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Title: CATALYTIC REARRANGEMENT OF CYCLODECA-1,2,5-TRIENE AND OXYMERCURATION OF BICYCLO-[7.1.0]-DECA-2,3-DIENE

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Dr. Richard W. Thies

The reaction of cyclodeca-1,2,5-triene with mercuric salts gave only rearranged hydrocarbon, tricyclo[4.4.0.$0^{2,4}$]deca-5-ene in acetic acid. Other catalysts $[Rh(CO)_2Cl]_2$ and $AgClO_4$ gave the same rearranged hydrocarbon. The isomerization is proposed to proceed through a "metal-complexed" carbenoid intermediate.

The reaction of bicyclo-[7.1.0]-deca-2,3-diene gave oxymercurated products.

CATALYTIC REARRANGEMENT OF CYCLODECA-1,2,5-TRIENE AND OXYMERCURATION OF BICYCLO-[7.1.0]-DECA-2,3-DIENE

by

Janice Lee Roop

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CATALYTIC REARRANGEMENT OF CYCLODECA-1,2,5-TRIENE

AND OXYMERCURATION OF BICYCLO-[7.1.0]-DECA-2,3-DIENE

Introduction

The problem of enviromental pollution is currently attracting a great deal of attention from nonscientists and scientists alike. There is particular concern by environmentalists about the disposal of industrial wastes containing heavy metals, such as mercury.[1,2,3] Mercury represents a serious health hazard because organisms can convert it to the highly toxic methylated form.[4,5]

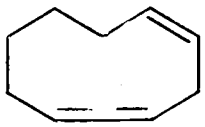
However, to the organic chemist mercury compounds have a useful role in synthesis. The oldest and most thoroughly studied reactions using mercuric compounds has been the oxymercuration of alkenes.[6,7,8] Oxymercuration provides a convenient route from an olefin to its corresponding Markovnikov solvent addition product (equation 1). Oxymercuration has been extended to allenes normally producing allylic alcohols, esters, or ethers (equation 2).

(1) $$>C{=}C< \;+\; Hg^{2+} \xrightarrow[2)\ NaBH_4]{1)\ SOH} >\overset{SO}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}<$$

(2) $$>C{=}C{=}C< \;+\; Hg^{2+} \xrightarrow[2)\ NaBH_4]{1)\ SOH} >\overset{SO}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}{=}C<$$

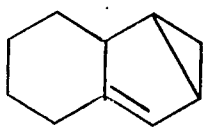
In 1972 a new development in the reaction of allenes with mercuric salts was presented by Thies and Hong.[9] They reacted mercuric sulfate with cyclodeca-1,2,5,8-tetraene in various solvents and found that, in contrast to most oxymercurations, only rearranged products were obtained.

The subject of this thesis supports that work by demonstrating that the reaction is not limited to a single case. Two allenes were studied. The more interesting one, cyclodeca-1,2,5-triene, reacted in acetic acid with various mercuric salts giving only one rearranged product, a hydrocarbon 2.



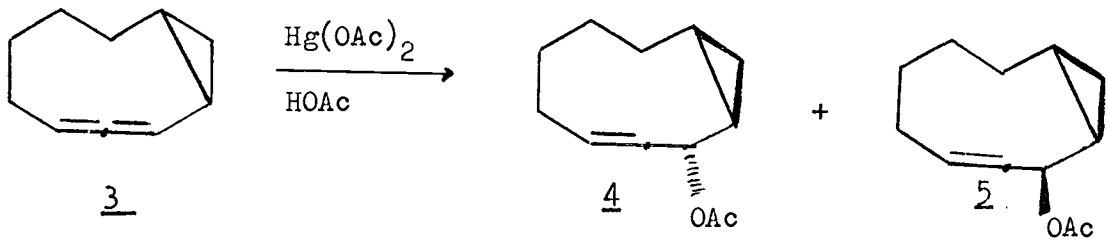
1

$\xrightarrow[\text{HOAc}]{Hg(OAc)_2}$



2

Other transition metal salts were used as catalysts yielding the same rearranged product, indicating that this isomerism can be catalyzed by other transition metal salts besides mercury salts. In addition, bicyclo [7.1.0] deca-2,3-diene 3 yielded only oxymercuration products 4 and 5 when the allene was subjected to the same reacting conditions as cyclodeca-1,2,5-triene with no rearranged products found.



History of Oxymercuration

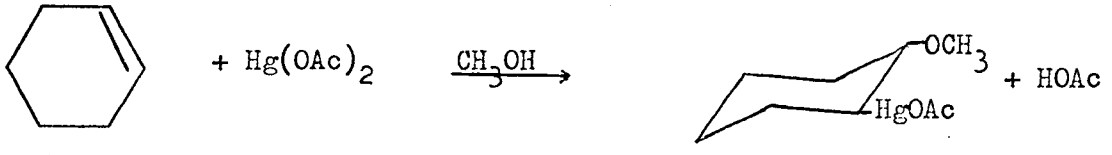
The very first addition reactions between mercury(II) salts and alkenes appear to have been in 1892 by Kucherov.[10]

General interest in the reaction between Hg(II) salts and alkenes was, however, first created by the work of Hofmann and Sand around 1900. These workers studied the reactions of olefins with basic mercury(II) salts in aqueous solution and were able to characterize the most important types of addition products for the first time.

The prolific investigations of Sand (1901-1908), Biilmann (1900-1912), Balbiana and Paolini (1901-1909), Schrauth and Scholler (1911-1922), Manchot (1920), Nesmeyanov (from 1936) and Wright (since 1935) have been discussed in a detailed review by Chatt[6] in 1951.

Stereochemical Course of Oxymercuration

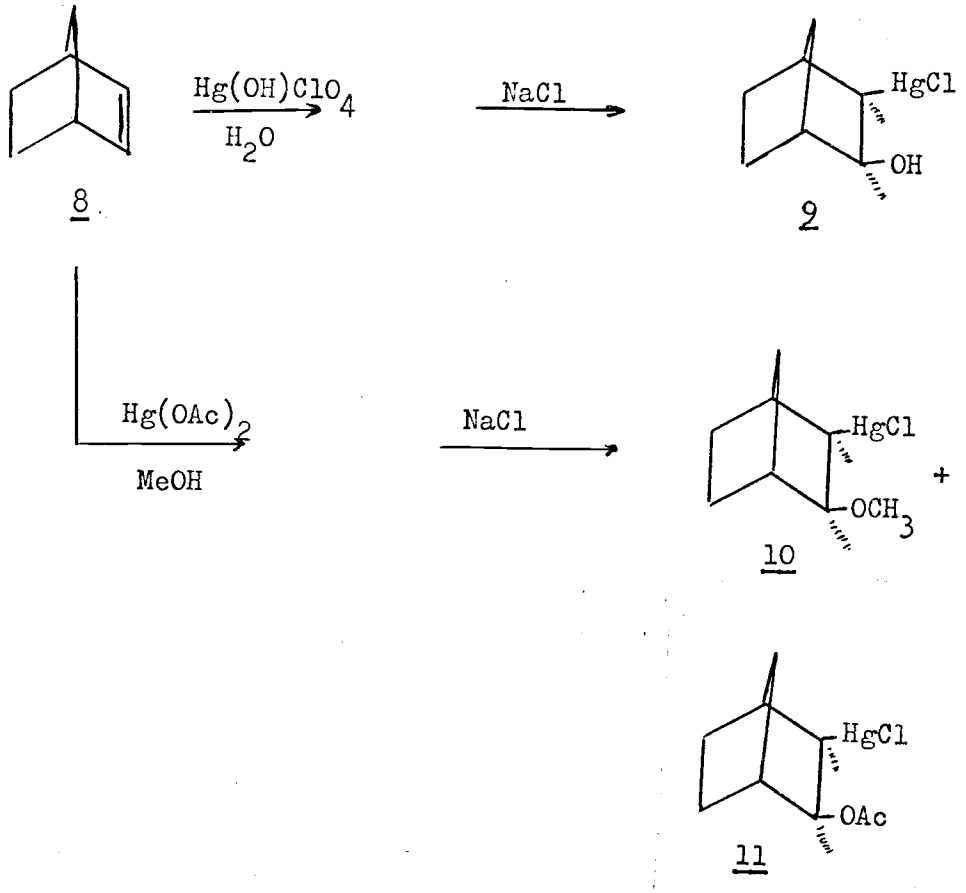
In a pioneering paper dealing with reaction of mercuric ion with cyclohexene, Lucas, Hepner, and Winstein[11] made the prediction based largely on analogy with behavior of bromonium ions, that oxymercuration of simple olefins may well be trans. The intuitive correctness of this prediction was subsequently established by studies of stereochemistry of isolated mercurial 7 from cyclohexene 6.[12,13]



6 7

Contrary to the oxymercuration of simple olefins, oxymercuration of norbornene and related olefins has cis-orientation of addition. The cis-exo nature of the norbornene-derived oxymercurials was first convincingly demonstrated by Traylor and Baker.[14] Norbornene 8 when reacted with $Hg(OH)ClO_4$ followed by workup in aqueous NaCl

solution gave product 9. And a similar reaction of norbornene 8 with mercuric acetate followed by subsequent workup in aqueous NaCl solution gave cis-exo products 10 and 11:



No skeletal rearrangement accompanied the addition process.

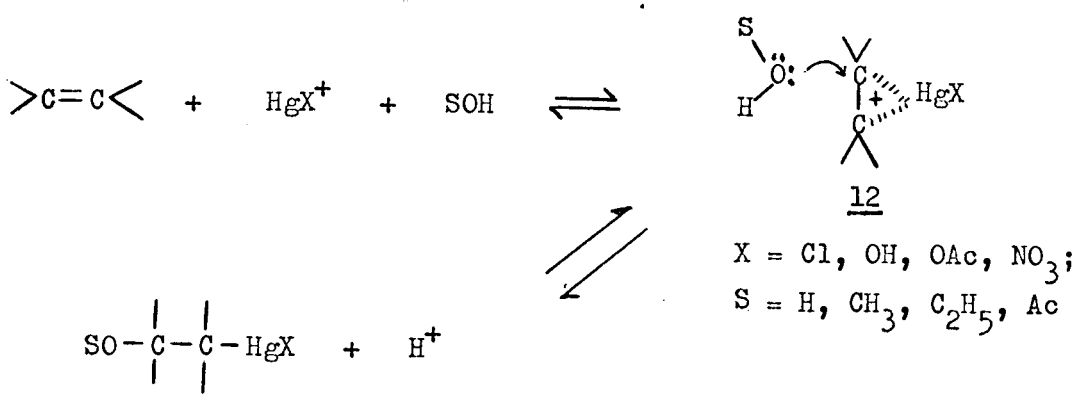
With regard to the stereochemistry and orientation of oxymercuration, the following generalizations have been made.[8]

1. Oxymercuration of cyclohexene and unstrained olefins is stereospecifically trans.
2. Oxymercuration of norbornenes is stereospecifically exo-cis.

3. Oxymercuration invariably occurs in the Markovnikov sense, so that the oxy group becomes attached to the more electropositive carbon and the mercuric group to the more electronegative carbon. Unless the polarities of the carbon atoms are almost identical, very fine discrimination occurs, so that only one positional isomer results.

Mechanisms of Oxymercuration

There are overwhelming arguments that show that oxymercuration proceeds through an initial electrophilic addition of mercury(II) species to the olefinic double bond to give a "mercurinium ion" 12 which is subsequently attacked by solvent (SOH) or another nucleophile.[6,7,8,15] In the case of acyclic olefins stereospecific trans-addition is observed:



The "mercurinium ions" have been formulated in mechanistic schemes in order to account for the stereochemistry.[16,17,18,19]

Several efforts have been made to detect mercurinium ions in solution by ^{1}H-nmr techniques,[20,21,22] but mercurinium ions are obviuously not present in measureable concentration in aqueous solutions. Stable, long-lived mercurinium ions have been identified recently by G. A. Olah and P. R. Clifford,[23,24] viz., 2-alkoxyetherylmercuric chloride, when added to the superacid merdium $FSO_3H-SbF_5-SO_2$, gave a solution which displayed an nmr spectrum corresponding to the mercurinium ion.

Not all investigators favor this mercurinium ion intermediate.[25]

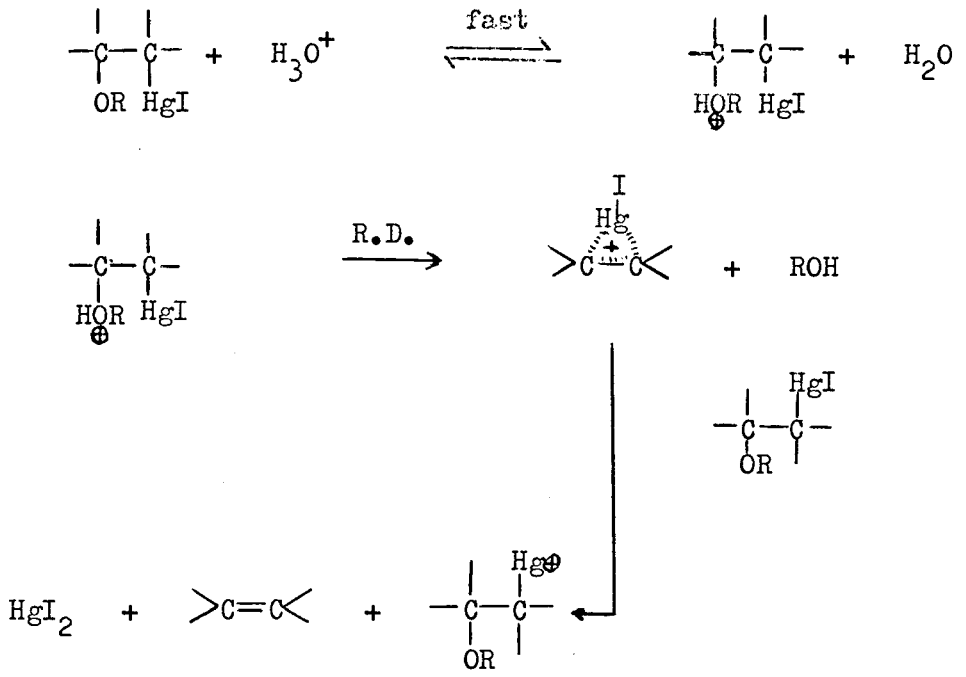
Kinetics of Oxymercuration

Kinetics of oxymercuration are clearly second order, first order with respect to mercuric species and with respect to olefin.[6,26]

Deoxymercuration

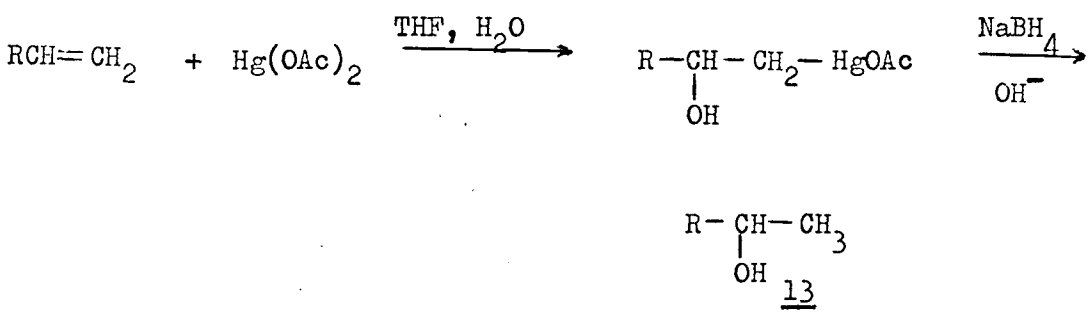
The reversibility of the reaction has been demonstrated by several investigators. Extensive work by Kreevoy[12,13,26,27] supports the following scheme:

Scheme 1



Synthetic Use of Oxymercuration

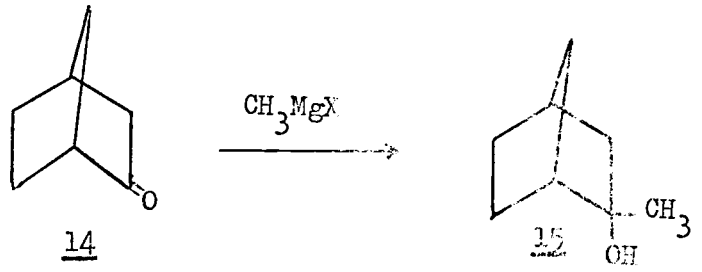
H. C. Brown and coworkers[28,29,30,31] in a series of papers presented the synthetic use of oxymercuration in the preparation of stereospecific alcohols. They reported a convenient method of preparing Markovnikov hydration product 13 from olefins.[28]



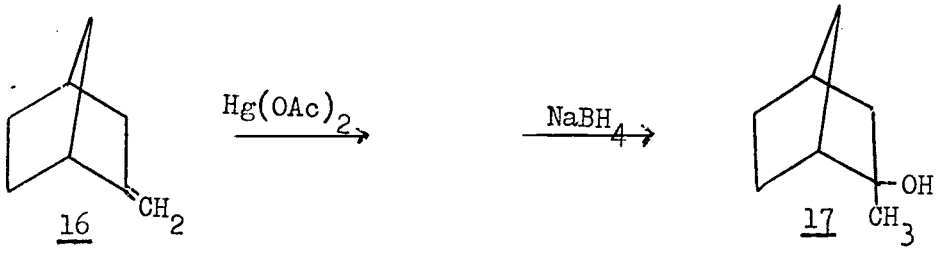
The reaction was clean, easy and usually gave a high yield of alcohols. This oxymercuration-demercuration procedure provides a highly convenient synthetic route to isomeric alcohols epimeric with those available *via* the Grignard synthesis. The Grignard reaction (equation 1) yielded the *endo*-alcohol 15, while the product of oxymercuration of compound 16 (equation 2) followed by reduction

gave an exo-alcohol 17:

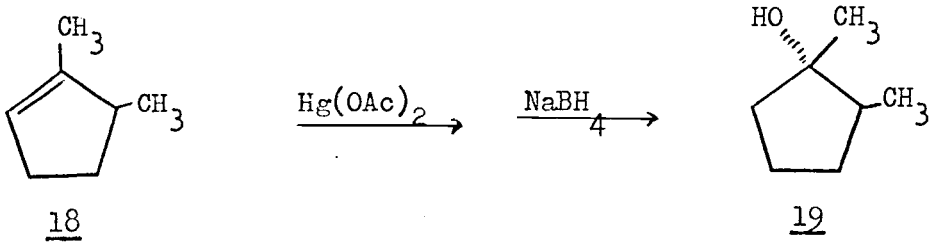
(1)



(2)

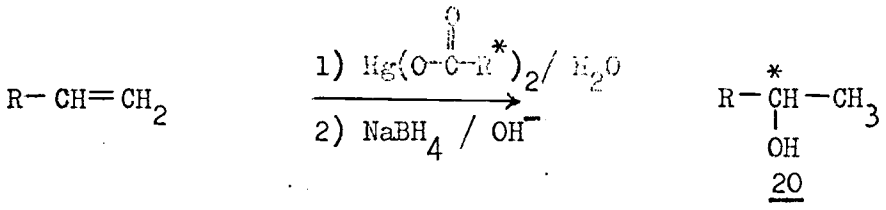


The data reveals that hydration of the initial mercury intermediate occurs predominately from the less hindered side of the molecule. This is illustrated by the following case:



Synthesis of optically active alcohols 20 can be accomplished by

using chiral mercury(II) carboxylates in the oxymercuration step:[32]

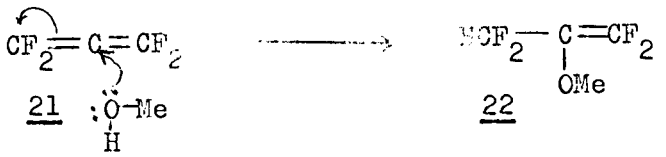


Within the last decade oxymercuration has been extended to allenes. Although there has been considerable literature on oxymercuration of alkenes, there has been little investigation of oxymercuration of allenes. In general, the reaction of allenes are similar to alkenes but more complicated. Investigators dealing with the oxymercuration of allenes try to draw much similarity [such as mode of oxymercuration, existence of mercurinium intermediate, kinetics of deoxymercuration and oxymercuration (although little work has been accomplished here)] to the oxymercuration of alkenes.

Reaction of Allenes

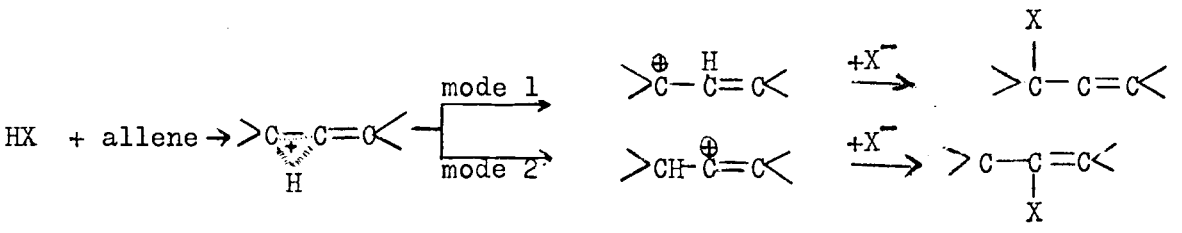
Allenes can react with either nucleophiles or electrophiles. There is no evidence to suggest that allene or its lower homologs are susceptible to nucleophilic attack but the presence of strongly electron-withdrawing groups leads to additions initiated by a nucleophile

attacking the central atom:[33]



Other typical electron-withdrawing groups besides fluorine are nitrile, carboxylic acid, carbonyl and ester, which activate the allenic bond to initiate the attack by amines, water (mercuric catalysts), Grignard reagents, and hydrohaloacids (metal catalyst).[34,35]

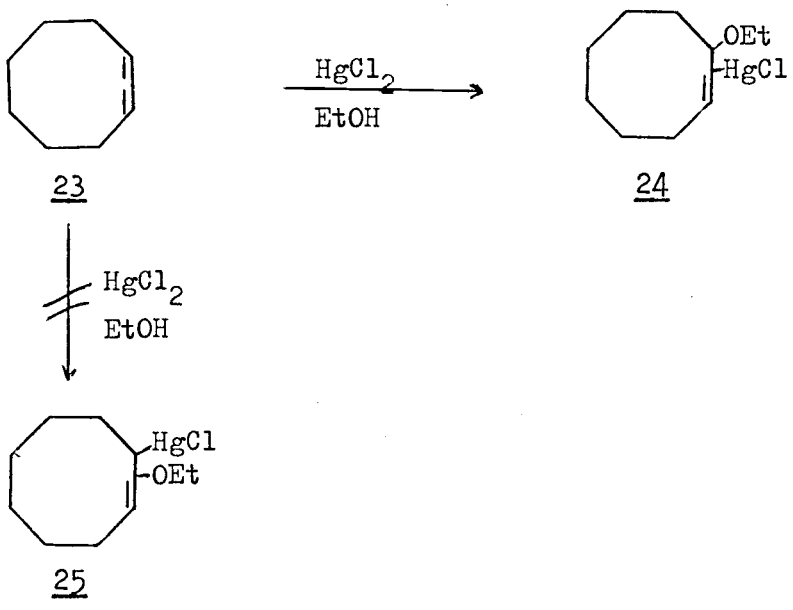
Although allenes must have strong eleotron-withdrawing groups in order to undergo nucleophilic addition, allenes readily undergo electrophilic addition of halogens and acids. With acids the proton adds first to the more electron rich double bond, which is dependent on the substituents, and either an allylic or vinylic carbonium ion forms:



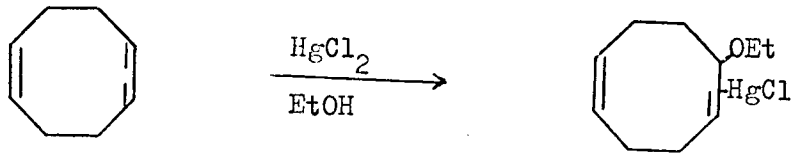
Systematic studies of this reaction have been carried out by Jacobs and Johnson[36] and by Griesbaum, et. al.[37]

Oxymercuration of allenes has been considered as a "type" of electrophilic addition in which mercury salts have been found to add selectively to the central carbon of the double bond (like mode 1 above) except for allene itself (mode 2). The first reported attempt to assign structures to initial allene-mercuric salt adducts was by Gardner and coworkers.[38] They determined the orientation of addition of mercuric acetate to 1,2-cyclononadiene, 1,2,6-cyclononatriene, and 2,3-pentadiene in ethanol.

Gardner reacted 1,2-cyclononadiene 23 with ethanolic mercuric chloride and afforded only compound 24.

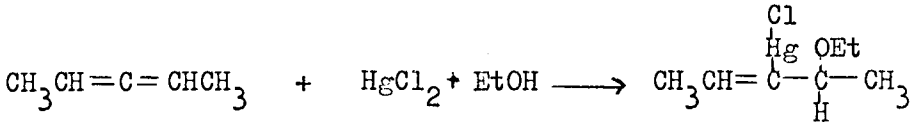


Oxymercuration of 1,2,6-cyclononatriene 26 followed the same path of addition and also supported the claim that allene bonds are more reactive than olefin bonds:



26 27

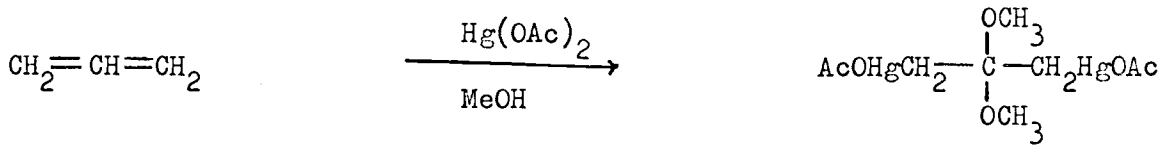
In the only aliphatic allene Gardner studied, $HgCl_2$ added to the allene 28 as it did with cyclic allenes, selectively to the central carbon.



28 29

Waters and Kiefer[39] extended the study of oxymercuration of aliphatic allenes by investigating the oxymercuration of allene 30

and its five methyl-substituted derivatives using mercuric acetate in methanol. They reported that unsubstituted allene resulted in the formation of the diadduct 31:

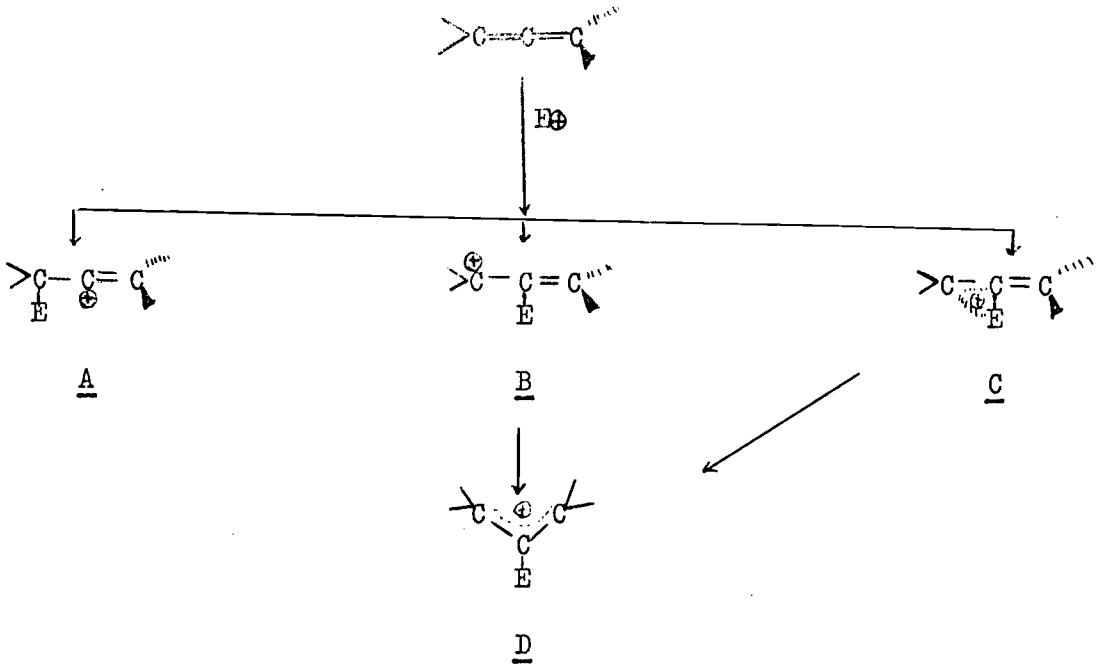


30 31

Substitued allenes added only one -HgOAc group, and usually to the central carbon atom.

Waters and Kiefer also investigated the mechanism of addition of mercuric salts to allenes. The mechanism of addition reaction of allenes is complex. The addition of an electrophile (E^+ or ^+HgX) to the cumulated orthogonal π-bond system can initially give rise to either a vinyl cation A, an orthogonal, non-resonance stabilized allylic-like cation B, or a bridged ion C. There is a considerable driving force[40] (12.6 ± 1.0 kcal/mol, Benson's calculations) for ions B and C to go through a 90° bond rotation about C_1 and C_2 to form a planar resonance stabilized carbonium ion D. (See Scheme 2)

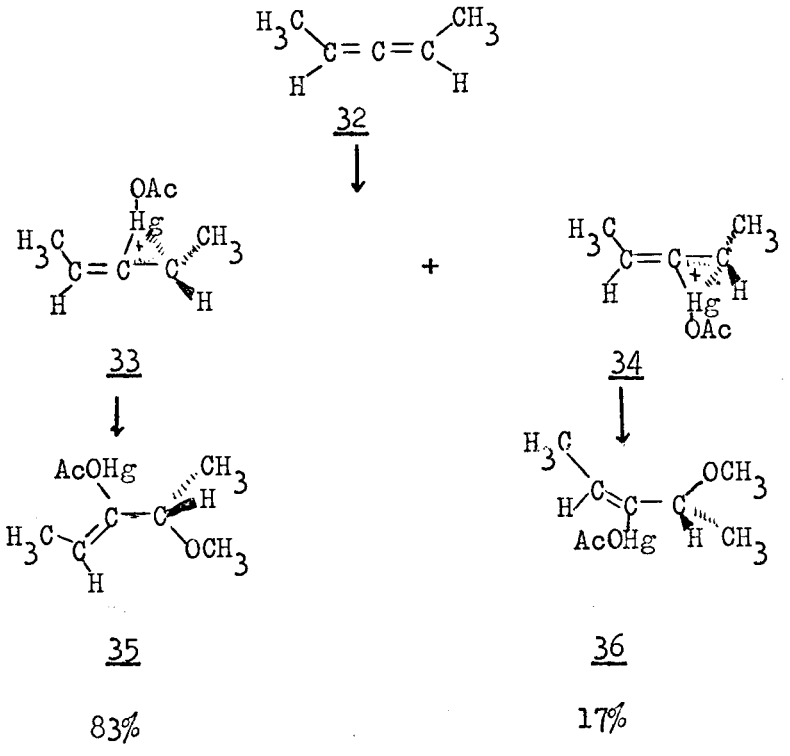
Scheme 2



So there exists theoretically several different types of reaction intermediates: A, B, C, or D, or a combination of a mixture of any of them. Waters and Kiefer supported the σ-bonded mercurinium ion C as intermediate for the oxymercuration of allenes based on the following data: the rate of oxymercuration of substituted allenes was found to be some 10^4 times faster than that of tetramethylethylene suggesting that oxymercuration of allenes proceeds through a stable intermediate. The σ-bonded mercurinium intermediate is more stable than the σ-bonded mercurinium ion of alkenes. They also found that addition of mercuric acetate in methanol to the 1,2-dimethylallene 32 gave

in high yield an 83:17 mixture of trans-cis-3-acetoxy-mercuri-4-methoxy-2-pentanes, 35 and 36 and suggested the following scheme to account for stereospecificity.

Scheme 3



The reaction involved the preequilibrium formation of σ-bonded mercurinium ions, 33 and 34, which in the rate-determining step collapsed to products by a trans-rearward attack of solvent at the methyl

substituted carbon. Thus approach of the nucleophile trans to the mercury bridge is expected to be less sterically hindered by the substitutents at the vinyl terminus in 33 than in 34 and trans product 35 would therefore be formed at the faster rate. This explains the 83:17 ratio of 35:36.

This mechanism requires that the reaction be a stereospecific trans addition, but it cannot be assumed this is the case. Cis-oxymercuration of alkenes is not unknown,[41,42,43,44] and one cannot exclude the possibility that allylic ions analogous to D may intervene.

That intermediate D was not involved was determined by Caserio[45] and coworkers who reported that addition of mercuric acetate to optically active 2,3-pentadiene 32 yielded essentially optically pure 35 (see Scheme 3), establishing that 32 to 35 proceeded stereospecifically ruled out intermediates which did not preserve stereochemistry of reaction and corroborated the bridged carbonium intermediate which should.

Bach[46] reported on results of alkoxymercuration of optically active 1,2-cyclononadiene with mercuric oxide and boron trifluoride etherate as an effective catalyst. Bach had obtained optically active products thus supporting the σ-bridged mercurinium ion.

Further study on the oxymercuration of cyclic allenes in ethanol was carrried out by R. Vaidyanathaswamy and D. Devaprabhakara.[47] Methoxymercuration of cyclic allenes 1,2-cyclononadiene, 1,2-cyclodecadiene, 1,2-cycloundecadiene and 1,2-cycltridecadiene with mercuric chloride was studied. The organomercurial was determined to be the

cis product or the trans product by mon.[57,58] There are two modes of attachment of the electrophile $^{+}HgCl$. One is from the hydrogen side resulting in a cis double bond (fig. 1). Cis product infers attack of ^{+}HgX cis to the hydrogen on the adjacent bond, i.e., from outside the ring.

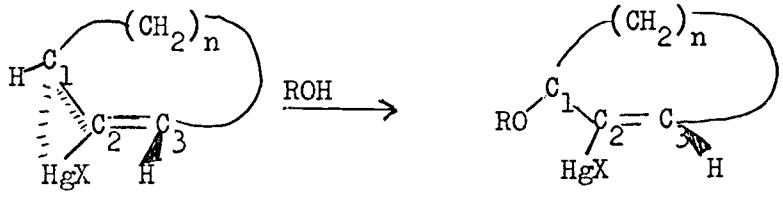


Figure 1 cis product

Trans product is obtained when the electrophile $^{+}HgCl$ attacks from inside the ring resulting in a trans double bond (fig. 2).

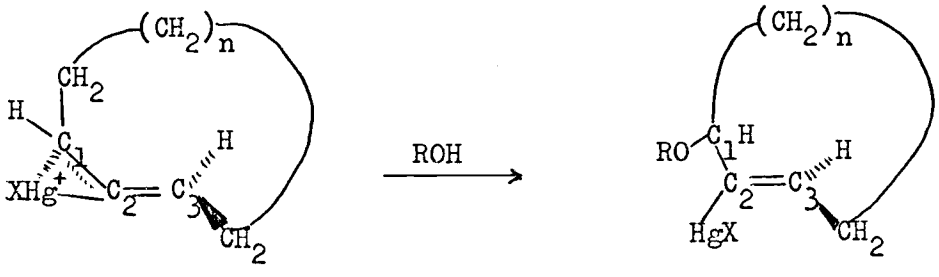


Figure 2 trans product

The results obtained for the various mercurials were as expected, viz., C-10 allenes gave rise to cis adduct and C-11 allene predominately cis whereas addition to C-12 and C-14 allenes resulted in the formation of predominately trans product.

Bach[50] did more extensive work on the oxymercuration mechanism of allenes and showed that upon investigation of oxymercuration of optically active 1,2-cyclononadiene the amount of racemization depended on the mercuric salt used. Refer to Table I.

In addition Bach proposed the following mechanism to support his findings:

Scheme 4

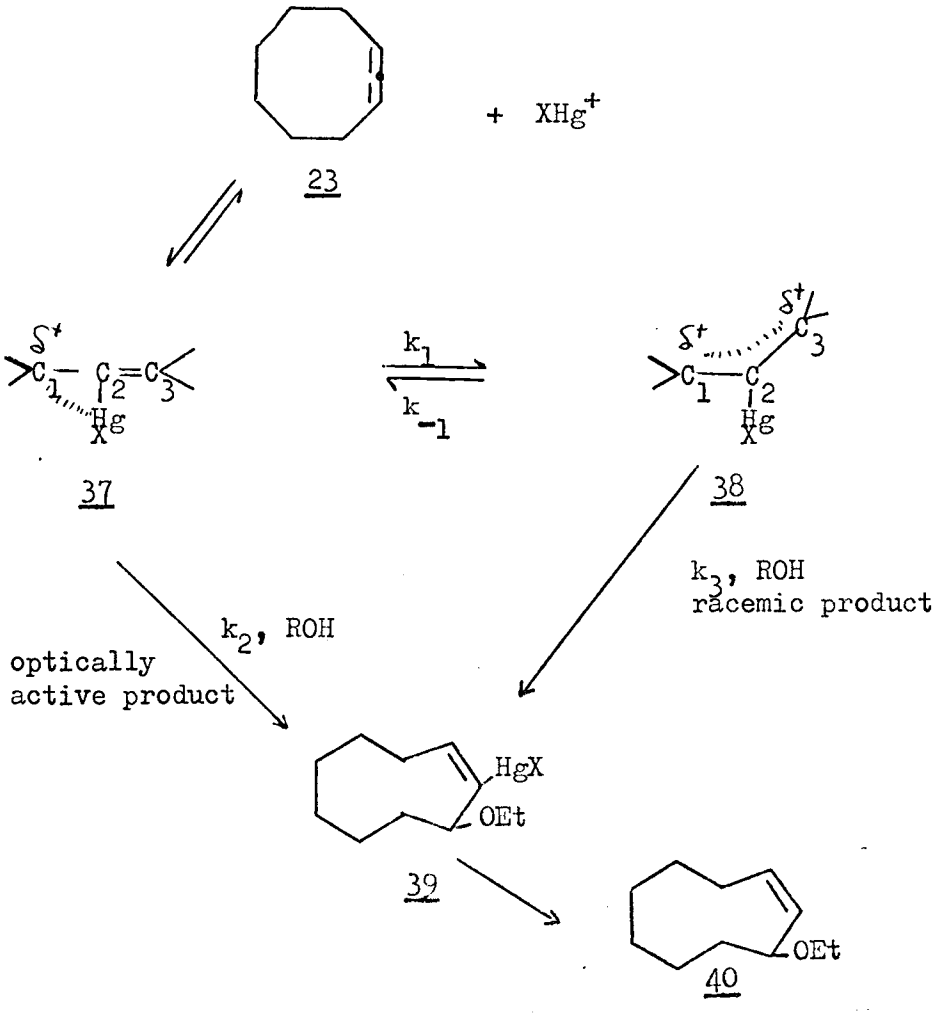


Table I

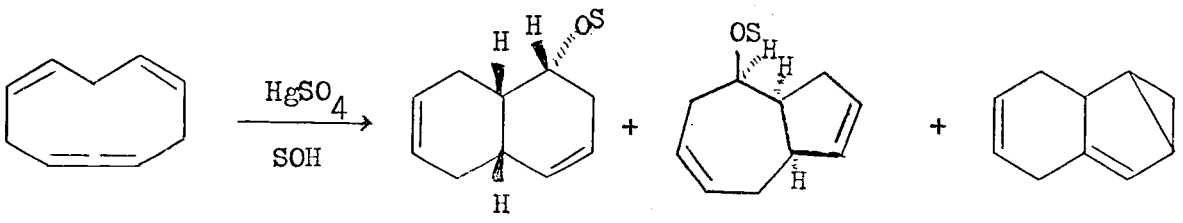
Reaction of Different Mercuric Salts with Optically Active 1,2-Cyclononadiene[a]

Mercuric Salt	Catalyst	Isolated Yield of 3-ethoxycyclonone	$[\alpha]^{25}D$, deg
C_2H_5HgOAc	BF_3	85	+15.3
C_6H_5HgOAc	BF_3	42	+13.6
$Hg(OAc)_2$			+12.4
$Hg(OAc)_2$	BF_3	67	+12.6
$Hg(ClO_4)_2 \cdot 9H_2O$	BF_3	82	+12.1
HgO	BF_3	73	+11.1
$HgSO_4$	BF_3	72	+10.4
$Hg(NO_3)_2$		51	+ 9.9
$Hg(NO_3)_2$	BF_3	70	+ 9.9
$HgCl_2Hg(OAc)_2$			+ 6.2
HgF_2	BF_3		+ 1.4
$HgCl_2$			0.1-0.2

[a]In ethanol

The important connotation of Scheme 4 is that there exists an equilibrium between 37 and 38. Each supports the fact that the electronegativity of the atom attached to Hg effects that equilibrium. Thus a more electronegative atom should increase the carbonium character at C_1, destabilizes 37 and enhances the formation of other resonance stabilized allylic carbonium ion, 38. This hypothesis was supported by the fact that the five oxygen-bearing ligands lead to a decrease in the stereospecificity of the reaction. (Table I)

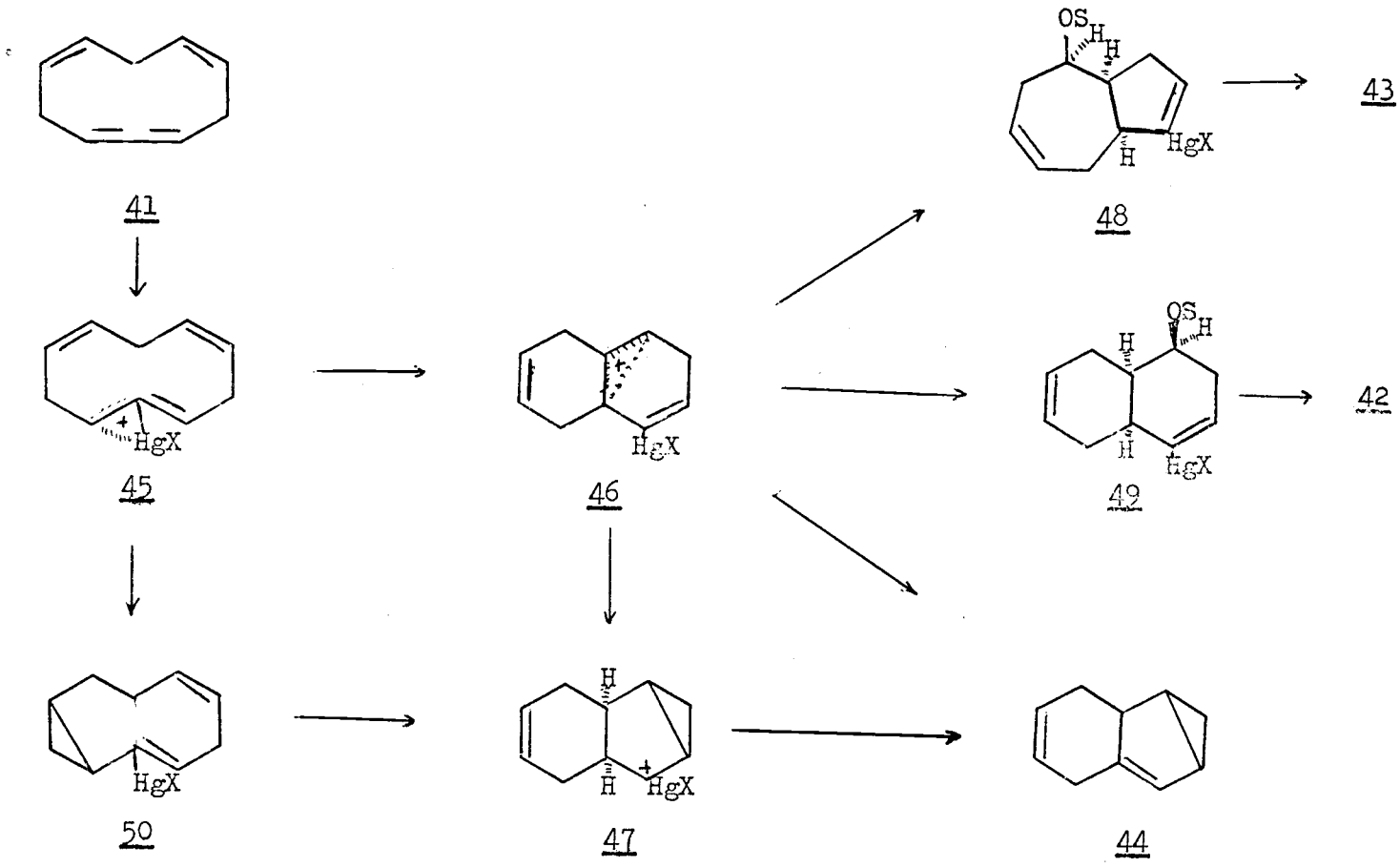
In contrast to most oxymercurations, Thies, Hong, and Buswell[9] reported the reaction of a cyclic allene, cyclodeca-1,2,5,8-tetraene, with a mercury salt in acetic acid gave only rearranged products.



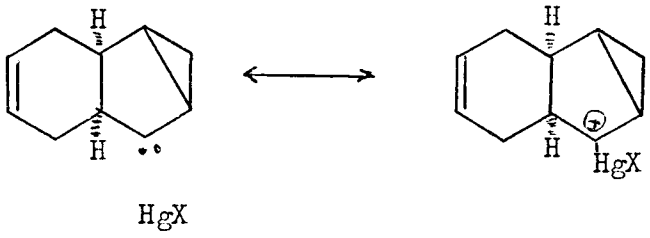
41 42 43 44

They proposed the following scheme to account for the products:

Scheme 5



Intermediate 45 is analogous to oxymercuration of cyclic allene. Solvated species 48 and 49 arose from solvent-captured intermediate 46. The hydrocarbon arose possibly from the paths outlined in Scheme 5. The proposed intermediate is of prime significance. Thies et. al. proposed the intermediate 47 to be a "metal complex carbenoid" 51 (which is shown here as a resonance form).



51 47

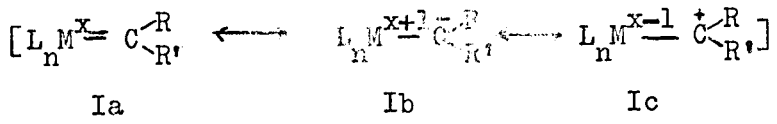
Hydrogen migration typical of metal carbenoids[51] results in hydrocarbon 44.

The character of "metal-complexed" carbenoid proposed by Thies may be an important factor in determining the yield of hydrocarbon. Thies reports approximately 50% yield of hydrocarbon in acetic acid using mercury salts as catalyst. Some work has been done concerning the nature of the "metal-complexed" carbenoids.

Nature of "Metal-complexed" Carbenoids

A complex of a transition metal M^xL_n (x = oxidation number, L = ligand) and a carbene :CRR' (R, R' = H or carbon function) has three resonance forms: ylene form Ia, metal-bonded carbanion Ib and the

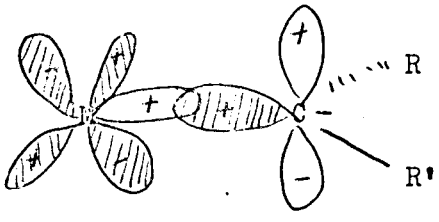
metal-bonded carbocation Ic.[52,53]



Ia Ib Ic

The relative significance of each resonance form is determined by the nature of the metal, its ligands, and the carbene substituents.

One theoretical model has been suggested, as represented by Model II. Two bond situtations occur simultaneously: lone-pair electrons in the carbene sp^2 hybrid orbital are donated into a vacant orbital of M forming a sigma bond, and simultaneous back-donation from an appropriate d or hybridized orbital of M to the vacant 2p orbital of carbene carbon forming a pi bond.



II

Therefore the bonding situation is related to promotion energy of the metal M (pi-interaction) and its electron affinity (sigma-interaction). The actual charge distribution M-C bond is determined by the σ and π components. The direction of the bond dipole is dominated primarily by the electronegativity of M compared with that of the carbon atom. (Refer to Table II)

Noyori[54] used Table II as a general source of information concerning the nature of carbenoids generated from bicyclo [1.1.0] butanes and transition metal complexes. He proposed the following generalizations: that reactivity of the carbenoid intermediate is dependent on the electronegativity of the metal vs. the carbon. Since a Ni(0) atom is more electropositive than carbon, nickel carbenoid behaves as a nucleophile.[55] By contrast, Rh(I), Ir(I), Pt(II), Pd(II), and Hg(II) ions are highly electronegative and their respective carbenoids undergo typical electrophilic reactions.

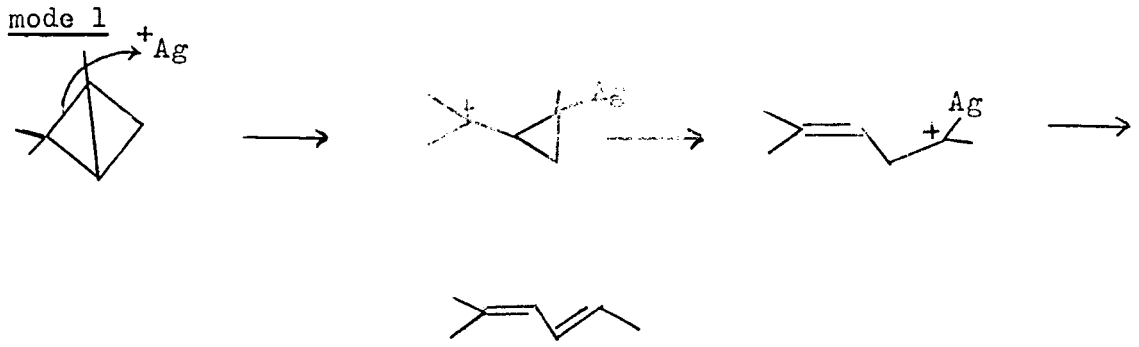
Noyori referred to Table II to explain the different products obtained from reacting unsymmetrically substituted bicyclobutane with different metal catalysts. He explained the products through three modes of interaction. Cu(I) and Ag(I) carbenoids (if indeed formed)[56] are relatively poor π donors and would have an intermediate like Ic, a metal-bonded carbocation. Cleavage occurs between bonds C_1-C_3, C_2-C_1 when using Cu(I) or Ag(I) in order to provide the most stable metal-bonded carbocation. The methyl group attached to the positive carbonium site stabilizes this intermediate and is the directive influence in bond breaking. Rh(I) or Ir(I) follows the mode 2 either because these metals are efficient π donors or because of their bulkiness.

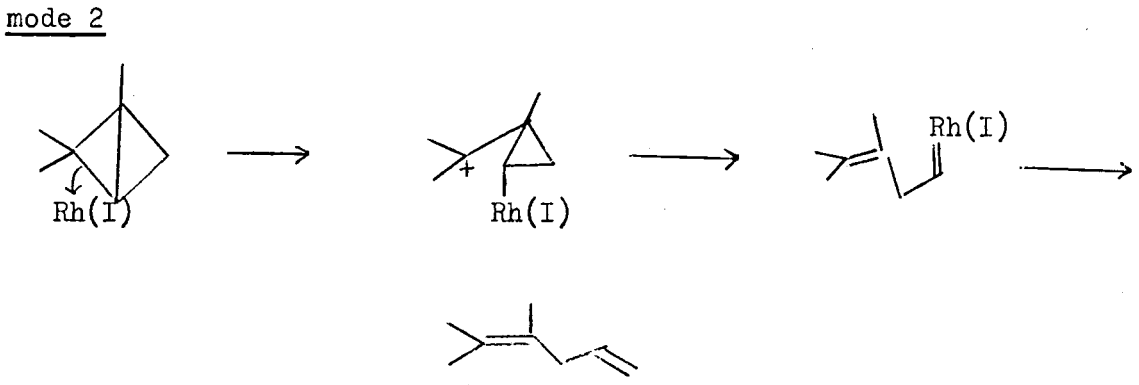
Table II

Properties of Certain Transition Metal Atom and Ions

Atom or ion	Electronic configuration	Promotion energy, eV[a,b]	Electron affinity, eV[a]	Electro-negativity, X[c]
Ni(0)	d^{10}	1.72	1.2	1.1
Rh(I)	d^{8}	1.60	7.31	4.1
Ir(I)	d^{8}	2.4	7.95	4.0
Pt(II)	d^{8}	3.05	18.56	7.5
Pd(II)	d^{8}	3.39	19.42	8.5
Cu(I)	d^{10}	8.25	7.72	4.4
Ag(I)	d^{10}	9.94	7.57	4.6
Hg(II)	d^{10}	12.8	18.75	8.4
Cd(II)	d^{10}	16.6	16.9	9.7

[a]Taken from R. S. Nyholm, Proc. Chem. Soc., 273 (1961). [b]Energy required for the $(n-1)d \rightarrow np$ transition. [c]Mulliken-type value adjusted to Pauling's scale, (ionization potential + electron affinity)/(2 x 3.15).

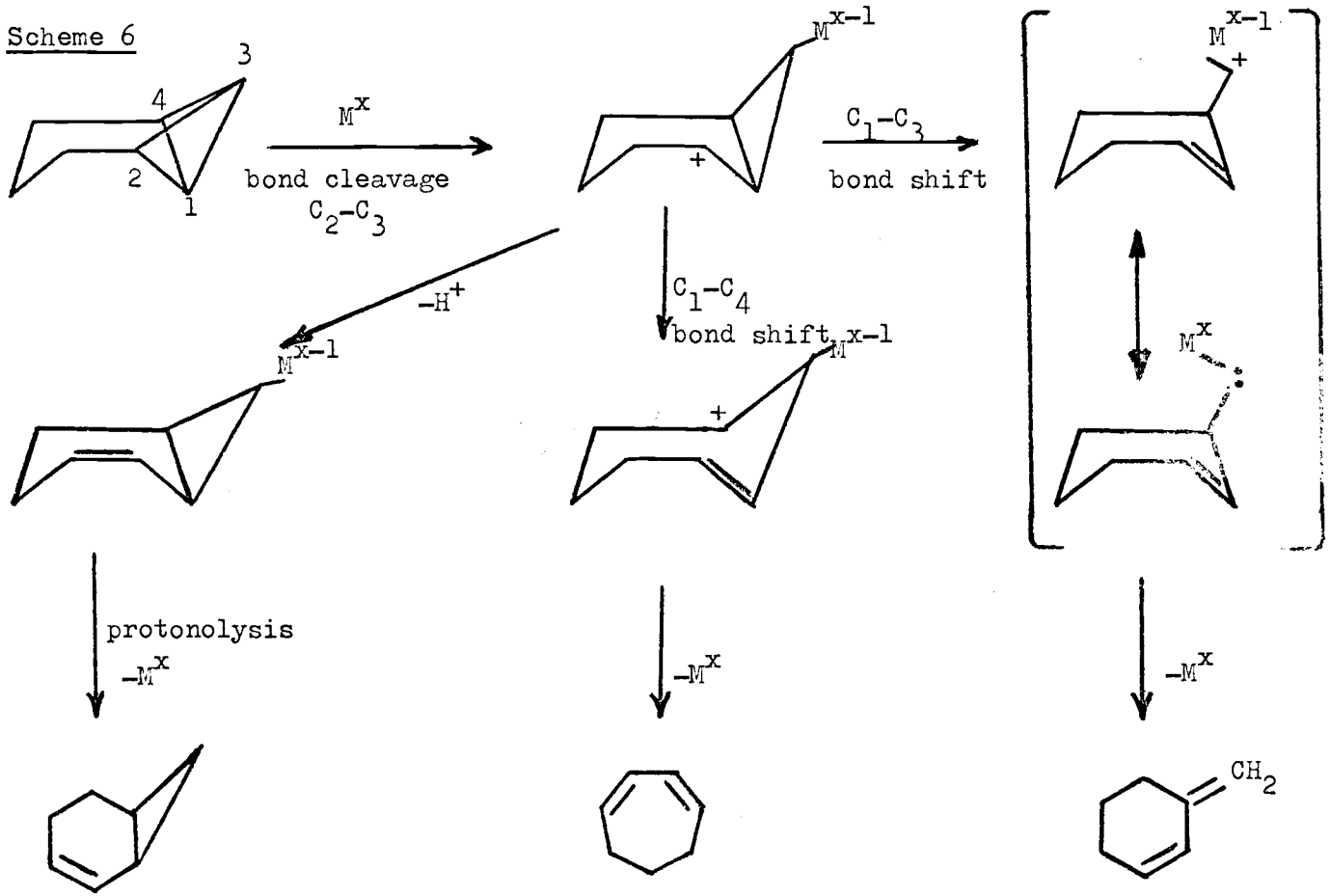




Other strained ring systems have also been studied. The transition metal complex promoted isomerization of tricyclo [4.1.0.0^{2,7}] heptane was studied in detail by Gassman and Atkins.[57] Derivatives of Cu(I), Ir(I), Hg(II), Pd(II), Pt(II), Ru(II), Sn(II), and Zn(II) were found to readily bring about the rearrangement of tricyclo [4.1.0.0^{2,7}] heptane to norcarene, 3-methylenecyclohexene, or 1,3-cycloheptadiene.

They proposed the following scheme to account for the products:

Scheme 6

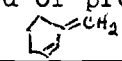

3
4
2
1
M^x
bond cleavage
C_2-C_3
M^{x-1}
+
C_1-C_3
bond shift
M^{x-1}
+
M^x
$-H^+$
M^{x-1}
C_1-C_4
bond shift
M^{x-1}
+
protonolysis
$-M^x$
$-M^x$
$-M^x$
CH_2

The mechanism utilizes the transition metal complex as a highly selective Lewis acid which generates a cyclopropylcarbinyl cation in cleaving the C_2-C_3 bond. Subsequent rearrangements yielded the respective hydrocarbons.

The yields and nature of the products formed were shown to be very dependent on the nature of the metal and the ligands attached to the metal. (Refer to Table III) However, Gassman and coworkers did not provide satisfactory answers why the metal catalysts formed the different hydrocarbons specifically. They hypothesized that the specificity of the reaction was somehow related to the strength of the carbon-metal "ions" in the metallic carbenoid formed in the first step of the rearrangement process.

Table III

Metal-Promoted Isomerizations of Tricyclo $[4.1.0.0^{2,7}]$ heptane.

Catalyst	Conditions (temp, °C; time; solvent)	% yield of products		
				
$AgBF_4$	ca. 40 minutes $CDCl_3$			100
ZnI_2	25°, 16 hr, Et_2O		11	88
$HgBr_2$	50°, 48 hr, Et_2O		8	89
$[Rh(CO)_2Cl]_2$	25°, 15 min, CH_3CN		98	
$[Ir(CO)_3Cl]_2$	25°, 14 hr, $CHCl_3$		91	
$[(\pi\text{-}CH_2{:}CHCH_2)PdCl]_2$	25°, 30 min, $CHCl_3$		94	
$[(C_6H_5CN)_2PdCl_2]$	25°, 20 hr, CH_3CN		69	
$[C_6F_5Cu]_4$	25°, 2hr, $CHCl_3$		74	
$[(C_6H_5)_3P]_2Rh(CO)Cl$	65°, 48 hr, CH_3CN	5	92	
$[Ru(CO)_3Cl_2]_2$	25°, 40 hr, CH_3CN	12	44	
PtO_2	65°, 48 hr, CH_3CN	24	62	
$SnCl_2 \cdot 2H_2O$	60°, 24 hr, $CHCl_3$	40		

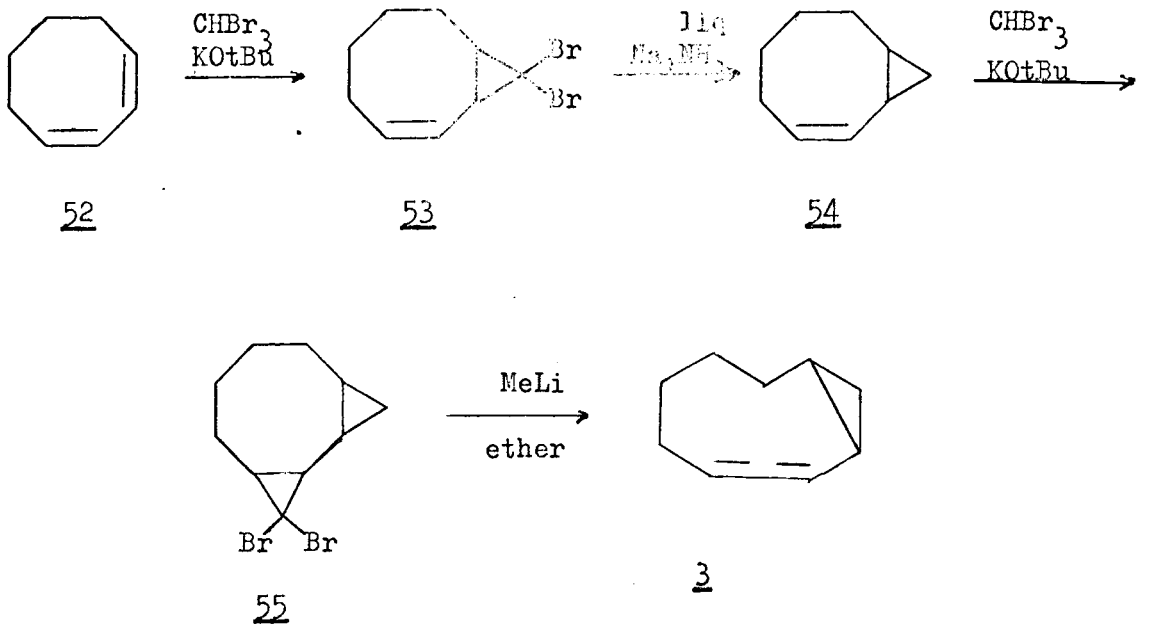
RESULTS AND DISCUSSION

Preparation of Bicyclo [7.1.0] deca-2,3-diene.

Bicyclo [7.1.0] deca-2,3-diene 3 was synthesized according to Scheme 7. The pathway for the synthesis of the allene 3 was chosen to proceed through bicyclo [6.1.0] non-2-ene 54. There are different routes to achieve this product. The Simmons-Smith reaction which is the addition of methylene group to a double bond by means of diiodomethane and zinc-copper couple, is one way of preparing bicyclo [6.1.0] non-2-ene in one step. E. Walton[58] has shown that the reaction of 1,3-cyclooctadiene results in the preferential formation of diadduct, i.e., methylene addition to both double bonds. Also, the monoadduct was difficult to separate from the diadduct. The reaction pathway that was chosen proceeds through a dibromocarbene addition to 1,3-cyclo-octadiene to give 9,9-dibromobicyclo [6.1.0] non-2-ene 53. The yield of the monoadduct 53 was 50-60%. Diadduct is also formed; however, vacuum distillation provides a clean, easy method for separating the monoadduct from the diadduct.

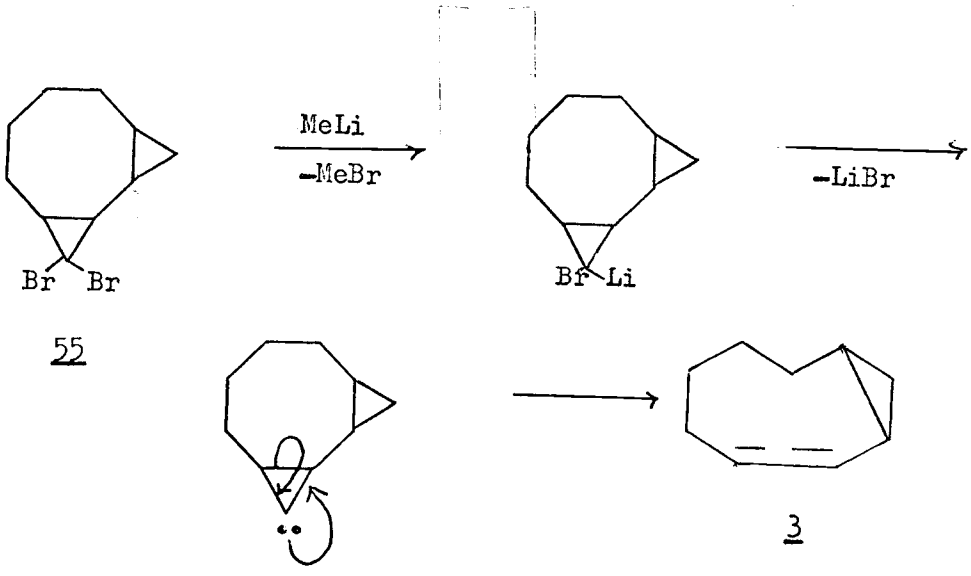
Reduction of dibromide 53 to bicyclo [6.1.0] non-2-ene 54 presented some problems. The best method (57% yield) was reduction of the dibromide to cyclopropane by sodium metal in liquid ammonia. Other methods proved less successful. Excess lithium aluminum hydride in ether[59] or THF gave reduced product very slowly. An

Scheme 7

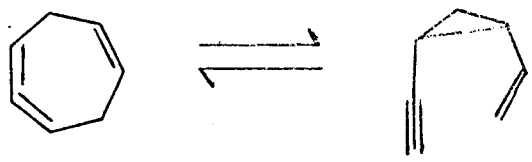

CHBr3
KOtBu
Br
Br
liq
NaNH2
CHBr3
KOtBu
52
53
54
MeLi
ether
Br
Br
55
3

excess of lithium metal in tert-butanol and diglyme[60] gave only partially reduced product. Another method using butyllithium[61] in n-hexane with ethanol proved inconvenient (transfer of butyllithium in n-hexane via syringe and under nitrogen) and gave low yield. The reduction with sodium metal in liquid ammonia, however, is easy and can be accomplished conveniently on any scale.

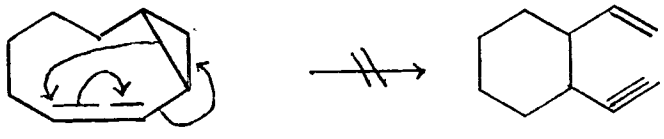
Addition of dibromocarbene to the reduced product 54 followed by vacuum distillation gave 10,10-dibromo tricyclo [7.1.0.$0^{2,4}$] decane 55; then addition of methyllithium in ether to the dibromo-adduct yielded the allene 3. The reaction proceeds through an intermediate carbene which undergoes rearrangement to the allene[51], as illustrated below.



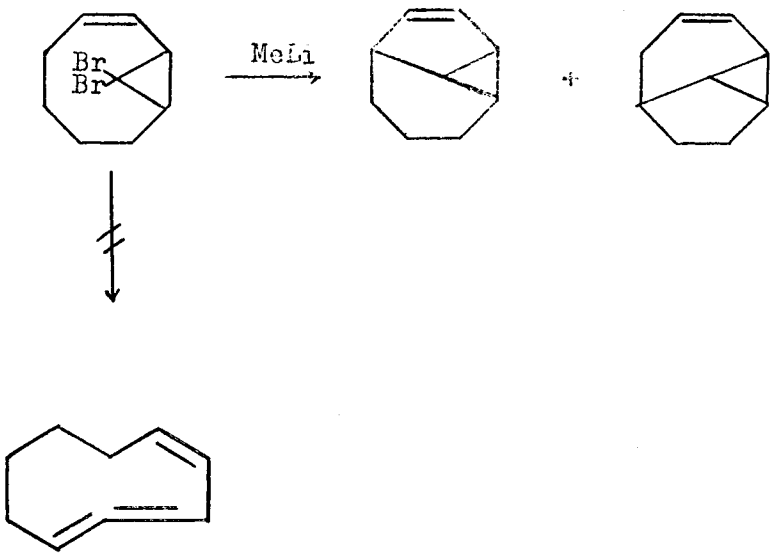
This allene is fairly stable; however, some cyclic allenes are known to form acetylenes.[63]



No characteristic acetylene absorptions were observed in the infrared spectrum of the allene. In addition this allene was mixed with tetralin (an internal standard) in ether and kept at 10-20° for some time (ca. one month) and the relative peak areas in the glc for the tetralin and allene remained approximately the same indicating very little decomposition to acetylene or polymerization.



The literature reports the reaction of 9,9-dibromobicyclo [6.1.0] non-2-ene with methyllithium in ether gives only tricyclic products.[64]

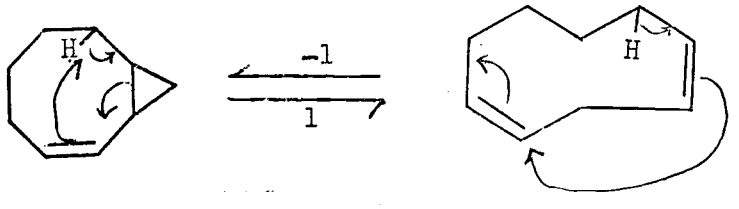


In the preparation of allene 3 from dibromoadduct 55 no tricyclic products were observed as a result of transannular insertion of the carbene rather than 1,2 insertion to form the allene. Overall, the yield of bicyclo [7.1.0] deca-2,3-diene 3 from starting material 1,3-cyclooctadiene was 19%, (based on limiting reagents).

Preparation of Cyclodeca-1,2,5-triene

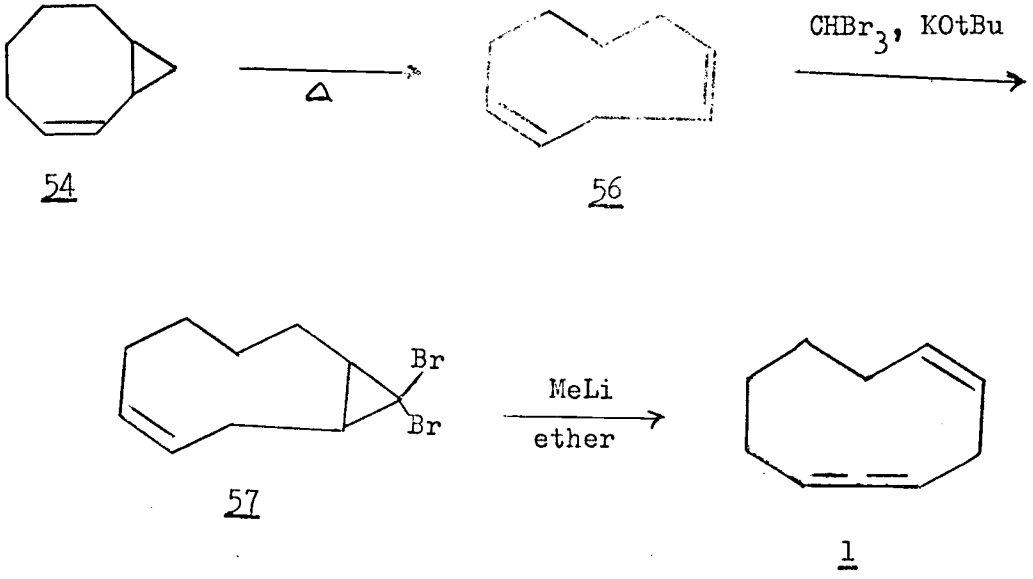
Cyclodeca-1,2,5-triene, 1, was synthesized as indicated by Scheme 8. Bicyclo [6.1.0] non-2-ene was used as shown in Scheme 8 for making allene 1 as well as allene 3 (refer to Scheme 7).

1,4-Cyclononadiene was prepared by simply refluxing pure bicyclo [6.1.0] non-2-ene in an oil bath at 150-160° for 7-9 hours. It was necessary to insure that no ether or low boiling hydrocarbons, remained since any amount of low boiling solvent lowers the temperature of refluxing resulting in only partial conversion. A homodienyl 1,5-hydrogen shift proceeds as illustrated below:



The kinetics of the equilibrium according to Glass and coworkers[65] has $H_1^{\neq}$ = 31.4 and $S_1^{\neq}$ = -6 e.u. thus favoring the formation of 1,4-cyclononadiene. The reaction was followed by nmr and was terminated when the upfield cyclopropyl proton disappeared.

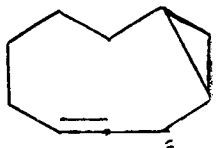
Scheme 8



The dibromoadduct 57 was prepared by dibromocarbene addition to the double bond and separated from diadduct by vacuum distillation. Allene 1 was obtained by the usual method of methyllithium in ether. Cyclodeca-1,2,5-triene was prepared in 64% yield from the dibromoadduct 57. No tricyclic systems were formed as a result of transannular carbene insertion. Formation of allene results in ring expansion to a ten carbon ring system. The allene unit has been previously reported in ten carbon ring systems: R. Vaidyanathaswamy reported the formation of 1,2-cyclodecadiene[47]; more significantly Thies and Hong[9] prepared 1,2,5,8-cyclodecatetraene from its appropriate analogous dibromoadduct. The allene appeared fairly stable when kept at 10-20° for ca. two months without appreciable decompostion. The overall yield of allene 1 from starting material bicyclo [7.1.0] non-2-ene was 35% based on limiting reagents.

Reaction of Mercuric Acetate with Bicyclo [7.1.0] deca-2,3-diene

When bicyclo [7.1.0] deca-2,3-diene 3 was treated with mercuric acetate in acetic acid, the major products obtained after reduction with lithium aluminum hydride were exo- and endo-bicyclo [7.1.0] deca-3-en-2-ol 58 and 59, respectively. These products represent "normal" oxymercuration without rearrangement.

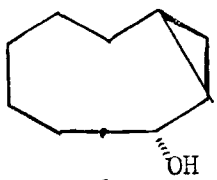


58

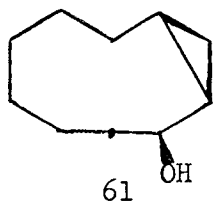
59

The reaction is assumed to proceed like any other allene oxymercuration through a σ-bonded "mercurinium" ion followed by addition-elimination mechanism with acid to obtain two acetates. The acetates were not isolated but reduced by lithium aluminum hydride. The alcohols were then isolated. Alcohol 59 was 92% of isolated products; the other alcohol 58 was minor product accounting for 8% of product, according to glc integration.

The major alcohol was purified by liquid chromatography over SilicAR. The minor alcohol was not separated from the other alcohol. Complete identification of products was achieved by hydrogenation of the two alcohols and comparing mass spectra with known samples.[48]



60

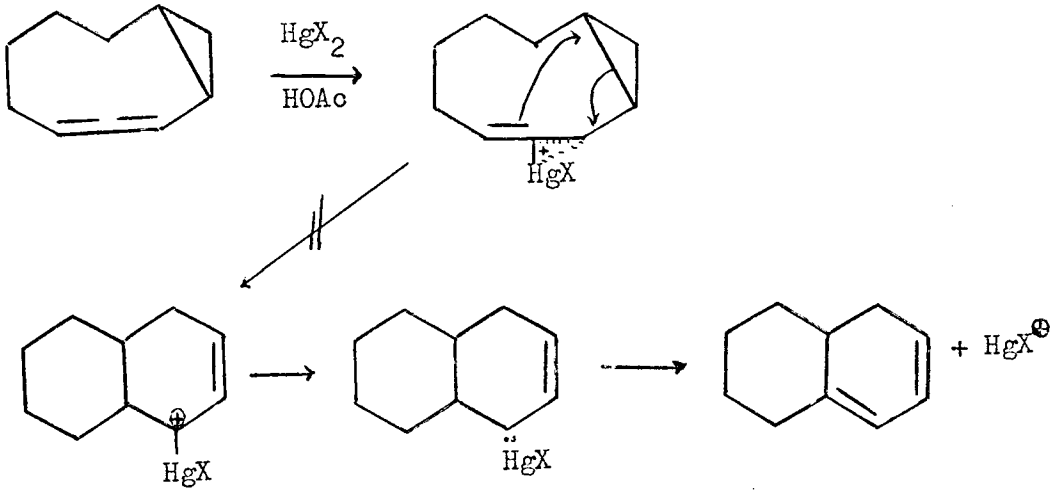


61

In addition, the nuclear magnetic resonance spectrum of alcohol 59 with added shift reagent ($Eu(fod)_3$) was consistent with the

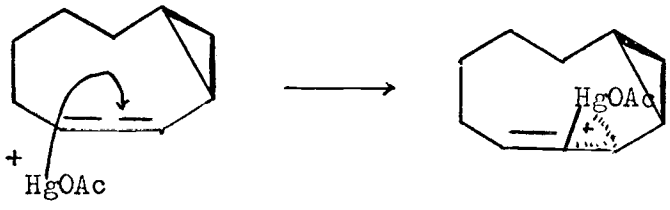
alcohol's structure.

Reaction of mercuric acetate with bicyclo [7.1.0] deca-2,3-diene 3 gave only oxymercurated products. No rearranged products were found, so the following reaction that was anticipated did not take place.



This reaction would require participation of the cyclopropane ring; i.e., breaking of the cyclopropane bond with migration of electrons to the mercurinium center with simultaneous migration of the double bond (concerted 1,5 sigmatropic shift).

Only two alcohols were obtained: exo-bicyclo [7.1.0] deca-3-en-2-ol and endo-bicyclo [7.1.0] deca-3-en-2-ol can be explained in the following manner: models indicate that the $^{+}$HgOAc could more easily attack the alkene center on the same side as the cyclopropyl ring forming the precedented σ-bridged mercurinium ion.



The exo-alcohol can be accounted for by trans-rearward attack of σ-bridged mercurinium intermediate. The endo alcohol can arise from frontside attack of the mercurinium ion. Bach[46] in the oxymercuration of 1,2-cyclononadiene suggested that solvent attacks to the mercurinium ion by trans addition or by frontside displacement of HgX affecting the configuration at that carbon. The ratio of endo to exo alcohol suggest that frontside attack of the mercurinium ion is more favorable and is supported by the model which shows the stearic hindrance of backside approach.

Another explanation for the formation of exo and endo alcohol arises from experimental data. Glc showed a shoulder to the allene 3, precursor to these alcohols. Fragmentation in the mass spectra of the peak and shoulder were the same, suggestive of peak and shoulder being isomers. The large peak which had the shorter retention time was approximated to be 80% of the two isomers and the shoulder with the longer retention time was estimated as 20% of the allene mixture. Models suggest that one diastereomer would favor exo attack while the other would favor endo attack.

Reaction of Catalysts with Cyclodeca-1,2,5-triene

When cyclodeca-1,2,5-triene was reacted with mercury salts (Table IV) in acetic acid only rearranged hydrocarbon 2 was observed. The cyclodeca-1,2,5-triene 1 was stable to the reaction conditions. Catalyst was necessary for the isomerization.

The mechanism as shown in Scheme 9 for the formation of tricyclo $[4.4.0.0^{2,4}]$ deca-5-ene is hypothesized to proceed through a σ-bridged mercurinium ion, typical initial step of oxymercuration. Homoallyl-cyclopropyl carbinyl rearrangement leads to an intermediate which can be represented as a metal-bonded carbonium ion, 63a, and the metal complex carbenoid, 63b, resonance forms. Similar species have been proposed earlier for strained hydrocarbon rearrangements. In addition, such carbenes are known to undergo 1,2 hydrogen migration which would account for the double bond in the bicyclic ring system. Verification of structure 2 was based on the spectra and chemical reduction.

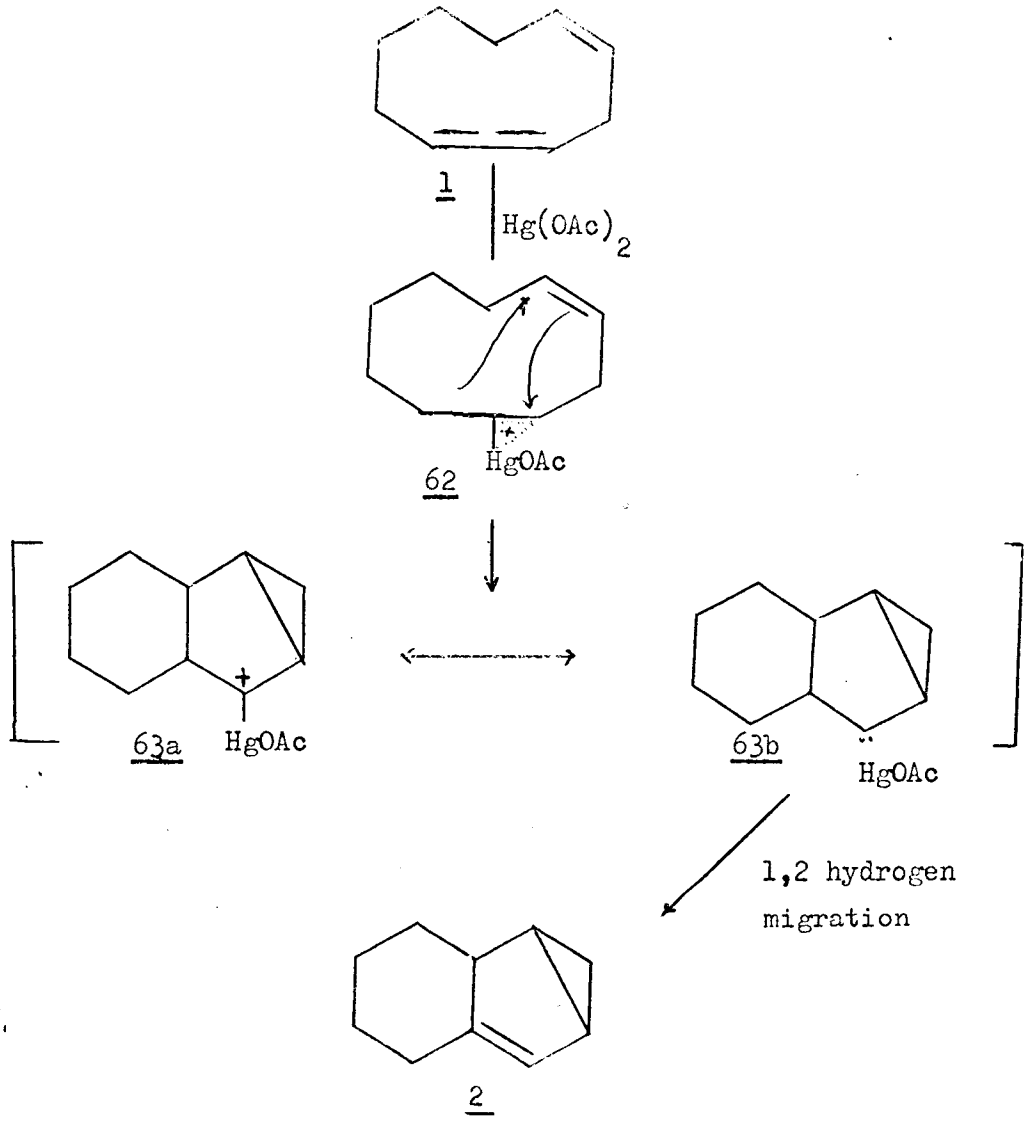
The mass spectrum had a parent peak of 132 and $M^{+\cdot}$ - 15 fragment which is characteristic of the cyclopropyl unit. High resolution mass spectrum gave $M^{+\cdot} = 134.10 \pm .01$ where the calculated molecular weight was 134.10. The nmr fit the proposed hydrocarbon. Its nmr characteristically showed an upfield cyclopropyl proton δ 0.0 as a quartet with a J = 4 Hz. and another cyclopropyl proton at δ 0.6 as a triplet of doublets, J = 4 and 7 Hz. A singlet appeared at δ 5.3; the only vinyl proton present. Integration also accounts well for the fourteen protons.

Table IV

Catalytic Isomerization of Cyclodeca-1,2,5-triene

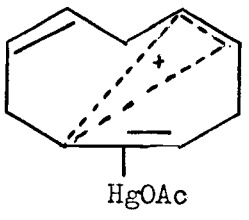
Catalysts	Amt of Initial Allene	Amt of H.C. 2 Produced	% Yield
$Hg(OAc)_2$	205 mg	106 mg	55
$HgSO_4$	105	58	55
$HgCl_2$	101	72	72
$Hg(COOCF_3)_2$	100	34	34
$[Rh(CO)_2Cl]_2$	102	102	100
$AgClO_4$	100	47	47

Scheme 9

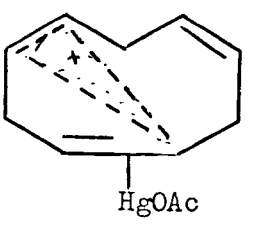

1
Hg(OAc)2
62
HgOAc
63a
HgOAc
63b
HgOAc
1,2 hydrogen
migration
2

The ir had absorption bands characteristic of the proposed structure. The ir for hydrocarbon 2 had bands at 3080, 3060, and 3025 cm^{-1}, as of cyclopropyl structure and an absorption at 1480 cm^{-1} for the double bond. Hydrogenation over Adams catalyst in acetic acid resulted in a mixture of cis and trans decalin (ca. 50:50 mixture) which was verified by mass spectra and glc retention time, thus supporting the basic ring structure. The hydrocarbon is also analogous to the hydrocarbon isolated by R. Thies et. al.[9] which was obtained by a similar proposed Scheme. (See Scheme 5).

Reacting cyclodeca-1,2,5,8-tetraene 41 in acetic acid with mercuric acetate, Thies and coworkers obtained not only the hydrocarbon but solvent captured species as well. The only difference between the two allenes (cyclodeca-1,2,5,8-tetraene 41 and cyclodeca-1,2,5-triene 1) is the double bond between C_8 and C_9. Cyclodeca-1,2,5,8-tetraene allows for transannular participation from both sides of the ring.

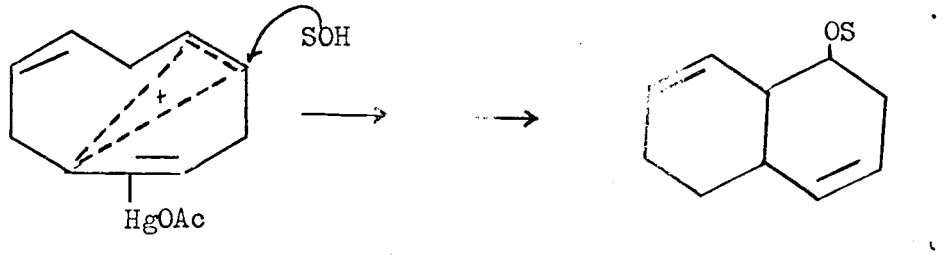


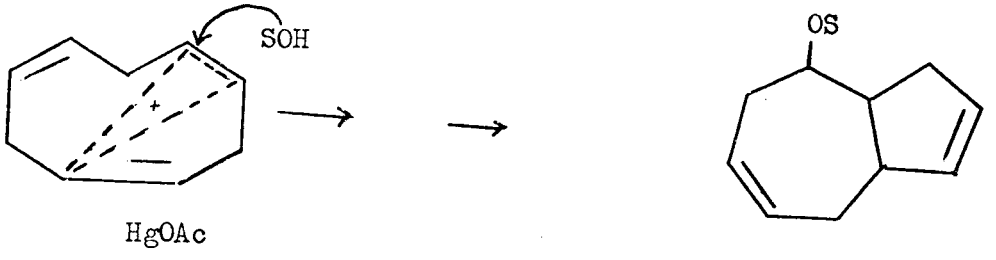
64a



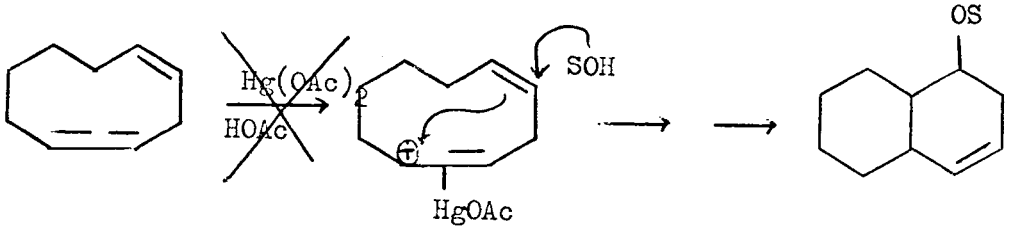
64b

Solvent attack of the above intermediates explains both products.

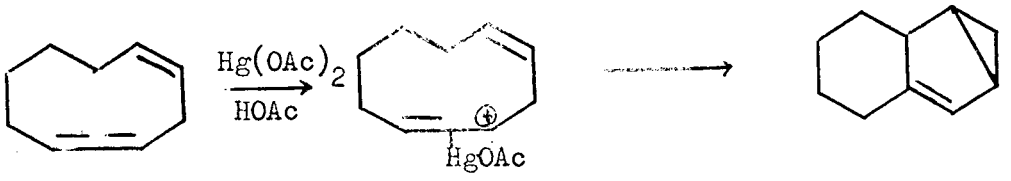




Cyclodeca-1,2,5-triene yields only hydrocarbon with no solvent captured products.



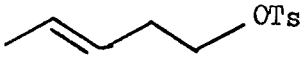
Only hydrocarbon was obtained.



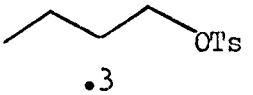
Even when a good nucleophilic solvent (i.e., 60% aqueous acetone) was used very little solvent-captured products were attained.

There are two possible explanations for this:

(1) There exists a competition between solvent-captured product and rearranged hydrocarbon. The solvent-captured product arises from transannular participation of C_5-C_6 or C_8-C_9 double bond. The hydrocarbon arises from homoallylic participation of the C_5-C_6 double bond. Roberts[68] has shown that homolylic participation increases the rate of solvolysis 210:0.3,

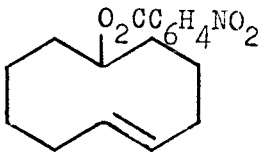


210

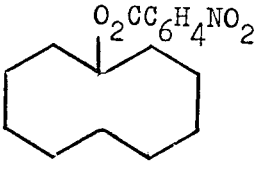


.3

while Goering *et al.*[69] illustrated in a ten carbon ring system that transannular participation of *cis*-double bond increased solvolysis rate five times.



5



1

The preferred homoallyic participation over transannular participation supports preferential hydrocarbon formation.

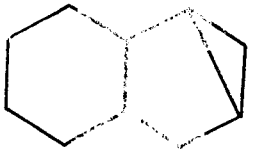
(2) The reaction leading to the hydrocarbon could also proceed through a concerted pathway which would not allow for solvent-captured species.

In either case it is not certain only the system involving cyclodeca-1,2,5-triene shows no solvent-captured products like those seen for the system of Thies and Hong's cyclodeca-1,2,5,8-tetraene. One possibility is that the extra double bond changes the preferred conformations in such a way that the transannular path is favored relative to homoallylic participation or concerted formation of hydrocarbon.

The "metal-complex carbenoid" is hypothesized in the mechanism of the formation of hydrocarbon 2. This type of intermediate is postulated in the bicyclobutane rearrangements as well. Gassman[57] reported in addition to mercury salts, other transition metal salts catalyzed bicyclobutane rearrangement. One such catalyst $[Rh(CO)_2Cl]_2$ was added to allene 1 (mole ratio 1:5) in glacial acetic acid and the reaction was followed by glc and found to be complete within fifteen minutes. The yield of hydrocarbon was quantitative based on tetralin as internal standard. The hydrocarbon was verified by mass spectrum, glc retention time and nmr comparison with a known sample of hydrocarbon obtained from the catalysis of allene with mercuric salt. $AgClO_4$, another catalyst used by Gassman, was reacted with allene 1 in the same manner. Two products were obtained according to analytical glc: a hydrocarbon (47% yield, based on internal standard) and a solvent-captured product (53% yield, based on internal standard). The hydrocarbon had the same retention time (coinjection with known sample of hydrocarbon 2) and mass spectra comparable with the pure hydrocarbon 2.

The reaction with mercury salts and $[Rh(CO)_2Cl]_2$ were found to be first order with respect to catalyst. (See figure 3 and figure 4).

The fact that other transition metal salts catalyzed the rearrangement supports the general carbenoid intermediate:



MX

where M is Ag(I), Rh(I), and Hg(II). M could be other similar transition metals; the work with $AgClO_4$, $[Rh(CO)_2Cl]_2$, and mercury salts represents only preliminary study to further work involving catalytic rearrangment of allene cyclodeca-1,2,5-triene and possibly other allenes.

Figure 3

Catalytic Effect of the Isomerization of Cyclodeca-1,2,5-triene with Mercuric Acetate

A^o = initial amount of allene		A = the amount of allene left after 15 minutes
A^o	A	Mercuric Acetate
1. 30 mg (2.24×10^{-4} mol)	18.9 mg	2 mg (6.28×10^{-6} mol)
2. 30 mg	8.0 mg	4 mg
3. 30 mg	4.6 mg	6 mg
4. 30 mg	2.0 mg	8 mg

*Ran in 2 ml of glacial HOAc

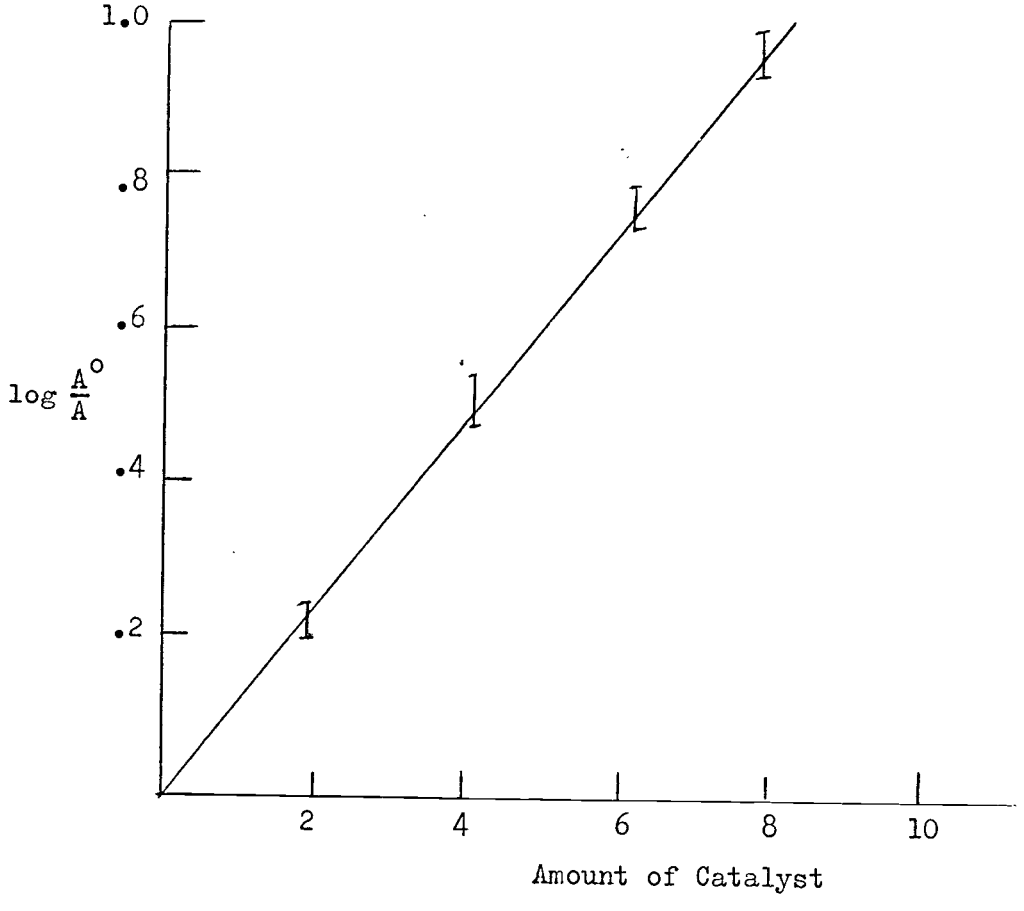


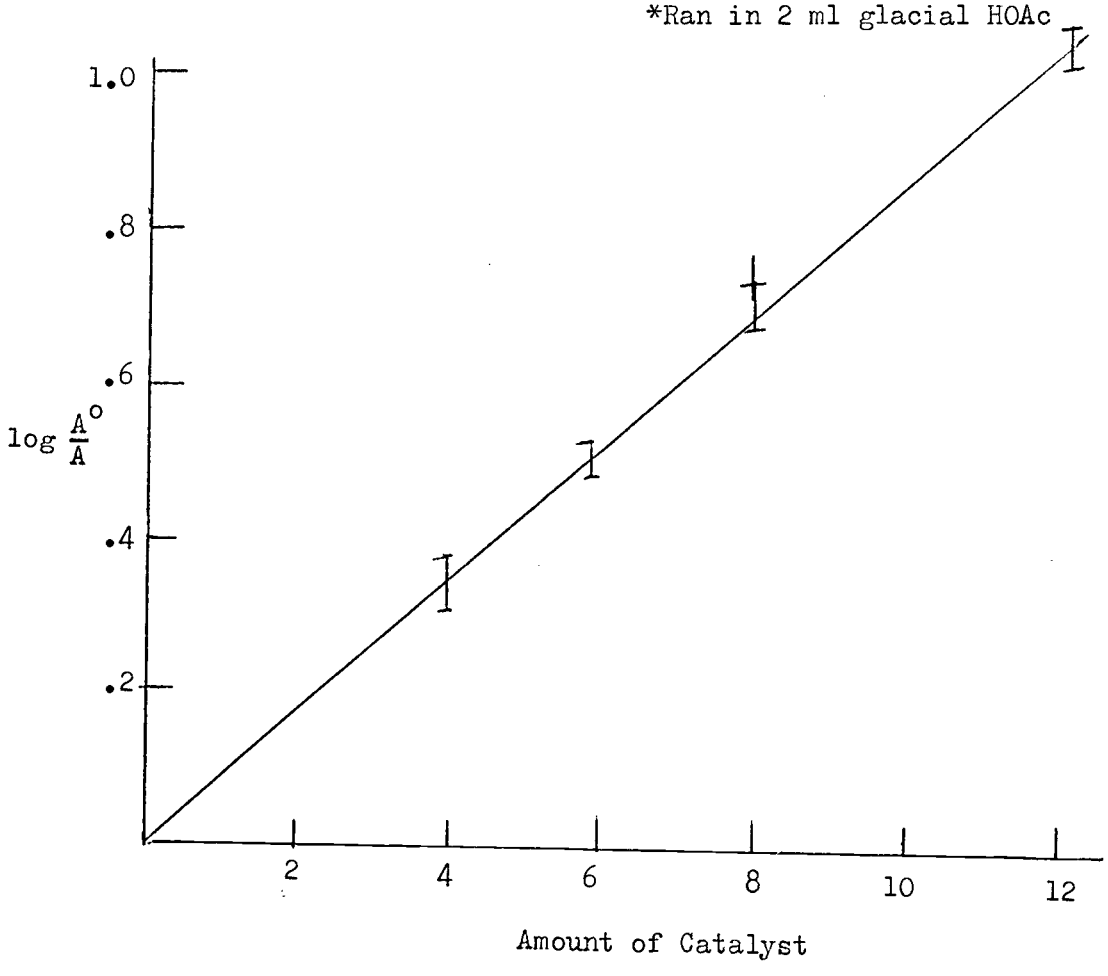
Figure 4

Catalytic Effect of the Isomerization of Cyclodeca-1,2,5-triene with $[Rh(CO)Cl]_2$*

A^o = initial amount of allene A = the amount of allene left after 15 minutes

A^o	A	$[Rh(CO)_2Cl]_2$
1. 20.6 mg (1.54×10^{-4} mol)	9.15 mg	4 mg (1.02×10^{-5} mol)
2. 20.6 mg	6.33 mg	6 mg
3. 20.6 mg	3.69 mg	8 mg
4. 20.6 mg	1.78 mg	12 mg

*Ran in 2 ml glacial HOAc



SUMMARY

Further Development of Catlytic Rearrangement of Allenes Using Transition Metal Salts.

This thesis presented the rearrangement of cyclodeca-1,2,5-triene to tricyclo $[4.4.0.0^{2,4}]$ deca-5-ene. The reaction was shown to be first order in mercuric ion and could also be catalyzed by $[Rh(CO)_2Cl]_2$ and $AgClO_4$ but the latter catalyst gave solvent captured products also. The catalyzed reaction was found to be first order with respect to the rhodium catalyst as well. The bicyclobutane work has been studied enthusiastically by Gassman[57] and others. In these investigations, as well as kinetics, solvent effects and structure studies were employed to probe the mechanism. Since the allene rearrangement proceeds through the same intermediate "metal-complex" carbenoid, the allene rearrangement could be investigated in a similar manner. Gassman had found that a wide variety of transition metals gave bicyclobutane rearrangement: $[C_6H_5Cu]_4$; $AgClO_4$ or $AgBF_4$; $HgBr_2$ or $Hg(OAc)_2$; ZnI_2, $[(\emptyset CN)_2PdCl_2]$; $[Rh(CO)_2Cl]_2$; and $[Ru(CO)_3Cl_2]_2$. Further work can be done in this area to determine whether the catalyst can effect rearrangement to obtain hydrocarbon or solvent-captured product. Gassman's results suggest that the "metal complexed carbene" intermediate is favored by catalysts that are good π donors. Noyori[54,55] suggested that promotional energy can be used as a guide to π donor ability and

he proposed that electronegativity of the metals influences the reaction. The electronegativity of metals increases in the following manner: Ni(0) < Ir(I) ≅ Rh(I) < Cu(I) ≅ Ag(I) < Pt(II) < Hg(II) ≅ Pd(II). Ni(0) being more electropositive than carbon would prefer nucleophilic reactions. The other extreme Cu(I) and Ag(I) would favor the electrophilic behavior. The combination of π donor ability and electronegativity would favor allene rearrangement <u>via</u> the carbene for Rh(I), Ir(I), and Ni(0) and more carbonium ion would favor solvent capture. The behavior would be anticipated for Cu(I), Ag(I), and Hg(II).

Other allenes could be studied.

EXPERIMENTAL

General

Infrared spectra were measured on a Beckman IR 8 infrared spectrometer or a Perkin Elmer 621 infrared spectrometer. Nmr spectra were measured on Varian Associates A-60, EM 360, 60 MHz nmr spectrometer and HA-100 instruments. Mass spectra were obtained on an Atlas CH7 mass spectrometer equipped with a gas chromatograph inlet system. High resolution mass spectra were obtained on the CEC 110B at the University of Oregon, Eugene Oregon. Elemental analyses were performed by Chemalytics, Inc. Anayltical gas liquid chromatography (glc) utilized a Varian Aerograph Model 1200 instrument with flame ionization detector and the following columns: (A) 0.01 in. x 75 ft. UCONLB550X capillary, (B) 0.125 in. x 5 ft. 5% SE 30 (C) 0.125 in. x 10 ft. 2.5% KOH Carbowax, (D) SF 96 using Carle Model 8000. Preparative glc was performed using Gow Mac Instrument Series 550 and column 0.250 in. x 4 ft., DC 200 Chromosorb-P. Integration of glc peaks was obtained by using a Hewlett-Packard Model 3373 B integrator.

Section A: Preparation of Alkenes

Preparation of 9,9-Dibromobicyclo [6.1.0] non-2-ene 53.[66] A dry, 1000 ml, 3-necked flask was fitted with a mechanical stirrer, a Graham condensor, and a pressure-equalizing dropping funnel. The system was swept out with nitrogen and a slight positive pressure of nitrogen was maintained. In the flask was placed 42 g (0.374 mol) of dry potassium-t-butoxide*, and the flask was cooled in an ice-salt bath. A solution of redistilled 1,3-cyclooctadiene (53.4 g, 0.48 mol, 64.2 ml) (bp 70°/10 mm) in 100 ml of dry pentane+ was added to the flask in one portion. Bromoform, undistilled, but clear not yellowed, (84 g, 29.6 ml, 0.332 mol) was placed in the dropping funnel and added dropwise with stirring over a period of one hour (color changed from light yellow to brown). At the completion of the addition, the cooling bath was removed, the flask was allowed to come to room temperature and stirring was continued at room temperature for 18-20 hours. Afterwhich water was added (100 ml), followed by sufficient hydrochloric acid (10% aqueous solution) to render the solution neutral. The organic layer was separated, and the aqueous layer extracted with pentane (3 x 30 ml). The combined pentane solutions were washed with (3 x 30 ml) water, then dried over anhydrous magnesium

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*Obtained from Ventron Alfa Inorganics; Beverly, Mass.

+Distilled over concentrated sulfuric acid.

sulfate, filtered and solvent removed by rotatry evaporation. The residue (98.9 g) was vacuum distilled affording 54.3 g (58.4% yield) of slightly yellow liquid 9,9-dibromobicyclo [6.1.0] non-2-ene 53: bp 110-115°/3 mm, (lit.[66] bp 86°/0.3 mm); ir (neat) 3020 (sh), 2950, 2890, 1450, 1430 (sh), 1420, 1215, 1165, 1085, 765, 740, 710, and 668 cm^{-1}; nmr (CCl_4, δ) 5.82 (broad s, 1), 5.22-5.56 (m, 1), and 0.66-2.6 (m, 10); mass spectrum m/e (rel intensity) 282 (2), 280 (4), 278 (1), 209 (25), 200 (5), 199 (25), 198 (2), 121 (8), 120 (2), 119 (82), and 91 (100).

Preparation of Bicyclo [6.1.0] non-2-ene 54[67] To a one liter 3-necked round-bottom flask equipped with a Dry-Ice condensor, one addition funnel and magnetic stirring bar, ammonia gas was added through the condensor after first being passed through a KOH drying tower. The flask was in a Dry-Ice bath and the temperature was maintained -70 to -40° during the entire course of the reaction. To 250 ml of liquid ammonia was added sodium metal (15 g, 0.65 mol). The solution turned blue. Then the dibromoadduct (27.2 g, 9.71×10^{-2} mol) in approximately 50 ml of dry ether was added dropwise over a period of 1.5 hr. The reaction was vigorous. Stirring and low temperature was maintained for another hour. Then ammonium chloride (23 g) was slowly added to terminate the reaction. The liquid ammonia was allowed to evaporate. The reaction mixutre was worked up by adding 100 ml of ether to the residue left in the flask after the evaporation of liquid ammonia. Then 100 ml of distilled water was slowly added to the mixture.

The water layer was washed with ether (3 x 30 ml). The combined ether layers were subsequently washed with 10% aqueous HCl until rendered neutral (5 x 30 ml).

The ethereal fraction was dried over anhydrous magnesium sulfate, filtered and distilled to concentrate the hydrocarbon. The hydrocarbon residue was then vacuum distilled to give 6.10 g (51.7% yield) of clear liquid bicyclo [6.1.0] non-2-ene 54: bp 50°/5 mm, 62°/29 mm; ir (neat) 3060, 3000, 2930, 2845 (sh), 2840, 2820 (sh), 1430, 1425 (sh), 1410, 1108, 1015, 1000 (sh), 840, 830, 785, 775, 755, and 695 cm^{-1}; nmr (CCl_4, δ) 5.3-5.9 (m, 2), 0.5-2.6 (m, 11), and -0.2 (q, J = 4 Hz, 1); mass spectrum m/e (rel intensity) 122 (20), 121 (5), 94 (26), 93 (56), 92 (5), 91 (22), 81 (56), 80 (78), and 79 (100).

Prepartion of 1,4-Cyclononadiene 56.[65] 6.1 g of bicyclo [6.1.0] non-2-ene 54 was refluxed for 10 hours in a silicone oil bath (temperature range 150-170°) under nitrogen. Reaction turned yellow during the course of heating. Vacuum distillation gave (5.3 g, 89% yield) 1,4-cyclononadiene 56 as a clear liquid: bp 90°/78 mm ; ir (neat) 3030, 2940, 2920, 1465, 1440, 1225, 878, 820, 740, 720, and 708 cm^{-1}; nmr (CCl_4, δ) 5.24-5.70 (m, 4), 2.68-2.98 (m, 2), 1.96-2.44 (m, 4), and 1.06-1.76 (m, 4); mass spectrum m/e (rel intensity) 122 (4), 121 (16), 120 (4), 95 (4), 94 (20), 93 (36), 92 (8), 91 (24), 82 (4), 81 (52), 80 (60), 79 (100), 78 (12), and 77 (36).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.32; H, 11.66.

Preparation of 10, 10-Dibromobicyclo [7.1.0] dec-3-ene 57. To a dry 100 ml 3-necked flask equipped with a West condensor was added 4.2 g (0.0374 mol) potassium-t-butoxide. The system was swept out with nitrogen and a slight positive pressure was maintained and the flask was cooled in an ice-salt bath. Subsequently a solution of distilled 1,4-cyclononadiene 56 (3.46 g, 0.0284 mol) with 10 ml dry pentane was added to the flask in one portion. Bromoform (5.02 g, 3 ml, 0.0334 mol) was added dropwise via syringe through the condensor. A color change was noted at this time: bromoform turned the reaction mixture from a faint yellow to a light brown. At the completion of the addition which required about 30 minutes the reaction was allowed to warm up to room temperature and allowed to stir for 18 hours. A five ml portion of water was added followed by five ml of pentane to terminate the reaction. The pentane and water layers were separated. The water layer was washed with pentane (3 x 7 ml). The pentane fractions were combined and washed with dilute 10% aqueous hydrochoric acid until neutral (5 x 7 ml).

The pentane layer was dried over anhydrous magnesium sulfate and then rotary evaporated to remove pentane. The residue which was subsequently darker through concentration was vacuum distilled to give 4.0 g (48.7% yield) of slightly yellow liquid 10,10 dibromobicyclo [7.1.0] dec-3-ene 57: bp $100^{\circ}/1.7$ mm; ir (film) 3040, 2950, 2890, 2880, 1660, 1485, 1365, 1460, 1410, 1400, 1370, 1360, 1285, 1270, 1250, 1235, 1220, 1200, 1130, 1115, 1090, 1070, 1040, 1025, 985, 970, 910, 870, 840, 825, 790, 755, and 745 cm^{-1}; nmr

(CCl_4, δ) 5.15-5.81 (m, 2) and 0.79-2.63 (m, 12); mass spectrum m/e (rel intensity) 296 (<1), 294 (<1), 292 (<1), 215 (1), 214 (<1), 213 (<1), 136 (16), 135 (24), 134 (20), 133 (8), 132 (12), 131 (8), 130 (8), 124 (20), 123 (12), 122 (16), 121 (12), 120 (20), 119 (12), 118 (12), 117 (8), 116 (12), 115 (8), 111 (16), 110 (40), 109 (8), 107 (12), 106 (32), 105 (12), 99 (20), 98 (20), 97 (56), 96 (48), 95 (49), 94 (36), and 93 (100).

Anal. Calcd for $C_{10}H_{14}Br_2$: C, 40.85; H, 4.80; Br, 54.35. Found: C, 40.45; H, 4.62; Br, 54.89.

Preparation of 10,10-Dibromotricyclo [7.1.0.$0^{2,4}$] decane 55.

A dry 50 ml 3-necked flask was equipped with a West condensor. The system was swept out with nitrogen and a slight positive pressure was maintained. In the flask was placed 2.1 g (0.0187 mol) of dry potassium-t-butoxide and the flask was cooled in an ice-salt bath. A solution of bicyclo [6.1.0] non-2-ene 54 (1.63 g, 1.34 x 10^{-2} mol) in 5 ml of pentane was added to flask. Bromoform (3.35 g, 2 ml, 0.025 mol) was added dropwise via a syringe (color changed from light yellow to brown). At the completion of addition the flask was allowed to come to room temperature and stirring was maintained under the nitrogen atmosphere for 18-20 hours. The reaction was terminated by the addition of 3 ml of water. Five ml of pentane was then added. The aqueous layer was washed with pentane (3 x 5 ml) and the pentane washings were combined with the pentane layer and was washed several times with 10% aqueous solution of HCl until neutral. The pentane layer was then dried over anhydrous magnesium

sulfate, filtered, rotary evaporated to remove the pentane, and then vacuum distilled to give 2.08 g (56% yield) of slight yellow dibromoadduct 55: bp 93°/1.0 mm; ir (neat) 3065, 3000, 2920, 2860, 1450, 1190, 1155, 1120, 1075, 1030, 1000, 975, 840, and 765 cm^{-1}; nmr (CCl_4, δ) 0.30–2.45 (m, 15) and 0.16 (q, J = 4, 1); mass spectrum m/e (rel intensity) 296 (<1), 294 (<1), 292 (<1), 215 (<1), 214 (<1), 213 (<1), 136 (10), 135 (10), 134 (50), 133 (20), 132 (10), 131 (10), 130 (10), 120 (25), 119 (10), 118 (20), 107 (20), 106 (100), 105 (15), 104 (10), 95 (10), 94 (15), and 93 (70).

Anal. Calcd for $C_{10}H_{14}Br_2$: C, 40.85; H, 4.80. Found: C, 40.89; H, 4.63.

Preparation of Bicyclo [7.1.0] deca-2,3-diene 3. A solution of 83 mg (2.8×10^{-4} mol) of dibromoadduct 55 in 2 ml of ether was cooled under nitrogen to −70° with stirring. Two ml of methyllithium (2 M in ether) was added over a period of one hour and the temperature was brought to −40° and kept there for 40 min, then taken to 0° and 1.5 ml of water was added to terminate the reaction. Five ml of ether was then added to the reaction mixture, the aqueous layer was washed with ether (3 x 3 ml), and the ether washings were then added to the ether fraction which was washed with dilute 10% aqueous HCl until rendered neutral. The ether layer was then dried over anhydrous magnesium sulfate and the hydrocarbon mixture was concentrated by distilling off the ether. The crude allene was purified by bulb-to-bulb vacuum distillation which gave 30 mg (80% yield) of allene 3: ir (neat) 3075, 3030 (sh), 3000, 2930, 2860, 1950, 1450, 1445 (sh),

1440, 1360, 1325, 1290, 1265, 1240, 1210, 1195, 1160, 1100, 1075, 1055, 1035, 1005, 950, 930, 880, 845, 835, and 720 cm^{-1}; nmr CCl_4, S) 4.7-5.8 (m, 2), 0.6-0.5 (m, 11), 0.1-0.4 (m, 1); mass spectrum m/e (rel intensity) 134 (1), 133 (3), 132 (3), 131 (50.5), 130 (1), 129 (1), 128 (1), 127 (1), 124 (3), 120 (2.5), 119 (12.5), 118 (2), 117 (5), 116 (2), 115 (3), 114 (1), 113 (1), 112 (3.5), 111 (1), 107 (2), 106 (8), 105 (18.5), 104 (3), 103 (3.5), 100 (11), 96 (2), 95 (13), 94 (16), 93 (52.5), 92 (1), 91 (1), and 69 (100).

Preparation of 1,2,5-Cyclodecatriene 1. A solution of 1.09 (3.71 x 10^{-3} mol) of dibromoadduct 57 in 2 ml of ether was added to a 25 ml two-necked round-bottom flask equipped with a West condensor and nitrogen inlet. The reaction was carried out under nitrogen. The vessel was cooled to -70° by a Dry-Ice-acetone bath and 2 ml of methyllithium (2 M in ether) was added through the condensor over a period of 45 minutes. The temperature of the reaction was gradually brought up to 0° and one ml of water was added to terminate teh reaction. Then work up was accomplished by adding 10 ml of ether and 3 more ml of water. The water fraction was washed with ether (3 x 5 ml) and washings were added to the ether layer which was washed repeatedly with dilute 10% aqueous HCl (5 x 5 ml) until netural.

The ether layers were dried over anhydrous magnesium sulfate and hydrocarbon was concentrated by distillation of most of the ether. Bulb-to-bulb vacuum distillation afforded 206 mg of allene

(42% yield): bp 90°/10 mm; ir (neat) 3000, 2965, 2915, 2845, 1950, 1470, 1450, 1330, 1115, 1040, 935, 910, 875, 850, 825, 800, 780, 730, 710, and 685 cm^{-1}; nmr (CCl_4; S) 5.14–5.19 (m, 4) and 0.8–3.2 (m, 10); mass spectrum m/e (rel intensity) 134 (5), 133 (10), 132 (3), 121 (4), 120 (25), 107 (5), 106 (20), 105 (40), 94 (24), 93 (40), and 92 (100).

Section B: Oxymercuration of Bicyclo [7.1.0] deca-2,3-diene and Catalytic Reactions of Cyclodeca-1,2-diene.

Oxymercuration of Bicyclo [7.1.0] deca-2,3-diene 3. Carefully, 280 mg (1.96×10^{-3} mol) of allene 3 and 200 mg of tetralin in ether was concentrated by passing nitrogen over the 10 ml Erlenmeyer flask. Tetralin was used as an internal standard. A solution of 5 ml of glacial acetic acid containing (640 mg, 2.01×10^{-3} mol) mercuric acetate. The mole ratio of allene to catalyst was 1:1. The reaction was complete after 30 minutes (shown in the glc). Two products were on the glc. The reaction was worked up in the following manner: five ml of ether was added to the reaction mixture, then transferred into 50 ml separatory funnel, washed with 10% aq. sodium bicarbonate solution until carbon dioxide was no longer generated. Then the ethereal solution was dried over anhydrous magnesium sulfate. Reduction of these products was accomplished by adding ca. 100 mg of lithium aluminum hydride. The reaction was stirred for 40 minutes. After that time, the reduction was terminated by the careful addition of 10% aq. Rochelles solution. The reaction required slow addition. The ether layer was dried over anhydrous magnesium sulfate for at least 15 minutes. Rotary evaporation yielded a white solid. Glc analysis showed a major product (92%) and a minor component (8%).

The major product, alcohol 59, was purified by careful liquid chromatogrphy from the minor product, alcohol 58. The mixture of alcohols, 110 mg, was chromatographed over 10 ml of SilicAR using a

mixture of solvents 10:1 (pentane*: ether). Fractions of 3 ml were collected. Fractions 43-46 contained pure alcohol 59. Fraction 47 and fraction 48 contained a mixture of alcohol 58 and 59. Alcohol 59 endo-bicyclo[7.1.0] deca-3-en-2-ol had the following: mp 85-88° ir (CCl_4) 3620, 3100, 3080, 3040, 3000 (sh), 2940, 2870, 1485, 1470, 1270, 1100, 1075, 1030, 910, 865, 850, 820, and 685 cm^{-1}; nmr (CCl_4,δ) 5.6 (d of d, J = 8, 10; 1), 5.3 (t of d, J = 6, 10; 1), 4.0 (t, J = 8; 1), 0.6-2.4 (m, 12), 0.1 (m, 1).

Hydrogenation of Exo-bicyclo [7.1.0] deca-3-en-2-ol 58 and Endo-bicyclo [7.1.0] deca-3-en-2-ol 59. Hydrogenation of alcohols 58 and 59 from fraction 47 and fraction 48 above was accomplished by stirring an ether solution of 58 and 59 over Adam's catalyst (ca. 50 mg) under an atmosphere of hydrogen for two hours. The resulting products exo-bicyclo [7.1.0] deca-2-ol 58 and endo-bicyclo [7.1.0] deca-2-ol 59 were identified by comparing mass spectrums of known samples+ and glc retention times.

Reaction of Cyclodeca-1,2,5-triene with Mercuric Acetate. In this experiment, 205 mg (1.53×10^{-3} mol) of allene 1 and 100 mg of tetralin in ether was concentrated carefully by passing

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*The pentane must be absolutely dry to get the separation desired. Distillation from sulfuric acid and storing over molecular sieve 3A for at least 24 hours provided the desired dryness.

+Samples were provided by Jim Billingmeyer.

nitrogen over the 10 ml erlenmeyer flask. Tetralin was used as an internal standard. A solution of 2 ml of glacial acetic acid containing 96 mg (3.06×10^{-4} mol) of mercuric acetate was pipetted into the erlenmeyer flask. The mole ratio of allene to catalyst was 5:1. The reaction was complete after 30 minutes (as indicated by glc) and worked up in the following manner: Five ml of ether was added to the reaction mixture and then transferred into a 50 ml separatory funnel. First the ether mixture was washed with water then with 10% aq $NaHCO_3$ (5 x 4 ml) until CO_2 was no longer generated. The ether layer was then dried over anhydrous magnesium sulfate and concentrated by a gentle flow of nitrogen over the erlenmeyer flask. The only product found was hydrocarbon 2 (110 mg based on internal standard tetralin, 55% yield). The hydrocarbon was isolated by careful liquid chromatography, over seven ml of SilicAR using dry pentane as elutant.* Fractions of 3 ml each were taken. The first 15 ml (i.e., fraction 1-5) contained only solvent. Fraction 6 and 7 contained pure hydrocarbon. Fractions 8 through 13 contained a mixture of hydrocarbon and tetralin. In some cases the hydrocarbon 2 was also separated from tetralin by preparative gas chromatogrphy.

Either procedure gave 2 that showed a single peak on glc: ir (CCl_4) 3080, 3060, 3025, 2980, 2920, 2845, 2825 (sh), 1950, 1800, 1480, 1440, 1030, 1000, 960, and 920 cm^{-1}; nmr (CCl_4, δ)

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*The pentane must be absolutely dry to get the separation desired. Distillation from sulfuric acid and storing over molecular sieve 3A for at least 24 hrs provided the desired dryness.

5.3 (s, 1), 2.6 (m, 1), 0.8-2.5 (m, 10), 0.0 (t of d, J = 4, 7; 1), and 0.0 (q, J = 4; 1); mass spectrum m/e (rel intensity) 134 (25), 133 (7), 120 (4), 119 (21), 105 (18), 104 (29), 103 (4), 102 (4), 92 (18), 91 (35), 90 (100), 78 (18), 77 (22), and 76 (18).

Hydrogenation of Hydrocarbon 2. Approximately 20 mg of hydrocarbon 2 based on internal standard of tetralin was stirred over a pinch of PtO_2 in 2 ml of glacial acetic acid overnite. Glc showed two peaks of approximately equal size (besides tetralin). Mass spectra of these hydrogenated products agreed with that of known samples of cis and trans decalin. Yield based on the summation of both peaks was quantitative. Cis decalin prepared from the hydrogenation of hydrocarbon 2 had the following mass spectrum: m/e (rel intensity) 138 (72), 110 (7), 109 (30), 97 (10), 96 (90), 95 (50), 83 (11), 82 (60), 81 (90), 69 (22), 68 (65), and 67 (100); which compared well with the mass spectrum of known sample: 138 (77), 110 (10), 109 (30), 97 (10), 96 (90), 95 (50), 83 (10), 82 (60), 81 (90), 69 (20), 68 (60), and 67 (100). Trans decalin, the second peak in the glc which was prepared from the hydrogenation of hydrocarbon 2, had the following mass spectrum: m/e (rel intensity) 138 (86), 110 (7), 109 (15), 97 (8), 96 (60), 95 (6), 83 (15), 82 (70), 81 (60), 69 (50), 68 (100), and 67 (96); which also compared well with a known sample of trans decalin's mass spectrum m/e (rel intensity) 138 (90), 110 (10), 109 (15),

97 (10), 96 (60), 95 (5), 83 (35), 82 (70), 81 (60), 69 (50), 68 (100), and 67 (95).

Stability of Cyclodeca-1,2,5-triene to Reaction Conditions. Allene 1 in ether was added to 15 mg of tetralin in 1 ml of ether in a 10 ml flask until the areas (based on integration) were approximately the same. The ether solution containing the allene and tetralin was concentrated by a gentle flow of nitrogen above the surface of the liquid; the 1 ml of glacial acetic acid was added. About one-third of the sample was worked up over intervals of 30 minutes with no sign of decay.

Reaction of Cyclodeca-1,2,5-triene with Mercuric Sulfate. Allene 1 (105 mg, 7.65×10^{-4} mol) in ether was added to 51 mg of tetralin in a 10 ml erlenmeyer flask. The allene and tetralin was concentrated and one ml of glacial acetic acid containing 47.5 mg (1.53×10^{-4} mol) of $HgSO_4$ was pipeted in. The allene to catalyst ratio was 5:1. The reaction was terminated after 30 minutes adn worked up. Yield based on glc was 53%. Mass spectrum was consistent with the hydrocarbon 2. No other products were observed.

Reaction of Cyclodeca-1,2,5-triene with Mercuric Chloride. The reaction was repeated exactly as the experiment with mercuric sulfate. Y eld was 72% based on internal standard of tetralin. Mass spectrum consistent with hydrocarbon 2.

Reaction of Cyclodeca-1,[illegible]ne [illegible] Mercuric Trifluoracetate. Reaction was repeated as in previous runs with mercuric trifluoroacetate used as catalyst. Yield: [illegible]% based on the internal standard of tetralin. Mass spectrum was consistent with hydrocarbon 2.

Reaction of Cyclodeca-1,2,5-triene with $[Rh(CO)_2Cl]_2$. The reaction was performedaas in the previous experiments with $[Rh(CO)_2Cl]_2$ used as catalyst. Yield was quanitative based on internal standard of tetralin. Mass spectrum and nmr was consistent with hydrocarbon 2.

Reaction of Cyclodeca-1,2,5-triene with $AgClO_4$. The reaction was performed as in the previous catalytic experiments using $AgClO_4$ as the catalyst. Two products were observed according to analytical glc. Hydrocarbon 2 (yield 47% based on internal standard of tetralin using glc integration) and an unidentified second product (53%). The retention time of the second product was similar to acetate and when reduced the unidentified second product then had a glc retention time of an alcohol. The hydrocarbon had the same mass spectrum as a known sample of hydrocarbon 2.

Reaction of Cyclodeca-1,2,5-triene with Mercuric Acetate in Deuterated Acetic Acid. The reaction was performed as above using mercuric acetate as catalyst and deuterated acetic acid as solvent. Mass spectra of the sole product had the same mass spectrum of a known sample of hydrocarbon 2.

Kinetic Run Using Mercuric Acetate as Catalyst. An ether solution containing 30.0 mg allene 1 and 12.0 mg of tetralin in 10 ml of ether was prepared. Then 1 ml of this solution was pipetted into four separate erlenmeyer flasks. The ether was evaporated by a gentle flow of nitrogen above each erlenmeyer flask. Four different solutions were also prepared containing the catalyst mercuric acetate in glacial acetic acid and had the following concentrations: 2 mg of $Hg(OAc)_2$/ml HOAc, 4 mg/ml, 6 mg/ml, and 8 mg/ml respectively. One ml of the first concentration was added to the first erlenmeyer by pipet. One ml of the second concentration was added to the second erlenmeyer by a separate pipet. One ml of the third concentration was added to the third erlenmeyer by a third pipet. One ml of the fourth concentration was added to the fourth erlenmeyer by a fourth pipet. The reactions were terminated after 25 minutes and subsequently worked up. The first erlenmeyer run had 18.9 mg of allene left according to glc integration. The second erlenmeyer run had 8 mg of allene left and the third and fourth had 4.5 and 2.0 mg left respectively.

Kinetic Run Using $[Rh(CO)_2Cl]_2$ as Catalyst. The kinetic run was performed as above with the following exceptions the amount of starting allene 1 was 20.6 mg. The four erlenmeyers had the following concentration of catalyst/ml of glacial acetic acid: 4 mg/ml, 6 mg/ml, 8 mg/ml, and 12 mg/ml. The amount of remaining allene were 9.15 mg, 6.33 mg, 3.69 mg, and 1.78 mg respectively.

Stability of Hydrocarbon 2 in Reaction Conditions. 30 mg of hydrocarbon 2 and 10 mg of tetralin was added to 1 ml of glacial acetic acid containing 4 mg of mercuric acetate. The mixture was observed by glc over intervals of time. The hydrocarbon peak showed appreciable decay. After 30 minutes 27 mg of hydrocarbon 2 remained. At the end of one hour, 24 mg of hydrocarbon remained. And after 12 hours, only 15 mg of hydrocarbon 2 was left.

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APPENDIX

Table V Glc Data

Compound	Column[a]	Temp[b]	Flow-rate[c]	Retention Time (min)
1,3-Cyclooctadiene	A	100	8.8	1.6
9,9-Dibromobicyclo[6.1.0]-non-2-ene	D B	137 120	9.0 2.2	4.0 6.2
Bicyclo[6.1.0]non-2-ene	A B	135 80	9.0 3.0	2.6 1.6
1,4-Cyclononadiene	B	80	3.0	1.6
10,10-Dibromobicyclo-[7.1.0]dec-3-ene	B	142	2.2	3.8
10,10-Dibromotricyclo-[7.1.0.$0^{2,4}$]decane	B	130	3.0	3.2
1,2,5-Cyclodecatriene	B	80	2.2	3.3
Bicyclo[7.1.0]deca-2,3-diene	B	80	2.3	4.4
Tricyclo[4.4.0.$0^{2,4}$]deca-5-ene	B	80	2.3	3.0
Endo-bicyclo[7.1.0]deca-3-en-2-ol	C	150	2.5	4.6
Exo-bicyclo[7.1.0]deca-3-en-2-ol	C	150	2.5	9.6

[a]See General of the Experimental Section for details on columns.

[b]In °C.

[c]In ml/sec.