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Transition-metal catalyzed rearrangements of substituted cyclobutene systems have been observed by various workers to proceed in a symmetry "forbidden" manner, suggesting either that the electronic constraints which govern such reactions are relaxed or reversed. Systems which have been used previously to probe the mechanism of such reactions have suffered from formidably high-energy transition states, involving for example trans-double bonds within six-membered rings.

The present study was initially intended to investigate the mechanism of rearrangement of cyclobutenes by transition metals in systems in which both symmetry "allowed" and symmetry "forbidden" reaction products were energetically attainable. In the course of this study, however, a much more facile rearrangement pathway was discovered, which involved hydrogen migration rather than the ring-opening observed in earlier studies. The reaction appears to involve a mechanism not previously observed. Bicyclo[4.2.0] oct-7-ene and bicyclo[6.2.0] dec-9-ene rearrange essentially quantitatively and at high reaction rates to products which possess the same carbon framework, but in which the double bond has shifted to a thermodynamically more stable position.

Transition-Metal Catalyzed Rearrangements
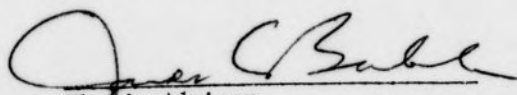
In Cyclobutene Systems

by

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Thanks to Jimmy,

my Mom

and all those who taught me.

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INTRODUCTION

In 1965 Woodward and Hoffmann introduced a theoretical treat-
ment of concerted reations.[1] An especially large impact in the field
of organic chemistry has been felt, and the first generally accepted
explanation of the nature of concerted reations has been the result.[2]
The basic principle simply states that reactions occur readily when
there is congruence between orbital symmetry characteristics of
reactants and products, and only with difficulty or not at all when
that congruency is not satisfied. More succinctly, orbital symmetry
is conserved in concerted reactions.

The crucial terms which must be considered, terms having to do
with the basic requirements for the successful application of the
Woodward and Hoffmann rules, are these: concerted reaction--unless
the reaction is concerted the symmetry rules may not be applied;
symmetry conservation --for predictive purposes symmetry must be shown
to be conserved.

To understand the scope of the investigations reported in this
thesis, a working knowledge of the Woodward and Hoffmann rules is
necessary. In the application of the Woodward and Hoffmann rules the
molecular orbitals associated with bonds that are broken or formed
during a concerted reaction are described either as symmetric or
antisymmetric with respect to common elements of symmetry. As the
reaction proceeds, if the orbitals of the reactant correlate (are of
the same symmetry) with the bonding orbitals of the product, then the

reaction is described as "symmetry allowed." If, however, the bonding reactant orbitals do not correlate with bonding product orbitals, then the reaction is termed "symmetry forbidden."

The conversion of 1,3-butadiene to cyclobutene is an example of an electrocyclic ring closure. Initially the molecular orbital energy diagrams of both butadiene and cyclobutene must be drawn. Only orbitals that are involved in the transition state are considered. The orbitals of interest in butadiene are ψ_1, ψ_2, ψ_3, and ψ_4; in cyclobutene they are π and π^* of the double bond and the σ and σ^* orbitals of the single bond that are formed. Other orbitals not mentioned remain symmetrically unchanged and will be neglected since their effects on the reaction are minimal.

The molecular orbital energy diagram of polyenes follows the concept of the particle in the box. Thus the lowest molecular orbital has no nodes and each molecular orbital of higher energy has n-1 nodes, where n is the molecular orbital being treated. The four molecular orbitals of butadiene necessary for symmetry determinations are illustrated in Figure 1.

Symmetry determinations are made with respect to the mathematical sign of the orbitals. Lobes marked "+" are all of like sign. Correspondingly, those unmarked are also of like sign. Overlap of like-sign orbitals result in a bonding situation, while those of unlike sign are antibonding. As mentioned previously, the π and π^* and the σ and σ^* of the bonds being formed must be included in the orbital energy diagram of cyclobutene, as shown in Figure 2.
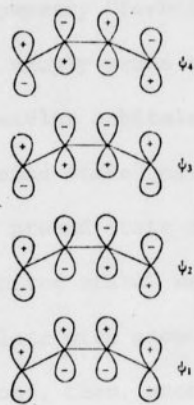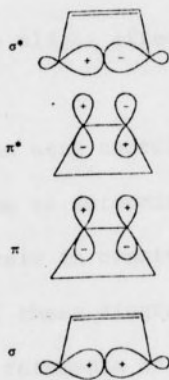
Figure 1

Figure 2

When the involved orbital's energy levels are drawn, the symmetry "allowedness" or symmetry "forbiddeness" can be determined. The term "symmetry allowed" simply means that a correlation exists between the appropriate molecular orbitals of reactants and products. "Symmetry allowed in the ground state" means that ground state orbitals of reactants correlate with ground state orbitals of products, whereas "symmetry allowed in the excited state" means that excited state orbitals of reactants correlate with ground state orbitals of products. Ground-state allowed reactions, then, proceed thermally, whereas excited-state allowed reactions take place (usually) under the influence of high-energy electromagnetic radiation. Pericyclic reactions are termed allowed or forbidden without reference to classical effects (steric, inductive, angle strain, etc.). These are referred to as secondary effects and have slight effect on the initial categorization of pericyclic reactions.

Woodward and Hoffmann used correlation diagrams constructed from the orbital energy diagrams to determine "allowedness" of a reaction. Symmetry plays a crucial role in construction of these diagrams. A critical characteristic of these diagrams is that symmetry of the orbitals transformed from reactants to product must be conserved in a continuous manner if the reaction is to occur.

The closure of butadiene to cyclobutene occurs when the terminal methylene carbons rotate in a conrotatory or in the opposite disrotatory fashion as illustrated in Figure 3.
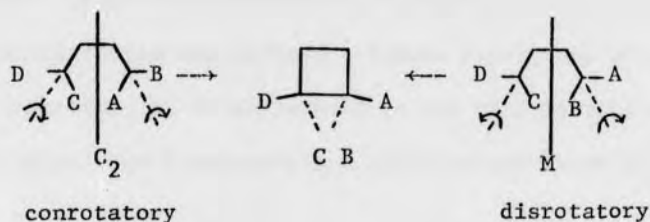
conrotatory   disrotatory

Figure 3

When A and D are not the same substituted groups, different
stereospecific products would be formed for each type of rotation.
Obviously both types of rotation could proceed in the opposite direction
from those shown in Figure 3. In some cases this will result in
stereochemically different products. The actual preferred direction
of rotation of each conrotatory or disrotatory process will be
determined by classical effects. For example, in the cycloreversion of
cyclobutene to butadiene in a conrotatory fashion two products could
result. If the conrotatory process of the cyclobutene ring shown in
Figure 3 were allowed to proceed in a clockwise motion, D would be
placed in the endo position and A in the exo position of butadiene. A
counterclockwise conrotatory process would conversely place A in the
endo position and D in the exo position. The favored rotation will
yield the least sterically strained product.

Correlation diagrams aid in determining which of the two processes
is allowed. The reaction could proceed either in the conrotatory
fashion in which a two-fold rotational axis (C_2) of symmetry is

preserved, or in a disrotatory fashion where a plane of symmetry (m) is maintained. Both are illustrated in Figure 3.

In demonstrating conrotatory movement first, the orbitals are classifed symmetric (S) or antisymmetric (A) with respect to the C_2 rotational axis. The symmetries and orbitals are shown in Figure 4.
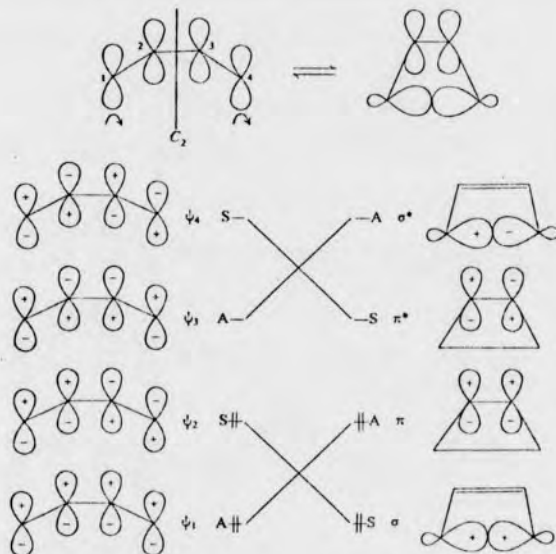

Figure 4

Joining of orbitals of like symmetry completes the correlation diagram. Thus, ψ_1 of butadiene correlates with π of cyclobutene, both of these being asymmetric, and ψ_2 correlates with σ. The four electrons occupying ψ_1 and ψ_2 in the normal ground state of butadiene can therefore be placed in the π and σ bonding orbitals of cyclobutene without involving a high energy transition state. The reaction is thus symmetry allowed in the ground state for the conrotatory mode. In the disrotatory reaction, however, if orbital symmetry is to be

maintained, the electrons in ψ_2 can only pass into π^*, because of symmetry constraints (Figure 5). In order to overcome this barrier an energy well must be created so ψ_3 can be occupied; now smooth transition to π is possible because these symmetries coincide. This reaction must pay a price in terms of a high activation energy, and can be achieved in practice photochemically.
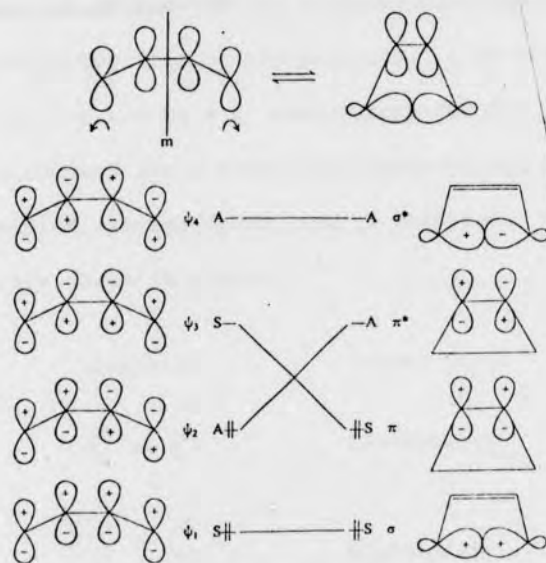

Figure 5

These correlation diagrams demonstrate that butadiene cyclization is "symmetry allowed" in conrotatory movement in the ground state, and that disrotatory cyclization is "symmetry allowed" in the excited state. The process of using correlation diagrams is reversible. Approaching these diagrams, namely the cycloreversion of cyclobutene to butadiene, from the opposite direction, will yield identical results. By a simple extension of what has just been presented, ring opening reactions of both smaller and larger systems can be analyzed.

Woodward and Hoffmann found that correlation diagrams need not be drawn in their entirety for predictive purposes. The highest occupied molecular orbitals (HOMO) play a dominant role in these correlations. Their importance is easily justified since they contain the valence electrons of the molecule, most easily perturbed during the incipient reaction.

The general properties for electrocyclic reactions are derived from the nodal properties of the polyenes. A $k\pi$ electron system will be disrotatory for $k = 4q + 2$, conrotatory for $k = 4q (q = 0, 1, 2, 3...)$. In the first excited state these relationships are reversed, since the lowest unoccupied orbital (LUMO) now is occupied. Some examples of these rules are shown in Figure 6.[1]
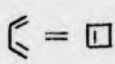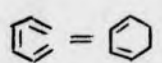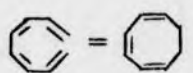
Reaction	Ground State	Excited State
$\xi = \boxdot$	Conrotatory	Disrotatory
$\xi = \bigcirc$	Disrotatory	Conrotatory
$\bigcirc = \bigcirc$	Conrotatory	Disrotatory

Figure 6

One of the two possible directions of conrotatory or disrotatory movement will be favored, if different products result. This will be determined by secondary effects as mentioned previously. When these effects become significant in systems described herein, they will be examined in detail.

Transition Metal Catalysis of Forbidden Reactions

Many reactions predicted to be forbidden in the ground state by the Woodward and Hoffmann symmetry rules have been observed to proceed rapidly in the ground state when a transition metal is introduced into the system. Pettit has shown, for example, anti-tricyclo [4.2.0.0^{2,5}] octa-3,7-diene (I) isomerizes completely to cyclooctatetraene (III) with AgBF$_4$ in refluxing acetone, with a reaction half-life of approximately five minutes.[3] Without the transition metal present there is practically no isomerization after 24 hours. Similar results obtain using CuCl in acidified methanol solution. This same conversion without a transition metal present has been achieved with a half-life of 20 minutes at 140°c by Nenitzescu.[4]
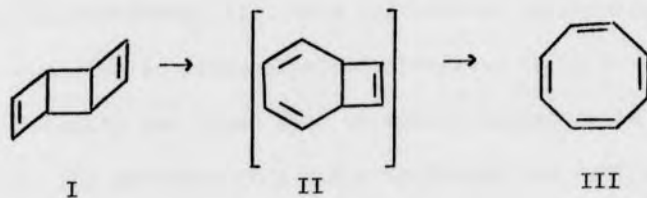

Figure 7

Because of the anti nature of the rings in I, a one step isomerization to III is unlikely. The initial step probably involves the triene (II) which is recognized merely as a valence tautomer of III. The initial formation of II appears to proceed through a disrotatory

opening of a cyclobutene ring; this is, in the absence of a transition

metal, a ground-state-forbidden isomerization. The transition metal

obviously catalyzes this process. The normal path of isomerization

of I, according to the Woodward and Hoffmann rules, would be

conrotatory ring opening, resulting in the cis, cis, trans-triene (IV),

which is practically disallowed due to formidable strain (Figure 8).

Figure 8

The effect of silver ion is also dramatized in the case of

dibenzotricyclooctadiene (V). This hydrocarbon is reported to

thermally isomerize to dibenzocyclooctatetraene (VII) at 180^0 in

4-5 hours.[5] Pettit has found that at room temperature in tetra-

hydrofuran in the presence of a molar equivalent of $AgBF_4$, complete

isomerization occurs in ten seconds.[3] No detectable amount of

isomerization occurs after one week under these conditions without

silver ion.

Here again it is believed the transition metal initially allows

a cyclobutene ring to open in a disrotatory fashion resulting in VI

(Figure 9) which immediately opens in a symmetry allowed process to the

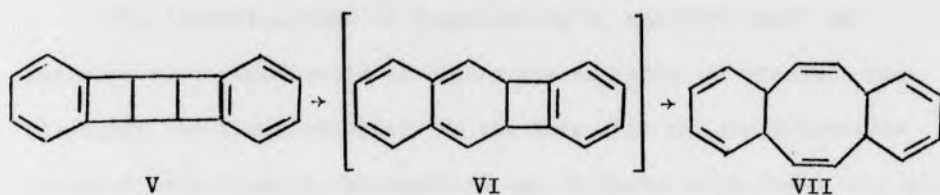final product VII. Proof of the existence of VI was obtained by

Figure 9

trapping the intermediate in a Diels-Alder reaction as soon as the intermediate was formed.[3]

Another interesting case is the silver ion isomerization of benzotricyclooctadiene (VIII). Addition of $AgBF_4$ to an etherel solution of VIII at 25° produces an instantaneous precipitate of the silver complex of benzocyclooctatetraene (X). Decomposition of the complex results in a 90% yield of X.[3] Isolation of the Diels-Alder adduct of IX suggests that IX is an intermediate in this rearrangement. Formation of IX would have to occur in a disrotatory manner. Without silver ion present no isomerization occurs.
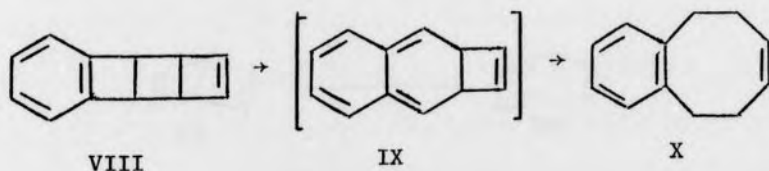
VIII   IX   X

Figure 10

The isomerizations of compounds I, V, and VIII would be expected to be exothermic reactions due to relief of strain. The compounds owe their stability to the fact that the isomerizations expected according to the Woodward and Hoffmann rules would take place in conrotatory fashion. In these instances such rotations cannot occur because of secondary effects. Hence the constraints on the nature of the rings to be formed are great enough that isomerization by this process is practically impossible (see figure 8). One of the most dramatic examples of a system which owes its stability to such a phenomenon is bicyclo[2.2.0] hexa-2,5-diene (Dewar benzene) (XI). Strain considerations alone, and the relatively large amount of energy lost in isomerization to Kekulé benzene, would cause one to be surprised that XI could exist at all. Conservation of orbital symmetry dictates that ring opening of XI should proceed in a conrotatory manner, to give cis, cis, trans-cyclohexa-1,3,5-triene (XII); where XI is badly strained, XII is simply unattainable. Turro and coworkers have in fact demonstrated that the conversion of XI to Kekulé benzene is a nonconcerted process.[6]

Figure 11

One explanation for transition metal catalysis of forbidden reactions, or an actual reversal of the Woodward and Hoffmann symmetry rules via transition metals, was proposed by Pettit.[3] Isomerization is allowed to proceed through a concerted disrotatory process via an intermediate metal π-complex. Once the complex is formed, the symmetry of the appropriate orbitals of cyclobutene are altered to include the metal center so that a disrotatory process is now symmetry allowed, as indicated in Figure 12.
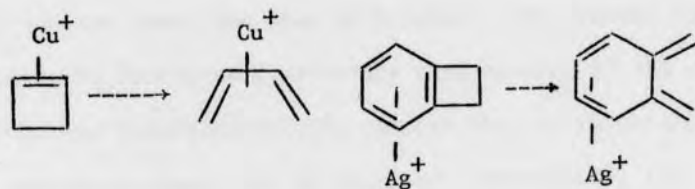
Figure 12

Therefore, the reversal of the Woodward and Hoffmann symmetry rules is the result of altering of orbital symmetry so that a formally forbidden process is now allowed. The concerted process that is required by symmetry rules occurs after metal-ligand complexation has already taken place. Any other treatment would involve stepwise processes, the ultimate result of which is not governed by symmetry rules.

Further work carried out by Pettit to prove that the transition metal forms a π-complex and does not actually insert into a σ-bond involved iron carbonyl complexes. It had been suggested and demonstrated

in a few cases by Eaton that the transition metal actually inserts
into a σ-bond in an oxidative-addition type reaction.[7]

syn-Tricyclo[4.2.0.0^{2,5}] octa-3,7-diene (XIII) treated with
$Fe_2(CO)_9$ yields syn-tricyclooctadieneiron tetracarbonyl (XIV). This
complex is known to be of metal-olefin π-type coordination.[8]
Conversion of XIV to bicyclooctatrieneiron tricarbonyl (XVI) is
readily achieved in refluxing hexane.[9] Before the organic ligand
isomerizes, it was shown that XIV loses CO thermally to yield the
monoolefin-$Fe(CO)_3$ complex (XV), in which the effective atomic number
of iron is now two less than that of krypton. The organic ligand in
XV then undergoes concerted disrotatory ring opening of the coordinated
ring to yield the butadiene-$Fe(CO)_3$ complex XVI, in which the electronic
inert gas structure about iron is regained. Presumably, the product
of the isomerization has the anti-configuration, which is sterically
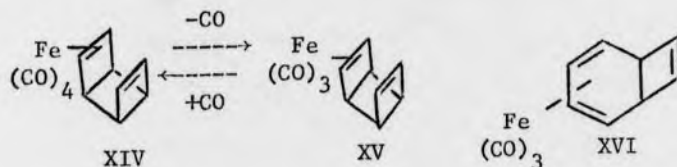favored.

Figure 13

The disrotatory ring opening occurring in the isomerization of XIV
to XVI is termed concerted only in the process in which the carbon
framework is undergoing rearrangement. The formation of the complex
is not part of the concerted reaction in question. The phrase

"catalysis of forbidden reactions" describes the conversion of uncomplexed starting material to uncomplexed product, and does not describe the intermediate complexes where the suspected symmetry alteration takes place.

In an analogous manner, anti-tricyclooctadieneiron tetracarbonyl (XVII), and syn-tricycloocteneiron tetracarbonyl (XVIII) rearrange in refluxing hexane yielding syn-bicyclooctatrieneiron tricarbonyl (XIX) and anti-bicyclooctadieneiron tricarbonyl (XX) respectively.[9]
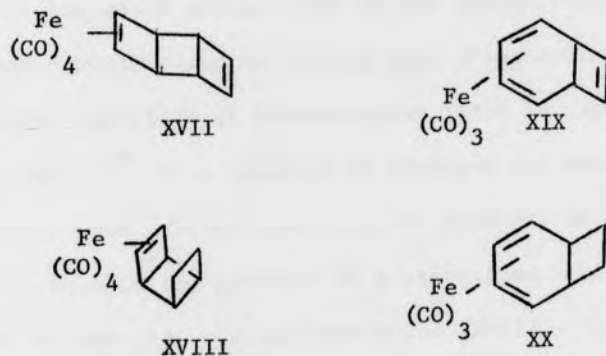

Figure 14

The half-lives for the ring opening of both complexes are less than three hours. The half-lives of the ring opening of the free ligands are 16 hours and 3 weeks respectively, under identical conditions.

Transition Metal Catalysis of Forbidden
Reactions of Monocyclobutene Systems

While much work has been compiled on transition metal catalysis of forbidden reactions, it is nonetheless insufficient. It is important to extend this transition metal work into systems where secondary constraints of the products are not the most important directing influence. All previous systems were obviously very much governed by secondary constraints (Figures 7, 8, and 9). One such system which would be expected to be much less influenced by secondary factors is cis-bicyclo[4.2.0] oct-7-ene (XXI). Application of symmetry rules would predict that in the ground state conrotatory ring opening would occur to produce cis, trans-cyclooctadiene (XXII). The observed half-life of bicyclooctene (XXI) is reported to be two hours at 350° .[10] If a reversal of Woodward and Hoffmann symmetry rules occurs when a transition metal is present, as has been suggested, then in the presence of a transition metal XXI would be expected to give cis, cis-cyclooctadiene (XXIII). Obviously if this assumption were true then trans-bicyclo[4.2.0] oct-7-ene (XXIV), were it known would yield the opposite products as illustrated in Figure 15.

Isomerizations allowed in the excited state are forbidden in the ground state; however, in the presence of a transition metal, these reactions should occur in the ground state if Pettit's predictions, as discussed earlier, are correct.

Conversion of XXI to XXIII has already been shown to occur to the extent of 50% in 1.5 hours using silver ion as the catalyst at
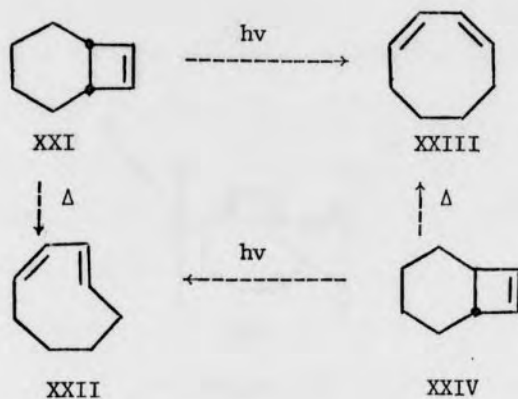
Figure 15

160-165° .[11]   Under identical conditions without catalyst less than

1% isomerization was seen.   One possibility not considered in this

investigation is that this isomerization may have proceeded through a

Ag^{+}-cis, trans-1,3-cyclooctadiene complex intermediate first, then

rearranged under these strenuous conditions. Cis-trans isomerization

of olefins by transition metals are well known.[8]   In this event silver

ion may simply have facilitated an allowed process. Figure 16

summarizes these reaction possibilities.

Silver is known to complex to cis, trans-1,3-cyclooctadiene,[12]

and at high temperatures, isomerization of the olefin could very well

occur.   Therefore, the Ag^{+}-cis, trans-1,3-cyclooctadiene complex XXV

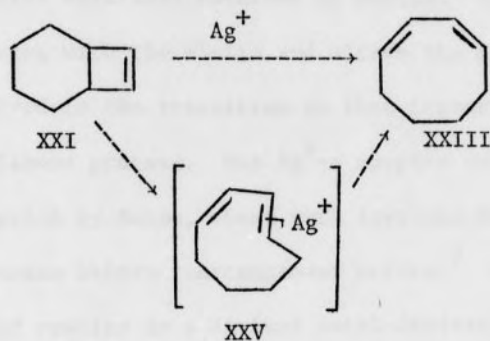should have been placed under conditions identical with those of the

Figure 16

silver-catalyzed isomerization of XXI to XXIII, to observe if
rearrangement occurs.

Another problem that arises from the use of Ag^{+} is that the
initial complex could form at two sites in the ligand. Both Ag^{+}-π
complexes and Ag^{+}-σ complexes[13] have been observed. Figure 17
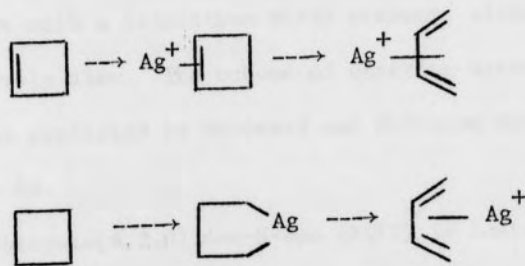demonstrates both types of possible interactions.

Figure 17

The Ag^+–olefin π complex probably is the bonding type required for the concerted reactions observed by Pettit. The transition metal coordinates with the olefin and alters the symmetry of the orbitals involved in the transition so that isomerization that takes place is an allowed process. The Ag^+–σ complex exemplifies oxidative addition suggested by Eaton, whose work involves Rh insertion into a σ-bond of cubane before rearrangement occurs.[7] Complexation into a strained σ-bond results in a dialkyl metal derivative which decomposes with notorious ease.[13] One result of this decomposition could be conversion to the diolefin. Whether the decomposition is concerted or not has not been investigated.

An alternate system for treatment with a transition metal known to form π-complexes is cis-bicyclo[6.2.0] dec-9-ene (XXVI). Bicyclo-decene is a good candidate for this type of investigation because both the thermally allowed and forbidden products are known to be reasonably stable.[15] However, some isomerization might occur between the two products with a transition metal present, although this process might be relatively slow. The scheme of starting material–product interconversions predicted by Woodward and Hoffmann symmetry rules is shown in Figure 18.

When cis-bicyclo[6.2.0] dec-9-ene (XXVI) is heated at 200° for one hour, a 95% conversion to cis, trans-1,3-cyclodecadiene (XXVIII) occurs.[16] This stereoisomer is the result of the predicted conrotatory process. In the presence of a transition metal and with altering of orbital symmetry, a disrotatory opening might occur if the concept of symmetry altering effects is correct. In this case cis, cis-1,3–
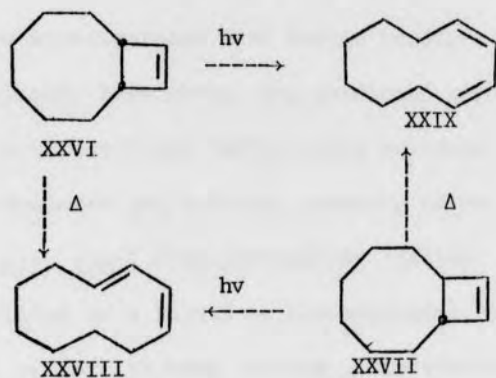
Figure 18

cyclodecadiene (XXIX), the normally forbidden ground state product, would now be the allowed product. Here again the transition metal could facilitate an allowed process with subsequent rearrangement to the final product. Analogously, trans-bicyclo[6.2.0] dec-9-ene (XXVII) would yield exactly opposite products because of the different stereochemistry of the starting material; however, at this time no thermal isomerization of XXVII has been reported. Radlick has shown that the cis, trans-diene XXVIII isomerizes to the cis, cis-diene XXIX by irradiation.[16] Quite possibly if cis, trans-diene XXVIII is generated in the presence of a transition metal, it may isomerize immediately on the metal to the cis, cis-diene XXIX, although again this isomerization could be slow. This possibility was pointed out in discussion of Pettit's Ag^{+}-catalysis of bicyclo[4.2.0] oct-7-ene.

In order for any conclusions to be drawn from the results of these monocyclobutene derivatives, that is if the predicted products are obtained, a few anticipations must become reality.

As has already been shown, the predicted product of cis-bicyclo[4.2.0] oct-7-ene (XXI) in the presence of a transition metal, if the Woodward and Hoffmann symmetry rules are reversed as suggested, is cis, cis-1,3-cyclooctadiene (XXIII). If the rearranged product is isolated as a ligand or uncoordinated, a decision as to the occurrance of initial ring opening in disrotatory fashion would be impossible. The possibility of initial conrotatory ring opening to cis, trans-1,3-cyclooctadiene and subsequent isomerization to the cis, cis-product on the transtition metal is real. In order for any conclusions to be drawn it is necessary to isolate cis, trans-1,3-cyclooctadiene (XXII) and observe the product formed in the presence of iron. If the product is entirely cis, cis-1,3-cyclooctadiene (XXIII), then cis, trans-1,3-cyclooctadiene (XXII) intermediate is a distinct possibility. Consequently, to eliminate this two-step mechanism it will be necessary to show that the cis, trans-to cis, cis-1,3-cyclooctadiene conversion is slower than the iron catalysis of cis-bicyclo[4.2.0] oct-7-ene (XXI) to product. If the olefin isomerization cannot be demonstrated to be slower then both mechanisms must still be considered possible mechanisms of the iron rearrangement.

These arguments extend directly to the bicyclo[6.2.0] dec-9-ene system as both systems would be expected to react in analogous manner in the presence of iron; therefore, subsequent investigations on this system should be carried out in similar fashion.

RESULTS AND DISCUSSION

The investigations described here were designed to gain a better understanding of the effects of transition metals on reactions to which the Woodward and Hoffmann symmetry rules can be applied. The investigations reported herein are limited to cyclobutene systems, of which the symmetry-predictive products have been described in the preceeding section.

The initial system chosen for these purposes was cis-bicyclo[4.2.0] oct-7-ene (XXI). The predicted products according to the Woodward and Hoffmann symmetry rules are reasonably stable and not subject to geometric constraints to the degree that previously-studied compounds have been. The primary transition metal chosen for catalysis was iron in the form of one of its carbonyls; iron carbonyls are known to form π-complexes,[8] and thus oxidation addition mechanisms[7] can be ruled out.

cis-Bicyclo[4.2.0] oct-7-ene (XXI) could be prepared by several methods, two of which were attempted. On a large scale cis, cis-1,3-cyclooctadiene (XXIII) could be irradiated at an elevated temperature for an extended period.[17] However, a steady-state equilibrium was apparently reached which contained 10% cyclooctadiene. The only successful method of separation of the two isomers was by preparative gas chromatography. On a smaller scale XXI was prepared by irradiation of XXIII with isolation of cis, trans-1,3-cyclooctadiene (XXII) by silver complexation and subsequent thermal

isomerization of XXII to XXI. This method produces essentially pure XXI.[12]
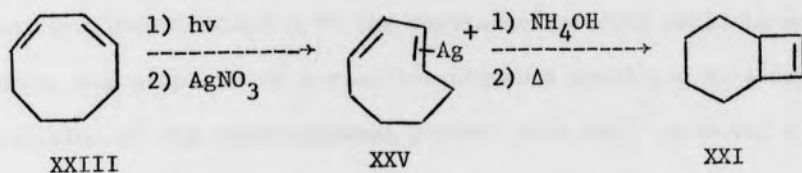
Figure 19

cis-Bicyclo[4.2.0] oct-7-ene (XXI) was placed in refluxing hexane with $Fe_2(CO)_9$, and subsequent identification of product indicated that neither of the expected symmetry "allowed" or "forbidden" products had formed. Instead, cis-bicyclo[4.2.0] oct-2-ene (XXX) was the major product (Figure 20).

Figure 20

Initially, confirmation of the skeletal system of the rearranged product was made by hydrogenation of both starting material and rearranged product, over Pt and chemically with diimide.[18] Both hydrogenation products gave identical infrared spectra indicating

no carbon skeletal rearrangement had occurred. cis-Bicyclo[4.2.0] oct-3-ene (XXXI) and cis-bicyclo[4.2.0] oct-2-ene (XXX) were authentically synthesized for comparison of spectra and consequently positive identification of the rearranged product could be made. The former was prepared by a reaction sequence developed by Alder.[19] Oxidation of the rearrangement product with MnO_4^- produced a different dicarboxylic acid from that produced under similar conditions from Alder's olefin (XXXI). Since bicyclo[4.2.0] oct-1(8)-ene (XXXII) and bicyclo[4.2.0] oct-1(2)-ene (XXXIII) could be ruled out on the basis of NMR spectral data, and since the rearrangement product was known to possess the cis-bicyclo[4.2.0] octane skeleton, the only structural alternative was XXX (independently synthesized by the sequence shown in Figure 21).
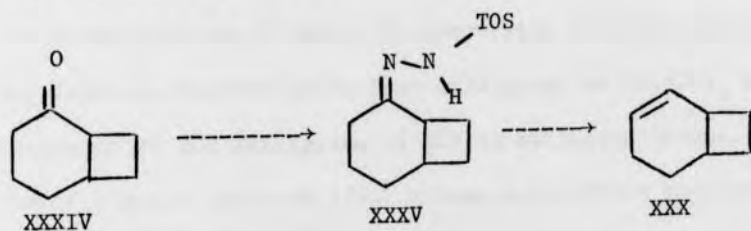

Figure 21

cis-Bicyclo[4.2.0] octan-2-one[20] (XXXIV) was converted to the p-toluenesulfonyl hydrazone derivative (XXXV), which was treated with n-butyllithium[21] to give XXX. Hydrogenation of XXX and XXI both gave the same hydrogenated products as XXI and its iron-catalyzed rearrangement product. NMR and infrared spectral data of authentically

synthesized XXX and the rearrangement product were identical.
Therefore, the rearrangement product was assigned the structure XXX.

Optimized conditions of the iron reaction yielded 95% of the
major product XXX and 5% of an unidentified minor product. Gas
chromatographic analysis showed the minor product was neither starting
material nor cis-cis-1,3-cyclooctadiene (XXIII). Conversion was
possible regardless of the molar ratio used. However, using
20% molar equivalent or greater gave complete conversion within a
half-hour period. Most reactions appeared to be complete within
five minutes as the reaction solution turned blackish-green, indicating
thermal decomposition of the metal complex; the blackish-green color
is due to formation of $Fe_3(CO)_{12}$, which was isolated from the reaction
mixture.

A dramatic case of catalytic conversion is shown when a half-life
of four days is observed using four milligrams of $Fe_2(CO)_9$ to catalyze
rearrangement of 200 milligrams of XXI in refluxing hexane, which
represents a molar ratio of 175. Attempts to affect rearrangement of
XXI using $AgBF_4$ in refluxing acetone and refluxing methanol failed,
regardless of the allowed duration of reaction. Under conditions
identical with those of the iron rearrangement reaction, but with
the metal excluded, no isomerization of XXI occurred.

Isolation of the iron-olefin complex was attempted by addition
of $Fe_2(CO)_9$ to a solution of XXI in refluxing petroleum ether. When
addition was complete and the $Fe_2(CO)_9$ had been consumed, the
reaction was immediately stopped and the solvent evaporated. Unreacted
hydrocarbon was removed by flash-distillation. The residue yielded

an unstable red oil believed to be complex XXXVI which upon
oxidative decomposition with $Ce(NH_4)_2(NO_3)_6$, left only starting
material. Thermal decomposition of the complex resulted in formation
of the rearranged product (XXX) (Figure 22). The instability of
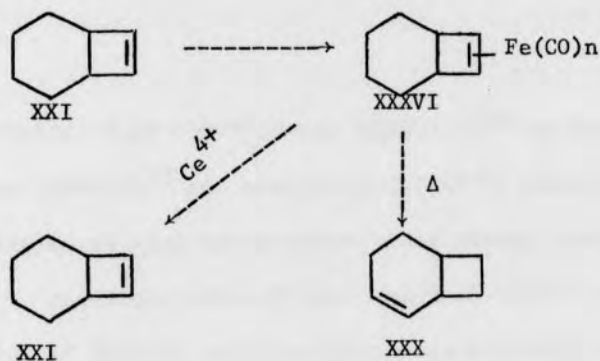XXXVI precluded the gathering of spectral data.

Figure 22

In an attempt to establish the mechanism of the iron-catalyzed
rearrangement, various compounds possessing the cis-bicyclo[4.2.0]
oct-7-ene skeleton were investigated under conditions identical with
those of the $Fe_2(CO)_9$-catalyzed rearrangement of XXI, and analyzed for
new products. Methyl or deuterium labels would have been the preferable
derivatives, since their addition to the parent system would allow
the least perturbation. However, preliminary attempts to synthesize
these systems have not been successful. The derivatives that were
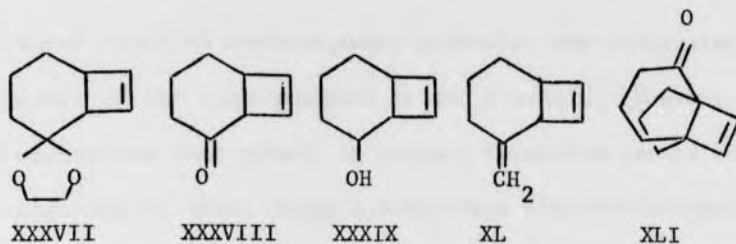tested with iron carbonyls are illustrated in Figure 23.

Figure 23

cis-Bicyclo[4.2.0] oct-7-en-one (XXXVIII),[22] the ethylene ketal
of that ketone (XXXVII)[22] and tricyclo$[4.3.2.0^{1,6}]$ undec-10-en-2-one
(XLI)[23] all failed to give new products under normal reaction conditions
with $Fe_2(CO)_9$. cis-Bicyclo[4.2.0] oct-7-en-2-ol (XXXIX) prepared by
$NaBH_4$ reduction of XXXVIII and 2-methylene-cis-bicyclo[4.2.0]
oct-7-ene (XL) also prepared from XXXVIII via a Wittig reaction failed
to give any new products upon treatment with excess $Fe_2(CO)_9$.

Failure of catalyzed rearrangements of the oxygenated systems
could be the result of prevention of initial π-complex formation
by the oxygen atom. Possibly the two lone pairs of electrons on
oxygen could compete successfully with the π-electrons of the olefin
for coordination sites. No obvious explanation of the failure of the
rearrangement of XL is presently available. Sp^2 hybridization at
position 2 in the six-membered ring could alter the ring configuration
enough to prevent rearrangement; alternatively, a strong metal-olefin
complex formation at the external olefin position could prevent initial
complexation at the olefin in the cyclobutene ring.

Without labelled rearrangement products, any conclusion as to

the mechanism of the rearrangement is not possible. However,

several mechanisms that result in product formation can be suggested.

A sequence of short range 1,3-hydrogen shifts catalyzed by iron

is a distinct possibility. Precedence has shown 1,3-hydrogen shifts

to be common in the presence of iron. Two examples are the conversion

of cis, cis-1,5-cyclooctadiene (XLII) to cis, cis-1,3-cyclooctadiene

(XXIII)[8] and the formation of tricyclo[5.2.1.0^{26}] decan-3-one (XLIV)

from the corresponding allyic alcohol (XLIII) through an enol

intermediate.[24]

XLII   XXIII
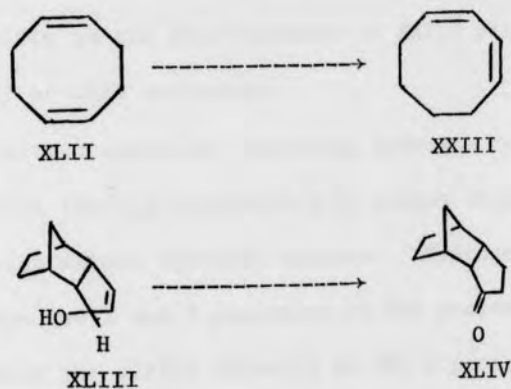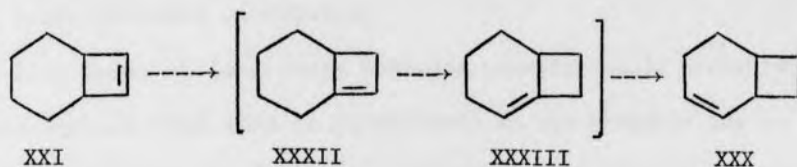
HO   H   O

XLIII   XLIV

Figure 24

In the series of 1,3-hydrogen transfer of an iron-catalyzed

reaction, the first transfer would yield XXXII, the second transfer

XXXIII, and the final transfer would result in product XXX (Figure 25).

Stepwise Hydrogen Transfer (SHT)

Figure 25

Hydrogen shifts occurring in a 1,3-manner are not known to proceed as rapidly as the rearrangement of XXI,[8] placing in question the possibility of this mechanism.

An alternative approach, involving hydrogen transfer on iron while maintaining the cis-bicyclo[4.2.0] octane skeleton is possible through direct hydrogen transfer. Hydrogens could be transferred from the 2 and 3 positions to the respective 7 and 8 positions forming the olefin directly in the 2 position avoiding any intermediates (Figure 26). The unsymmetrical hydrogen transfer makes this type of transfer implausible. Direct transfer of hydrogen from position 3 and 4 to the olefin with formation of XXXI as an intermediate would be the more likely process of long range hydrogen transfer, maintaining geometric symmetry through the transfer. XXXI could subsequently rearrange to the final product XXX on the metal (Figure 26).

Evidence supporting this two step hydrogen transfer process involved total conversion of authentically synthesized XXXI to XXX under iron-catalysis conditions.

Both types of long range hydrogen transfer would probably require another iron atom to participate in the transfer due to the nature of the initial π-complex. The first iron atom would probably approach the olefin from the exo-side of the cyclobutene ring, making long-range hydrogen transfer from one ring to the other virtually impossible. A second iron atom could approach from the endo-side of the four-membered ring and perform the transfer more readily (Figure 26). The possibility of intermolecular hydrogen transfer cannot be ruled out.

Fe(CO)n
XXI

XXX
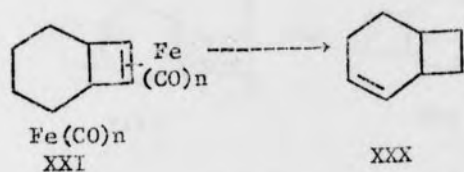
Direct Hydrogen Transfer (DHT)

Fe(CO)n
XXI

XXXI

XXX
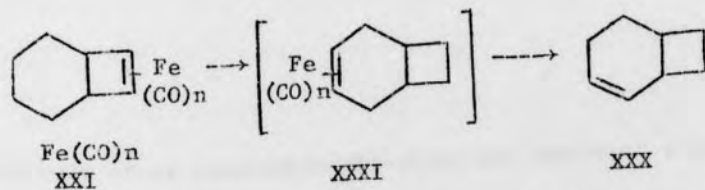
Indirect Hydrogen Transfer (IHT)

Figure 26

Diradical intermediates are an alternative to hydrogen transfer. After initial π-complex is formed a diradical could be produced by the rupture of the 1,6-bond, subsequent double hydrogen radical transfer from adjacent methylene carbons could occur and then collapse of the diradical to reform a cyclobutane ring (Figure 27). cis-Bicyclo[4.2.0] oct-3-ene (XXXI), the result of this mechanistic process, has already been shown to rearrange in the presence of iron to XXX.
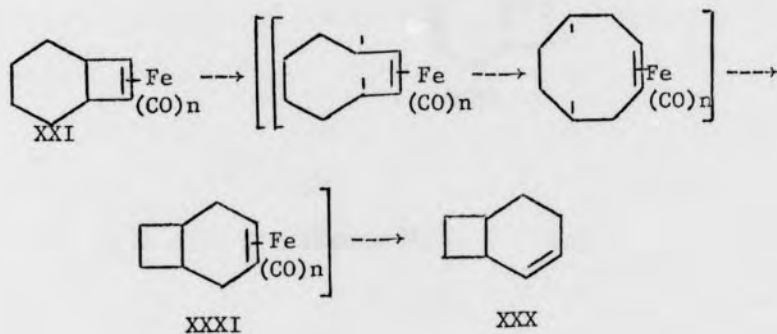
Figure 27

The only other reasonable mechanism not mentioned thus far also involves hydrogen transfer by iron. Hydrogens from the two bridge heads could be transferred directly across the four-membered ring leaving bicyclo[4.2.0] oct-1(6)-ene (XLV) as an intermediate. This intermediate could rearrange on iron via any of the three hydrogen

transfer mechanisms previously described. All possibilities of
rearrangement from this intermediate are shown in Figure 28.
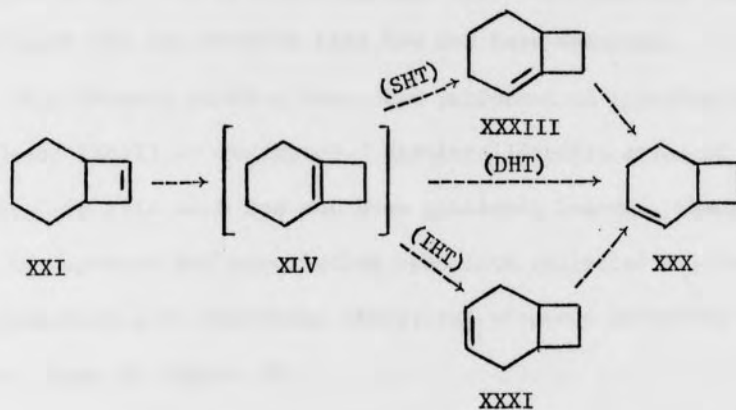
Figure 28

At this time no substantial evidence has been found that would
indicate that XLV is a true intermediate in the catalysis reaction.
However, some preliminary investigations on cis-bicyclo[6.2.0]
dec-9-ene (XXVI) apply directly to this problem. Preliminary findings
infer that XXVI rearranges in the presence of $Fe_2(CO)_9$ to
bicyclo[6.2.0] dec-1(8)-ene (XLVI); data collected thus far concerning
this system will be discussed below.

Due to the facile rearrangement of XXI to XXX, conclusions pertaining to transition metal catalysis of symmetry "forbidden" reactions could not be accomplished in these systems. Mechanistic studies of this facile rearrangement were unsuccessful. However, opening of the cyclobutene ring has not been detected.

Preliminary studies have been performed on cis-bicyclo[6.2.0] dec-9-ene (XXVI) as indicated. Absolute identification of compounds involved in this work has not been achieved; however, observations will be reported and speculation upon data collected will be made. cis-Bicyclo[6.2.0] dec-9-ene (XXVI) was prepared according to the scheme shown in Figure 29.
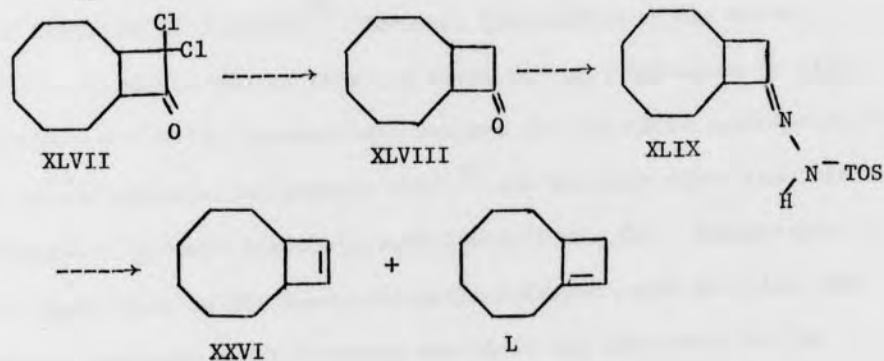

Figure 29

cis-Bicyclo[6.2.0] dec-9-one[25] (XLVIII) was prepared in several steps starting initially with dichloroketene addition to cis-cyclooctene,[25] and subsequent bis-dechlorination with zinc and

acetic acid.[26] Ketene additions are known to occur in a cis-manner.[1]

Gas chromatography indicates that the product of dechlorination

consists of only one product XLVIII. The p-toluenesulfonyl hydrazone

derivative XLIX was prepared from XLVIII and subsequent treatment with

lithiumdiisopropylamide[27] resulted in three products analyzed by

gas chromatography to be in the ratio of 40:50:10. By careful column

chromatography on 20% $AgNO_3$/silica gel, two major products could be

separated from the minor product. Hexane was used as the elution

solvent and the minor product (removed from the column first) appeared

to be a saturated hydrocarbon and remains unidentified. NMR of the

two inseparable major products showed two singlets in the olefin

region at 5.95-5.90ppm. The vinyl hydrogen absorption for XXVI has

been reported at 5.95ppm.[28] However, integration of the mixed

reaction products showed that the ratio of vinyl hydrogens to alkyl

hydrogens was 1:10, intermediate between the 1:7 ratio anticipated for

the normal elimination product XXVI,[27] and the only other reasonable

elimination product bicyclo[6.2.0] dec-1(8)-ene (L). Integration

of L would show an olefin-to-aliphatic hydrogen ratio of 1:15. The

ratio of isolated major products was 55:45 and XXVI would be the

expected major product due to the stability of the intermediate anion

that forms in the elimination mechanism.[29] Based on this assumption,

a mixture of the two suggested products would yield an olefin-to-

aliphatic hydrogen ratio of 1:10.5, which compared favorably with

the experimental data.

The mixture of the two elimination products was treated with a

molar equivalent of $Fe_2(CO)_9$ under identical conditions as

cis-bicyclo[4.2.0] oct-7-ene (XXL). The reaction was monitored by gas chromatography and it was found that both compounds had rearranged to new products in a half hour. Only minute amounts of starting material could be detected. Separation attempts of the two new products were not successful; therefore, no absolute identification of the iron-catalyzed rearrangement products was possible. It is significant that the ratio of the products formed was equal to the ratio of starting material. NMR spectra of the iron-catalyzed rearrangement mixture showed slight olefinic absorption; infrared showed slight vinylic hydrogen absorption and no carbon-carbon double bond absorption.

Hydrogenation over Pt of the mixed products of the elimination reaction resulted in formation of two new products showing no olefin absorption in the NMR spectrum. Analysis by gas chromatography indicates the ratio of the hydrogenation products was identical to that of the mixed products of the elimination reaction. This can be easily rationalized in that hydrogenation will occur from the least hindered side and thus L, which could give two products depending upon the side of addition, would be expected to yield only one product, trans-bicyclo[6.2.0] decane (LI), as the product of hydrogen addition to the least hindered side. Regardless of the side of addition, XXVI would give only one product cis-bicyclo[6.2.0] decane (LII); therefore, the ratio of the products of hydrogenation should be consistent with the ratio of starting material.

The mixed products of the iron catalysis were also hydrogenated over Pt. A mixture of the hydrogenated products of XXVI and L and

the hydrogenation products of the iron-catalyzed product of XXVI and L were examined by gas chromatography, results of which showed only two compounds present, and these two compounds showed equivalent retention times regardless of their source. This indicates that the hydrogenation products are the same compounds. NMR spectra of the hydrogenation products consisted of an unresolved envelope not suitable for comparative purposes; however, infrared spectra of both hydrogenation products were identical, again indicating the hydrogenation products were the same.

With data presently compiled no definite conclusions can be reached as to the products of the iron catalysis of XXVI and L.

At this point it is only speculation, but it is suggested from accumulated data that one of the products of the iron catalysis of XXVI and L is bicyclo[6.2.0] dec-1(8)-ene (XLVI). This suggested product is based on NMR spectrum indicating no vinylic hydrogens present. Infrared and gas chromatographic data of the hydrogenation product of XXVI and L and the iron-catalyzed rearrangement product of XXVI and L indicate no skeletal rearrangement had taken place, thus XLVI would yield LII upon hydrogenation. The infrared spectrum of the products of iron catalysis of XXVI and L showed no olefinic absorption; XLVI, due to absence of vinylic hydrogens and the nature of its symmetry, would be expected to show no signs of being olefinic. The iron-catalyzed rearrangement product did absorb Br_2 indicating olefin present. The nature of the second product formed in the iron-catalysis reaction is not known and no erudite suggestion can be offered at this time.

A possible mechanism for formation of LIII could be direct hydrogen transfer by iron from the bridgeheads to the olefin (Figure 30).

XXVI   XLVI

Figure 30

If L is the other starting material of the iron catalysis reaction, then stepwise 1,3-hydrogen transfers can be ruled out as a mechanism in this particular type of rearrangement. L would be an intermediate in 1,3-hydrogen transfer mechanism and subsequently only one product would result instead of the observed two.

The validity of XLVI as a product can be reasoned in that the double bond is probably more stable at the bridgeheads than in the ring. The normal bond angles of sp^2 hybridization is 120° and if the double bond migrates into the eight membered ring it must accomodate the strain due to a larger angle associated with the cyclootyl ring. This mechanism as previously stated could apply directly to the iron rearrangement of cis-bicyclo[4.2.0] oct-7-ene (XXI); however, in this case once the double bond is transferred to the bridgeheads it continues to move into the six membered ring which nicely accomodates the 120° bond angle required for sp^2 hybridization, resulting in a more

thermodynamically stable product.   The more thermodynamically stable product in the bicyclo[6.2.0] decene system is probably the bridge (tetrasubstituted) olefin.

Both products of the iron catalysis of XXVI and L are not definitely known; however, rearrangement of both in the presence of iron is a fact.   Neither symmetry predicted "allowed" or "forbidden" ring opening products occur, since both symmetry products are known and spectral data reported.

EXPERIMENTAL

All NMR spectra were obtained with a Varian T-60 NMR
spectrophotometer. Infrared spectra were obtained on a Perkin-
Elmer 457 grating spectrophotometer using NaCl cells. Gas chroma-
tographic analyses were performed on a Varian Aerograph Hi-Fy
Model 600-D, and a Hewlett-Packard 5720A gas chromatograph. Melting
points were obtained from a Fisher-Johns melting point apparatus;
melting points and boiling points are uncorrected.

<u>cis</u>-Bicyclo[4.2.0] oct-7-ene (XXI)[12]

A solution of 60g (0.55mol) of <u>cis</u>, <u>cis</u>-1,3-cyclooctadiene
and 2g (17mmol) of accetophenone in approximately 500ml of 30-60°
petroleum ether is placed in an irradiation vessel equipped with a
water-cooled internal (quartz) immersion well containing a 450 watt
Hanovia medium pressure lamp and magnetic stirrer. The solution is
irradiated, maintaining a solution temperature of 10-15° with an
external ice bath, while N_2 is bubbled through the solution for 12 hrs
with stirring (the immersed well is removed and washed with acetone
every four hours). The solution is then transferred to a 2-1., three
neck, round bottom flask equipped with a mechanical stirrer. The
solution is cooled to 0° and with stirring 200ml of 20% $AgNO_3$ is
added at a rate that maintains a solution temperature of <5° ; vigorous
stirring is continued for 2 hrs at 0°. The solution is filtered and
the white precipitate washed with water and several portions of

petroleum ether. The product is air-dried overnight; 32.5g of Ag^+-cis, trans-1,3-cyclooctadiene is isolated.

To a stirred solution of 32.5g of Ag^+-complex in 130ml of heptane is added dropwise over a 30 minute period 35ml of concentrated aqueous NH_3, the layers are separated and the aqueous layer is extracted with 2 x 100ml of heptane. The combined organic layers are washed with 2 x 100ml of H_2O, 1 x 100ml of brine solution, and dried over $MgSO_4$. The drying agent is removed by filtration and the solution is then refluxed under N_2 for 12 hrs. The solvent is removed by distillation at reduced pressure and the residue distilled at 130mm yielding 5.5g (9%) of essentially pure XXI; bp 71-78°.

Generalized Olefin-$Fe_2(CO)_9$ Rearrangement Procedure

The hydrocarbon (30mmol) is dissolved in 150ml of hexane and $Fe_2(CO)_9$ is added in one portion. The mixture is magnetically stirred and placed in a preheated oil bath (95-100°), reaching reflux almost immediately. The solid iron carbonyl is consumed within a few minutes and the entire mixture in most cases turns blackish-green in less than 10 minutes (the change in color is due to production of $Fe_3(CO)_{12}$). After a half hour of reflux the solution is cooled, filtered through Celite and concentrated. The solution is poured into acetone and $Ce(NH_4)_2(NO_3)_6$ is added slowly with stirring. Evolution of CO is observed; addition is stopped when gas evolution stops. The yellow solution is poured into water and the aqueous solution is extracted several times with 30-60° petroleum ether. The organic layers are combined and dried over $MgSO_4$. The solvent is removed by distillation

and the residue is purified by distillation or column chromatography through alumina. The ratio of reaction products is determined by gas chromatography using a 10% SE-30 column.

cis-Bicyclo[4.2.0] oct-2-ene (XXX)

To a solution of 2.6g (21mmol) of cis-bicyclo[4.2.0] octan-2-one (XXXIV)[20] in 25ml of chloroform is added with stirring 4.0g (21mmol) of p-toluenesulfonyl hydrazide; stirring is continued overnight. Na_2SO_4 is then added to remove the liberated water and stirring is continued for several hours. The solution is filtered and the solvent removed at reduced pressure leaving 5.5g (95%) of the tosylhydrazone XXXV, mp 150-152° (unrecrystallized).

To a stirred suspension of 5.5g (19mmol) of XXXV in 20ml of hexane is added dropwise, under N_2 at room temperature, 31ml (60mmol) of 15% n-butyllithium in hexane. The solution is stirred overnight at ambient temperature and 100ml of H_2O is added and stirring continued for a half hour. The layers are separated and the aqueous layer washed with 40ml of hexane. The organic layers are combined and dried over $MgSO_4$. The drying agent is removed and the solvent distilled at room temperature through a 15cm Vigreaux column. The residue is distilled at 130mm yielding 0.25g (12%) of cis-bicyclo[4.2.0] oct-2-ene (XXX): bp 74° , NMR (δ, CCl_4) 5.7 (s, 2H), 2.9-2.4 (m, 2H) and 2.4-1.3 (m, 8H); ir (CCl_4) 3025 (w), 1645 (w), 1451 (m) 1441 (m), 703 (m) and 690 (m)cm^{-1}.

cis-Bicyclo[4.2.0] octane (LIV)

A solution of 0.95g (8.8mmol) of XXX and 3.28g (17.6mmol) of p-toluenesulfonyl hydrazide in 20ml of diglyme (dried over molecular sieves) is heated under N_2 to reflux and maintained there for 1 hr. N_2 evolution is observed and subsides by the end of the hour. The mixture is cooled, poured into water, and extracted several times with 30-60° petroleum ether. The combined organic layers are washed with water and dried over $MgSO_4$. The solvent is removed by distillation and the residue distilled in a micro-distillation apparatus at 130mm, yielding 0.4g (50%) of LIV; ir 2980 (m), 2940 (s), 2870 (m), 1468 (w), 1452 (m) and 1440 (w)cm^{-1}.

cis-Bicyclo[4.2.0] oct-7-en-2-ol (XXXIX)

To a solution of 0.5g (4.1mmol) of XXXVIII[22] in 10ml of methanol is added with stirring 0.15g (4.1mmol) of $NaBH_4$ in small quantities over a half hour period. The solution is allowed to stir an additional 4 hours and the volume is then concentrated under reduced pressure. The residue is poured into H_2O and the aqueous solution is extracted several times with ether. The combined etheral layers are dried over $MgSO_4$ and the solvent is removed under reduced pressure, yielding 0.5g (100%) of the crude alcohol XXXIX: NMR (δ, $CDCl_3$) 6.35-6.0 (d, 2H), 5.0-4.8 (s, 1H), 4.05-3.8 (m, 1H), 3.1-2.9 (s, 2H) and 1.8-1.2 (m, 6H); ir 3600-3100 (s), 3045 (w), 1050 (s), 790 (m) and 770 (w)cm^{-1}.

2-Methylene-<u>cis</u>-bicyclo[4.2.0] oct-7-ene (XL)

Methyltriphenylphosphonium iodide (4.65g, 11.5mmol) dissolved in 16ml of dimethylsulfoxide (distilled from CaH_2) is added to a solution of 1.3g (11.7mmol) of potassium <u>t</u>-butoxide in 16ml of dimethyl sulfoxide under N_2 and stirred for 3 hrs. To this solution is added dropwise 1.4g (11.5mmol) of XXXVIII[22] dissolved in 5ml of dimethylsulfoxide, stirring is continued for an additional 3 hrs where upon 50ml of 30-60° petroleum ether is added and the mixture is stirred for 0.5 hrs. The layers are separated and the dimethyl-sulfoxide layer is poured into ice water and extracted several times with 30-60° petroleum ether. The combined petroleum ether layers are washed with H_2O and dried over $MgSO_4$. The solvent is removed under reduced pressure and the residue is distilled at 160mm yielding 0.7g (50%) of XL: bp 105° ; NMR (δ, CCl_4) 5.8-5.4 (m, 2H), 4.4-4.2 (s, 2H), 3.1-2.5 (q, 2H) and 2.0-1.0 (m, 6H); ir 3080 (w), 3050 (w), 2942 (s), 888 (m), 788 (m) and 698 (w)cm^{-1}.

<u>cis</u>-Bicyclo[6.2.0] dec-9-ene (XXVI)
and Bicyclo[6.2.0] dec-1(8)-ene (L)

A. <u>10,10-dichloro-<u>cis</u>-bicyclo[6.2.0] decan-9-one (XLVII)</u> A solution of 20.9g (207mmol) of triethylamine (distilled from KOH) in 140ml of <u>cis</u>-cyclooctene is added through a pressure-equalizing addition funnel over a 1 hrs period with stirring to a mixture of 30.6g (207mmol) of dichloroacetylchloride in 250ml of <u>cis</u>-cyclooctene preheated by an oil bath at 65° in a 1-1., three neck round bottom flask equipped with a mechanical stirrer and a condenser with drying

tube. A white precipitate forms immediately upon addition of the amine. When the addition is complete the oil bath temperature is raised to 80° and the solution is stirred for an additional 2 hrs. The solution is cooled and with continued stirring H_2O is added until all the precipitate has dissolved. The layers are separated and the organic phase is washed with 2 x 100ml of 5% HCl, 2 x 100ml of 10% $NaHCO_3$ and dried over $CaSO_4$. The solvent is removed under reduced pressure. The residue is distilled at 0.75mm yielding 32.7g (72%) of XLVII: bp 88-96° ; ir 1807 (s), 1468 (m), 1462 (w) and 1450 (w)cm^{-1}.

B. <u>cis</u>-Bicyclo[6.2.0] decan-9-one (XLVIII) A solution of 30g (136mmol) of XLVII in 400ml of glacial acetic acid in a 1-1. round bottom flask equipped with a condenser and magnetic stirrer is placed in a preheated oil bath at 120°. Zinc dust (17.9g, 272mmol) is added neatly and very cautiously since the reaction becomes violently exothermic during addition. After addition, stirring is continued at the elevated temperature for 20 minutes. The solution is then cooled, filtered through Celite, concentrated under reduced pressure and poured into H_2O. The aqueous solution is extracted several times with ether; the combined ethereal layers are washed copiously with H_2O, several portions of 10% $NaHCO_3$, dried over $MgSO_4$, charcoaled, filtered through Celite and solvent removed under reduced pressure. The residue is distilled at 0.1mm yielding 10g (66%) of XLVIII: bp 62-64° ; ir 1780 (s), (1468 (m), 1462 (w) and 1450 (w)cm^{-1}.

C. <u>Tosylhydrazone of XLVIII (XLIX)</u> To a solution of 2g (13.2mmol) of XLVIII dissolved in 20ml of chloroform is added 2.7g (14.5mmol) of <u>p</u>-toluenesulfonyl hydrazide. The mixture is stirred overnight, $MgSO_4$

is added, stirring is continued for an additional 3 hrs and the solution
is then filtered through Celite. The solvent is removed under
reduced pressure and the residue is placed under high vaccuum for a
half hour, leaving a waxy yellow solid. Recrystalization from absolute
ethanol yields 2.9g (69%) of white crystaline XLIX; mp 128-130°.

D. XXVI and L To a solution of 1.52g (15mmol) of
diisopropylamine (distilled from KOH) in a solvent mixture of 45ml
tetrahydrofuran (distilled from $LiAlH_4$) and 5ml ethyl ether (distilled
from Na), placed in a 100ml three neck round bottom flask equipped
with a rubber septum, magnetic stirrer, and N_2 bubbler, is slowly
added 9.75ml (15mmol) of 15% n-butyllithium in hexane via syringe;
resulting in formation of a yellow solution, which is allowed to stir
for 1 hrs under N_2. To this mixture 2.4g (7.5mmol) of XLIX dissolved
in 20ml tetrahydrofuran/5ml ethyl ether is slowly added via syringe;
the reaction is slightly exothermic, and results in a maroon red color.
The solution is stirred for 10 hrs; 30-60° petroleum ether is added
and stirring is continued for an additional half hour. The mixture
is poured into H_2O; the organic layer is separated, washed copiously
with H_2O, 2 x 50ml of 5% HCl, 1 x 50ml $NaHCO_3$, dried over $MgSO_4$ and
the solvent removed under reduced pressure. The residue is
chromatographed on silica gel with hexane as the eluent. Gas
chromatographic analysis shows three products formed and NMR indicates
vinylic hydrogens present. The purified products are chromatographed
on 20% $AgNO_3$/silica gel with hexane as the eluent; the minor elimination
product believed to be a saturated hydrocarbon is removed from the
column first. The two major elimination products are removed next

essentially pure in a ratio of 55:45 yielding 200mg (20%) of XXVI and

L; NMR (δ, CCl_4) 6.0-5.9 (d, 1H) and 2.5-1.0 (unresolved multiplet, 10H).

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