**-d_0 above. For proton magnetic resonance spectrum, see Figure 3. Additional products **5**-d_8, **6**-d_8, and **7**-d_8 were also isolated.

Rhodium(I) Catalyzed Photorearrangement of 1,4-Cyclooctadiene (4). Irradiation (254 nm) of **4** (80 mg) in the presence of rhodium(I) complex **2** (8 mg) in ether (20 ml) was carried out as for **1**-d_0 above. Products were isolated after 25% conversion and identified by comparison with authentic samples as for **1**-d_0 above.

Rhodium(I) Catalyzed Photorearrangement of 1,3-Cyclooctadiene (14). Irradiation (254 nm) of **14** (300 mg) in the presence of **2** (8 mg) in ether (50 ml) gave a 50% conversion to a single product **5** after 75 hr. The product was isolated and identified by comparison with an authentic sample as for **1**-d_0 above.

Rhodium(I) Catalyzed Photorearrangement of a 1:1 Mixture of 1-d_0 and 1-d_8. A mixture of **1**-d_0 (80 mg), **1**-d_8 (80 mg), **2**-d_0 (8 mg), and adamantane (60 mg, internal standard) in ether (20 ml) was irradiated (254 nm), and the composition of the reaction product mixture was analyzed periodically during the reaction by gas-liquid phase chromatography on a 15 ft × ⅛ in. column packed with 20% FFAP on 60–80 Chromosorb P at 70°. Relative retention times on this column are **1**-d_8 (0.62), **1**-d_0 (0.65), and adamantane (1.00). Complete (baseline) separation of **1**-d_0 and **1**-d_8 was not achieved. However, the detector response to these compounds is essentially the same. Therefore, it was possible to calculate the absolute concentrations of **1**-d_0 and **1**-d_8 from a determination of their total concentration (total peak area relative to internal standard) and relative peak heights by the use of a calibration curve (which was a straight line) relating relative peak heights to mole ratio. After almost complete conversion of **1**-d_0, the mixture of labeled 1,4-diene products **4** was isolated after the usual workup by gas-liquid phase chromatography as for **1**-d_0 above. Care was taken to collect all **4** and not to fractionate variously labeled material. This mixture of labeled **4** was analyzed by mass spectroscopy for isotopic composition at low ionizing voltage (18–22 eV). The precision of the isotope ratio determination was about ±1%; d_0 = 49%, d_1 = 1%, d_2–d_6 = 0%, d_7 = 7%, and d_8 = 43%.

Rhodium(I) Catalyzed Photorearrangement of 3,3-Dimethyl-1,5-hexadiene (8). A solution containing **8** (80 mg) and the corresponding rhodium(I) complex **12** in pentane (20 ml) was irradiated (254 nm) with magnetic stirring and water cooling in a cylindrical quartz tube. The reaction was essentially complete after 65 hr. After the usual work-up (see for example the photorearrangement of **1**-d_0 above), the sole volatile products, **10** and **11** (18 and 82%, respectively), were analyzed and isolated by gas-liquid phase chromatography on a 10 ft × 0.25 in. column packed with 40% of a saturated solution of $AgNO_3$ in glycerol on 30–60 Chromosorb P at 55°. Relative retention times on this column are *trans*-1,4-diene **11** (1.0), *cis*-1,4-diene **10** (1.7), and 1,5-diene **8** (4.4). The products were identified by spectral comparison with authentic samples.

Irradiation of *cis*-3,3-Dimethyl-1,4-hexadiene (10) in the Presence of 12. A solution of **10** (40 mg) and the rhodium complex **12** (8 mg) in pentane (15 ml) was irradiated (254 nm). The reaction mixture gradually deposited an orange-yellow solid on the walls of the quartz vessel, and the solution went from yellow to colorless over a period of 49 hr. The resulting solution contained *cis*-1,4-diene **10** (89%) and *trans*-1,4-diene **11** (11%).

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, and to the Chemistry Department of Case Western Reserve University for support of this research. We also thank Dr. John Sanders and the T. R. Evans Research Center of the Diamond Shamrock Corp. for assistance and the use of their GC-mass spectroscopy instrument.

References and Notes

(1) Freshman undergraduate research participant.
(2) For reviews see: (a) E. K. von Gustorf and F.-W. Grevels, *Fortschr. Chem. Forsch.*, **13**, 366 (1969); (b) J. Halpern, *Adv. Chem. Ser.*, **No. 70**, 1 (1968); (c) R. Crammer, *Acc. Chem. Res.*, **1**, 186 (1968); (d) J. P. Collman, *ibid.*, **1**, 136 (1968); (e) W. Keim in "Transition Metals in Homogeneous Catalysis", G. N. Schrauzer, Ed., Marcel Dekker, New York, N.Y., 1971, pp 59–92; (f) C. A. Tolman, *Chem. Soc. Rev.*, **1**, 337 (1972).
(3) M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Organomet. Chem.*, **70**, 283 (1974), and references cited therein.
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Nonlinearity in Buffer–Rate Relationships. The Significance of Carboxylate–Acid Complexes[1]

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Abstract: The observed rate constants for nitroethane ionization increase linearly with acetate buffer concentration up to 2 *M* when the ionic strength is maintained at 2.0 *M* with potassium trifluoroacetate. A small upward curvature when the ionic strength is maintained with potassium nitrate is attributed to a specific salt effect. A larger upward curvature for cyclohexanone enolization is found with both trifluoroacetate and nitrate and is attributed to bifunctional acid-base catalysis. No evidence for buffer association was found for these reactions. However, plots of observed rate constants against formate buffer concentrations of up to 2 *M* for the reaction of formate with iodine and for the protonation of nitroethane anion exhibit downward curvature that can be accounted for by the formation of an unreactive $(HCOOH{\cdot}OOCH)^-$ anion with an association constant $K_{12} = 0.25\ M^{-1}$. The hydrolysis of benzylhydrylidenedimethylammonium ion exhibits "negative catalysis" by formic acid that can be accounted for by the decrease in water concentration in concentrated buffer solutions if it is assumed that four water molecules are required for water-catalyzed hydrolysis. Other causes of nonlinear plots of rate against buffer concentration are illustrated and discussed.

A break in a plot of rate against buffer concentration that is caused by a change in rate-determining step is one of the most useful results that can be obtained from kinetic experiments because such a break demonstrates that the reaction must proceed through at least two steps and an intermediate. The identification of such a break is usually straightforward when it occurs at low buffer concentration at a constant ionic strength and pH, but curvature in plots of rate against buffer concentration is more difficult to interpret in concentrated buffer solutions because buffer complexation and other factors can also give rise to curvature. The experiments reported here were undertaken after the appearance of several reports describing a nonlinear dependence of rate on the concentration of acetate and formate buffers, in the hydrolysis of ketene acetals and lactonization, that was attributed to the formation of inactive