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RHODIUM CATALYZED REACTIONS OF BICYCLIC HYDROCARBONS. PRODUCTS, MECHANISM, AND THE NATURE OF THE CATALYST *

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Summary

The rhodium complexes $Rh(PPh_3)_3Cl$ and $Rh(PPh_3)_2(CO)Cl$ catalyze the ring opening of *endo*-6-carbomethoxybicyclo[3.1.0]hex-2-ene (I) forming the five possible isomeric carbomethoxycyclohexadienes II—VI. The rate of the reaction is dramatically accelerated by the presence of O_2, and the dioxygen complex $[Rh(PPh_3)_2(Cl)O_2]_2$ has been shown to be an active catalyst precursor for the reactions. A mechanism involving the intermediacy of cyclohexadienylrhodium hydride complexes accounts for the products formed and their subsequent interconversions.

Introduction

Structural rearrangements of strained hydrocarbons have been of interest to organic chemists for some time. The discovery [3] that metal complexes with appropriate electronic configurations and ancillary ligands can relax symmetry restraints imposed by the Woodward—Hoffman Rules [4] not only intensified the interest of organic chemists, but introduced inorganic chemists to the area as well. Primary emphases have been the detailed mechanisms of metal-catalyzed transformations of strained organic molecules, the metal—hydrocarbon orbital and electronic interactions, and the nature of the active metal catalysts.

We have investigated the metal complex promoted reactions of bicyclic hydrocarbons which have available to them a variety of reaction pathways. The most intensively studied organic substrate was *endo*-6-carbomethoxybicyclo[3.1.0]-hex-2-ene (I) and we describe herein the results obtained for this molecule in the presence of a variety of metal catalysts. A dramatic effect of dioxygen on the catalysts $Rh(PPh_3)_3Cl$ and $Rh(PPh_3)_2(CO)Cl$ has been discovered [1] and is also

* A preliminary report of portions of this work has appeared [1]. Abstracted from the thesis of D.L. Beach [2].

discussed herein. Results for related systems which demonstrate the effects of structural changes in the organic substrate are reported in the following paper [5].

Experimental

Proton NMR spectra were recorded on Varian T-60 or Perkin—Elmer R-20 High Resolution Spectrometers, using tetramethylsilane as internal standard for chemical shift measurements. Infrared spectra were obtained on a Perkin—Elmer 337 or 521 High Resolution Grating Spectrophotometer. Matched 0.1 mm KBr solution cells from International Crystal Laboratories (Irvington, New Jersey) were used and frequencies calibrated with the 1601.4 cm^{-1} band of polystyrene. Ultraviolet spectra were determined on a Perkin—Elmer 202 or Beckman ACTA MVI Ultraviolet Visible Spectrophotometer using matched 1.0 cm path length quartz cells. Calibration of absorptions was accomplished with the 361 nm band of holmium oxide. Mass spectra were recorded on an AEI MS-9 mass spectrometer at an ionizing voltage of 70 eV. VPC analyses were performed on Varian Aerograph Model 700 or 705 gas chromatographs, equipped with preparative collection accessories.

All solvents used were reagent grade and dried over appropriate materials prior to use. Catalyst poisoning was observed when commercial samples of $CDCl_3$ were used, presumably from the presence of HCl. For that reason, experiments were conducted in $CHCl_3$ containing 0.75% ethanol as a free-radical inhibitor. All glassware was rinsed successively with dilute sodium bicarbonate solution and deionized water and oven-dried before use.

The following metal compounds were purchased from Strem Chemicals, Inc.: $(PPh_3)_2Ir(CO)Cl$, $[Rh(CO)_2Cl]_2$, $[Rh(C_2H_4)_2Cl]_2$, $(PPh_3)_2PdCl_2$, $(PPh_3)_2Pd(C_6H_5CN)_2$, $(PPh_3)_4Pd$, $Fe_2(CO)_9$. They were used without further purification and stored according to the label instructions. $(PPh_3)_3RuCl_2$ was purchased from Alfa Inorganics and used as received. $(PPh_3)_3RhCl$ [6], $(PPh_3)_2Rh(CO)Cl$ [6], and $[(PPh_3)_2RhCl]_2$ [7] were prepared by the literature methods cited.

Preparation of bis(triphenylphosphine)dioxygen rhodium chloride dimer. This compound was prepared by bubbling air through a methylene chloride solution of $(PPh_3)_3RhCl$ under the conditions described by Bennett and Donaldson [8]. Existence of the O_2 complex was confirmed by the presence of an O—O stretch [8] in the IR spectrum ($CHCl_3$) at 850 cm^{-1}. Elemental analysis before reaction with I: Found: C, 54.66; H, 5.40; Cl, 10.00; P, 8.43; Rh, 14.39. $C_{72}H_{60}Cl_2O_4P_4Rh_2 \cdot CHCl_3$ calcd.: C, 58.08; H, 4.07; Cl, 11.74; P, 8.21; Rh, 13.64%. Elemental analysis after reaction with I: C, 52.19; H, 4.42; Cl, 14.78; P, 7.98; Rh, 15.70%.

Preparation of organic substrates. I was prepared by esterification of the parent carboxylic acid with diazomethane [9]. II, III and IV resulted from flash vacuum pyrolysis of I (565°C, 10^{-1} mmHg) followed by preparative VPC (30' × 3/8" XF - 1150 on Chromosorb G, 130°C). V and VI were prepared by the Diels—Alder reaction of 1,3-butadiene with methylacetylenecarboxylate [10a] and esterification of the corresponding acid [10b], respectively. The dienes were characterized by NMR (Table 1) and mass spectroscopy *m/e* 138 (parent ion) in all cases. X and XI resulted from room temperature hydrogenation (Adams catalyst) of the respective bicyclo[3.1.0]hex-2-ene until 1.2 mmol of

H_2 were taken up. Products were identified by NMR and mass spectroscopy.

General procedures for ring-opening of bicyclo[3.1.0]hex-2-enes with $(PPh_3)_3RhCl$ in the presence of oxygen. Typically, 1.0 mmol of the bicyclohexane and 0.1 mmol of $(PPh_3)_3RhCl$ were mixed with 1.0 ml spectral grade $CHCl_3$ and compressed air vigorously bubbled through the solution for 60 s. The solution was then transferred to an NMR tube, which had been previously washed with dilute base to remove traces of acid and then thoroughly rinsed with deionized water and oven dried. The tube was capped and stored in the dark at room temperature. NMR spectra were recorded at appropriate intervals. (Attempted kinetic analyses were carried out with varying concentrations of $(PPh_3)_3RhCl$ and I, see text.)

After complete reaction, catalyst was removed from the solution by precipitation with hexanes. The solution containing the organic products was then analyzed by appropriate methods (IR, UV, NMR, mass spectrometry, VPC) and when necessary, the products were purified by preparative VPC.

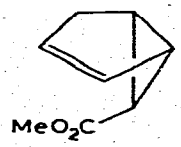
Reaction of I with $[(PPh_3)_2RhCl]_2$. In a dry box were mixed stoichiometric quantities of PPh_3 (0.0525 g, 0.20 mmol) and $[(C_2H_4)_2RhCl]_2$ (0.01925 g, 0.05 mmol) in $CHCl_3$ to generate $[(PPh_3)_2RhCl]_2$. I (0.1380 g, 1.0 mmol) was added and the resulting solution pipetted into an NMR tube. The tube was capped, sealed with parafilm, and removed from the dry box. It was stored in the dark at room temperature. No reaction was noted after three days, based on the NMR spectrum of the solution. The tube was then opened and air bubbled vigorously through the solution for 60 sec. Ring-opening commenced and after two days, the NMR spectrum showed ~67% reaction to give 1-carbomethoxy-1,3-cyclohexadiene and 5-carbomethoxy-1,3-cyclohexadiene.

Reaction of $[(PPh_3)_2Rh(O_2)Cl]_2$ with I. Into an NMR tube equipped with a standard taper fitting suitable for attachment to a vacuum system were added 0.078 g (0.05 mmol) of $[(PPh_3)_2Rh(O_2)Cl]_2$ and 0.138 g (1.0 mmol) of the *endo* ester I. The tube was evacuated to $<10^{-3}$ mmHg and 1.0 ml spectral grade $CHCl_3$, which had been rigorously degassed by repeated freeze—pump—thaw cycles, was distilled into the tube. The tube was immersed in a liquid nitrogen bath and then sealed with a torch. Reaction progress was followed by recording NMR spectra at appropriate intervals. Ring-opening occurred (~50% conversion after 48 h), yielding the conjugated carbomethoxycyclohexadiene isomers II and III.

Reaction of I with $(PPh_3)_3RhCl/O_2$ in the presence of X. This experiment was conducted with 1.0 mmol of I and 0.1 mmol of $(PPh_3)_3RhCl$ as previously described, except 1.0 mmol of X was added as well. The ring-opening reaction of I proceeded as usual and X remained unchanged.

Results and discussion

The initial system chosen for investigation was *endo*-6-carbomethoxybicyclo[3.1.0]hex-2-ene (I). It was hoped that the C_2—C_3 double bond would promote



(I)

interaction between the bicyclic molecule and transition metal compound. In addition, the substituent at C_6 provides a convenient spectroscopic "handle" for observing rearrangements which might occur. The metal complex used was Wilkinson's catalyst, $(PPh_3)_3RhCl$. Reactions were conducted on a small scale in NMR tubes in order to minimize the use of the expensive rhodium compound, and for ease in monitoring reaction progress. Early in our investigations we discovered [1] that oxygen dramatically affected the reaction and hence its presence in the system was controlled. This "oxygen effect" is the subject of later discussion.

In principle there are a variety of reaction pathways open to this and related molecules including valence isomerization, epimerization at C_6, external cyclopropane bond cleavage, and internal cyclopropane bond cleavage. I and related substrates [5] follow the latter pathway exclusively in the presence of the rhodium catalyst, the reaction products being cyclohexadienes.

The proton NMR spectrum of *endo*-6-carbomethoxybicyclo[3.1.0]hex-2-ene (I), is shown in Fig. 1. The two olefinic protons give rise to a broad singlet at δ 5.63 ppm; the three methyl hydrogens on the *endo*-carbomethoxy function produce a sharp singlet at δ 3.57 ppm; and the methylene and cyclopropane proton resonances show complex multiplets at δ 2.37—2.80 and δ 1.57—2.17 ppm, respectively. The complex multiplet centered at ~7.4 ppm is from the phenyl hydrogens of the triphenylphosphine ligands of the catalyst, $(PPh_3)_3$-RhCl.

Figure 2 shows the proton NMR spectrum after 80% reaction in the presence of oxygen (vide infra). The two new singlet resonances in the $-CO_2Me$ region are readily attributed to products. In addition, new olefin resonances at δ 5.90, 6.08, and ~6.9 ppm, and changes in the alkyl region are apparent. The continuous

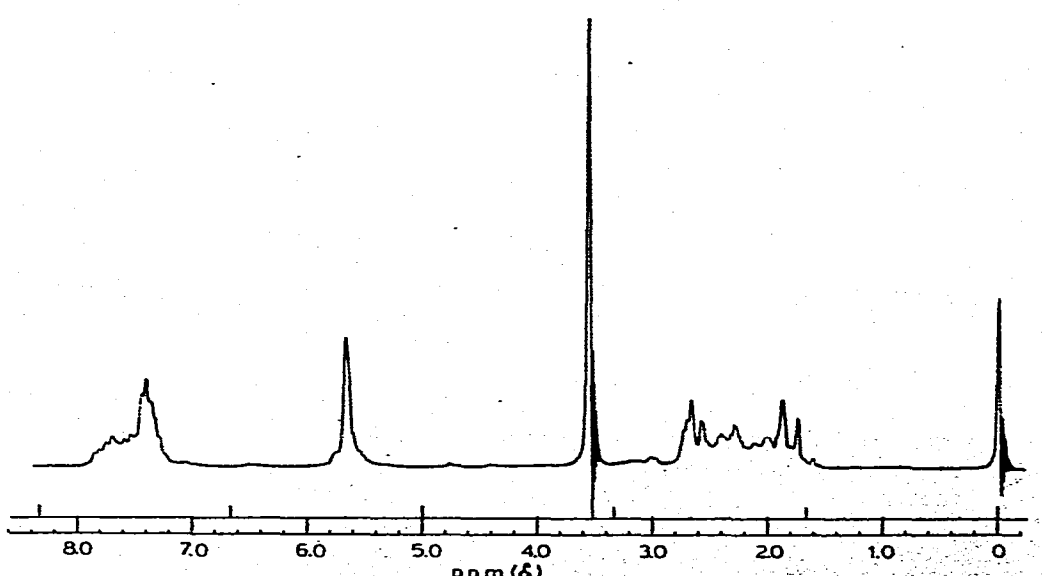


Fig. 1. Proton NMR spectrum of *endo*-6-carbomethoxybicyclo[3.1.0]hex-2-ene and $(PPh_3)_3RhCl$.

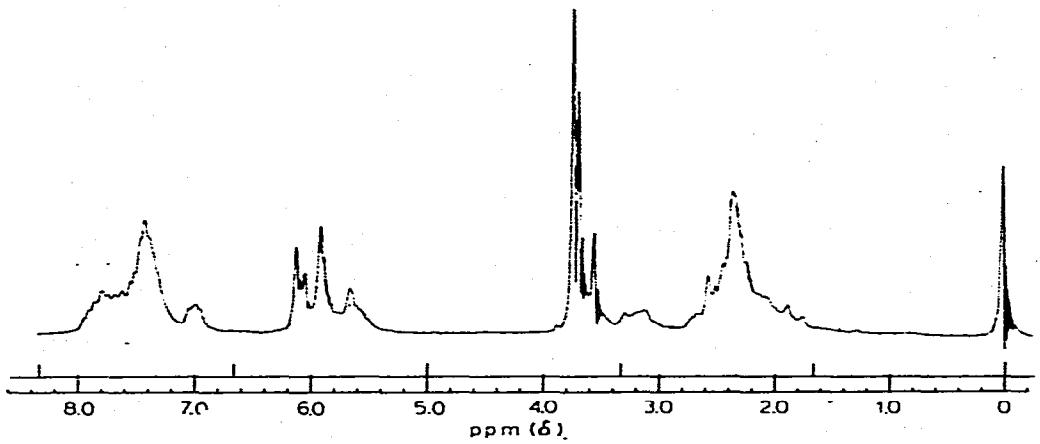
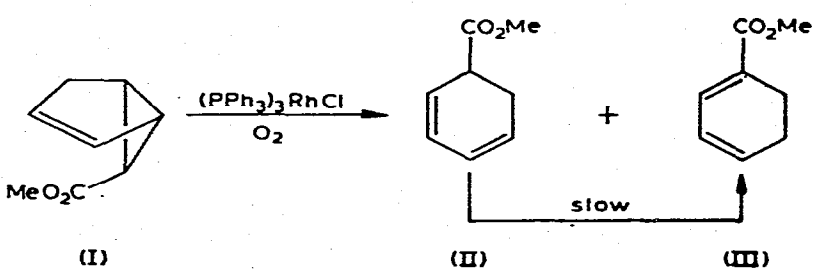


Fig. 2. Proton NMR spectrum of *endo*-6-carbomethoxybicyclo[3.1.0]hex-2-ene and $(PPh_3)_3RhCl$ after 80% reaction.

diminution of cyclopropane proton signals (<2.0 ppm) indicates that valence isomerization is not occurring to a detectable extent.

Once all starting material has reacted (based on the total disappearance of the $-CO_2Me$ singlet at δ 3.57) a slow disappearance of the resonances at δ 3.73 and 5.90 is observed, and a single product then remains. If the reaction is terminated by precipitation of the catalyst when all starting material is gone, two products are obtained. Both were isolated in pure form by preparative VPC (6′ × 1/4″ Carbowax on Chromosob W) and characterized by mass spectrometry, UV, and proton NMR spectroscopy.

The NMR spectra have been discussed above and are consistent with the formulation of the products as the conjugated cyclohexadiene isomers, II and III. The reaction may be summarized as follows:



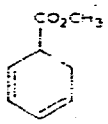
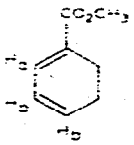
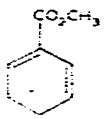
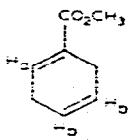
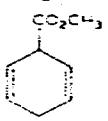
Proton-NMR data for II, III, and the remaining isomeric carbomethoxycyclohexadienes are presented in Table 1.

Although only cyclohexadienes II and III were observed in amounts detectable by NMR spectroscopy, analysis of the crude products by VPC-mass spectrometry revealed the presence of all five possible carbomethoxycyclohexadienes II—VI (see Table 1 for structures). Compounds IV—VI constituted ~5% of the product mixture after complete reaction of I.

The mass spectra of I—VI showed ions at *m/e* 138, 123, 107, and 79 which

TABLE 1

PROTON NMR DATA FOR CARBOMETHOXYCYCLOHEXADIENES [a]

Compound	Chemical shift (δ, ppm) (multiplicity) [b]	Assignment
 (II)	3.73 (s) 5.90(d) 2.32—2.63 (m) 3.05—3.33 (m)	$-CO_2CH_3$ olefin methylene methyne
 (III)	3.78 (s) 6.82—7.08 (m) 6.08 (d) 2.20—2.52 (m)	$-CO_2CH_3$ olefin (H_a) olefin (H_b) methylene
 (IV)	3.72 (s) 5.62—6.78 (m) 2.38—3.22 (m)	$-CO_2CH_3$ olefin methylene
 (V)	3.77 (s) 7.00 (s) 5.73 (s) 2.88 (s)	$-CO_2CH_3$ olefin (H_a) olefin (H_b) methylene
 (VI)	3.72 (s) 5.87 (s) 1.52—2.80 (m)	$-CO_2CH_3$ olefin methylene, methyne

[a] $CDCl_3$ solution, TMS internal standard. [b] s, singlet; d, doublet; m, multiplet.

were assigned as P^+, $[P - CH_3]^+$, $[P - OCH_3]^+$, and $[P - CO_2CH_3]^+$, respectively. The presence of the 138 peak in all spectra further supports the assignment of the products as arising from rearrangement rather than degradation of starting material.

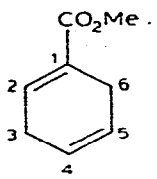
To obtain information concerning the mechanism of the ring-opening process, we investigated the possible cyclohexadiene interconversions which could occur under conditions identical to those employed in the ring-opening reaction of I. Cyclohexadienes IV—VI were synthesized and subjected to ring-opening conditions. Figure 3 summarizes the rearrangements observed.

In all cases NMR spectroscopy proved useful in monitoring isomerization. Qualitative half-lives (defined as the time necessary for 50% of the starting material to rearrange) were determined by integration of appropriate resonances. Under conditions of the ring-opening, in the presence of oxygen, V isomerized rapidly ($t_{1/2} < 1$ h) to the fully conjugated cyclohexadiene III. (The half-life of the ring-opening reaction itself was reproducibly measured at 48 h).

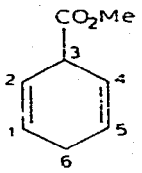
The other nonconjugated cyclohexadiene isomer, VI, behaved similarly to V,

dent [11]. It is interesting to note, however, that V rearranges to III, and not to II or IV; and that VI isomerizes to II, and not to IV.

A single 1,3-sigmatropic shift in compound V can lead to formation of all three conjugated cyclohexadienes, II—IV. Migration of a hydrogen from $C_3 \rightarrow C_5$ or from $C_6 \rightarrow C_2$ leads to the observed isomer III. If a 1,3-sigmatropic shift occurs



(V)



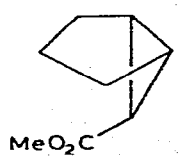
(VI)

via $C_3 \rightarrow C_1$ or $C_6 \rightarrow C_4$, isomer II or IV would be produced, respectively. The fact that only isomer III is formed from V supports the postulated intermediacy of the cyclohexadienylrhodium hydride VIII.

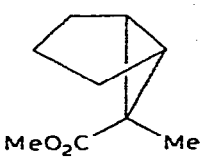
Similarly, in the non-conjugated cyclohexadiene isomer VI, a 1,3-sigmatropic shift can produce conjugated cyclohexadienes II and IV. Hydrogen migration from $C_6 \rightarrow C_4$ or C_2 leads to II, while a $C_3 \rightarrow C_1$ or C_5 hydrogen shift would produce IV. Again, the fact that only isomer II is produced from VI is consistent with the proposed existence of the cyclohexadienylrhodium hydride, IX.

There are, of course, other isomeric monosubstituted cyclohexadienylrhodium hydrides that one could draw, but there is no need to invoke their existence since they do not arise from the ring-opening process itself (see Fig. 4). Furthermore, VIII and IX account for all of the cyclohexadiene interconversions observed. The rapid isomerizations V → III and VI → II (vide infra) suggest that VIII and IX are easily formed. The sluggishness of the conjugated cyclohexadiene interconversion, II → III, would seem to indicate that IX → VIII is not as easily accomplished.

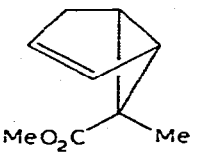
Experiments with dihydro-derivatives of bicyclo[3.1.0]hex-2-ene, i.e. in which the C_2—C_3 double bond has been hydrogenated, were important in arriving at the mechanism shown in Fig. 4. When subjected to the catalytic conditions effecting ring-opening of I, solutions of X and XI were unreactive, even when heated at 55°C for two months, whereas XII is even more reactive than I (Table



(X)



(XI)



(XII)

2). Thus while C_6 substituents affect reaction rates to a considerable extent [5], the C_2—C_3 double bond is absolutely essential in order to initiate ring-opening.

A kinetic study of the reaction of I with $(PPh_3)_3RhCl$ in the presence of oxygen was attempted in order to examine what dependence the rate showed

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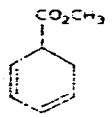
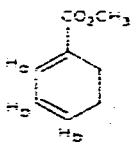
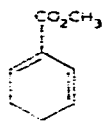
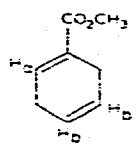
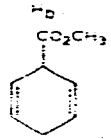
 (II)	3.73 (s) 5.90(d) 2.32—2.63 (m) 3.05—3.33 (m)	$-CO_2CH_3$ olefin methylene methyne
 (III)	3.78 (s) 6.82—7.08 (m) 6.08 (d) 2.20—2.52 (m)	$-CO_2CH_3$ olefin (H_a) olefin (H_b) methylene
 (IV)	3.72 (s) 5.62—6.78 (m) 2.38—3.22 (m)	$-CO_2CH_3$ olefin methylene
 (V)	3.77 (s) 7.00 (s) 5.73 (s) 2.88 (s)	$-CO_2CH_3$ olefin (H_a) olefin (H_b) methylene
 (VI)	3.72 (s) 5.87 (s) 1.52—2.80 (m)	$-CO_2CH_3$ olefin methylene, methyne

[a] $CDCl_3$ solution, TMS internal standard. [b] s, singlet; d, doublet; m, multiplet.

were assigned as P^+, $[P - CH_3]^+$, $[P - OCH_3]^+$, and $[P - CO_2CH_3]^+$, respectively. The presence of the 138 peak in all spectra further supports the assignment of the products as arising from rearrangement rather than degradation of starting material.

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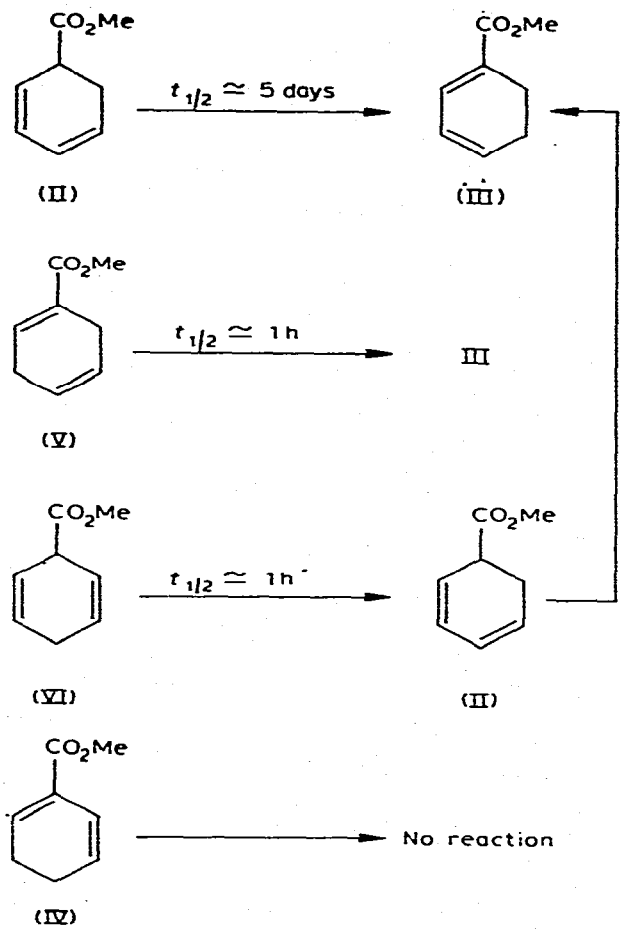


Fig. 3. Carbomethoxycyclohexadiene interconversions catalyzed by $(PPh_3)_3RhCl$ in the presence of O_2. (See text for "$t_{1/2}$" definition.)

rearranging rapidly ($t_{1/2} \approx 1$ h) to II, which then slowly converted to III, as in the original ring-opening reaction (vide supra).

Cyclohexadiene IV was found to be unreactive under ring-opening conditions and hence must not be formed in appreciable amount. If the nonconjugated cyclohexadienes, V and VI, are produced during the ring-opening process, their rapid catalytic isomerizations to III and II, respectively, would make them undetectable by NMR spectroscopy, in accord with our observations.

A proposed mechanism for the ring-opening reaction of I is presented in Fig. 4. (Other ligands bonded to rhodium have been omitted and Co_2Me abbreviated R.) The initial step involves a formal oxidative addition of the bicyclic molecule to rhodium, and is probably rate-determining. The internal cyclopropane carbon—carbon σ bond is broken and two new rhodium—carbon σ bonds are formed. Furthermore, interaction between the olefinic part of the bicyclic

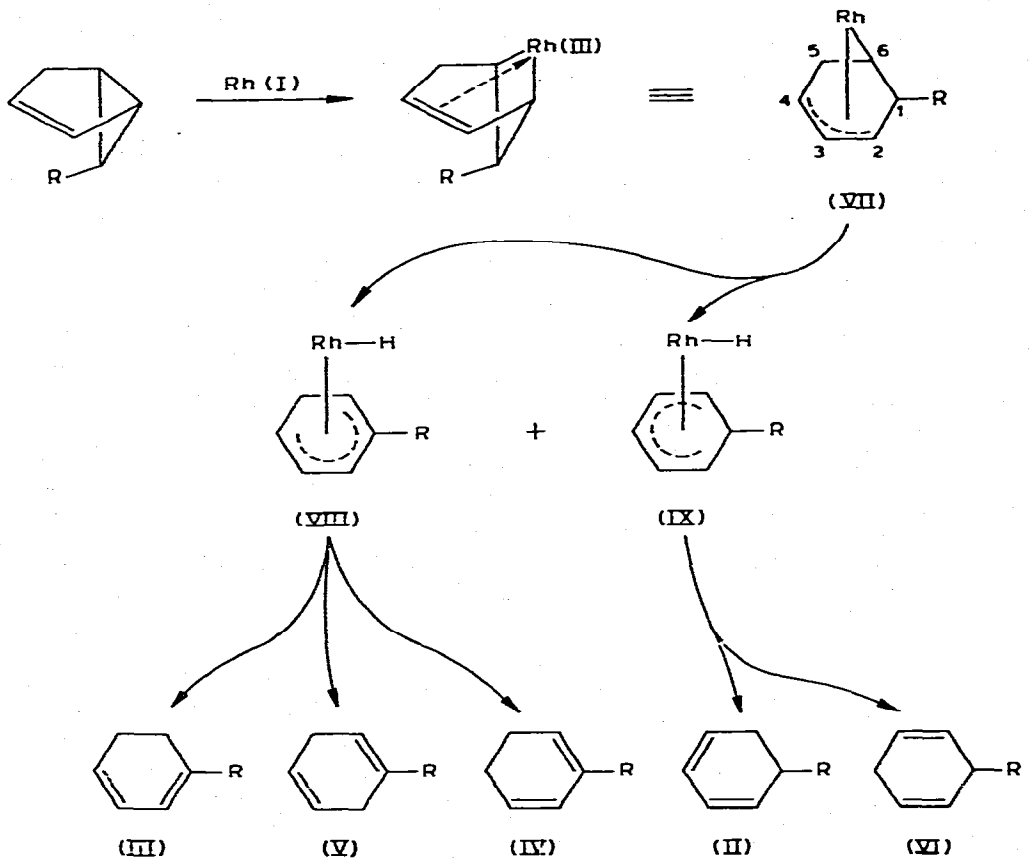


Fig. 4. Proposed mechanism for the Rh(I) catalyzed isomerization of bicyclo[3.1.0]hex-2-enes.

molecule and rhodium is suggested. This postulate has considerable precedent [3]. Evidence which supports this postulate is discussed below.

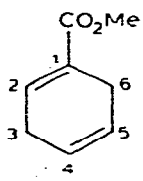
The rhodium(III) intermediate which is formed may be rewritten as an η^3-allyl complex with a fourth σ-bond to C_6, VII. Migration of a hydrogen from either C_1 or C_5 to rhodium results in formation of isomeric cyclohexadienyl rhodium hydrides, VIII and IX. It is possible, as shown in Fig. 4, to generate all the isomers for a monosubstituted cyclohexadiene from these two intermediates.

In VIII, migration of a hydrogen to C_6, C_4, or C_2 produces cyclohexadiene III, IV, or V, respectively. Similarly, in IX, reattachment of the hydrogen at either C_2 or C_6 forms II, while migration to C_4 produces VI.

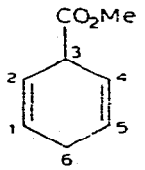
This mechanism is not only consistent with all data from the ring-opening reaction of I, but is also capable of explaining the observed carbomethoxycyclohexadiene interconversions (Fig. 3). That is, a convenient route for the conversion of V → III exists through VIII and for VI → II through IX. The ability of the catalyst to isomerize non-conjugated to conjugated dienes has ample prece-

dent [11]. It is interesting to note, however, that V rearranges to III, and not to II or IV; and that VI isomerizes to II, and not to IV.

A single 1,3-sigmatropic shift in compound V can lead to formation of all three conjugated cyclohexadienes, II—IV. Migration of a hydrogen from $C_3 \rightarrow C_5$ or from $C_6 \rightarrow C_2$ leads to the observed isomer III. If a 1,3-sigmatropic shift occurs



(V)



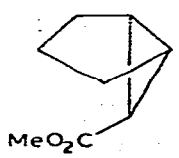
(VI)

via $C_3 \rightarrow C_1$ or $C_6 \rightarrow C_4$, isomer II or IV would be produced, respectively. The fact that only isomer III is formed from V supports the postulated intermediacy of the cyclohexadienylrhodium hydride VIII.

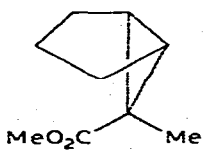
Similarly, in the non-conjugated cyclohexadiene isomer VI, a 1,3-sigmatropic shift can produce conjugated cyclohexadienes II and IV. Hydrogen migration from $C_6 \rightarrow C_4$ or C_2 leads to II, while a $C_3 \rightarrow C_1$ or C_5 hydrogen shift would produce IV. Again, the fact that only isomer II is produced from VI is consistent with the proposed existence of the cyclohexadienylrhodium hydride, IX.

There are, of course, other isomeric monosubstituted cyclohexadienylrhodium hydrides that one could draw, but there is no need to invoke their existence since they do not arise from the ring-opening process itself (see Fig. 4). Furthermore, VIII and IX account for all of the cyclohexadiene interconversions observed. The rapid isomerizations V → III and VI → II (vide infra) suggest that VIII and IX are easily formed. The sluggishness of the conjugated cyclohexadiene interconversion, II → III, would seem to indicate that IX → VIII is not as easily accomplished.

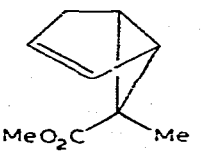
Experiments with dihydro-derivatives of bicyclo[3.1.0]hex-2-ene, i.e. in which the C_2—C_3 double bond has been hydrogenated, were important in arriving at the mechanism shown in Fig. 4. When subjected to the catalytic conditions effecting ring-opening of I, solutions of X and XI were unreactive, even when heated at 55°C for two months, whereas XII is even more reactive than I (Table



(X)



(XI)



(XII)

2). Thus while C_6 substituents affect reaction rates to a considerable extent [5], the C_2—C_3 double bond is absolutely essential in order to initiate ring-opening.

A kinetic study of the reaction of I with $(PPh_3)_3RhCl$ in the presence of oxygen was attempted in order to examine what dependence the rate showed

TABLE 2

THE EFFECT OF OXYGEN ON RATES OF RING-OPENING OF 6-SUBSTITUTED BICYCLO[3.1.0]-HEX-2-ENES

Substrate	Catalyst	Conditions[a]	$t_{1/2}$ (h)[b]
I	$(PPh_3)_3RhCl$	O_2	48
I	$(PPh_3)_3RhCl$	Ar	336
I	$(PPh_3)_2Rh(CO)Cl$	O_2	120
I	$(PPh_3)_2Rh(CO)Cl$	Ar	>720
XII	$(PPh_3)_3RhCl$	O_2	12
XII	$(PPh_3)_3RhCl$	Ar	144

[a] See experimental. [b] Defined as time required for 50% of starting material to react. See text for discussion.

on the concentrations of bicyclic hydrocarbon and rhodium. Chloroform solutions containing 0.1 *M* rhodium compound and varying amounts (0.3—1.5 *M*) of I were monitored by NMR and exhibited first order kinetic behavior initially. Eventually, however, reaction slowed considerably and the rate changed erratically, especially at higher concentrations of I. One explanation for this behavior is that the rhodium catalyst was poisoned by product complexation. This is not an unreasonable postulate in view of the large number of cyclohexadiene—metal complexes which are known [12] to exist.

Experimental support for the latter hypothesis was obtained by intentionally doping a reaction solution of I with an equimolar amount of the eventual ring-opening product II. A twin reaction solution, containing no cyclohexadiene product was run simultaneously. Integrations of the carbomethoxy region of the proton-NMR spectrum of each solution showed a pronounced inhibition of the rate of reaction by the cyclohexadiene II. After 24 h, the solution containing I and catalyst showed 28% products, while the solution containing equimolar amounts of I and II showed only 2% conversion.

Rhodium complex concentrations above 0.1 *M* could not be investigated due to the limited solubility of the O_2 complex [8] and 0.01—0.05 *M* solutions did not give reproducible results. The system is additionally complicated by the presence of oxygen, whose reaction with $(PPh_3)_3RhCl$ is not clearly understood (vide infra). Several O_2 complexes have been reported, including $[RhCl(PPh_3)_2(O_2)] \cdot xCH_2Cl_2$ (x = 0.5—5) [8], $[RhCl(PPh_3)_2(O_2)]O$ [13], $[RhCl(PPh_3)(OPPh_3)O_3] \cdot C_6H_6$ [14], and $Rh(PPh_3)_3ClO_2 \cdot 2CH_2Cl_2$ [15]. In view of the uncertainty concerning the nature of the actual catalyst in our system and the difficulties cited above, attempts at a detailed kinetic analysis were abandoned.

The "oxygen effect": nature of the catalyst

The presence of oxygen was found [1] to dramatically affect the ring-opening reactions of compounds I and related substrates [5]. In each case, when the catalyst employed was $(PPh_3)_3RhCl$, a significant difference in the half-life of ring-opening was observed, depending on whether or not oxygen was excluded from the reaction system. In addition, a similar effect of oxygen on the rate of ring-opening was observed for the $(PPh_3)_2Rh(CO)Cl$ promoted ring-opening of I. If the reactions are carried out under an inert atmosphere with argon-purged solvents, a significant rate decrease is observed, as compared to reactions con-

ducted in the presence of oxygen. These rate differences are sumarized in Table 2.

One possible explanation for this oxygen-induced rate enhancement is that molecular oxygen oxidizes the triphenylphosphine ligand to triphenylphosphine oxide and produces $[(PPh_3)_2RhCl]_2$ which could be the active species. Bis(triphenylphosphine)rhodium chloride dimer was synthesized by a conventional route [7] and placed in solution with I under conditions of air-exclusion. No reaction was observed after three days. Upon bubbling oxygen through the solution, however, ring-opening was initiated to give the previously described cyclohexadiene products, with $t_{1/2} < 48$ h. The potentially catalytically-active $[(PPh_3)_2RhCl]_2$, therefore, does not promote ring-opening of I in the absence of oxygen.

The reports that both $(PPh_3)_3RhCl$ [8,13—15] and $(PPh_3)_2Rh(CO)Cl$ [16] form complexes with O_2 suggested another possibility for the observed effect of oxygen on catalyst reactivity. Hence, the complex $[(PPh_3)_2RhCl(O_2)]_2$ was synthesized, isolated, and placed in an NMR tube equipped with a vacuum fitting, and the *endo*-ester I added. The tube was placed under a vacuum (10^{-3} mmHg) and chloroform, which had been rigorously degassed by multiple freeze—pump—thaw cycles, was distilled into the NMR tube. This tube was then sealed under vacuum and reaction progress monitored by proton-NMR spectroscopy. Ring-opening was found to occur to give the conjugated cyclohexadiene products previously described, with $t_{1/2} < 48$ h. It thus appears likely that the $[(PPh_3)_2RhCl(O_2)]_2$ species is the actual catalyst precursor in this system.

Proof of the presence of the dioxygen ligand in the catalyst before and after reaction with I was obtained from solution infrared spectra [8]. The oxygen—oxygen stretch at ~850 cm^{-1} (cf. 1554.7 cm^{-1} in the Raman spectrum of free O_2 [17]) was present in the rhodium complex before reaction, and in the recovered catalyst. Elemental analyses indicated a 2 : 1 phosphorus/rhodium ratio, supporting formulation of the rhodium complex as containing two phosphorus ligands per rhodium atom before and after reaction with I. Satisfactory analyses were also obtained for carbon, hydrogen, and chlorine, although variation in the latter (see Experimental) was noted, presumably from the existence of varying amounts of solvated $CHCl_3$ in the solids. Other workers [8,15,18] have also obtained varying analyses of this rhodium—dioxygen complex.

The reported [16] formation of an O_2 complex of $(PPh_3)_2Rh(CO)Cl$ suggests that the mode of activation may be similar to that of the $(PPh_3)_3RhCl—O_2$ system. It should be emphasized that the actual catalytic species in the systems studied is very much in doubt and no claim is made that the O_2-complexes are in themselves catalytically active, only that they more accurately describe the catalyst precursors than do $(PPh_3)_3RhCl$ and $(PPh_3)_2Rh(CO)Cl$.

It has been well established [3] that $[Rh(CO)_2Cl]_2$ in the presence of olefins produces complexes of the type $[Rh(olefin)_2Cl]_2$ which are frequently much more powerful catalysts than their dicarbonyl precursors. An example is the rapid catalytic isomerization of quadricyclane to norbornadiene by [Rh(norbornadiene)Cl]$_2$ [19]. In order to test whether a similar complex of the type [Rh(bicyclic olefin)$_2$Cl]$_2$ was formed and catalytically active its synthesis was attempted. Treatment of I with stoichiometric amount of $[Rh(CO)_2Cl]_2$ or $[Rh(C_2H_4)_2Cl]_2$ in chloroform solution in the dry box and subsequent addition of

hexanes failed to yield isolable organorhodium complexes. Repeated attempts to isolate such a complex from stoichiometric reactions of I and $(PPh_3)_3RhCl$, in the presence or absence of oxygen, also met with failure. Nevertheless, if such a complex were formed in low concentrations and showed the activity toward isomerization of strained hydrocarbons exhibited by the norbornadiene rhodium species, it could be envisioned to ring-open the dihydro species X, previously found unreactive. When a 1 : 1 mole ratio of I and X was treated in $CHCl_3$ solution with 1 mole % of $(PPh_3)_3RhCl$ in the presence of oxygen, the bicyclohexene I was ring-opened to give the previously described products and the dihydro bicyclic X remained unchanged. If a bicyclohexene—rhodium or cyclohexadiene—rhodium complex is formed, its activity as a catalyst is not sufficient to ring-open X.

The behaviour of I in the presence of transition metal compounds known to catalytically rearrange other strained hydrocarbons was also investigated. The primary aim of this study was to see if new rearrangement pathways could be opened with different metal complexes. The phenomenon of the mode of rearrangement depending on the metal catalyst used has been observed in a number of other systems [3]. For example, *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene has been shown [20] to undergo internal cyclopropane ring-opening with $[Rh(CO)_2Cl]_2$, but not with $[Rh(norbornadiene)Cl]_2$ or $(PPh_3)_2Rh(CO)Cl$. As previously mentioned, $[Rh(CO)_2Cl]_2$ was unreactive toward I at room temperature. However, when heated to 55°C, ring-opening to carbomethoxycyclohexadiene isomers was observed. No other mode of rearrangement was evident. No reaction occurred when I was treated with 1 mole % of $[(C_2H_4)_2RhCl]_2$ in chloroform at room temperature. At 50—55°C, however, reaction was initiated and NMR showed the presence of II, III, methylbenzoate, and traces of other, unidentified products. Disproportionation to give aromatics has sample precedent in related systems [21]. $Ir(PPh_3)_2(CO)Cl$, $Ru(PPh_3)_3Cl_2$, $Pd(PPh_3)_4$, and $Pd(PPh_3)_2Cl_2$ all failed to react, even at 50—60°C for prolonged periods. $Fe_2(CO)_9$ produced a mixture of II and III, consistent with its ability to ring-open the unsubstituted bicyclo[3.1.0]hex-2-ene [22]. $(C_6H_5CN)_2PdCl_2$ and I formed II, III, methylbenzoate, and small amounts of several unidentified products. Thus no indication was given in any of these systems that changing the central metal or ancillary ligands of the catalyst opened reaction channels other than internal cyclopropane bond cleavage to a significant extent.

Acknowledgements

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