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PART I  TRANSITION METAL COMPLEX PROMOTED REARRANGEMENTS

PART II  ORGANOLITHIUM CHEMISTRY

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Thomas Joseph Atkins, B.S.

The Ohio State University
1972

Approved by

[Signature]
Adviser
Department of Chemistry
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VITA

Thomas Joseph Atkins, son of Dave and Lillian Atkins, was born on September 6, 1946, in Dayton, Ohio, where he received his primary and secondary education. In September, 1964, he entered the University of Cincinnati where he received his B.S. in Chemistry in June, 1968. In December, 1966, he married Ann Louise Chisholm of Cincinnati, Ohio, who presented him with a daughter, Lisa Anne, in July, 1967. In June, 1968, he entered the Graduate School of The Ohio State University, where he held the position of National Science Foundation Trainee until he received his Ph.D. in Chemistry in August, 1972.
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PART I

TRANSITION METAL COMPLEX PROMOTED REARRANGEMENTS

INTRODUCTION

The use of transition metal complexes in organic synthesis has received much attention in the past two decades. Chemists have investigated the role of the transition metal in a wide variety of synthetic applications. Perhaps the best known of these reactions is the "oxo" process, used industrially to add hydrogen and carbon monoxide to olefins. The overall reaction is shown below and the process has been shown to involve the intermediacy of a transition metal hydride, hydrido-cobalttetra carbonyl. Transition metal hydrides have been used in a variety of related reactions and their utility in organic synthesis is now widely recognized.

\[
\text{CH}_2=\text{CH}_2 + \text{H}_2 + \text{CO} \rightarrow \text{CO} \rightarrow \text{CH}_3\text{CH}_2\text{CHO}
\]

In addition to the "oxo" process, transition metal complexes have also been used to catalyze the oligomerization of unsaturated molecules.

For example, acetylene can be coupled to give its cyclic trimer, benzene or its cyclic tetramer, cyclooctatetraene, depending upon the conditions and the catalyst used. Transition metal complexes have been shown to promote disproportionation of olefins, or olefin metathesis, and a general example is given below. The isomerization of olefins is another useful reaction of transition metal complexes. An example of the versatility of this type of reaction can be seen in the reactions of 1,5-cyclooctadiene (1) and 1,3-cyclooctadiene (2) with transition metal deriv-

\[
\begin{array}{c}
\text{R} \quad \text{C} = \text{C} \quad \text{R} \\
\text{R'} \quad \text{C} = \text{C} \quad \text{R'} \\
\end{array}
\quad \xrightarrow{[\text{M}]} \quad
\begin{array}{c}
\text{R} \quad \text{C} = \text{C} \quad \text{R'} \\
\text{R'} \quad \text{C} = \text{C} \quad \text{R} \\
\end{array}
\]

\[
\begin{array}{c}
1 \\
2
\end{array}
\]

vatives. Treatment of 1 with pentacarbonyliron(0) gave 2, whereas treatment of 2 with rhodium trichloride afforded a complex from which 1 could be liberated.

The isomerization of highly strained hydrocarbons by treatment with transition metal complexes has recently received much attention. The

facile isomerization of quadricyclene to norbornadiene has been reported. In a completely independent study, Gassman et al., found that the quadricyclene derivative, 3, was thermally stable to 200°, but reverted to the norbornadiene derivative, 4, in seconds upon treatment with certain transition metal complexes at low temperatures. However, an unrecognized example of this type of isomerization had been observed much earlier, and various mechanistic interpretations of the basis for these rearrangements have appeared.

Molecules containing at least three fused cyclobutane rings have been readily isomerized by silver ion and cuprous ion. Numerous


have extended Pettit's silver ion catalysis to cubane-type molecules and have found that other transition metal compounds also promote rearrangements of cubane and its analogues. Two modes of rearrangement have been noted. These may be represented in the following manner: treatment of cubane (5) with silver(I) or palladium(I) derivatives effected isomerization to cuneane (6), whereas treatment of rhodium(I) complexes afforded syn-tricyclo[4.2.0.02,5]octa-3,7-diene (7). In general, it was found that silver or palladium ions caused

12-15 workers

rearrangement of the fused cyclobutane moiety to two cyclopropane moieties. This mode of rearrangement was distinctly different from the rhodium complex promoted rearrangements of $\Delta$ to give $\Sigma$ or of $\Delta$ to give $\Xi$. The rhodium complex promoted rearrangement effected cleavage of a cyclobutane to a diene.

In addition to those examples of isomerizations of strained molecules already mentioned, isomerizations of prismane and Dewar benzene derivatives promoted by various transition metal complexes have also been reported. Intramolecular transition metal complex promoted interactions between a cyclopropane moiety and an olefin have been reported both as a suggested mechanistic pathway and as a preparative tool. Treatment of \textit{exo}-tricyclo[3.2.1.0$^2$4]oct-6-ene (9) with

\begin{itemize}


\end{itemize}
rhodium dicarbonyl chloride dimer, \([\text{Rh}(\text{CO})\text{Cl}_2]_2\), quantitatively afforded tetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane (10).\(^{13a}\) The formation of 10 from 2 may be viewed as a **formal** cycloaddition of an olefin and a cyclopropane moiety.

The lability of compounds such as 3, 5, and 6 in the presence of transition metal complexes can be associated with the strain energy.\(^{20}\) This fact raised the question of whether less strained ring systems, such as bicyclo[1.1.0]butane and bicyclo[2.1.0]pentane derivatives which have strain energies of ca 64 and 54 kcal per mol, respectively, would be susceptible to transition metal complex promoted rearrangements. Since many of the transition metal complex promoted rearrangements of the various strained polycyclic molecules have been discussed in conjunction with the thermal chemistry associated with these molecules,\(^{10-14,16}\) it is necessary to review the thermochemistry of bicyclo[1.1.0]butanes and bicyclo[2.1.0]pentanes.

Since the first reported synthesis of bicyclo[1.1.0]butane and its derivatives, numerous workers have investigated its thermal isomerization to 1,3-diene derivatives. The mechanism of this rearrangement has been discussed in detail, and has been shown to involve a conrotatory mode of ring opening of one cyclopropane ring concomitant with a disrotatory mode of ring opening of the other cyclopropane ring. For example, exo,exo-2,4-dimethylbicyclo[1.1.0]butane (11) gives 93% of cis,trans-2,4-hexadiene (12) and endo,exo-2,4-dimethylbicyclo[1.1.0]-butane (13) gives 95% of trans,trans,2,4-hexadiene (14). The formation of 12, for example, may be viewed as occurring by cleavage of either of the opposite pairs of side bonds (ab and cd, or ad and bc)


followed by conrotatory rotation of one pair of developing orbitals and disrotatory rotation of the other set of orbitals to give the observed stereochemistry.

![Diagram](image)

The molecule chosen for this study of transition metal complex promoted rearrangements of bicyclo[1.1.0]butane derivatives was the highly strained tricyclo[4.1.0.0²7]heptane (15). This structure has "flaps" of the bicyclobutane moiety connected by a three carbon bridge. The thermal opening of 15 has been reported to give bicyclo[3.2.0]-hept-6-ene (16). It was suggested that cis,trans-1,3-cycloheptadiene (17) was initially formed. It was further postulated that 17 was very unstable due to the strain of the trans double bond and thus, underwent rapid ring closure under the thermolysis conditions to give 16. It should be noted that there is no currently available convincing evidence that the center bond of the bicyclo[1.1.0]butane skeleton is ever
cleaved in a purely thermal reaction to produce 1,3-butadiene derivatives. Opening of the bicyclobutane moiety has been effected by acids and resulted in the formation of vinylcyclopropyl derivatives as in the isomerization of 15 to give 2-norcarene (18)\textsuperscript{24} and of 19 to give 20.\textsuperscript{25}

\begin{itemize}
\end{itemize}
Another type of reaction of bicyclo[1.1.0]butanes which has been studied is hydrogenation. Almost invariably, two moles of hydrogen is taken up per mole of bicyclobutane derivative and the products are usually those caused by cleavage of a side bond and the central bond of the bicyclobutane. The hydrogenation of tricyclo[4.1.0.0^2,7]heptane (15) is a typical example. Hydrogenation of 15 over palladium-on-carbon gives methylcyclohexane (21) as the major product along with very minor amounts of cycloheptane (22) and norcarane (23). The formation of 21 indicates that two bonds, a side bond and the central bond, are broken. It has also been found that these hydrogenations do not involve stepwise reduction of the bonds as the intermediates in the reduction of bicyclobutane derivatives that would be generated are

\[\text{H}_2 \xrightarrow{\text{Pd-C}} \text{CH}_3\]
stable to the hydrogenation conditions.  

In addition to the thermochemistry of bicyclo[1.1.0]butanes, the thermolytic behavior of bicyclo[2.1.0]pentane (24) should be mentioned. In the pyrolytic preparation of 24 from 2,5-diazabicyclo[2.2.1]hept-2-ene (25) at 200°, 30° there was no detectable isomerization of 24.

Criegee and Rimmelin have reported that a temperature of 330° was needed in order to observe a reasonable rate of thermal isomerization of 24 to cyclopentene (26). The formation of 26 was said to occur via cleavage of the central bond of 24 to give a 1,3-diradical intermediate which could undergo a hydrogen migration to give 26.

In view of the successful utilization of transition metal complexes to effect isomerizations of quadricyclene and of simple, methylated

\[26, 27\]

---

27. Two methods are reported to give reduction of only the central bond of the bicyclo[1.1.0]butane moiety.  


bicyclo[1.1.0]butane derivatives reported from these laboratories, \(^{32}\) the detailed investigation of reactions of transition metal complexes with the rigid, strained tricyclo[4.1.0.0\(^2,7\)]heptane and the bicyclo-
[2.1.0]pentane ring systems was undertaken. It was hoped that this investigation would establish the scope of the reaction and lead to certain mechanistic conclusions, which would explain the formation of products and which would reasonably approximate the actual mechanism of these rearrangements.

PART A  Tricyclo[4.1.0.0²,⁷]heptane and 1-Methyltricyclo-
[4.1.0.0²,⁷]heptane

Although the bicyclo[1.1.0]butane nucleus has a strain energy of ca 64 kcal/mol,²⁰ temperatures of 150⁰ to 300⁰ and activation energies in excess of 40 kcal/mol²¹d,²¹g appear necessary for a reasonable rate of thermolysis. A number of different structures with higher strain energies⁶-⁸,¹¹-¹⁵ have been found to be labile in the presence of transition metal complexes. Therefore, the question is raised whether the bicyclo[1.1.0]butane nucleus would also be susceptible to transition metal complex promoted rearrangement. The bicyclobutane derivative chosen for study was the tricyclo[4.1.0.0²,⁷]heptane ring system because of its ready availability and its highly rigid nature. The preparation of tricyclo[4.1.0.0²,⁷]heptane (¹⁵) was accomplished in two steps according to literature procedures.²⁴ Treatment of cyclohexene with potassium tert-butoxide and bromoform gave 7,7-dibromonorcarane (²⁷) which upon reaction with methyllithium afforded ¹⁵. The initial transition metal complex chosen for study was rhodium dicarbonyl chloride dimer because it was commercially available and appeared to be highly reactive in other transition metal complex promoted rearrange-
⁷,¹⁹,³²
When an acetonitrile solution of 15 was treated with 4 mol % of rhodium dicarbonyl chloride dimer, a rapid exothermic reaction occurred to give 3-methylenecyclohexene (28) in 93% yield after 15 min. This material was identical in all respects to an authentic sample of 28 prepared via the Wittig reaction of 2-cyclohexenone with methylenetri-phenylphosphine. The formation of 28 differs markedly from the thermal isomerization of 15. The rhodium dicarbonyl chloride dimer promoted rearrangement of 15 clearly requires a hydrogen migration. The isomerization of 15 to 28 may be viewed as occurring via cleavage of one

34. Kindly provided by Mr. H. R. Drewes.
side bond and the central bond of the bicyclobutane nucleus to give an intermediate which may be represented as either the metal-bonded carbene complex, $2^2$, or its resonance structure, the metal-bonded carbenium ion, $30$. The intermediate $2^2$ $30$ could then experience hydrogen migration with loss of $M^X$ to give $23^3$. This mode of ring cleavage amounts of a formal retro-carbene reaction. Species such as $23$ or $30$ might be expected to gain stability from the metal bond. Examples of stable, isolable complexes of divalent carbon bonded to a metal atom are known, and a bonding scheme such as that depicted below has been presented to account for the stability of these molecules. Donation of the electron pair of the carbene to form a carbon-metal sigma bond

![Diagram](image)

stabilizes the carbene. The increased amount of electron density on
the metal is alleviated through \( d_π - p_π \) interactions (back bonding) from
the filled \( d \)-orbital of the metal and the empty \( p \)-orbital of the carbene.

In order to gain some insight into the nature of the proposed
intermediate \( 32 \leftrightarrow 30 \), the study of the effect of an alkyl substituent
at the bridgehead position was undertaken. 1-Methyltricyclo[4.1.0.0\(^{2,7}\)]-
heptane \( (31) \) was prepared by the method of Closs and Closs, through
formation of the anion of \( 15 \) with \( n \)-butyllithium-tetramethylethylene-
diamine \( 1:1 \) complex in ether, and methylation of the anion with methyl
iodide as shown in Scheme I. When a chloroform solution of \( 31 \) was
treated with 5 mol \% of rhodium dicarbonyl chloride dimer, a rapid exo-
thermic reaction occurred to yield \( 96\% \) of 2-methyl-3-methylenecyclo-
hexene \( (32) \). The structure proof of \( 32 \) was based on its characteristic
spectral data [nmr: \( \tau \ 4.37 \) (1H, multiplet), 5.17 (1H, broad singlet),
and 5.30 (1H, broad singlet); ir: 6.09, 6.22 (conjugated diene) and
11.28 \( \mu \) (terminal methylene); uv: \( \lambda_{\text{max}} \) \( \text{hexane} \ 234 \) nm (\( \varepsilon = 16,200 \))]. In
addition, \( 32 \) was catalytically hydrogenated to give a mixture of cis-
and trans-1,2-dimethylcyclohexane and dehydrogenated to give \( \alpha \)-xylene.
Cleavage of a side and central bond of the bicyclobutane moiety could
occur (in a manner similar to the cleavage of bonds in \( 15 \)) to give the
proposed transition metal-complexed carbene \( (33) \leftrightarrow \) transition metal-
bonded carbonium ion \( (34) \) hybrid as an intermediate. Hydrogen migration

with loss of $X$ from the intermediate would produce $32$. The isomerization showed amazing stereospecificity in that only the side bond attached to the unsubstituted bridgehead carbon was cleaved (in addition to the central bond of the bicyclo[1.1.0]butane moiety). This specificity parallels observations on the reaction of 1,2,2-trimethylbicyclo[1.1.0]butane (19) with rhodium dicarbonyl chloride dimer. $^{32a}$

In order to determine what effect different transition metal compounds might have upon the mode of isomerization of the strained bicyclo[1.1.0]butane portion of $15$ and $31$, these compounds were treated with a wide variety of metal derivatives. The conditions used for the reactions of the various metal derivatives and $15$ and the results are shown in Table I. From the table it can be seen that derivatives of some eleven different metals have been used to effect the isomerization of $15$ and that these derivatives gave varying proportions of three different products: $18$, $28$ and 1,3-cycloheptadiene ($35$). $^{39}$ Surprisingly, stannous chloride and aluminum chloride gave the “normal” acid catalyzed product, 2-norcarene ($18$), but the known Lewis acids, zinc iodide and mercuric bromide, gave mixtures of $28$ and $35$. The formation of $35$ as the major product in these reactions closely parallels the silver ion catalyzed rearrangement of $15$. $^{37,38}$ The behavior of

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39. The structure was conclusively established by comparison with an authentic sample.
Table I

Metal-Promoted Isomerizations of Tricyclo[4.1.0.0²,⁷]heptane (I₅)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conditions</th>
<th>% Yield of Products^a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(temp, time, solvent)</td>
<td>18</td>
</tr>
<tr>
<td>AgBF₄</td>
<td>(ca. 40°, “minutes,” CDCl₃)³⁷,³⁸</td>
<td>--</td>
</tr>
<tr>
<td>ZnI₂</td>
<td>25°, 16 hr, Et₂0</td>
<td>--</td>
</tr>
<tr>
<td>HgBr₂</td>
<td>50°, 48 hr, Et₂0</td>
<td>--</td>
</tr>
<tr>
<td>[Rh(CO)₂Cl]₂</td>
<td>25°, 15 min, CH₃CN</td>
<td>--</td>
</tr>
<tr>
<td>[Ir(CO)₃Cl]₂</td>
<td>25°, 14 hr, CHCl₃</td>
<td>--</td>
</tr>
<tr>
<td>[(π-allyl)PdCl]₂</td>
<td>25°, 30 min, CHCl₃</td>
<td>--</td>
</tr>
<tr>
<td>(ηCN)₂PdCl₂</td>
<td>25°, 20 hr, CH₃CN</td>
<td>--</td>
</tr>
<tr>
<td>[C₆F₅Cu]₄</td>
<td>25°, 2 hr, CHCl₃</td>
<td>--</td>
</tr>
<tr>
<td>(η₃-P)₂Rh(CO)Cl</td>
<td>65°, 48 hr, CH₃CN</td>
<td>5</td>
</tr>
<tr>
<td>[Ru(CO)₃Cl₂]₂</td>
<td>25°, 40 hr, CH₃CN</td>
<td>12</td>
</tr>
<tr>
<td>PtO₂</td>
<td>65°, 48 hr, CH₃CN</td>
<td>24</td>
</tr>
<tr>
<td>SnCl₂·2H₂O</td>
<td>60°, 24 hr, CHCl₃</td>
<td>40</td>
</tr>
<tr>
<td>AlCl₃</td>
<td>(ether)^2⁴</td>
<td>b</td>
</tr>
</tbody>
</table>

a) All yields reported from this laboratory represent the average of at least two runs.

b) Yield not reported.
iridium tricarbonyl chloride dimer, \((\pi\text{-allyl})\)palladium chloride dimer, bis-benzonitrile-palladium chloride, and pentafluorophenylcopper tetramer \(^{40}\) simulated that of rhodium dicarbonyl chloride dimer. However, none of the complexes which mimic rhodium dicarbonyl chloride dimer appear to be as reactive nor as quantitative. \textit{trans-}Chlorocarbonyl-bis(triphenylphosphine)rhodium(I), ruthenium tricarbonyl dichloride dimer and platinum oxide give products which form a connecting link between the products formed in the presence of zinc iodide and mercuric bromide, and those formed in the presence of aluminum chloride or mineral acid.

The results from the transition metal complex promoted isomerizations of 1-methyltricyclo[4.1.0.0\(^{3,7}\)]heptane \(^{31}\) are shown in Table II. Again, a range of products was obtained depending on the metal derivatives used. Treatment of an ethereal solution of \(^{31}\) with 7 mol \% of stannous chloride in a sealed tube at 60\(^\circ\) for 24 hr afforded 53\% of the expected protic acid catalyzed product, 1-methyl-2-norcarene \(^{36}\). The structure proof of \(^{36}\), as outlined in Scheme II, was based on comparison with an authentic sample prepared from the reaction of 2-methyl-2-cyclohexenone \(^{39}\) with dimethylsulfoxonium methyldide, \(^{42}\) which afforded 1-methyl-2-norcaranone \(^{40}\) in 76\% yield. Treatment of \(^{41}\) with \(p\)-toluene-

\(^{40}\) Kindly provided by Dr. William Sheppard of the duPont Co.


### Table II

Metal-Promoted Isomerizations of 1-Methyltricyclo[4.1.0.0²⁷]heptane (31)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conditions (temp, time, solvent)</th>
<th>36</th>
<th>32</th>
<th>31</th>
<th>38</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Rh(CO)₂Cl]₂</td>
<td>25°, 15 min, CHCl₃</td>
<td>--</td>
<td>96</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>[Ir(CO)₃Cl]₂</td>
<td>25°, 14 hr, CHCl₃</td>
<td>--</td>
<td>93</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>[(μ-allyl)PdCl]₂</td>
<td>25°, 30 min, CHCl₃</td>
<td>--</td>
<td>56</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>[C₆F₅Cu]₄</td>
<td>25°, 6 hr, CHCl₃</td>
<td>--</td>
<td>--</td>
<td>48</td>
<td>12</td>
</tr>
<tr>
<td>ZnI₂</td>
<td>25°, 16 hr, Et₂O</td>
<td>--</td>
<td>--</td>
<td>24</td>
<td>42</td>
</tr>
<tr>
<td>HgBr₂</td>
<td>60°, 24 hr, Et₂O</td>
<td>53</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

% Yield of Products

![Chemical Structures]
Scheme II

32 $\xrightarrow{\text{CH}_3\text{MgI}}$ 40 $\xrightarrow{\text{TsOH}}$ 41 $\xrightarrow{h\nu}$ 36

42 $\xrightarrow{1. \text{CH}_3\text{MgI}}$ 410° $\xrightarrow{h\nu}$ 43 $\xrightarrow{450°}$ 44

43 $\xrightarrow{h\nu}$ 31 $\xrightarrow{450°}$ 36
sulfonylhydrazine gave 41 which was treated with 2 eq of methyllithium to give a 54% yield of 36.

The reactions of 31 with zinc iodide and mercuric bromide resembled the recently published silver ion catalyzed rearrangement 37,38 of 31. The two products which were obtained were 2-methyl-1,3-cycloheptadiene (37) and 6-methylbicyclo[3.2.0]hept-6-ene (38). Their structures were established through independent synthesis as shown in Scheme II. The reaction of 2-cycloheptenone (42) with methylmagnesium iodide followed by dehydration with p-toluenesulfonic acid gave a 2:1 mixture of 43 and 34, respectively, in 65% combined yield. Photolysis of a mixture of 43 and 37 gave a 24% yield of a mixture of 44 and 38, which was separated by preparative vpc. The structural correlation of 37 with 38 was unequivocally established by pyrolysis of 38 at 450° to give only 37. Similarly, 44 gave only 33 on pyrolysis at 410°.

As in the case of 25, iridium tricarbonyl chloride dimer, (π-allyl)palladium chloride dimer and pentafluorophenylcopper(I) tetramer gave the same product as rhodium dicarbonyl chloride dimer in the transition metal-complex promoted isomerization of 31. Interestingly, although 31 bears a structural resemblance to 1,2,2-trimethylbicyclo[1.1.0]butane (19) (one bridgehead carbon atom of the bicyclo[1.1.0]-butane moiety has a methyl substituent and the other has a hydrogen).

their reactions with pentafluorophenylcopper(I) differed markedly. Treatment of 19 with the aryl copper compound 32b resulted in products arising from cleavage of the side and central bonds in the manner indicated below to give the proposed intermediate species $45 \leftrightarrow 46$. Treatment of 31 with $(\text{C}_6\text{F}_5\text{Cu})_4$, however, gave 32 which arose from cleavage of a different side bond and the central bond. This mode of cleavage would be best explained in terms of the intermediate species $32 \leftrightarrow 34$, in which the metal is attached to the carbon atom not bearing the methyl group. Apparently, transition metal complex promoted isomerizations of the bicyclo[1.1.0]butane nucleus are as sensitive to the nature of the ring system as they are to the nature of the transition metal complex.
Since the discovery that transition metal compounds promote the facile rearrangement of a wide variety of strained ring compounds, many mechanisms have been proposed to account for the products obtained. In studies of the reactions of simple bicyclo[1.1.0]butane derivatives, the formation of a transition metal-complexed carbene - transition metal-bonded carbonium ion resonance hybrid has been proposed. This intermediate would arise via cleavage of a side and central bond of the bicyclo[1.1.0]butane moiety as in the case of 15 to give 32 ↔ 30 and 31 to give 33 ↔ 34. Evidence cited in support of this proposal included deuterium labelling studies in the rearrangement of 1,2,2-trimethylbicyclo[1.1.0]butane (19). Treatment of 19 with rhodium dicarbonyl chloride dimer afforded 2,3-dimethyl-2,4-pentadiene (42) as the major product. Since 42 is also one of the thermolysis products of 19, the question was raised whether it arose via bond cleavage in a manner similar to the thermolysis, namely cleavage of bonds ad and bc; or whether it arose via cleavage of bonds ac and bc with hydrogen migration.

The answer to this question was elucidated by replacing the bridgehead hydrogen of 19 by deuterium to give 50. When the reaction with
rhodium dicarbonyl dimer was carried out, only the diene with the deuterium located in 5-position, 52, was isolated and none of the corresponding 4-deuterio compound, 51, was found. This indicated that cleavage of the ac and bc bonds occurred in 50 and thus the formalism of a retro-carbene reaction to give a transition metal-complexed carbene -transition metal-bonded carbonium ion was adopted.

The validity of using resonance structures such as 32 ↔ 30 and 33 ↔ 34 in describing reactions of bicyclo[1.1.0]butane with metal catalysts has been supported in two ways. Intermolecular “trapping” of a carbenoid species has been reported. Treatment of bicyclo[1.1.0]-butane derivatives such as 19 with bis(acrylonitrile)nickel(0) in the presence of methyl acrylate afforded cyclopropane adducts of the type 52. This reaction can be viewed as occurring via cleavage of a side and central bond in 19 in the manner shown to give 34 ↔ 35, which can then undergo addition to give the cyclopropane derivative 53. The formation of these adducts may therefore be viewed as the result of a

formal intramolecular retro-carbene reaction followed by an intermolecular carbene addition.

The utility of both the transition metal-complexed carbene and the transition metal-bonded carbonium ion in the explanation of products from reactions of bicyclo[1.1.0]butane derivatives and transition metal complexes has also been capably demonstrated. Treatment of 1-methyl-2,2-diphenylbicyclo[1.1.0]butane (56) with rhodium dicarbonyl chloride dimer afforded three primary products: 1-diphenyl-2-methyl-1,3-butadiene (57), 2-methyl-1-phenyl dihydroazulene (58), and 2-methyl-1-phenyl-3,4-dihydronaphthalene (59). The mechanism proposed for the formation of 57, 58, and 59 is presented below. Cleavage of a side and central bond of 56 would give the transition metal-complexed carbene (60) - transition metal-bonded carbonium ion (61) intermediate. Hydrogen migration with loss of the metal ion would give 57. The formation of 58 could be explained on the basis of intramolecular addition of the carbenoid species 60 to one of the aromatic rings to give the norcaradiene structure (62) which, upon tautomerization to the cyclo-
heptatriene, gives 58. The formation of 59 may be explained on the basis of either resonance form 60 or 61. Insertion of the carbenoid into a carbon-hydrogen bond of the aromatic ring would give 59. Alternatively, Friedel-Crafts alkylation of the carbonium ion center of 61 onto one of the aromatic rings and subsequent hydrogen migration and loss of the metal ion would also give 59. Thus, both the transition metal-complexed carbene and the transition metal-bonded carbonium ion are useful representations of the proposed intermediate in the transition metal promoted rearrangements of bicyclo[1.1.0]butane derivatives.

The data presented in Table I shows that there is a gradual crossover of products for the metal derivatives used for the rearrangement
of 15. The entire range of products can be explained in terms of the mechanism shown in Scheme III, which details a stepwise bond cleavage process for the bicyclo[1.1.0]butane nucleus. In this mechanism, the various transition metal derivatives act as highly specific Lewis acids. Initial attack of the transition metal derivative would produce the cyclopropylcarbinyl cation, $6_2$, via cleavage of the C$_2$-C$_3$ bond. All of the observed products can be adequately explained on the basis of the intermediacy of $6_2$. Subsequent cleavage of the C$_1$-C$_3$ bond would produce the hybrid intermediate $22 \rightarrow 30$ represented by the resonance contributors shown. A hydrogen shift from C$_4$ to C$_3$ and loss of M$^X$ at this point, would produce $28$. Loss of a proton from $6_2$ would give $6_4$ which on protonolysis of the carbon-metal bond would give $18$. 1,3-Cycloheptadiene (35) could be viewed as arising by cleavage of the C$_1$-C$_4$ bond in $6_2$ to give the homoallylic cation 65, which upon loss of M$^X$ would give 35.

45. In some respects there is a similarity between the stepwise mechanism for the rearrangement of 15 proposed in Scheme III and that which has been suggested for the metal catalyzed rearrangement of tri-tert-butylprismane [K. L. Kaiser, R. F. Childs, and P. M. Maitlis, J. Amer. Chem. Soc., 93, 1270 (1971)]. Both mechanisms use the transition metal catalyst as an electron acceptor. For an additional discussion see J. E. Byrd, L. Cassar, P. E. Eaton, and J. Halpern, Chem. Commun., 40 (1971).


47. This is the pathway taken in the "normal" protic acid catalyzed reaction of 15.
Scheme III

15 \[ \xrightarrow{M^X} \] \[ \text{C}_2\text{-C}_3 \text{ bond cleavage} \] \[ \xrightarrow{-H^+} \] 64

63 \[ \xrightarrow{\text{C}_1\text{-C}_3 \text{ bond shift}} \] 30

65 \[ \xrightarrow{-M^X} \] 22

protonolysis

18 \[ \xrightarrow{-M^X} \] 35 \[ \xrightarrow{-M^X} \] 28
In order to add substance to this hypothesis, an attempt was undertaken to trap \( \text{63} \) by running the reaction in a more nucleophilic solvent. Treatment of \( \text{15} \) with rhodium dicarbonyl chloride dimer in methanol resulted in the formation of 75% isolated yield of a 4:1 mixture of the methyl ethers \( \text{66} \) and \( \text{67} \) shown in Scheme IV. This is the same ratio of ethers as was found in the methanolation of \( \text{15} \) catalyzed by sulfuric acid. The structures were conclusively proven by spectral comparison with authentic samples synthesized by a modification of the procedure used by Dauben and Berezin. 2-Cyclohexenone (\( \text{68} \)) was treated with dimethylsulfoxonium methyliide \( \text{42} \) to give \( \text{69} \), which was reduced with lithium aluminum hydride to give a 30:70 mixture of \( \text{70} \) and \( \text{71} \), respectively. Methylation of the mixture of these alcohols with sodium hydride - methyl iodide afforded a mixture of \( \text{66} \) and \( \text{67} \) in 85% yield.

When a methanolic solution of \( \text{15} \) was treated with 1 mol % of (\( \pi \)-allyl)palladium chloride dimer or 6 mol % of zinc iodide, again rapid

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48. Control experiments demonstrated that the dimer could be recovered unchanged from methanol and that the addition of enough sodium methoxide to make the reaction mixture strongly basic did not stop the reaction. Hence, it would appear that the observed reaction was not due to the formation of some new catalyst from methanol and rhodium dicarbonyl chloride dimer nor by generation of a Brönsted acid in the solution.


Scheme IV

\[
\begin{align*}
&\text{15} & \xrightarrow{[\text{Rh(CO)}_2\text{Cl}]_2, \text{CH}_3\text{OH}} & \text{66} + \text{67} \\
&\text{68} & \rightarrow & \text{69} \quad \rightarrow \quad \text{70} + \text{71}
\end{align*}
\]
addition of methanol occurred to give essentially the same mixture of \(34\) and \(35\). This indicates that the transition metal compounds can behave as very specific Lewis acid catalysts. Furthermore, the trapping of a carbonium ion type intermediate by nucleophilic solvent tends to support the hypothesis that the multiple bond cleavages promoted by transition metal derivatives is a stepwise process which leads, in some instances, to an intermediate which can be represented by resonance hybrids such as \(29\) and \(30\).

Table II lists the products observed in the reaction of various transition metal derivatives with \(31\). The metal derivatives which converted \(15\) to \(28\) have been previously discussed, and evidence was presented in support of the resonance structures \(29 \leftrightarrow 30\) as an intermediate in this isomerization. Similar arguments can be utilized in support of the intermediacy of the resonance hybrid \(33 \leftrightarrow 34\) in the isomerization of \(31\) to \(32\). The formation of the “expected” acid-catalyzed product, \(36\), may be viewed in the same manner as the formation of \(18\) as shown in Scheme V. However, the formation of \(37\) and \(38\) when zinc iodide or mercuric bromide was used as the reaction initiator, deserves some mechanistic comment. Initial attack of the complex on \(31\) would be expected to lead to the cleavage of the C\(_2\)-C\(_3\) bond to give the cyclopropyl carbinylication \(72\). Cleavage of the C\(_1\)-C\(_3\) bond would lead to formation of \(33 \leftrightarrow 34\) and subsequently to \(32\), while proton loss and protonolysis of the carbon-metal bond of \(72\) would produce \(36\). Alternatively, \(72\) could undergo a shift of the C\(_1\)-C\(_4\) bond to give the homallylic cation \(73\). Upon loss of the metal ion, \(73\) would give \(37\). A cyclopropyl car-
Scheme V

32

33

34

35

36

37

38
vinyl - cyclobutyl cation rearrangement of 72 would produce the tertiary cation 74, which would yield 38 upon loss of M+. It is presumably the added stability of the tertiary cation 74, which differentiates the formation of 38 from 31, from the lack of formation of any bicyclo[3.2.0]heptane derivative from 15.

Evidence in support of a stepwise mechanism similar to that proposed for the rearrangement of 15, was obtained by treatment of a methanolic solution of 31 with 1 mol% of rhodium dicarbonyl chloride dimer. The trapping of the carbonium ion type intermediate, 72, was substantiated by the formation, in 82% isolated yield, of an 80:10:10 mixture of exo-2-methoxy-1-methylnorcarane (75), endo-2-methoxy-1-methylnorcarane (76), and 4-methoxy-2-methylcycloheptene (77) as shown in Scheme VI. The structures of 75 and 76 were conclusively proven by independent synthesis in the following manner. Reduction of 70 with lithium aluminum hydride afforded a 5:1 mixture of 78 and 79. Methylation of the mixture of alcohols with sodium hydride - methyl iodide yielded a mixture of 75 and 76. The structure of 77 was based

\[ 51 \text{ Alternately, 74 could be formed by homoallylic participation of the double bond in 72. A multistep mechanism which involves initial cleavage of the central bond of 31 could also be constructed to explain the origin of 38.} \]

\[ 52 \text{ An infrared spectrum of authentic 79 was kindly provided by Professor W. Dauben.} \]

\[ 53 \text{ Compound 77 could also be obtained by treatment of the mixture of 78 and 79 with p-toluenesulfonyl chloride in pyridine followed by refluxing the crude product in methanol.} \]
Scheme VI

31 $\rightarrow$ [Rh(CO)$_2$Cl]$_2$ $+$ CH$_3$OH 

$\rightarrow$ 75 $+$ 76 $+$ 77

40 $\rightarrow$ 78

$\rightarrow$ 79 $\rightarrow$ 80 $\rightarrow$ 81 $\rightarrow$ 82
upon its spectral data [ir (CCl₄ solution) 8.98, 9.10, and 9.21 μ; nmr (CDCl₃) τ 4.40 (1H, triplet, J = 7 Hz), 6.71 (3H, singlet), 7.0 (1H, multiplet), 7.6-9.0 (11H, broad multiplet containing a 3H singlet at τ 8.29)], and by reduction of 77 to give a 3:2 mixture of 80 and 81, which were prepared independently by methylation of 82 and 83, respectively.

The evidence presented provides strong support for the mechanistic postulate that the transition metal promoted rearrangement of bicyclo[1.1.0]butane derivatives involves a stepwise bond cleavage process in which the transition metal acts as a very specific Lewis acid. Furthermore, the trapping experiments with the nucleophilic solvent, methanol, supports the contention that the first step of the rearrangement occurs via cleavage of a side bond of the bicyclo[1.1.0]butane moiety to yield a cyclopropylcarbinyln cation. In general, this postulate provides a unified picture of the overall patterns of reactions which derivatives of bicyclo[1.1.0]butane, and in particular, derivatives of tricyclo[4.1.0.0²,7]heptane, can follow in transition metal complex promoted rearrangements.

The concept of the retrocarbene reaction, although not mechanistically accurate, is, in the formal sense, a useful method of bookkeeping. Stepwise cleavage of a side and the central bond of the bicyclo[1.1.0]-butane nucleus gives an intermediate which is that predicted by a formal retrocarbene reaction. The ability of the intermediate postulated in

the transition metal complex promoted rearrangements of bicyclo[1.1.0]-butane derivatives to account for many of the products obtained indicates that the proposal is useful in predicting products. The desirability of using two resonance forms of this intermediate has also been presented.

Finally, the study of transition metal complex promoted rearrangements of tricyclo[4.1.0.0^2,7]heptane and other bicyclo[1.1.0]butane derivatives offers the first experimentally supported rationale which could explain hydrogenation patterns of these derivatives. When the bicyclo[1.1.0]butane derivative is adsorbed on the surface of the hydrogenation catalyst, facile rearrangement to diene derivatives could occur. Hydrogenation of the diene could then be rapid and occur before the diene is liberated from the catalyst surface. The similarities in the mode of bond cleavage in hydrogenations and in transition metal complex promoted rearrangements of bicyclo[1.1.0]butane derivatives and in the types of metals which facilitate these reactions make this explanation plausible.

The specificity of the metal complex; i.e., why different metals and even different ligands on the metal effect a crossover in the mechanistic pathways, is a question which remains to be answered. This specificity may be related to the strength of the various carbon-metal "bonds" formed in the rearrangement process. Probably all of the factors which influence the Lewis acidity of the metal will have an effect on the specificity of these rearrangements. A substantially larger body of information is needed before the influence of these factors will be fully understood.
The ease with which various transition metal complexes promote the rearrangement of derivatives of bicyclo[1.1.0]butanes has been discussed. The facility with which these highly strained ring systems isomerize has been attributed in part to ca. 64 kcal/mol of strain energy incorporated into this fused ring system. In addition, the transition metal complex promoted isomerization of quadricyclenes,\textsuperscript{8,7} and of other cage type molecules,\textsuperscript{11-17} have been associated with the strained nature of these molecules. It would therefore be of interest to study the transition metal complex promoted isomerization of bicyclo[2.1.0]pentane (24), a molecule whose strain energy (54 kcal/mol) is considerably less than most other saturated molecules which have been found to rearrange in the presence of transition metal complexes.

Cleavage of the central bond of bicyclo[2.1.0]pentane results in the release of ca. 47 kcal/mol of strain energy.\textsuperscript{20,55} Despite the large amount of energy which can be released through cleavage of this bond, 24 possesses remarkable thermal stability. A temperature of 330° has been reported necessary for the thermal isomerization of 24 to

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cyclopentene (26). In contrast, treatment of a chloroform or acetonitrile solution of 24 with 5 mol % of rhodium dicarbonyl chloride dimer, at 25°, resulted in the smooth isomerization of 24 into 26. The half-life for the reaction at 25° was ca. 8 hr. At 65°, no trace of 24 could be detected after 48 hr, when 2 mol % of rhodium dicarbonyl chloride dimer was used to promote the isomerization. Vpc analysis indicated that the conversion of 24 into 26 was essentially quantitative.

The transformation of 24 into 26 represents an interesting example of a transition metal complex promoted isomerization. It is distinctly

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56. From one point of view this rearrangement can be classified as a cyclopropyl to allyl type isomerization. Although such transition metal complex promoted rearrangements are known, they generally do not occur readily at room temperature. For typical examples see ref. 18, 19b, 19e, 19g; K. G. Powell and F. J. McQuillen, Chem. Commun., 931 (1971); D. M. Roundhill, D. N. Lawson, and G. Wilkinson, J. Chem. Soc. (A), 845 (1968); and R. J. Ouellette and C. Levin, J. Amer. Chem. Soc., 90, 6889 (1968).
different from the isomerization of bicyclo[1.1.0]butanes, in which two
carbon-carbon bonds were cleaved. Furthermore, in the transition metal
complex promoted isomerization of bicyclo[1.1.0]butanes, it has been
suggested that cleavage of a side bond preceded cleavage of the center
bond. Formally, with bicyclo[2.1.0]pentane, only the center bond was
broken. In view of the obvious differences between the transition
metal complex promoted isomerizations of bicyclo[1.1.0]butane and bi-
cyclo[2.1.0]pentane, a more detailed mechanistic insight into the mode
of rearrangement of \( \text{C}_4 \) was sought. In principle, numerous mechanisms
could be invoked to rationalize the observed isomerization of \( \text{C}_4 \) in
the presence of rhodium dicarbonyl chloride dimer. Three of the more
likely possibilities are outlined in Scheme VII, which shows the reac-
tion routes possible via initial cleavage of the C1-C2 bond (path a),
the C1-C4 bond (path b), or the C1-C5 bond (path c). Initial cleavage
of the C1-C2 bond would yield an intermediate, \( \text{C}_4 \), \(^{57}\) which, on 1,3-
hydrogen shift, could produce vinylcyclopropane (\( \text{C}_5 \)). If the rhodium
dicarbonyl chloride dimer could catalyze a vinylcyclopropane to cyclo-
pentene rearrangement, this route would be feasible. This mechanistic
possibility was readily tested by exposing vinylcyclopropane to rhodium
dicarbonyl chloride dimer. The lack of any rearrangement of \( \text{C}_5 \) under

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57. The nature of the intermediate formed in the first step of the
    cleavage has not been determined. It seems likely that the tran-
    sition metal must be strongly associated with the intermediate
    (whether \( \text{C}_4 \), \( \text{C}_6 \), or \( \text{C}_7 \) is the intermediate of importance). Hence,
    the structures shown for \( \text{C}_4 \), \( \text{C}_6 \), and \( \text{C}_7 \) are only meant to show
    which bonds were broken, not how they were broken nor the role of
    the transition metal complex.
Scheme VII

86 \xrightarrow{c} 84

\[ 2k \]

86 \xrightarrow{b} 2k

87 \xrightarrow{a} \rightarrow \xleftarrow{\text{pentane}}

85
these conditions indicated the unlikelihood of path a as a route from 24 to 26. Paths b and c are quite different in that different bonds are initially broken to convert 24 into 56 and 27. Since 56 would have to undergo a ring expansion to yield the observed product, paths b and c become indistinguishable experimentally.

In view of the intriguing nature of the rearrangement of 24 by transition metal complexes, more information about this reaction was sought via a study of deuterium labeled 24. In order to determine which of the hydrogens were migrating during the rearrangement, the preparation of exo-2,3-dideuteriobicyclo[2.1.0]pentane (88), endo-2,3-dideuteriobicyclo[2.1.0]pentane (82), and 5,5-dideuteriobicyclo[2.1.0]pentane (92) was undertaken as shown in Scheme VIII. A 2.9:1 mixture of 88 and 82, respectively, was prepared in 65% yield via pyrolysis of exo-5,6-dideuterio-2,3-diazabicyclo[2.2.1]hept-2-ene (91) at 200°.59 The relative ratios of 88 and 82 were determined by nmr spectroscopy which showed peaks at τ 7.92 (0.51 H, exo-protons at C2 and C3) and τ 8.67 (1.49 H, endo-protons at C2 and C3). Photolysis of 91 in an n-butanol glass at -70° with a high pressure mercury lamp afforded a 37% yield of a 1.3:1 mixture of 88 and 82, respectively.

The synthesis of 5,5-dideuteriobicyclo[2.1.0]pentane (92) was accomplished in 23% yield through the reaction of cyclobutene (92)60

58. W. Greenlee, personal communication.
59. This is essentially the procedure of W. Roth and M. Martin, Justus Liebigs Ann. Chem., 702, 1 (1957).
Scheme VIII

\[
\begin{align*}
\text{21} & \xrightarrow{\text{hv or } \Delta} \text{88} + \text{82} \\
\text{22} + \text{ICD}_3\text{ZnCD}_2\text{I} & \rightarrow \text{23}
\end{align*}
\]
with bis(dideuteriodiomethyl)zinc (D3) utilizing a modification of the
procedure of Wittig and Wingler to prepare D4. The sample of D2
prepared by this procedure was 84% deuterated at the 5-position as shown
by the nmr spectrum of D2 which had peaks at 7 9.35 (exo H) and 9.52
(endo H).

Treatment of the 2.9:1 mixture of D3 and D5, the 1.3:1 mixture of
D3 and D6, or the sample of D2 with 2 mol % of rhodium dicarbonyl
chloride dimer in chloroform at 65° gave identical mixtures of deuterated
cyclopentenes. The nmr and ir spectra of these product mixtures
were identical. The nmr spectra of the mixtures of deuterated cyclo-
pentenes showed a ratio of low field vinylic protons to upfield protons
(both allylic and non-allylic) of 1:3.21 ± 0.10, respectively. Totally
random distribution of the deuterium should give a ratio of 1:3, assum-
ing no deuterium isotope effects on the product distribution. It
became clear at this point that essentially complete scrambling of the
deuterium label was occurring during the course of this reaction. In
order to determine the stage of the reaction at which scrambling of the
deuterium occurred, several control experiments were carried out. The

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62. The nmr assignments are those of Roth and Martin (ref. 59).
63. Measurements of cyclopentene, cyclohexene, and cycloheptene gave
ratios of 1:3.31, 1:4.49, and 1:5.72 (average of three determina-
tions), respectively, on the nmr spectrometer used for these analy-
ses. These values indicate that the ratio of 1:3.21 represents
complete scrambling of the label.
rearrangement of the 2.9:1 mixture of \( \mathbf{88} \) and \( \mathbf{82} \) was run to 50% completion. The remaining labeled bicyclo[2.1.0]pentane was recovered and shown by nmr spectroscopy to be unscrambled. Next, 1-deuteriocyclopentene (\( \mathbf{94} \)) was prepared by reduction of cyclopentanone (\( \mathbf{25} \)) with

\[
\begin{align*}
\text{\( \mathbf{94} \)} & \xrightarrow{\text{LiAlD}_4} \text{\( \mathbf{26} \)} \\
\text{\( \mathbf{24} \)} & \xrightarrow{\Delta} \text{\( \mathbf{27} \)} \\
\end{align*}
\]

lithium aluminum deuteride to yield \( \mathbf{26} \), followed by acetylation of \( \mathbf{26} \) with acetic anhydride in pyridine to give \( \mathbf{27} \) in 65% overall yield. Pyrolysis of \( \mathbf{27} \) in the vapor phase at 450° gave an 80% yield of \( \mathbf{24} \). The nmr spectrum of \( \mathbf{94} \) showed a ratio of olefinic to saturated aliphatic hydrogens of 1:6.22, respectively. Using the correction factor required by the data in footnote 63, this ratio indicated 93% deuterium incorporation at the 1-position by nmr analysis.

Treatment of \( \mathbf{24} \) with rhodium dicarbonyl chloride dimer at 65° in chloroform, for a time equivalent to four half-lives for the bicyclo-
[2.1.0]pentane isomerization, gave no detectable isomerization of the 1-deuteriocyclopentene. This control indicated that the deuterium scrambling in the isomerization of 88, 99, and 90 was either occurring during the interaction of the bicyclo[2.1.0]pentane with the transition metal complex and before the isomerized product had dissociated from the transition metal complex, or that an intermediate was being generated in the reaction of bicyclo[2.1.0]pentane with the transition metal complex which was capable of promoting the rearrangement of the labeled cyclopentene product in an intermolecular reaction. In order to distinguish between these two possibilities, a series of experiments was undertaken in which small amounts of highly strained bicyclic molecules were added to a chloroform solution of 1-deuteriocyclopentene and rhodium dicarbonyl chloride dimer. Addition of 10 mol % of 24 to a deuteriochloroform solution of 24 and rhodium dicarbonyl chloride dimer gave, after only 3.5 hr at 10°, a solution of cyclopentene which showed an olefinic hydrogen to saturated aliphatic hydrogen ratio of 1:3.6, respectively. This indicated that the 1-deuteriocyclopentene was almost completely equilibrated during the course of the reaction of 24 with the rhodium dicarbonyl chloride dimer. Once the added bicyclo[2.1.0]pentane was completely isomerized, no further scrambling of the labeled cyclopentene was observed. This indicated that it was a transitory intermediate, involved in the rearrangement of 24 which was the active catalyst for the isomerization of the labeled cyclopentene and not some new derivative of the transition metal (which would have remained after 24 had completely disappeared).
In view of the extensive evidence for the role of metal hydrides in the transition metal promoted isomerization of olefins, it is possible that the active intermediate which promotes the deuterium scrambling of $\mathbf{24}$ may be the same intermediate which accounts for the hydrogen transfer step in the isomerization of $\mathbf{24}$ to $\mathbf{26}$. It is also possible that this intermediate is a metal hydride as is shown in either structure $\mathbf{23}$, $\mathbf{22}$, or $\mathbf{100}$, in which the transition metal is coordinated to both the residue from the bicyclo[2.1.0]pentane and the hydrogen which is being transferred. This would formally involve a rhodium(III) hydride. Intermolecular addition-elimination of the metal hydride to $\mathbf{24}$ would lead to deuterium scrambling in $\mathbf{24}$, whereas collapse of the hydride would produce cyclopentene. However, it was shown in a control experiment that a preformed rhodium(I) hydride was not satisfactory for deuterium scrambling of $\mathbf{24}$ under the reaction conditions. After 24 hr at $10^\circ$ with 1 mol % of the soluble catalyst, tris(triphenylphosphine)carbonylrhodium(I) hydride, no detectable isomerization of $\mathbf{24}$ had occurred.

The unusual nature of the isomerization of $\mathbf{24}$ in comparison to the transition metal complex promoted isomerization of derivatives of bicyclo[1.1.0]butane was demonstrated by the failure of added 1,2,2-trimethylbicyclo[1.1.0]butane (19) or added tricyclo[4.1.0.0²,7]heptane.

---


(15) to facilitate rearrangement of \( 2^4 \) in a chloroform solution of \( 2^4 \).

![Diagram](attachment:image.png)

containing rhodium dicarbonyl chloride dimer. No change in the nmr spectrum of \( 2^4 \) was observed after the transition metal complex promoted rearrangement of \( 15 \) or \( 15 \) was complete and the catalyst had been removed from the solution. If an intermediate metal hydride is generated in the transition metal complex promoted rearrangement of \( 15 \) or \( 19 \), it must either be too short-lived or too unreactive to promote the deuterium scrambling of \( 2^4 \). In the hope of trapping an electrophilic species (intermediate), the isomerization of \( 2^4 \) was carried out in the more nucleophilic solvent, methanol. Whereas, bicyclo[1.1.0]butane derivatives gave high yields of methyl ethers under these conditions, \( 2^4 \) gave only cyclopentene (26).

66. If the reaction solution containing 3-methylene-cyclohexene (28), and \( 2^4 \) was allowed to remain in contact with the rhodium dicarbonyl dimer for long periods of time, some changes were noted in the nmr spectrum of \( 2^4 \). However, this was most likely due to interactions of 28 and \( 2^4 \) and not due to an intermediate in the reaction of \( 15 \) and rhodium dicarbonyl chloride dimer. If the solution of \( 2^4 \) was vacuum transferred as soon as \( 15 \) had completely disappeared, no change in the nmr spectrum of \( 2^4 \) was observed.

67. Within the limits of analysis by vpc, no methyl ether could be detected from the reaction of \( 2^4 \) with rhodium dicarbonyl chloride dimer in methanol.
Therefore, on the basis of the observed data, a mechanistic scheme for the transition metal complex promoted rearrangement of bicyclo-
[2.1.0]pentane (24) could be constructed which differs markedly from
the mechanistic scheme proposed for the isomerization of bicyclo[1.1.0]-
butane derivatives (Scheme III and Scheme V). Such a mechanistic pro-
posal is outlined in Scheme IX. Oxidative addition of the transition
metal across the C1-C4 central bond of the bicyclo[2.1.0]pentane would
give the bicyclic intermediate (101). Alternatively, 101 could
arise via oxidative addition of the metal to the side bond of the
cyclopropane ring (C1-C5) to give 102, followed by rearrangement of
102 to give 101. Cleavage of one carbon metal bond of 101 and hydrogen
transfer would give a metal hydride intermediate, which may be one of
the three structures 99, 99, or 100. Collapse of the metal hydride
would then give 26.

68. The postulate of the formation of a hydride intermediate in the
isomerization of 24 was supported by recent observations from the
laboratory of Prof. K. B. Wiberg. These workers observed that the
use of methanol-D2 as solvent for this isomerization of 24 led to
the incorporation of deuterium into the cyclopentene. K. E. Wiberg,
personal communication.

69. For recent discussion see J. P. Collman, Accounts of Chem. Res.,
1, 136 (1968); J. A. Roth, J. Amer. Chem. Soc., 92, 6658 (1970);
L. Cassar, P. E. Eaton, and J. Halpern, J. Amer. Chem. Soc., 92,
Soc., 22, 7499 (1970); J. E. Byrd, L. Cassar, P. E. Eaton, and J.
Halpern, Chem. Commun., 40 (1971); T. J. Katz and S. A. Cerefice,

70. For a recent proposal analogous to this addition see R. Noyori,
Scheme IX

24

102

M

101

or

M'

or

M'

98

M'

100

26
The mechanism proposed in Scheme IX could account for all of the observations made in the rearrangement of $2^4$ to $2^6$. The metal hydride, $2^3$, $2^2$, or $100$, would account for the deuterium scrambling of 1-deuteriocyclopentene provided that the intermediate was long-lived and reactive enough to accomplish this rearrangement. The metal hydride also could account for deuterium incorporation in methanol-$D_2$ and, of course, for the product, cyclopentene. Unfortunately, none of the proposed intermediates $2^5$ through $10^2$, could be isolated or trapped in the reaction mixture. However, *a priori*, the pathway $2^4 \rightarrow 10^1 \rightarrow 2^9 \rightarrow 2^6$ would be the expected pathway on the basis of previous observations.

In order to evaluate the effect of an electron-withdrawing substituent at C-1 on the rearrangement of $2^4$, the study of the rearrangement of 1-carbomethoxybicyclo[2.1.0]pentane ($10^2$) in the presence of 5 mol \% of rhodium dicarbonyl chloride dimer in chloroform was undertaken. After 22 hr at $65^\circ$, $10^2$ was converted into 1-carbomethoxybicyclo (104) and 3-carbomethoxybicyclo (105) in 36 and 33\% yield, respectively. In addition, less than 1\% each of two unidentified products were produced. The structures of 104 and 105 were established by spec-


CO₂CH₃

103

CO₂CH₃

104 +

CO₂CH₃

105

CO₂CH₃

CO₂CH₃

tral and vpc comparisons with independently synthesized authentic samples. Reduction of methyl cyclopentanone-2-carboxylate with sodium borohydride, dehydration with phosphorus pentoxide, and equilibration of the product mixture with sodium methoxide gave 104 as the major product. The synthesis of 105 involved addition of one mole of hydrogen chloride to cyclopentadiene, Grignard formation, and carboxylation, followed by esterification with diazomethane.

In summary, it has been shown that the moderately strained bicyclo[2.1.0]pentane structure and its derivatives rearrange readily in the presence of rhodium dicarbonyl chloride dimer. The mechanism of the rearrangement of 2₄ appears to be significantly different from that proposed for the transition metal complex promoted rearrangement of derivatives of bicyclo[1.1.0]butane in the presence of the same complex. Although both proposed mechanisms provide an electrophilic role for the transition metal complex, the modes of cleavage in the two mechanisms appear to differ. Whereas the products from the rhodium dicarbonyl chloride dimer promoted rearrangement of bicyclo[1.1.0]butane derivatives arise via cleavage of two bonds of the bicyclo[1.1.0]butane
moiety, namely a side bond and the central bond, the products from bicyclo[2.1.0]pentane and its derivatives formally arise via cleavage of the central bond.
PART II ORGANOLITHIUM CHEMISTRY

INTRODUCTION

During an investigation designed to determine whether the 7-norbornenyl cation was best represented by a classical or non-classical cation, Gassman and Patton had need of certain methylated norbornene derivatives. These researchers found no suitable synthetic procedures in the literature for the preparation of compounds such as anti-7-hydroxy-2-methylnorbornene (106) and thus they began an investigation of the reactions of 2-chloronorbornene (107) and its derivatives with organolithium reagents in the hopes of obtaining a suitable synthetic route to 106. They reported that treatment of 107 with ethereal

\[
\begin{align*}
106 & \quad \text{HO} \quad \text{H} \\
107 & \quad \text{Cl} \\
108 & \quad \text{CH}_3
\end{align*}
\]


methylolithium for 8 days at 25° afforded 73% of 2-methylnorbornene (108). Treatment of 107 with n-butyllithium in hexane gave only starting material, whereas treatment of 107 with sec-butyllithium in hexane gave an 80% yield of norbornene (109).

In order to obtain a suitable precursor to 106, 7,7-dimethoxy-2-chloronorbornene (110) was treated with methylolithium. However, only 5% of the desired 7,7-dimethoxy-2-methylnorbornene (111) was found. The major product, isolated in 54% yield, was the nortricyclene derivative 112. Treatment of 110 with n-butyllithium in a similar manner gave 4% of 7,7-dimethoxy-2-n-butylnorbornene (113) and 72% of the nortricyclene derivative 114. Finally, they reported that treatment of

\[
\text{110} \quad \rightarrow \quad \text{111} \quad + \quad \text{112}
\]

\[
\text{110} \quad \rightarrow \quad \text{113} \quad + \quad \text{114}
\]

a mixture of syn- and anti-7-hydroxy-2-chloronorbornene, 115 and 116, respectively, with methylolithium afforded the alcohol 117 and its epimer
In view of these intriguing observations, a detailed investigation of the reaction of 2-chloronorbornene (107) and methyllithium was undertaken in order to determine what, if any, mechanistic conclusion about this reaction could be reached. Secondly, the reinvestigation of the treatment of 107 with other organolithium reagents was begun in the hopes of obtaining reactions of the organolithium reagents with the vinyl chloride. Finally, the investigation of reactions of 7,7-dimethoxy-2-chloronorbornene and, other 2-chloronorbornene derivatives with organolithium reagents was undertaken in order to measure the scope of these reactions of vinyl halides with organolithium reagents.

Some of the chemistry of organolithium reagents which might be pertinent to the discussion should be mentioned briefly. One of the most widely used reactions of organolithium reagents is the exchange of the lithium of the organometallic reagent with an organic halide. This process, known as metal-halogen interconversion, has been widely used to generate new organolithium reagents. The organic substrates used in these reactions have been primarily aryl halides. However, several vinyl halides, e.g. β-bromostyrene (118), α-bromostyrene (119),
and cis-bromostilbene (120) have been reported\(^{77,78}\) to undergo metal-halogen interconversion. The order of reactivity of organolithium reagents in ether in metal-halogen interconversion has been reported\(^{76a,79}\) to be \(n\)-C\(_3\)H\(_7\)Li > C\(_2\)H\(_5\)Li > \(n\)-C\(_4\)H\(_9\)Li > PhLi > CH\(_3\)Li. The reagent methyl-lithium was reported to be of little or no value for the metal-halogen interconversion reaction.

An aspect of the lithium-halogen interconversion reaction which has received much attention in recent years has been the formation of "carbene"\(^{80a}\) intermediates from gem-dihalides and organolithium reagents. For example, treatment of benzal bromide (121) with an organolithium reagent gave a metal-halogen conversion reaction with one of bromines to give the \(\alpha\)-bromolithium derivative 122. The chemistry of

the species derived from 122 was similar to that of a carbene and the term carbenoid was used to describe the intermediates in these reactions. Carbenoid intermediates generated in this manner were found to undergo addition to olefins, as in the case of 122 which gave 123, and the carbon-hydrogen insertion reaction. The organolithium reagents used for the generation of carbenoid intermediates have been n-amyl lithium, ethyllithium, n-butyllithium, and methyllithium. It is somewhat surprising that methyllithium is effective in view of Gilman's observations, but in at least one case, methyllithium appeared to be better than n-butyllithium in effecting a smooth carbenoid transformation.

The coupling reactions of organolithium reagents and organic halides is closely related to the metal-halogen interconversion reaction. Jones and Gilman classified the reaction as an "interfering side reaction" and did not attempt a mechanistic interpretation. Several groups have recently reported on the use of Chemically Induced Dynamic

Nuclear Polarization (CIDNP) for determining the presence of radicals in metal-halogen interconversions. They reported that alkyl iodides and organolithium reagents underwent metal-halogen interconversion and coupling via an intermediate which could be represented by \[ \text{[R',X,M,R']} \].

Similarly, studies of CIDNP emissions in the reactions of gem-dihalo-cyclopropanes and organolithium reagents led to the proposal of a one electron transfer (radical process) occurring before either coupling reactions or subsequent carbenoid chemistry was observed. Unfortunately, the CIDNP techniques have not been applied equally well to other coupling reactions of vinyl halides and aryl halides.

The strongly basic nature of organolithium reagents has long been known. The relative efficacy of organolithium reagent in abstracting protons from aromatic substrates under comparable conditions has been reported to be \( \text{n-butyllithium} > \text{ethyllithium} > \text{n-amyllithium} > \text{phenyllithium} > \text{methyllithium} \). Proton abstraction from simple vinyl halides often resulted in dehydrohalogenation to give the acetylene as shown.

---

below for vinyl bromide (125).

An example of the multifarious nature of organolithium reagents can be typified by the reaction of $\beta$-bromostyrene (116) with $n$-butyllithium. In 1927, Marvel and coworkers reported that treatment of 118 with $n$-butyllithium in petroleum ether for 38 days gave $\beta$-$n$-butylstyrene (127) and 128. Gilman and coworkers reinvestigated the reaction

\[ \text{H}_2\text{C}=\text{C}<\text{Br} \quad \xrightarrow{n-\text{BuLi}} \quad \text{H}\text{C}=\text{C}<\text{Br} \quad \xrightarrow{\Theta} \quad \text{H}\text{C}=\text{C}<\text{H} \]

\[ \text{Ph}\text{C}=\text{C}<\text{Br} \quad \xrightarrow{} \quad \text{Ph}\text{C}=\text{C}<\text{CO}_2\text{H} \]

tion and found that after shorter reaction periods, the product of metal-
halogen interconversion could be trapped with carbon dioxide to give
\[62\]. However, if \(\text{[\text{[text missing]}]}\) was treated with \(\text{n-butyllithium}\) in ether, the pro-
duct obtained after carbonation, \[130\], was the result of dehydrobromina-
tion and proton abstraction from the acetylene formed.

Another aspect of organolithium chemistry which has been observed
is the addition of organolithium reagents to olefins. It has been shown
that organolithium compounds will add to conjugated dienes and ethyl-
ene. \[84\] The secondary and tertiary organolithium reagents to appear to
be more reactive than the primary organolithium reagents. \[85\] A few
\[86\] reports of additions of organolithium reagents to other olefins,
mainly norbornenes, have also appeared. Wittig and coworkers \[86\] treated

\[84\] K. Ziegler, F. Crossmann, H. Kleiner, and O. Schafer, Justus Lie-
bigs Ann. Chem., 413, 1 (1929); K. Ziegler and H. Colonius, Justus
Liebig's Ann. Chem., 479, 135 (1930); K. Ziegler, F. Dersch, and H.
Wollthan, Justus Liebig's Ann. Chem., 511, 13 (1934); K. Ziegler,
H. Wollthan, and A. Weriz, Justus Liebig's Ann. Chem., 511, 164
(1934); E. Grovenstein, Jr., and G. Wentworth, J. Amer. Chem. Soc.,
89, 1852 (1967).

\[85\] (a) H. Ziegler and H.-G. Geller, Justus Liebig's Ann. Chem., 567,
179, 185, 195 (1950); (b) P. D. Bartlett, S. Friedman, and M.


\[88\] (a) R. Caple, G. M.-S. Chen, and J. D. Nelson, J. Org. Chem., 36,
2874 (1971); (b) J. G. Welch and R. M. Magid, J. Amer. Chem. Soc.,
89, 5300 (1967).
7-alkoxynorbornadienes (131) with isopropyl- and tert-butyllithium and obtained 7-alkoxy-5-alkynorbornenes (132) via addition of the organo-lithium reagent. Mulvaney and Gardlund studied the addition of tert-

\[ \text{OR} \xrightarrow{R'Li} \text{OR} \]

\[ \begin{align*}
R &= \text{tert-buty} \\
R' &= \text{methyl} \quad R = \text{tert-buty} \\
R' &= \text{isopropyl} \quad R = \text{tert-buty}
\end{align*} \]

butyllithium to norbornene (109) and isolated the product either as 2-tert-butylnorbornane (133) (via hydrolysis) or as 2-tert-buty1-3-carboxynorbornane (134) (via carbonation). These authors assigned an exo-configuration for the tert-butyl group based on nmr data. Caple and coworkers found that n-butyllithium in ether as well as sec-butyllithium...
and tert-butyllithium could be added to benzonorbornadiene (135) to give 5-butylbenzonorbornenes (136). The butyl group was assigned the exo-configuration. Welch and Magid studied the addition of phenyllithium to cyclopropene and found that the stereochemistry of the addition was cis.
RESULTS AND DISCUSSION

The Methylithium Reaction.

In view of the unprecedented reactions of 2-chloronorbornene derivatives and organolithium reagents reported by Gassman and coworkers, the detailed investigation of the reactions of 2-chloronorbornene (107) and its derivatives with organolithium reagents was undertaken in order to obtain a better understanding of the mechanisms and scope of these reactions. The reinvestigation of the reaction of 107 with methylithium was begun in the hope of obtaining information useful for mechanistic interpretation. Because of the diverse nature of organolithium reagents, many mechanisms could be proposed to account for the formation of 2-methylnorbornene (108) from 107 and methylithium. Four reasonable mechanisms which would account for this transformation are discussed below.

The first possible mechanism could be called the "norbornyne" mechanism. In this route, outlined below, methylithium could abstract the vinyl proton of 107 to give the anion 137. The anion 137 could undergo loss of chloride ion to give the highly strained bicycloalkyne, norbornyne (138). Addition of methylithium to 138 would be expected to give 139 which, upon hydrolysis in the workup, would give 2-methylnorbornene (108). Dehydrohalogenations of vinyl halides have already been mentioned. The use of organolithium reagents to effect dehydro-
halogenations of aromatic halides to give benzyne and other aryne intermediates is now well established. Some reactions of endocyclic vinyl halides and phenyllithium have been shown to proceed via cycloalkyne intermediates. Montgomery and co-workers have provided compelling evidence based on deuterium- and $^{14}$C-labelling experiments that the reaction of 1-chlorocyclohexene (107) and phenyllithium to give 1-

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phenylcyclohexene (142) proceeds via cyclohexyne (141). This work was also extended to include cyclopentyn e formation in an analogous reaction. The formation of cyclopentyn e has been postulated in other reports and attempts have even been made, although unsuccessfully, to generate cyclobutyn e. The intermediacy of a bicycloalkyne, 4,4-dimethylbicyclo[3.2.1]oct-2-yn e (143) has also been postulated, although its generation was via a different route. Recently, stabiliz-

\[
\text{Cl} \quad \overset{\text{PhLi}}{\longrightarrow} \quad [\text{cyclohexyne}] \quad \overset{\text{PhLi}}{\longrightarrow} \quad \text{Ph}
\]

tion and isolation of cycloalkynes by complexation with metal derivatives has been reported.

The second plausible mechanistic pathway could be called the "carbeneoid" mechanism. Addition of methyllithium to 107 could occur to give

![Chemical Structures](image)

the α-chlorolithium derivative, 104. On the basis of electronic effects, this mode of addition might be expected because the electropositive lithium would be attached to the more electronegative end of the vinyl chloride dipole and the anionic methyl group would be expected to be attached to the more electropositive end of the dipole. α-Elimination of lithium chloride from 104 should give the carbeneoid species


depicted by $\text{145}$. The intermediate $\text{145}$ could convert to 2-methylnorbornene ($\text{103}$) in two ways. Migration of the hydrogen to the carbenoid center of $\text{145}$ would give $\text{103}$, as would migration of the methyl group. In view of the preference for hydrogen migration rather than methyl migration in carbene reactions, the hydrogen migration might be expected to predominate.

The third plausible pathway could be called the “addition-β-elimination” mechanism. Methyllithium could add to $\text{107}$ in the manner indicated below to give the β-chlorolithium derivative $\text{146}$. This mode of addition is opposite to that proposed in the “carbenoid” mechanism. The β-elimination of lithium chloride from $\text{146}$ would then give $\text{108}$ directly.

The final mechanistic proposal is the “coupling” mechanism. This mechanism is analogous to those nefarious side reactions which occur in Grignard reactions and organolithium reactions. Methyllithium and $\text{107}$ could come together in close association, as depicted by $\text{147}$, and exchange fragments to give $\text{108}$ and lithium chloride. This mechanism

98. H. Shechter, personal communication to P. G. Gassman.
could be analogous to that reported for the coupling of alkyl iodides, but the electronic structure of the fragments in 147 has not been well defined.

After reviewing these four mechanistic proposals, the "norbornyne" mechanism appeared to be the most aesthetically interesting and most easily tested. Thus, the investigation of its plausibility was undertaken. In the last step of this mechanism, the new vinyl-lithium derivative 139 must undergo hydrolysis to give 2-methyl-norbornene (108). Therefore, incorporation of deuterium via deuterium oxide hydrolysis, or carboxylation of 139 would be evidence for the presence of 139. When 2-chloronorbornene (107) was stirred with five equivalents of ethereal methyl-lithium for 8 days and hydrolyzed with deuterium oxide, no deuterium incorporation in 108 was observed. Similarly, carboxylation of the reaction mixture afforded no product identifiable as the acid expected from 139. These experiments do not preclude the possibility that partial hydrolysis of 139 could occur during the 8 day reaction period. So, in order to establish unequivocally whether or not the "norbornyne" mechanism was operative, the synthesis of 3-deuterio-2-chloronorbornene
(148) was undertaken. If the "norbornyne" mechanism is operative, the deuterium in 148 should be abstracted in the first step and subsequent hydrolysis of the reaction mixture should yield only 108 with no deuterium incorporation.

The preparation of 148 was accomplished in three steps as outlined in Scheme X. Treatment of norcamphor (149) with trifluoroacetic acid-0-d in deuterium oxide, according to the method of Farnum and Mehta, gave 3,3-dideuterionorcamphor (150). Treatment of 150 with phosphorus pentachloride gave 151, which upon treatment with potassium tert-butoxide gave 148. The deuterium content in the 3-position of 148 was found to be 83% by nmr analysis.

Treatment of 148 with five equivalents of methyllithium in ether for 5 days gave a mixture of both 149 and 3-deuterio-2-methylnorborne (152). Both compounds were isolated and nmr analysis indicated that each had 83% deuterium incorporation at the 3-position. The presence of 152 and the recovery of 148 with all of the original deuterium content present indicated that proton abstraction had not occurred (107, \ref{137}) and that the "norbornyne" mechanism was not operative in the transformation of 107 to 108.

After the elimination of the proposed "norbornyne" mechanism, the possibility of the "carbenoid" mechanism was considered. If hydrogen migration to the carbenoid center in 145 occurred, then the methyl group in 108 would be attached to the carbon originally bearing the.

Scheme X

142 → 150 → 151

152 ← 148
hydrogen, and the hydrogen would be attached to the carbon originally bearing the chlorine. By using racemic 2-chloronorbornene (107) this distinction cannot be detected. By treating optically active 2-chloronorbornene (153) with methylithium and correlating the absolute configuration of the optically active 2-methylborbornene, 154 or 155, with 153, the location of the methyl group could be discovered. As seen below, the optical isomer 154 would be expected if the carbenoid me-

![Chemical Structure](image)

chanism with hydrogen migration were to occur. However, if 155 was obtained, then this mechanistic pathway could be eliminated from consideration.

Optically active 2-chloronorbornene was prepared, as shown in Scheme XI, according to the procedure of McDonald and Steppel.

Treatment of norbornene (102) with diisopinocampheylborane (prepared

Scheme XI

102 → 156 → OH

Cl

H

153

Cl

Cl

152

OAc

"H

157

CH₃

H

155

CH₃

158

161

160
from \( \delta\)-\(\alpha\)-pinene and diborane) followed by hydrolysis and acetylation, gave \((+)-(15,23)\)-exo-norbornyl acetate \(156\). Reduction of \(156\) with lithium aluminum hydride gave \((-)-(15,23)\)-exo-norborneol \(157\), which had \([\alpha]_{D}^{25} = 1.4 \pm 0.1^\circ\) (c 10.0, CHCl\(_3\)), and oxidation of \(157\) with Sarett reagent afforded \((+)-(15)\)-norcamphor \(158\), \([\alpha]_{D}^{25} = 7.7 \pm 0.1^\circ\) (c 9.94, CHCl\(_3\)). Comparison of the observed rotation of \(158\) and the calculated maximum rotation of \(158\) indicated a maximum optical purity of 23% for \(158\) and all compounds derived from it. Treatment of \(158\) with phosphorus pentachloride afforded \((+)-(15)\)-2,2-dichloronorborne (159), \([\alpha]_{D}^{25} = +4.1 \pm 0.1^\circ\) (c 10.0, CHCl\(_3\)), and dehydrohalogenation of \(159\) with potassium tert-butoxide gave \((+)-(15)\)-2-chloronorborne (153), \([\alpha]_{D}^{25} = +1.3 \pm 0.1^\circ\) (c 9.72, CHCl\(_3\)).

Treatment of \(153\) with five equivalents of methyllithium in ether for 8 days afforded 59% of optically active 2-methylnorborne, \([\alpha]_{D}^{25} = +2.0 \pm 0.1^\circ\) (c 10.2, CHCl\(_3\)). The structural correlation of the 2-methylnorborne was obtained, as shown in Scheme XI, by hydrogenation to give \((-)-(15,2R)\)-endo-2-methylnorborne (161), \([\alpha]_{D}^{25} = -9.2 \pm 0.2^\circ\) (c 6.63, CHCl\(_3\)). Treatment of \(158\) with methylenetriphenylphosphine gave \((+)-(15)\)-2-methylene norborne (160), \([\alpha]_{D}^{25} = +33 \pm 5^\circ\) (c 6.0, CHCl\(_3\)), which was hydrogenated to give \(161\), \([\alpha]_{D}^{25} = -9.4 \pm 0.2^\circ\) (c 7.05, CHCl\(_3\)). On the basis of the correlation of the specific rotations of the samples of \(161\), the structure \((+)-(15)\)-2-methylene norborne (155), was

assigned to the product of the reaction of $^{153}$ and methyllithium.

The isolation of $^{155}$ and not $^{154}$ from the reaction of $^{153}$ and methyllithium indicated that the carbenoid mechanism with hydrogen migration was not occurring. The stereospecific replacement of the chlorine of $^{153}$ by a methyl group is still compatible with three possible mechanisms which are chemically indistinguishable. Addition of methyllithium to 2-chloronorbornene (153) could still occur to give 144, which upon loss of lithium chloride and methyl migration to the carbenoid center would account for the stereospecificity observed in the formation of 155. Additionally, both the “addition-β-elimination” mechanism and the “coupling” mechanism would also account for the observed stereospecificity.

Although these mechanisms cannot be distinguished chemically, arguments can be made which favor the “coupling” mechanism. The preference for hydrogen migration rather than methyl migration to carbenes has already been noted. Although addition of the methyllithium might be expected to occur in the manner which leads to the formation of the carbenoid species, none of the other products derived from such a proposed intermediate (vide infra) are observed in this system. Addition of the methyllithium to 109 in the “addition-β-elimination” mechanism must occur in the manner opposite to that expected on the basis of electronic effects. Subsequent elimination of lithium chloride would have to occur

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102. The formation of optically active products in this reaction also adds additional evidence against the “norbornyne” mechanism. Presumably, norbornyne would be symmetrical and loss of optical activity would be expected if it were an intermediate.
in a **trans** manner and should proceed **very** slowly. Therefore, some product resulting from hydrolysis of $^{146}$ would be expected. Unfortunately, no experimental evidence in support of the "coupling" mechanism can be offered. Techniques such as CIDNP$^2$ could not be applied in this case because the reaction is too slow under the conditions used.

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The n-Butyllithium Reaction.

In order to gain a better understanding of reactions of 2-chloronorbornenes and organolithium reagents, a reinvestigation of the reactions of 107 with other organolithium reagents was undertaken. Treatment of 107 with n-butyllithium in hexane had been reported to give no reaction. However, when the reaction solution of 107 and five equivalents of n-butyllithium in hexane was diluted with an equal volume of anhydrous ether and stirred for 7 days at 25°, the formation of a white precipitate (lithium chloride) was noted. Two products were isolated which were identified as 2-n-butylnorborne (162) (40% yield) and 3-n-butylnortricyclene (163) (21% yield).

The structural assignment of 162 was based on its infrared spectrum, which showed an olefinic stretching absorption at 6.18 μ; its nmr spectrum, which had absorptions at τ 4.51 (1H, broad s), 7.24 (1H, m), 7.33 (1H, m), 7.93 (2H, m), and 8.2-9.2 (13H, m); and its near-infrared spectrum, λ_max = 1.675 μ (ε = 0.229). In addition, the structure

was conclusively proven by hydrogenation to give endo-2-n-butynorbornane (164) which was identical in all respects to an authentic sample. The independent synthesis of 164 was accomplished by treatment of norcamphor (142) with n-butyllithium to give 95% of 165, which was dehydrated with phosphoric acid to afford 77% of 166. Hydrogenation of 166 gave 74% of 164. The structure proof of 163 was based on its infrared spectrum which showed a peak at 3.24 μ (cyclopropyl hydrogens), the absence of any downfield protons in its nmr spectrum, and its characteristic near-infrared absorption, $\lambda_{\text{max}} = 1.666 \mu$ ($\epsilon = 1.280$).

In contrast to the reaction of 107 with methyllithium, which gave only 108, the reaction 107 with n-butyllithium afforded not only the 2-alkynorbornene, 162, but an additional product, 163. The formation of the coupling product, 165, may be rationalized in a manner similar

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105. The term “coupling product” will be used henceforth in order to expedite the explanation of product types. However, its use is strictly in the formal sense since no chemical evidence was obtained to eliminate the other mechanistic possibilities.
to that proposed for the formation of $103$. However, the formation of $163$ merits additional discussion. In order to determine if the formation of $163$ occurred because of a solvent effect, the reaction of $107$ with methyl lithium was carried out in the same solvent system. No products other than $103$ were observed. A carbenoid mechanism may be proposed to account for the formation of $163$. Addition of $n$-butyllithium to $107$ in the manner predicted by electronic effects would afford the $\alpha$-chlorolithium derivative, $167$. Loss of lithium chloride from $167$

\[
\begin{align*}
\text{Cl} & \xrightarrow{\text{Li}} \text{Li}\text{N-Bu} \quad \xrightarrow{\text{LiCl}} \text{H} \\
107 & \quad 167 & \quad 168 \\
\end{align*}
\]

would give the carbenoid $168$ which could insert into the C$_8$-H bond of the norbornyl skeleton to give $103$. Since $n$-butyllithium has been reported to add to benzonorbornadiene and its derivatives, this carbenoid mechanism would seem reasonable. The stereochemistry of the

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106. This is a common reaction of this type of bicyclic carbene. For typical examples see (a) J. Bredt and W. Holz, J. Prakt. Chem., 203, 133 (1917); (b) A. Angeli, Gazz. Chim. Ital., 24, II, 317 (1894); (c) J. W. Powell and M. C. Whiting, Tetrahedron, 7, 305 (1959); (d) P. Clarke, M. C. Whiting, G. Papenmeier, and W. Reusch, J. Org. Chem., 27, 3356 (1962).
addition of the organolithium would be undetermined because 107 is racemic. *exoc-Addition of the n-butyl group would be predicted on the basis of previous observations.

The tert-Butyllithium Reaction.

Since tert-butyllithium has been reported to add readily to norbornene and its derivatives, the reaction of 107 with tert-butyllithium was investigated in order to obtain evidence in support of a carbenoid mechanism. Treatment of 107 with three equivalents of tert-butyllithium in pentane at 25° for 6 days afforded 36% of norbornene (109), 5% of 2-tert-butylnorbornene (162), and 44% of 3-tert-butylnortricyclene (170).

\[
\begin{align*}
\text{107} & \rightarrow \text{109} + \text{162} \\
& \hspace{1cm} \text{170}
\end{align*}
\]

The structural assignment of 162 was based upon its infrared spectrum, which had absorptions at 3.26 (olefinic hydrogen) and 6.22 μ (C=C); its nmr spectrum, which had absorptions at τ 4.50 (1H, d, J = 3 Hz), 7.12 (1H, m), 7.23 (1H, m), and 8.0-9.1 [15H, m, containing τ 8.92 (9H, s)]. The nmr data compare favorably with those found for
and also cf. Table III, Appendix. The structure proof of 170 was also based on its spectral properties. The infrared spectrum of 170 had an absorption at 3.25 μ (cyclopropyl hydrogens) and the nmr spectrum showed no downfield protons and a 9-proton singlet at δ 9.07, indicative of the tert-butyl group. In addition, the near-infrared spectrum of 170 showed the characteristic absorption, $\lambda_{\text{max}} = 1.667$ (ε = 1.011), of the nortricyclyl hydrogens.

The formation of substantial amounts of 102 can best be explained via a lithium-halogen interconversion to give the norbornenyl anion, followed by hydrolysis of the anion to give 102. The formation of a significantly larger ratio of nortricyclene derivative to norbornene derivative in the tert-butyllithium reaction than in the n-butyllithium reaction is consistent with the expected increase in reactivity of tert-butyllithium towards addition to the double bond. This larger ratio would support the carbeneoid mechanism proposed below for the formation

$$\begin{align*}
107 & \rightarrow 171 & \rightarrow 172 \\
\text{Cl} & \text{Li} & \text{LiCl} \\
\text{H} & \text{t-Bu} & \text{H} \\
\end{align*}$$
of 170. Addition of tert-butyllithium to 107 would give 171, which could lose lithium chloride to give the carbenoid intermediate 172. Insertion of the carbenoid center of 172 into the C3-hydrogen bond of the norbornyl skeleton would then give 170. The discussion of the mechanism of formation of the coupling product, 169, is subject to the same restraints that have previously been mentioned.

The Phenyllithium Reaction.

In order to obtain more information on the scope of the reaction of 107 with organolithium reagents, the reaction of 107 with phenyllithium was examined. When 107 was treated with five equivalents of commercial phenyllithium in benzene-ether at reflux for 24 hr, two new products were obtained. The minor product was isolated in 7% yield and was readily identified as 3-phenylnortricyclene (173) on the basis of its spectral properties. The infrared spectrum of 173 had absorptions at 3.35, 6.24, 12.33, 13.54, and 14.89 μ; the nmr spectrum of 174 had absorptions at τ 2.61 (5H, s), 7.17 (1H, s), 8.03 (1H, s), 8.53 (2H, s), and 8.67-9.13 (4H, m). In addition, its near-infrared spectrum showed an absorption, λmax = 1.665 μ, characteristic of nortricyclyl hydrogens.

The major product was isolated in 62% yield and was found to analyze for C13H14. However, it was shown not to be the expected coup-

107. Alfa Inorganics Inc., 2.2 M phenyllithium in 70:30 benzene-ether.
108. No ε could be accurately calculated due to overlap of an absorption presumably due to the aromatic hydrogens.
ling product, 2-phenylbornene (174), via spectral comparison with an authentic sample. The structure of the major product was tentatively assigned as 5-benzalbicyclo[2.1.1]hexane (175) on the basis of its spectral characteristics. The infrared spectrum of 175 had absorptions at 3.33, 5.90, 6.22, 13.15, and 14.33 μ; the nmr spectrum showed absorptions at τ 2.83 (5H, s), 4.22 (1H, s), 6.60 (1H, m), 7.07 (1H, m), 8.20 (5H, broad s), and 8.78 (1H, d, J = 7 Hz). The high olefinic stretching frequency (5.90 μ), and the nmr spectrum, which bore a strong resemblance to the published spectrum of bicyclo[2.1.1]-hexan-5-one, were quite compatible with the assigned structure, 175.

The structure of 175 was conclusively proven by chemical degradation to bicyclo[2.1.1]hexan-5-one (176) in two steps. Treatment of 175 with osmium tetroxide in pyridine afforded 92% of the glycol (177),


which was cleaved with periodic acid in ether to afford a 68% yield of benzaldehyde (178) and a 67% yield of 176, whose spectral properties were identical to those published.\textsuperscript{110,111} The transformation of 107 into 176 affords a five-step synthesis of 176 starting from commercially available norcamphor (149) in ca. 20% overall yield, and represents a marked improvement over the 11-step procedure for the preparation of 176 from the same starting materials!\textsuperscript{111}

The same intermediate could account for the formation of 173 and 175 in the reaction of 107 with phenyllithium. The addition of phenyllithium to 107 could occur in a manner analogous to that proposed for the \textit{n}-butyl- and \textit{tert}-butyllithium reactions of 107 to give the \(\alpha\)-chlorolithium derivative 179, which would give the carbenoid species 180 upon loss of lithium chloride. Insertion of the carbenoid center of 180 into the \(\text{C}_8\)-hydrogen bond of the norbornyl skeleton would give 172. A unique ring contraction of 180 would give 175. These reactions can be compared to the decomposition of diazocamphor (161), which, on

\textsuperscript{112} The tentative assignment of the stereochemistry of 177 was based on a comparison of its NMR spectrum with those of \textit{exo-} and \textit{endo-5-hydroxybicyclo[2.1.1]hexane}.\textsuperscript{110}
treatment with copper powder, gives primarily the insertion product 182, and on irradiation undergoes a photochemical Wolff rearrangement to yield 183. The lack of formation of any coupling product in this reaction was somewhat surprising and no rationale for this

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behavior can be offered. 2-Phenynorbornene (174) was treated under the reaction conditions and was found not to afford 175, indicating that 174 was not a precursor of 175.
Reactions of 7,7-Dimethoxy-2-chloronorbornene with Organolithium Reagents.

In order to extend the scope of reactions of organolithium reagents with bicyclic vinyl halides and to study the effects of substituents on the norbornyl ring skeleton, the investigation of reactions of organolithium reagents with 7,7-dimethoxy-2-chloronorbornene (184) was undertaken. The vinyl chloride 184 was prepared by the method of Patton. Treatment of 7,7-dimethoxynorbornene (185) with iodo-benzene dichloride afforded the dichloride 186, which upon treatment with potassium tert-butoxide gave 184.

When 184 was treated with five equivalents of methylthium at 25°, the complete disappearance of starting material was observed after 28 hr and two products were obtained. The minor product, obtained in 6.5% yield, was identified as the coupling product, 2-methyl-7,7-di-

methoxynorbornene (187) on the basis of its infrared absorptions at 3.26 (vinyl hydrogen), 6.13 μ (olefin stretch), 9.13 and 9.35 μ, and its nmr spectrum, τ 4.25 (1H, m), 6.92 (3H, s), 6.96 (3H, s), 7.45 (1H, m), 7.59 (1H, m), 8.23 (2H, m), 8.28 (3H, d), and 9.18 (2H, m). The major product, obtained in 70% yield, was identified as syn-3-methyl-7,7-dimethoxynortricyclene (188) on the basis of its infrared absorptions at 3.22 (cyclopropyl hydrogens), 7.54, 8.71, 8.88, 9.40, and 10.08 μ; its nmr spectrum, which showed no olefinic hydrogens, the six hydrogens of the two methoxy groups as a singlet at τ 6.85, and the methyl group as a doublet at τ 8.85, J = 7 Hz; and its near-infrared absorptions, which appeared as a doublet at λmax = 1.660 μ (ε = 0.892) and λmax = 1.666 μ (ε = 0.903) indicating the presence of the nortricyclyl ring. The assignment of the stereochemistry of the methyl group will be discussed in detail (vide infra).

```
\[\text{CH}_3\text{O} \quad 187\] \rightarrow \quad \text{CH}_3\text{O} \quad 188
```

Treatment of 184 with three equivalents of n-butyllithium in hexane (the addition of ether was not necessary) gave a vigorous exothermic reaction which afforded two products after 10 min at 25°. The minor product, obtained in 5% yield, was identified as 2-n-butyl-7,7-dimethoxynorbornene (189) on the basis of its infrared absorptions at
3.25 (vinyl hydrogen), 6.14 (weak, olefin stretch), 9.11 and 9.35 μ;

and its nmr spectrum, τ 4.48 (1H, m), 6.91 (3H, s), 6.96 (3H, s), 7.47 (2H, m), and 7.7-9.4 (13H, m). The major product, obtained in 83% yield, was identified as syn-3-n-butyl-7,7-dimethoxynortricyclene (190) on the basis of its infrared absorptions at 3.24 (cyclopropyl hydrogen), 7.55, 8.73, 8.90, and 9.40 μ; its nmr spectrum, which showed no olefinic hydrogens and had a six hydrogen singlet at τ 6.88 due to the methoxy groups; and its near-infrared absorptions, which appeared as a doublet at λ_{max} = 1.660 μ (ε = 1.009) and λ_{max} = 1.667 μ (ε = 1.038) indicating the presence of the nortricyclyl ring.

Treatment of 184 with three equivalents of phenyllithium afforded only syn-3-phenyl-7,7-dimethoxynortricyclene (191) in 82% yield (in addition to biphenyl) after 30 min at 25°. The structural assignment of
was based upon its infrared absorptions at 3.24 (aromatic and cyclo-
propyl hydrogens), 6.24, 7.57, 9.01, 9.40, 13.67, and 14.41 μ; its
nmr spectrum, τ 2.3-3.0 (5H, m), 6.86 (3H, s), 6.98 (1H, s), 7.52 (3H,
s), 7.8-8.1 (3H, m), and 8.3-8.7 (4H, m); and its near-infrared spec-
trum which showed an absorption at λ_max = 1.666 μ (ε = 1.155) indica-
tive of nortricycl hydrogen.

The effects of the methoxy substituent in the reactions of 184 with organolithium reagents are most notably manifested in two as-
pects—the rates of reaction and the nature of the products formed.
The reaction of 107 with methyllithium required 8 days for disappear-
ance of starting material whereas the corresponding reaction of 184
required only 28 hr (ca. a 7-fold rate enhancement). A much more dra-
matic effect was observed when n-butyllithium and phenyllithium were
used. Reactions of 107 and 184 with n-butyllithium required 7 days
(a two-fold dilution factor, notwithstanding) and 10 min, respectively.
Similarly, the reactions of 107 and 184 with phenyllithium required 24
hr at reflux and 30 min at 25°, respectively. This notable rate en-
hancement in the reactions of 184 with organolithium derivatives could
be explained via complexation of the organolithium reagent with the
electron rich oxygen atom of the methoxy group. Complexation of

117. The effects of complexation of organolithium reagents has been
widely discussed. For examples of discussion of reagents such
as tetramethylethenediamine see A. W. Langer, Trans. N.Y.
Acad. Sci., 27, 741 (1965); G. G. Eberhardt and W. A. Butte, J.
Org. Chem., 29, 2928 (1964); H. E. Zieger and E. M. Laski, Tetra-
hedron Lett., 3801 (1966); and the technical literature of the
Foote Mineral Co.
the organolithium reagent could have the effect of breaking down the molecular aggregates and thus make the "naked" organolithium reagent more reactive. A similar proposal has been made to account for the addition of organolithium reagents to allylic alcohols under reaction conditions in which the simple olefins were unreactive. The necessity of the added ether in the reaction of 107 and n-butyllithium could also be due to the same type of phenomenon. In the reactions of 184 with organolithium reagents, the major products obtained were nortricyclene derivatives. Only in the reactions of 184 with methyl-lithium and n-butyllithium were small amounts (6.5% of 157 and 5% of 159) of the coupling products obtained. This result can be compared to the reactions of 107 with methyllithium, which gave only the coupling product 108, and with n-butyllithium, which gave 40% of the coupling product 162 and 21% of the nortricyclene derivative 163. No coupling product or rearrangement product was found in the reaction of 107 with phenyllithium, which afforded only the nortricyclene derivative 191.

The increased rates of reaction and the formation of nortricyclene products in the reactions of 184 with organolithium reagents could be explained on the basis of the mechanism proposed in Scheme XII. Initial complexation of the organolithium reagent and 184 would give 192.

Scheme XII

\[
184 + [\text{RLi}]_X \rightleftharpoons 192 \rightarrow 193
\]

\[
\begin{align*}
R &= \text{CH}_3 \quad 188 \\
    &= \text{n-Bu} \quad 190 \\
    &= \text{Ph} \quad 191
\end{align*}
\]
Attack of the organolithium reagent from 192 could then occur to give the α-chlorolithium derivative 193, which, upon loss of lithium chloride, would yield the carbenoid intermediate 194. Intramolecular insertion of the carbenoid into the Cα-hydrogen bond of the norbornyl skeleton would afford the observed nortricyclene products, 188, 190, or 191. The stereochemistry of the addition of the organolithium reagent to 184 as outlined in Scheme XII would be expected to be the same as that previously observed in unsubstituted norbornenes, and would require that the products 188, 190, and 191 have the alkyl or aryl substituent syn to the methoxy group.

In accord with this postulate, the stereochemistry of the R-group in 188, 190, and 191 had been assigned as syn to the methoxy group. The assignment was based on the comparison of chemical shifts of the methoxyl hydrogens in the nmr spectra of 188, 190, and 191. The chemical shifts of the methoxyl hydrogens of 188 and 190 overlapped and appeared as a singlet at τ 6.85 and 6.88, respectively. However, the chemical shifts of the two methoxyl group hydrogens of 190 differed widely, appearing at τ 6.86 and 7.52. An upfield shift of the syn-methoxyl hydrogen absorption would be expected on the basis of the anisotropy of the benzene ring. The position of the methoxy group

120. For a comparison of chemical shifts of methoxyl hydrogens for other 7,7-dimethoxynortricyclyl derivatives see J. L. Marshall, Ph.D. Thesis, The Ohio State University, 1966.

above the plane of the aromatic ring would account for this phenomenon, whereas the absorption of the methoxyl hydrogens above the methylene group should and did occur at about the same chemical shift as the absorption of the methoxyl hydrogens in 188 and 190.

The mechanistic proposal outlined in Scheme XII could account for the formation of 188, 190, and 191 in the reactions of 184 with organolithium reagents. However, in the reactions of 184 with methyllithium and n-butyllithium, small amounts of the coupling products 187 and 189 were observed. The explanation of the formation of 187 and 189 is subject to the same considerations discussed earlier for the reactions of 107 and organolithium reagents. The lack of formation of any ring contraction products in the reaction of phenyllithium and 184 was quite surprising since the same type of carbenoid intermediate (193, R=Ph) was proposed in this reaction and in the reaction of 197 with phenyllithium, 180. A change in the nature or even the degree of dissociation of lithium chloride in the proposed carbenoid intermediate, 193 (R=Ph), could possibly account for this change in product formation, but these effects are unknown.
2,3-Dichloronorbornene and 3-Phenyl-2-chloronorbornene.

In order to determine the effect of replacing the vinylic hydrogen by chlorine in the reactions of 2-chloronorbornenes with organolithium reagents, the preparation of 2,3-dichloronorbornene (195) was undertaken. Treatment of 107 with iodobenzene dichloride afforded an 87% yield of 2,2,3-trichloronorbornanes (196), which upon dehydrochlorination with potassium tert-butoxide gave 85% of 195, whose spectral properties were in accord with the assigned structure. Treatment of 195 with five equivalents of methyllithium at reflux for 7 days gave only recovered starting material. Treatment of 195 with five equivalents of phenyllithium in benzene-ether at reflux for 7 days did, however, lead to the disappearance of starting material. Three products were isolated and identified as 2-phenylnorbornene (174) (17% yield), 3-phenyl-2-chloronorbornene (197) (12% yield), and 2,3-diphenylnorbornene (198) (28% yield) via spectral comparison with independently synthesized authentic samples. The synthesis of 174 had previously been described. The synthesis of 197 was accomplished via treatment of norcamphor (142) with sulfuryl chloride which gave exo-3-chloronor-
camphor \(^{122}\); \(^{122}\) treatment of 192 with phenyllithium gave 78% of 200 which was dehydrated to afford 93% of 197. The synthesis of 198 was

\[ \text{149} \xrightarrow{} \text{122} \xrightarrow{} \text{200} \xrightarrow{} \text{198} \]

accomplished via treatment of endo-3-phenylnorcamphor (201) with phenyllithium to give 202, which on dehydration afforded a 51% overall yield of 193.

The formation of coupling products in the reaction of 195 with phenyllithium can be contrasted to the reaction of 107 with phenyllithium which afforded no coupling product 174. Therefore, the intermediacy of 107 could be ruled out in the explanation of the formation of 174. The formation of 197 as a minor product could be explained on the basis of a mechanism similar to that operative in the formal coupling reactions previously mentioned. The vinyl chloride 197 could then undergo reaction with the excess phenyllithium to give a second coupling product 198. The formation of 174 could be due to a lithium-halogen interconversion of 197, which, on subsequent hydrolysis, would yield 174. Alternatively, 174 could arise via lithium-halogen interconversion of 195 to give the vinyl anion 137, originally proposed as a possible intermediate in the conversion of 107 to 108.

\[ \text{123. Kindly provided by Mr. J. Valcho.} \]
Loss of chloride ion from $^{137}$ would give norbornyne ($^{138}$), which could add phenyllithium to give $^{174}$ upon hydrolysis.

In order to test these possibilities, $^{197}$ was treated with five equivalents of phenyllithium in benzene-ether at reflux for 5 days. A 42% yield of $^{198}$ was obtained but no $^{174}$ was isolated. The lack of formation of $^{174}$ would indicate that $^{197}$ was not the precursor to its formation and would argue strongly in favor of a "norbornyne" mechanism to account for the formation of $^{174}$ in the reaction of $^{195}$ with phenyllithium. However, the conclusive piece of evidence for the existence of $^{138}$, i.e. trapping of $^{138}$ by cycloaddition with a reactive diene, $^{124}$ was not obtained.

In conclusion, a wide variety of new chemistry has been observed in the reactions of 2-chloronorbornene and its derivatives, with organolithium reagents. The reaction of $^{107}$ with methyllithium was shown to proceed stereospecifically to give $^{108}$ with retention of configuration and several mechanisms which would account for this observation were

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$^{124}$ Due to the nature of reactions of $^{195}$ and $^{197}$ with phenyllithium, several observations should be noted. Large amounts of biphenyl were produced in these reactions which complicated the isolation procedure. Fortunately, the products isolated eluted from basic alumina with pentane before the biphenyl. Continued elution with more polar solvents gave highly aromatic compound(s) as oils which could not be crystallized or purified by other means. Therefore, the low yields of $^{174}$, $^{197}$, and $^{108}$ do not preclude their instability under the reaction conditions. Furthermore, other products could initially be formed and be labile under the reaction conditions. These difficulties inherent in the reactions themselves and in the isolation techniques used, would severely restrict the use of an excellent trapping reagent, such as diphenylisobenzofuran.
discussed. A carbenoid mechanism was proposed to account for the formation of nortricyclene derivatives in the reactions of 107 with \( \text{\textit{n}} \)- and \( \text{\textit{t}} \)-butyllithium. This mechanism involved a hitherto unrecognized reaction sequence including addition of the organolithium reagent to the vinyl chloride, followed by \( \alpha \)-elimination of lithium chloride to give a proposed carbenoid intermediate. In the reaction of 107 with phenyllithium, a similar intermediate was proposed to account for the formation of 173 and the unique ring contraction product, 175. The conversion of 107 into 175 is an unusual reaction that has synthetic utility. The reactions of 184 and organolithium reagents were found to yield nortricyclene derivatives and, again an analogous carbenoid mechanism was proposed. The reaction of 195 with phenyllithium showed another unexpected change in the types of products formed and opened the possibility of generating norbornyne as an intermediate in this reaction.
Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Melting points and boiling points are uncorrected. Infrared spectra were taken on a Perkin-Elmer Model 137 Infracord as neat liquids, in solution in carbon tetrachloride or chloroform, or as powdered solids in potassium bromide discs. Nuclear magnetic resonance spectra were obtained on a Varian Associates A-60-A Spectrometer and are reported in tau (τ) units relative to tetramethylsilane (τ = 10.00) as the internal standard. Exact mass determinations were obtained on an MS-9 High Resolution Mass Spectrometer.
PART I
Transition Metal Complex Promoted Rearrangements

PART A  Tricyclo[4.1.0.0^2,7]heptane (15) and 1-Methyltricyclo-
[4.1.0.0^2,7]heptane (31)

General Procedures

Two procedures were used to determine the products from the reac-
tions of 15 and 31 with the various transition metal derivatives.

A. To a solution of ca. 2 mmol of 15 or 31 in 1 ml of solvent under ni-
trogen was added ca. 5 mol % of the transition metal derivative and the
mixture was stirred at 25^o for the described time. The volatile pro-
ducts were then vacuum transferred and the products were separated from
solvent by preparative vpc on a 10 ft x 1/4 in 20% DC Silicone Fluid #200,
1000 c.s. on 60/80 Columnpak column at 80^o.

B. A mixture of ca. 2 mmol of 15 or 31 in 1 ml of solvent was heated
in a sealed tube with ca. 5 mol % of the transition metal derivative at
the desired temperature for a prescribed period of time. The tube was
cooled, opened and the contents were vacuum transferred. The products
were isolated as in procedure A.

All yields reported in these reactions were determined by vpc vs.
an internal standard and represent the average of at least two runs.
The yields were determined on a 10 ft x $\frac{1}{8}$ in 20% DC Silicone Fluid #200, 1000 c.s. on $^{60}$/$^{80}$ Columnpak at 80° and are corrected for detector response. Both preparative and analytical analyses were obtained on an F and M Model 810 Gas Chromatograph.

All products were identified via comparison with authentic samples.

Tricyclo[4.1.0.0$_2$$_2$$_7$]heptane (15). This compound was prepared by the method of Moore, et al.

Reaction of 15 with Zinc Iodide. Procedure A. A 202.4 mg (2.15 mmol) sample of 15, 2 ml of anhydrous ether, and 44.6 mg (0.14 mmol, 6.5 mol % of anhydrous zinc iodide gave 11% of 3-methylenecycloheptene (28) and 88% of 1,3-cycloheptadiene (35) after stirring for 16 hr.

Reaction of 15 with Mercuric Bromide. Procedure B. A 142.1 mg (1.51 mmol) sample of 15, 2 ml of anhydrous ether, and 50.1 mg (0.139 mmol, 9 mol %) of mercuric bromide gave 8% of 28 and 85% of 35 after 43 hr at 50°.

Reaction of 15 with Rhodium Dicarbonyl Chloride Dimer. Procedure A. A 265 mg (2.8 mmol) sample of 15, 1 ml of acetonitrile, and 29 mg (0.075 mmol, 4 mol %) of rhodium dicarbonyl chloride dimer gave 93% of 28 after 15 min. Using chloroform as solvent under the same conditions, a 97% yield of 28 was obtained.

Reaction of 15 with Iridium Tricarbonyl Chloride Dimer. Procedure A. A 23.4 mg (0.025 mmol) sample of 15, 0.25 ml of chloroform, and 7 mg (0.012 mmol, 5 mol %) of iridium tricarbonyl chloride dimer yielded 91%
of 28 after 14 hr.

Reaction of 15 with (π-Allyl)palladium Chloride Dimer. Procedure A. A 153.0 mg (1.65 mmol) sample of 15, 1 ml of chloroform, and 7.3 mg (0.02 mmol, 1.2 mol %) of (π-allyl)palladium chloride dimer produced 94% of 28 after 30 min.

Reaction of 15 with bis(Benzonitrile)palladium Chloride. Procedure A. A 148.7 mg (1.58 mmol) sample of 15, 1 ml of acetonitrile, and 32.3 mg (0.079 mmol, 5 mol %) of bis(benzonitrile)palladium chloride gave 69% of 28 after 20 hr.

Reaction of 15 with Pentafluorophenylcopper Tetramer. Procedure A. A 158.0 mg (1.68 mmol) sample of 15, 1 ml of chloroform, and 32.1 mg (0.035 mmol, 2 mol %) of pentafluorophenylcopper tetramer gave 74% of 28 after 2.5 hr.

Reaction of 15 with trans-Chlorocarbonylbis(triphenylphosphine)rhodium-(I). Procedure B. A 174 mg (1.86 mmol) sample of 15, 1 ml of acetonitrile, and 62 mg (5 mol %) of trans-chlorocarbonylbis(triphenylphosphine)rhodium(I) gave 92% of 28 and 5% of 2-norcarene (18) after 48 hr at 65°.

Reaction of 15 with Platinum Oxide. Procedure B. A 155 mg (1.65 mmol) sample of 15, 1 ml of acetonitrile, and 18 mg (5 mol %) of platinum oxide yielded 62% of 28 and 24% of 18 after 48 hr at 65°.
Reaction of 15 with Stannous Chloride. Procedure B. A 148.9 mg (1.59 mmol) sample of 15, 1 ml of chloroform, and 40.2 mg (0.18 mmol, 11 mol %) of stannous chloride dihydrate gave 40% of 18 after 24 hr at 60°.

1-Methyltricyclo[4.1.0.0²⁷]heptane (31). To a magnetically stirred solution of 5.15 g (44.4 mmol) of dry tetramethylethylenediamine (TMEDA) in 10 ml of anhydrous ether was added 60 ml of 0.74 N n-butyllithium in ether (44.4 meq.) and the mixture was stirred for 20 min under nitrogen. Via a syringe, 3.00 g (31.9 mmol) of 15 was added dropwise and the solution was stirred for 5 hr at 25°; 6.00 g (42 mmol) of methyl iodide was slowly added while cooling the reaction mixture in ice and the mixture was then stirred for 3.5 hr at 25°. The solution was poured onto ice, the layers were separated, and the aqueous phase was extracted with 40 ml of ether. The combined organic layers were washed with three 50-ml portions of water, 50 ml of saturated salt solution, and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration. After careful distillation of the ether at atmospheric pressure, vacuum distillation of the residue through a 10 cm Vigreux column afforded 5.30 g of a hydrocarbon mixture, bp 56-65° (190 mm). Pure 31, 2.12 g (61%), was obtained after removal of the n-octane impurity by preparative vpc on a 10 ft x 1/4 in 15% Carbowax 1500 + 3% KOH on 60/80 Chromosorb G column at 50°.

Reaction of 31 with Rhodium Dicarbonyl Chloride Dimer. Procedure A. A 56 mg (0.53 mmol) sample of 31, 0.5 ml of chloroform, and 9 mg (0.023 mmol, 5 mol %) of rhodium dicarbonyl chloride dimer, after 15 min reac-
tion time, gave 96% of 2-methyl-3-methylene cyclohexene (32): \( \text{ir (CCl}_4 \text{ solution) } 3.21, 3.40, 6.09, 6.22, 6.95, \text{ and } 11.28 \mu; \text{ nmr (CCl}_4 \text{) } \tau 4.37 \) (1H, m), 5.17 (1H, broad s), 5.30 (1H, broad s), 7.5-8.1 (4H, m), 8.21 (3H, d, \( J = 1.5 \) Hz), 8.2-8.6 (2H, m); \( \lambda_{\text{max}}^{\text{hexane}} = 234 \) nm (\( \varepsilon = 16,200 \)).

**Anal. Calcd m/e for C\(_8\)H\(_{12}\): \( 108.0938 \).**

**Found (obs. m/e): 108.0937.**

Reaction of 31 with Iridium Tricarbonyl Chloride Dimer. **Procedure A.**

A 156.4 mg (1.44 mmol) sample of 31, 1 ml of chloroform, and 44 mg (0.7 mmol, 5 mol%) of iridium tricarbonyl chloride dimer gave 93% of 32 after 14 hr.

Reaction of 31 with (\( \pi \)-allyl)palladium Chloride Dimer. **Procedure A.**

A 104.4 mg (0.96 mmol) sample of 31, 0.5 ml of chloroform, and 4.8 mg (0.013 mg, 1.4 mol%) of (\( \pi \)-allyl)palladium chloride dimer gave 93% of 32 after 30 min.

Reaction of 31 with Pentafluorophenylcopper Tetramer. **Procedure A.**

A 161.1 mg (1.49 mmol) sample of 31, 1 ml of chloroform, and 24.4 mg (0.026 mmol, 1.8 mol%) of pentafluorophenylcopper tetramer yielded 56% of 32 after 6 hr.

Reaction of 31 with Zinc Iodide. **Procedure A.**

A 167.4 mg (1.42 mmol) sample of 31, 2 ml of anhydrous ether, and 42.0 mg (0.13 mmol, 9 mol%) of dry zinc iodide gave 48% of 2-methyl-1,3-cycloheptadiene (37) and 12% of 6-methylbicyclo[3.2.0]hept-6-ene (38) after 16 hr.
Reaction of $^1$ with Mercuric Bromide. Procedure B. A 143 mg (1.32 mmol) sample of $^1$, 2 ml of anhydrous ether, and 25 mg (0.069 mmol, 5.25 mol %) of mercuric bromide produced 24% of $^2$ and 42% of $^3$ after 24 hr at 60°.

Reaction of $^1$ with Stannous Chloride. Procedure B. A 188 mg (1.74 mmol) sample of $^1$, 1 ml of anhydrous ether, and 28.1 mg (0.125 mmol, 7 mol %) of stannous chloride dihydrate gave 53% of 1-methyl-2-norcarene ($^4$) after 24 hr at 60°.

Hydrogenation of $^4$. In a 15 ml round-bottom flask equipped with a magnetic stirrer and serum cap was placed 15 mg of 5% palladium-on-carbon and 59 mg of $^4$. The flask was charged with 10 cc of hydrogen gas via a syringe and the solution was stirred at 25°. At three half-hour in intervals additional 10-cc portions of hydrogen gas were added and the solution was stirred overnight under a positive hydrogen pressure. The solution was centrifuged and the supernatant liquid was found to contain a mixture of 43% of trans-1,2-dimethylcyclohexane, 24% of cis-1,2-di-methylcyclohexane, and 33% of o-xylene via vpc analysis. The components were isolated by preparative vpc at 90° on a 10 ft x $\frac{1}{4}$ in 20% DC Silicone Fluid #200, 1000 c.s. on $^60$/80 Columnale column and characterized by spectral comparison to authentic samples.

2-Methyl-1,3-cycloheptadiene ($^3$). Methylmagnesium iodide was prepared in the usual manner from 3.65 g (0.15 gram-atom) of magnesium turnings and 21.3 g (0.15 mol) of methyl iodide in a total volume of 125 ml of
anhydrous ether in a 300 ml three-necked flask equipped with a magnetic stirrer, addition funnel, reflux condenser and drying tube. A solution of 10.8 g (0.0983 mol) of 2-cycloheptenone (42) in 20 ml of anhydrous ether was slowly added over 1.5 hr and the mixture was stirred for an additional 1 hr at 25°. The mixture was poured onto ice-saturated ammonium chloride solution and the layers were separated. The aqueous layer was extracted with two 50-ml portions of ether and the combined organic layers were washed with saturated salt solution and dried over anhydrous magnesium sulfate. After filtration, distillation of the solvent afforded 11.0 g (89%) of crude alcoholic product.

The crude alcoholic product was dissolved in 25 ml of benzene in a 50 ml flask equipped with a Dean-Stark trap and the solution was refluxed with 0.5 g of p-toluenesulfonic acid for 75 min. The reaction solution was diluted with an equal volume of ether and washed with 25-ml portions of water, saturated sodium carbonate solution, saturated salt solution, and was dried over anhydrous magnesium sulfate. The solution was filtered and the solvents were carefully removed by distillation. Vacuum distillation of the residue through a short path column afforded 6.95 g (66%) of a 2:1 mixture of 1-methyl-1,3-cycloheptadiene (43) and 37, bp 73-78° (60 mm).125 Pure samples of 43 and 37 were obtained by preparative vpc on a 10 ft x ½ in 15% Carbowax 1500 + 3% KOH on 60/80 Chromosorb G column. Spectral properties of

were: \( \text{ir (CCl}_4 \text{ solution) 6.06, 6.16 (m) } \mu; \text{ nmr (CDCl}_3 \text{) } \tau 4.11-4.49 \) (3H, m), 7.5-8.4 (9H, m, containing 8.19 [3H, s]). Spectral properties of \( \text{3} \) were: \( \text{ir (CCl}_4 \text{ solution) 6.06, 6.16 (m) } \mu; \text{ nmr (CDCl}_3 \text{) } \tau 4.2-4.5 \) (3H, m), 7.45-7.83 (4H, m), 7.90-8.36 (5H, m, containing 8.16 [3H, s]).

6-Methylbicyclo[3.2.0]hept-6-ene (38). A solution of 4.00 g (0.037 mmol) of a 2:1 mixture of \( \text{4} \) and \( \text{3} \) in 350 ml of olefin-free pentane was irradiated for 2 hr at 0\(^\circ\) in a quartz photolysis apparatus equipped with a Vycor filter using a Hanovia high-pressure mercury lamp. The solution was dried over anhydrous magnesium sulfate and filtered. The pentane was removed by distillation and the residue was vacuum transferred. Preparative vpc of the crude material on a 10 ft x \( \frac{1}{8} \) in 20% DC Silicone Fluid #200, 1000 c.s. on \( \text{C}_{100}/80 \) Columpak column afforded 436 mg of 6-methylbicyclo[3.2.0]hept-6-ene (38) and 554 mg of 1-methylbicyclo[3.2.0]hept-6-ene (44) (26\% combined yield). In order to unequivocally establish the structural relationships, pure \( \text{44} \) was pyrolyzed at 410\(^\circ\) in the vapor phase to give \( \text{4} \) and pure \( \text{38} \) was pyrolyzed at 450\(^\circ\) to give \( \text{3} \). Spectral properties of \( \text{38} \) were: \( \text{ir (CCl}_4 \text{ solution) 6.10 } \mu (m); \text{ nmr (CDCl}_3 \text{) } \tau 4.45 (1H, m), 6.97 (2H, broad d), 8.0-9.3 [9H, m, containing a 3H doublet (J = 1.5 Hz) at } \tau 8.38); n\(^D\) = 1.4612. Spectral properties of \( \text{44} \) were: \( \text{ir (CCl}_4 \text{ solution) 5.99 } \mu (w); \text{ nmr (CDCl}_3 \text{) } \tau 4.1 (2H, broad s), 7.32 (1H, broad d), 7.9-9.3 (9H, m, containing a 3H singlet at } \tau 8.70); n\(^D\) = 1.4470.

Reaction of 15 with Rhodium Dicarbonyl Chloride Dimer in Methanol. To a stirred solution of 520 mg (5.5 mmol) of 15 in 5 ml of absolute methanol cooled in ice, was added 23.8 mg (0.06 mmol, 1 mol %) of rho-
A mixture of dimethyl dicarbonyl chloride dimer. After stirring for 5 min, no starting material could be detected by vpc analysis. The methanol was removed by distillation, and distillation of the residue afforded 521 mg (75%) of clear, colorless liquid, bp 91-92° (76 mm), which was identified as a 4:1 mixture of exo-2-methoxynorcarane (66) and endo-2-methoxynorcarane (67) by nmr and vpc comparison with authentic samples.

Reaction of 15 with Zinc Iodide in Methanol. In a similar manner, 392.9 mg (4.18 mmol) of 15, 2 ml of absolute methanol, and 78.6 mg (0.246 mmol, 6 mol %) of zinc iodide was stirred at 25° for 4 hr to afford 350.6 mg (67%) of ca. a 4:1 mixture of 66 and 67.

Reaction of 15 with (π-allyl)palladium Chloride Dimer in Methanol. In a similar manner, 336 mg (3.57 mmol) of 15, 2 ml of absolute methanol, and 14.8 mg (0.04 mmol, 1.1 mol %) of (π-allyl)palladium chloride dimer gave 347.2 mg (77%) of ca. a 4:1 mixture of 66 and 67.

2-Norcaranone (69). In a 500-ml three-necked flask equipped with a magnetic stirrer, addition funnel, reflux condenser with a gas outlet, and a gas inlet stopcock, was placed 4.4 g (60%, 0.11 mol) of sodium hydride - mineral oil dispersion. The mineral oil was removed by three hexane washings and the last traces of hexane were removed by evacuating the system. Dry nitrogen gas was admitted and 24.2 g (0.11 mol) of trimethylsulfoxonium iodide was added and the system was maintained under a nitrogen atmosphere. From the dropping funnel, 125 ml of dry dimethylsulfoxide (DMSO) was added with stirring and vigorous hydrogen
evolution. After 15 min, a solution of 9.6 g (0.10 mol) of 2-cyclohexene-
olone (68) in 20 ml of dry DMSO was slowly added to the milky white solu-
tion. After the initial exotherm, the clear red solution was stirred
at 50° for 2 hr, cooled to 25°, poured onto 250 ml of cold water, and
extracted with three 50-ml portions of ether. The extracts were washed
twice with water, then saturated salt solution, and were dried over
anhydrous magnesium sulfate. After filtering the solution and removing
the ether, distillation of the residue afforded 4.91 g (45%) of clear,
colorless 69, bp 93-95° (18 mm) [lit bp 85-85.5° (10 mm)]; nD^17 =
1.4947.

Reduction of 69 with Lithium Aluminum Hydride. In a 250-ml three-necked
flask equipped with a magnetic stirrer, addition funnel, reflux con-
denser, and drying tube, was placed 1.0 g (26.3 mmol) of lithium alu-
minum hydride and 80 ml of anhydrous ether. A solution of 4.9 g (44.6
mmol) of 69 was slowly added with stirring, and the mixture was re-
fluxed for 2 hr, cooled to 25°, decomposed by careful dropwise addition
of 4.0 g of 10% sodium hydroxide solution and stirred overnight. Anhy-
drous magnesium sulfate was added to dry the mixture and the solution
was filtered. The ether was removed and distillation of the residue
afforded 4.64 g (93%) of a 30:70 mixture of exp-2-norcaranol (70)^50
and endo-2-norcaranol (71)^50 respectively, bp 90-107° (19 mm). Pure
samples of 70 and 71 were obtained by preparative gas chromatography
at 110° on a 10 ft x ^1/2 in 10% Carbowax 20M:KOH (4:1) on 80/80 Chromo-
sorb W column.
exo-2-Methoxynorcarane (66) and endo-2-Methoxynorcarane (67). In a 250-
ml three-necked flask equipped with addition funnel, magnetic stirrer,
reflux condenser, and drying tube, was placed 1.8 g (60%, 45 mmol) of
sodium hydride - mineral oil dispersion. The mineral oil was removed
by three hexane washings and the last traces of hexane were then removed
by evacuation of the apparatus. Dry nitrogen was then admitted and 60
ml of anhydrous ether was added, followed by a solution of 2.00 g (17.7
mmol) of a 30:70 mixture of 70 and 71 in 5 ml of ether. After stirring
at 25° for 2 hr, 10.0 g (70 mmol) of methyl iodide was added and the mix-
ture was stirred at 25° for an additional 3 days. The excess sodium hy-
dride was decomposed by the addition of 1:1 ether-methanol. Saturated
ammonium chloride solution was added to precipitate the salts, the ether
was decanted and the salts were washed twice with ether. The combined
washings were washed twice with saturated salt solution and were dried
over anhydrous magnesium sulfate. After filtering the solution and dis-
tilling the ether, distillation of the residue yielded 1.87 g (85%) of
a mixture of 66 and 67, bp 92-97° (66 mm) [lit bp 60° (40 mm)], whose
spectral data compared favorably with the literature values.

Reaction of 31 with Rhodium Dicarbonyl Chloride Dimer in Methanol. A
stirred solution of 460 mg (4.26 mmol) of 31 in 5 ml of methanol at 0°
was treated with 24 mg (0.062 mmol, 1.5 mol %) of rhodium dicarbonyl
chloride dimer, which caused a vigorous exothermic reaction. After stir-
ring for 5 min, the methanol was distilled and distillation of the residue
afforded 490 mg (82%) of clear, colorless liquid, bp 90-92° (55 mm), which
was identified as an 90:10:10 mixture of \textit{exo}-2-methoxy-1-methylnorcarane (75), \textit{endo}-2-methoxy-1-methylnorcarane (76), and 4-methoxy-2-methylcycloheptene (77). The components were separated by preparative vpc at 90° on a 9 ft x \( \frac{1}{4} \) in 25% \( \beta,\beta' \)-oxydipropionitrile on \( \text{42/60} \) Firebrick column. The spectral properties of 77 were: ir (CCl\(_4\) solution) 8.93, 9.10, and 9.21 \( \mu \); nmr (CDCl\(_3\)) \( \tau \) 4.40 (1H, t, \( J = 7 \) Hz), 6.71 (3H, s), 7.0 (1H, m), 7.6-9.0 (11H, m containing a 3H singlet at \( \tau \) 8.29).

\textbf{Anal. Calcd m/e for C\(_9\)H\(_{18}O\): 140.1201.}

\textbf{Found (obs. m/e): 140.1203.}

1-Methyl-2-norcaranone (40). Using the procedure described for the preparation of 62, 4.4 g (60%, 0.11 mol) of sodium hydride - mineral oil dispersion, 24.2 g (0.11 mol) of trimethylsulfoxonium iodide and 11.0 g (0.10 mol) of 2-methylcyclohexenone (39) \( ^{41} \) gave 10.40 g (76.5\%) of clear, colorless \( \text{21, } 126^\circ \text{ bp } 88-90^\circ \text{ (19 mm)}, \text{ir (neat)} 3.91, 10.98 \mu; \text{nmr (CDCl}_3\text{)} \tau 7.6-9.6 \text{ (m), 8.93 (s); } n^\text{D}_{17} = 1.4828. \)

1-Methyl-2-norcaranone Tosylhydrazone (44). A solution of 1.86 g (10 mmol) of \( \text{p-toluene sulfonylhydrazine, } 30 \text{ ml of methanol, 1.24 g (10 mmol) of } 40, \text{ and two drops of conc. hydrochloric acid was refluxed for 2 hr. The methanol was removed and the resulting oil was triturated with ether. The ether was evaporated and the resulting off-white solid was recrystallized from methanol-water to give } 2.33 \text{ g (80\%) of } 44. \text{ Three recrystallizations gave an analytical sample, mp } 148-150^\circ; \text{ir (KBr)} 3.10, 6.26, 7.14, \text{ and } 8.66 \mu. \)

1-Methyl-2-norcarene (**). To a stirred solution of 2.3 g (7.9 mmol) of 22 in 100 ml of anhydrous 1:1 ether-tetrahydrofuran was added 12.5 ml of 1.62 M methyl lithium in ether via a syringe. The solution turned orange and a yellow-orange precipitate was deposited. After stirring for 15 min, the mixture was decomposed on ice-water. The layers were separated and the aqueous layer was extracted with two 25-ml portions of 1:1 ether-pentane. The combined organic layers were washed twice with water, once with saturated salt solution, and were dried over anhydrous magnesium sulfate. The solution was filtered, the solvents were distilled, and distillation of the residue afforded 0.46 g (94%) of clear, colorless 36, bp 75-77° (190 mm); ir (CCl₄ solution) 6.10 μ; nmr (CDCl₃) τ 4.10 (1H, broad d, J = 10 Hz), 4.4-4.8 (1H, m), 7.8-9.1 (8H, m containing a 3H singlet at τ 8.84), and 9.15-9.7 (2H, m); n_D²⁰ = 1.4650.

Anal. Calcd for C₉H₁₄NO₂S: C, 61.62; H, 6.86; N, 9.55; S, 10.93.
Found: C, 61.65; H, 6.91; N, 9.61; S, 10.94.

Reduction of ** with Lithium Aluminum Hydride. Using the procedure described for the reduction of 69, 6.00 g (48.4 mmol) of ** was reduced with 1.0 g of lithium aluminum hydride to give 5.65 g (93%) of a clear, colorless 5:1 mixture of exo-1-methyl-2-norcaranol (**8) and endo-1-methyl-2-norcaranol (**9), bp 84-87° (15 mm). Pure samples of **8 and **9 were obtained by preparative vpc at 100° on a 10% Carbowax
20M:KOH (4:1) on 60/80 Chromosorb W. The spectral properties of \( \text{78} \) were: \( \text{ir (CCl}_4 \text{ solution)} \) 2.91 and 9.73 \( \mu \); \( \text{nmr (CDCl}_3 \) 6.14 (1H, t), 7.7-9.4 (11H, m including variable 0-H singlet and a 3H singlet at \( \tau \) 8.84), 9.57 (1H, s), 9.68 (1H, d). The spectral properties of \( \text{79} \) were: \( \text{ir (CCl}_4 \text{ solution)} \) 2.86, 9.02, 9.48, 9.82, 10.18, and 10.34 \( \mu \); \( \text{nmr (CDCl}_3 \) \( \tau \) 5.99 (1H, m), 7.8-9.4 (11H, m including 0-H singlet and a 3H singlet at \( \tau \) 8.94), 9.5-10.0 (2H, m).

**Anal. Calcd for C\( \text{9H}_\text{14O} \): C, 76.14; H, 11.16.**

**Found: C, 75.84; H, 11.14.**

**exo-2-Methoxy-1-methylnorcarane (\( \text{75} \))** and **endo-2-Methoxy-1-methylnorcarane (\( \text{76} \)).** In a procedure similar to that used for the preparation of \( \text{66} \) and \( \text{67} \), 2.25 g (17.7 mmol) of a 5:1 mixture of \( \text{78} \) and \( \text{79} \), 1.8 g (60\%, 45 mmol) of sodium hydride - mineral oil dispersion, and 10.0 g of methyl iodide, gave 1.95 g (78\%) of clear, colorless liquid, bp 92-97° (64 mm) which was subjected to preparative vpc at 90° on a 9 ft x \( \frac{1}{2} \) in 25\% \( \beta, \beta' \)-oxydipropionitrile on 42/80 Firebrick to give pure \( \text{75} \) and \( \text{76} \). The spectral properties of \( \text{75} \) were: \( \text{ir (CCl}_4 \text{ solution)} \) 9.11 \( \mu \); \( \text{nmr (CDCl}_3 \) \( \tau \) 6.4-6.7 (1H, m), 6.67 (3H, s), 7.8-9.2 (10H, m containing a 3H singlet at \( \tau \) 8.91), 9.2-9.8 (2H, m).

**Anal. Calcd for C\( \text{9H}_\text{16O} \): C, 77.09; H, 11.50.**

**Found: C, 76.93; H, 11.37.**

The spectral properties of \( \text{76} \) were: \( \text{ir (CCl}_4 \text{ solution)} \) 9.03 and 9.19 \( \mu \); \( \text{nmr (CDCl}_3 \) \( \tau \) 6.5-6.7 (1H, m), 6.67 (3H, s), 7.8-9.5 (10H, m containing a 3H singlet at \( \tau \) 8.95), 9.5-10.0 (2H, m).
Found: C, 76.87; H, 11.47.

Hydrogenation of 4-Methoxy-2-methylcycloheptene (77). A solution of 220 mg (1.58 mmol) of 4 in 10 ml of absolute methanol over 50 mg of 5% palladium-on-carbon was hydrogenated on an atmospheric pressure hydrogenator to give 200 mg (90%) of a 3:2 mixture of cis-1-methoxy-3-methylcycloheptane (80) and trans-1-methoxy-3-methylcycloheptane (81) bp 89-93° (45 mm).

cis-1-Methoxy-3-methylcycloheptane (80). Pure cis-1-methoxy-3-methylcycloheptanol (82), [bp 91.6-91.8° (12 mm)] (1.00 g, 7.8 mmol), was methylated in the manner previously described for the preparation of 66 and 67, and 75 and 76 to give 0.97 g (90%) of 80, bp 90-92° (43 mm); [lit bp 77° (12 mm)]; nmr (CCl₄) δ 6.6-7.0 (1H, m), 6.82 (3H, s), 7.8-9.1 (11H, m). 9.06 (3H, d, J = 5 Hz).

trans-1-Methoxy-3-methylcycloheptane (81). Pure trans-1-methoxy-3-methylcycloheptanol (83) [bp 88.2-89.6° (12 mm)] (1.10 g, 8.6 mmol) was methylated in the manner previously described for the preparation of 66 and 67, and 75 and 76 to give 1.10 g (90%) of 81, bp 90-91° (45 mm) [lit bp 76° (12 mm)]; nmr (CCl₄) δ 6.5-6.9 (1H, m), 6.82 (3H, s), 7.9-9.1 (11H, m), 9.10 (3H, d, J = 6 Hz).
PART B Bicyclo[2.1.0]pentane (24) and 1-Carbomethoxybicyclo[2.1.0]-pentane (103).

Bicyclo[2.1.0]pentane (24). This compound was prepared according to the method of Gassman and Mansfield.

Reaction of 24 with Rhodium Dicarbonyl Chloride Dimer. A solution of 260 mg (3.82 mmol) of 24, 1 ml of deuteriochloroform and 29 mg (0.075 mmol, 2 mol %) of rhodium dicarbonyl chloride dimer was sealed in a tube and heated to 65° for 49 hr. After cooling to 25°, the contents were distilled to give 93% of cyclopentene (26) in deuteriochloroform, bp 40-56°, which was identified by spectral comparison to an authentic sample.

Preparation of a 2.9:1 Mixture of exo-2,3-Dideuteriobicyclo[2.1.0]-pentane (88) and endo-2,3-Dideuteriobicyclo[2.1.0]pentane (89). 5,5-Dideuterio-2,3-diazabicyclo[2.2.1]hept-2-ene (91) (7.6 g) was pyrolyzed as in the preparation of 24. Distillation of the pyrolysat e afforded 3.5 g (65%) of clear, colorless liquid, bp 44-45°; nmr (CCl4) 7.92 (0.51 exo-H at C2 and C3), 8.49 (2 bridgehead H), 8.67 (1.49 endo-H at C2 and C3), 9.35 (1 exo-H at C5), 9.52 (1 endo-H at C5).

127. The yield reported is an average of duplicate runs as determined by vpc at 25° on a 10 ft x 1/8 in 20% DC-Silicone 200, 1000 c.s. on 50/30 Columpak column vs an internal standard.
Preparation of a 1.3:1 mixture of 88 and 89. A solution of 3.00 g (30.6 mmol) of 87 in 150 ml of n-butanol was placed in a 200 ml photolysis cell which was immersed in a dry ice-isopropanol bath and isopropanol, at -70°, was circulated through the quartz immersion well.

Irradiation of the n-butanol glass was carried out at 5 min intervals due to excessive heating by the high pressure mercury lamp and the actual irradiation time was 2 hr. Distillation of the photolysis solution through a 10 cm Vigreux column gave 0.70 g (33%) of clear, colorless liquid, bp 44-46°, which, by nmr analysis, was found to be a 1.3:1 mixture of 88 and 89; nmr (CCl₄) 7.92 (0.87H), 8.49 (2H), 8.67 (1.13H), 9.35 (1H), and 9.52 (1H).

5,5-Dideuteriobicyclo[2.1.0]pentane (90). To an ice-cooled solution of 17.0 g (53 mmol) of anhydrous zinc iodide in 150 ml of anhydrous ether in a 500 ml, three-necked flask equipped with polished stopcock for nitrogen introduction, Nalgene addition funnel, mercury bubbler, and magnetic stirrer was added 230 ml of 0.30 M ethereal dideuteriodiazomethane under nitrogen over a 0.5 hr period with stirring.

After 15 min, the volume of ether was reduced to ca 30 ml by evacua-

128. A diazomethane solution, which was prepared from 20 g of nitrosomethylurea, 300 ml of ether and 60 ml of 45% potassium hydroxide solution, and dried over potassium hydroxide pellets overnight, was stirred over 8 ml of 1 N sodium deuterioxide in deuterium oxide and 6 ml of tetrahydrofuran for 3 hr at 0°. The solution was decanted and the process was repeated. The ethereal solution was then dried over anhydrous potassium carbonate and found to be 0.30 M in dideuteriodiazomethane by standard titration. This procedure was based on an excellent new preparation of dideuteriodiazomethane, P. G. Cassman and W. Greenlee, procedure submitted to Org. Syn.
tion of the apparatus and stirring at 0°. The solution of 23 was then cooled to ca. -30° and 3.0 g (55.5 mmol) of cyclobutene (92) was added. The tightly stoppered flask was warmed slowly (3 hr) to 14° and stirred for 12 hr. The volatile products were vacuum transferred to a cooled (-78°) receiver and the solution was carefully concentrated by distillation of the ether through a 30 cm glass helices packed column at a reflux ratio of 60:1. Preparative vpc of the residue on a 10 ft x 1/4 in 20% DC-Silicone #200, 1000 c.s. on 80/80 Columpack column at 25° gave 442 mg (23%) of 92. Nmr analysis indicated 84% of dideuteration at the 5-position. The nmr spectrum of 92 in CCl₄ showed peaks at τ 7.94 (2H), 8.4-8.9 (4H), 9.2-9.6 (0.32H).

Reaction of a 2.9:1 Mixture of 88 and 89 with Rhodium Dicarbonyl Chloride Dimer. A solution of 106 mg (1.55 mmol) of a 2.9:1 mixture of 88 and 89, respectively, 0.5 ml of deuteriochloroform and 11 mg (0.023 mmol, 2 mol %) of rhodium dicarbonyl chloride dimer was heated at 65° in a sealed tube for 70 hr. The products and solvent were distilled and analyzed by nmr spectroscopy (CDCl₃ solution) to show peaks at τ 4.22 (1H, s), and 7.4-8.5 (3.21H, m). This was consistent with the presence of only deuterated cyclopentenes.

An 80% yield based on dideuteriodiazomethane gives 27.6 mmol of reagent 23.
Reaction of 90 with Rhodium Dicarbonyl Chloride Dimer. Using the above
procedure, the product from the reaction of 90 with rhodium dicarbonyl
chloride dimer was analyzed by nmr spectroscopy (CDCl$_3$) to show peaks
at $\tau$ 4.22 (1H, s) and 7.4-8.5 (3.22H, m).

1-Deuterio-1-acetoxy cyclopentane (97). In a 500 ml round-bottom flask
equipped with a magnetic stirrer, addition funnel, reflux condenser,
and drying tube, was placed 2.0 g (47.7 mmol) of lithium aluminum
deuteride and 125 ml of anhydrous ether. To the stirred solution was
added 15.0 g (179 mmol) of cyclopentanone (95) in 75 ml of anhydrous
ether at a rate sufficient to reflux the solution. After 3 hr at reflux,
the solution was cooled to 25°, decomposed via dropwise addition
of 3 g of 10% sodium hydroxide solution and stirred at 25° for 4 hr.
After drying over anhydrous magnesium sulfate, the solution was filtered,
and the ether was removed by distillation. The residue was dis-
solved in 100 ml of pyridine, 40 g of acetic anhydride was added, and
the solution was stirred overnight, poured onto ice, and extracted
with two 100-ml portions of ether. The extracts were washed with di-
lute hydrochloric acid, water, saturated sodium bicarbonate solution
and dried over anhydrous magnesium sulfate. After filtering the solu-
tion, the ether was removed by distillation, and distillation of the
residue afforded 16.11 g (65%) of clear, colorless 27, bp 85-87° (80 mm); ir spectrum (neat): 4.57 (w), 5.85, 7.28, 7.90, 8.42, and 9.73 μ.

1-Deuteriocyclopentene (24). Pyrolysis of 27 (16.0 g) in the vapor phase under nitrogen at 450° in a Lindeber Hevi-duty pyrolysis oven afforded 6.32 g (80%) of 24, bp 41-43°, upon distillation of the pyrolysate. The ir spectrum of 24 (CCl₄ solution) showed absorptions at 4.42 and 9.96 μ. The nmr spectrum (CCl₄) consisted of peaks at τ 4.22 (1H, s) and 7.4-8.5 (6.22H, m).

Using the correction factor required by the data in footnote 63, 93% deuterium incorporation at the 1-position was determined by nmr analysis.

Scrambling of 1-Deuteriocyclopentene (24). In an nmr tube was placed 100 mg (1.45 mmol) of 24, 0.5 ml of deuteriochloroform, 5.6 mg (1 mol %) of rhodium dicarbonyl chloride dimer, and 10 mg (10 mol %) of 24. The solution was allowed to stand at 10° for 3.5 hr and then the nmr was recorded to show peaks at τ 4.22 (1H, s) and 7.4-8.5 (3.59H, m).

The control experiments utilizing derivatives of bicyclo[1.1.0]-butane and bis(triphenylphosphine)carbonylrhodium(I) hydride were run using the procedure described above.

1-Carbomethoxybicyclo[2.1.0]pentane (103). This compound was prepared according to the method of Gassman and Mansfield.

Reaction of 103 with Rhodium Dicarbonyl Chloride Dimer. A solution of 400 mg (3.13 mmol) of 103, 1 ml of chloroform, and 62 mg (0.159 mmol,
5 mol %) of rhodium dicarbonyl chloride dimer was heated in a sealed tube at 65° for 22 hr. After cooling to 25°, the volatile contents of the tube were vacuum transferred and the two major products were collected by preparative vpc at 120° on a 10 ft x ½ in 15% DEGS on 60/80 Chromosorb P column. These were shown to be 1-carbomethoxycyclpentene (104) and 3-carbomethoxycyclpentene (105) by spectral comparison with authentic samples. Vpc analysis of the product mixture in duplicate runs vs an internal standard at 130° on a 10 ft x ½ in 5% DEGS on 60/80 Chromosorb P column showed 36% of 1-carbomethoxycyclpentene (104), 33% of 3-carbomethoxycyclpentene (105), and ≤ 1% each of two minor products. The spectral properties of 104 were: ir (CCl₄ solution): 5.81, 6.13, 6.98, 7.40, 7.72, 7.92, 8.39, and 9.20 μ; nmr (CDCl₃) τ 3.21 (IH, broad t, J = ~ 2 Hz), 6.29 (3H, s), 7.1-8.4 (6H, m). The spectral properties of 105 were: ir (CCl₄ solution) 5.75, 6.20 (w), 6.96, 7.51, 8.33, 8.50, and 9.51 μ; nmr (CDCl₃) τ 4.13 (1H, d of d, J = 6.5 Hz, J = 2 Hz), 4.38 (1H, m), 6.33 (3H, s), 6.2-6.6 (1H, s), and 7.2-8.2 (4H, m).

1-Carbomethoxycyclpentene (104). The procedure used was a modification of the literature procedures. 130,132 2-Carbomethoxycyclpentanone was reduced with sodium borohydride to 2-carbomethoxycyclpent-

tanol, bp 83-91° (1.3 mm). Dehydration of the alcohol with phosphorus pentoxide in benzene afforded a mixture of carbomethoxycyclopentenes which was equilibrated by treatment with methanolic sodium methoxide. Distillation afforded impure töl, bp 71-75° (33 mm) [lit. bp 63-65° (10 mm), 1° 52° (12 mm) 133]. Purification by preparative vpc at 120° on a 10 ft x 1/8 in. 25% DEGS on 60/80 Chromosorb P column gave pure töl; n°D = 1.4830.

3-Carbomethoxycyclopentene 105. 3-Chlorocyclopentene was prepared by the method of Moffett 134 and was converted to the Grignard reagent and subsequently to cyclopentene-3-carboxylic acid by the method of Jørgensen and Berg. Esterification with diazomethane afforded 3-carbomethoxycyclopentene (105), bp 66-67° (26 mm), [lit. bp 60-65° (15 mm), 46° (10 mm) 135]: n°D = 1.4538.

2-Chloronorbornene (107). This compound was prepared according to the procedure of McDonald and Steppel.

Reaction of 2-Chloronorbornene (107) with Methyllithium. The procedure used was that of Gassman, Andrews, and Patton. In a 50-ml round-bottomed flask, equipped with a serum cap in a sidearm, magnetic stirrer, and reflux condenser under a nitrogen atmosphere, was placed 3.50 g (27 mmol) of 107 and 90 ml (147 mmol, 15.18%, 0.71 g/ml) of ethereal methyllithium via a syringe. After stirring at 25° for 8 days, the reaction mixture was cautiously poured onto ice and extracted with three 25-ml portions of ether. The combined extracts were washed with 25 ml of water, 25 ml of saturated salt solution, and dried over anhydrous magnesium sulfate. After filtering the solution, the solvent was removed by distillation. Distillation of the residue afforded 2.14 g (73%) of 2-methyllnorbornene, bp 63-65° (86 mm) which was identical in all respects to an authentic sample.

Reaction of 2-Chloronorbornene (107) with Methyllithium, Deuterium Oxide and Carbon Dioxide Workup. This reaction was carried out as previously described. After 8 days, 15 ml of deuterium oxide was slowly added to the reaction mixture and work-up proceeded in the removal manner. No deuterium incorporation in 108 was detectable by
nmr or mass spectral analysis. In a similar reaction, the reaction solution was poured onto powdered dry ice, acidified, extracted with ether, and worked up as above. Only 105 was obtained in addition to some acetic acid.

3,3-DideuterionorcAMPHOR (150). This compound was prepared according to the method of Farnum and Mehta, and had mp 94-96°, with ca 75\% d2 and 20\% d1 by mass spectral analysis. The infrared spectrum (CCl4 solution) showed absorptions at 4.55, 5.73, and 9.15 μ.

2,2-Dichloro-3,3-dideuterionorbornane (151). A solution of 15.00 g (0.134 moles) of phosphorous trichloride was placed in an ice cooled 250-ml, 3-necked, round-bottomed flask equipped with a magnetic stirrer, reflux condenser, drying tube, thermometer, and connected by means of Gooch tubing to a 125-ml Erlenmeyer flask containing 30.0 g (0.144 moles) of phosphorus pentachloride. The phosphorus pentachloride was added over a 2 hr period so that the temperature did not rise above 5° during the addition. After stirring at 25° for 20 hr, the reaction mixture was poured onto ice and extracted with three 100-ml portions of pentane. The combined organic extracts were washed with six 50-ml portions of water, two 50-ml portions of saturated salt solution, and were dried over anhydrous magnesium sulfate. After filtering the solution, the solvent was removed by distillation and vacuum distillation of the residue afforded 22.68 g (90\%) of clear, colorless liquid, bp 75-77° (14 mm) which was > 95\% 151 by
vpc analysis. The infrared spectrum (CCl₄ solution) of 15₁ showed strong absorptions at 7.68, 9.76, and 10.62 μ.

2-Chloro-3-deuteronorbornene (1₄₈). In a 1-l, three-necked round-bottomed flask equipped with mechanical stirrer, addition funnel, reflux condenser, and drying tube was placed 400 ml of tert-butanol and 10 g (0.25 gm-atom) of metallic potassium. The stirred solution was warmed to gentle reflux to dissolve the potassium. From the addition funnel, 22.00 g (0.132 mol) of 1₅₁ was added to the warm solution over 15 min. After refluxing for 108 hr, the reaction mixture was cooled, poured onto ice, and extracted with three 100-ml portions of pentane. The combined extracts were washed with six 50-ml portions of water and dried over anhydrous magnesium sulfate. After filtering, the solvents were distilled. Fractional distillation of the residue afforded 4.18 g (45% based on unrecovered dichloride) of clear, colorless liquid, bp 70-72° (60 mm), and 10.12 g of starting dichloride. The infrared spectrum (CCl₄ solution) of 1₄₈ showed strong absorptions at 6.40, 7.18, 9.10, and 14.15 μ. Integration of the nmr spectrum absorbances at 4.27 (vinyllic H, doublet) and 7.0-7.25 (bridgehead 2H multiplet) indicated 83% D-incorporation at the 3-position.

Reaction of 2-Chloro-3-deuteronorbornene (1₄₈) with Methyllithium. A mixture of 40 ml (1.6 M, 64 mmoles) of ethereal methyllithium and 1.40 g (10.8 mmoles) of 1₄₈ was stirred under a nitrogen atmosphere at 25° for 5 days. The cloudy reaction mixture was poured cautiously onto
ice and the layers were separated. The aqueous layer was extracted
with two 50-ml portions of ether and the combined organic layers were
washed with saturated salt solution and dried over anhydrous magnesium
sulfate. The solution was filtered and the solvent was removed by dis-
tillation at atmospheric pressure. The residue was purified by prepara-
tive vpc at 120° on a 20 ft x \( \frac{3}{8} \) in \( \times \) 0.005 in. in a 0.01 in. x \( \frac{3}{8} \) in. Chromosorb W
column and both starting material and 2-methyl-3-deuterionorbornene
(152) was isolated. Pure 152 had the following spectral properties:
ir (CCl\(_4\) solution), 4.43 (2), 6.23 (w), 6.93, 11.55, and 14.17 μ; nmr
(CCl\(_4\)/TMS) \( \tau \) 4.50 (0.17 H, m), 7.24 (1H, m), 7.40 (1H, m), 8.23 (3H,
s), 8.3-9.1 (6H, m). Both starting material and product had 33% of
deuterium incorporation in the 3-position by nmr analysis.

(+)-(1S)-2-Chloronorbornene (153). Optically active 2-chloronorbor-
nene was prepared according to the procedure of McDonald and Steppel.
The dextrorotatory isomer was prepared which had the 1S configuration
and \([\alpha]_D^{25} = +1.3 \pm 0.10^\circ\) (c 9.72, CHCl\(_3\)). The maximum optical purity
for 153 was 28%. The optical purity of (+)-(1S)-norcamphor (158)
from which 153 was obtained was calculated to be 28% based on the maxi-
mum specific rotation of 158. For the listing of specific rota-
tions of the precursors of 153, see the Results and Discussion, Part II.

Reaction of (+)-(1S)-2-Chloronorbornene (153) with Methyllithium. A
mixture of 120 ml (1.6 M, 0.192 moles) of ethereal methyllithium and
5.00 g (39 mmol) of 153 was stirred at 25° for 8 days. The solution
was cautiously poured onto ice and the layers were separated. The
aqueous phase was extracted with two 25-ml portions of ether and the combined organic layers were washed with saturated salt solution and dried over anhydrous magnesium sulfate. The solution was filtered and concentrated by distillation at atmospheric pressure. The residue was distilled through a 15 cm Vigreux column to afford 2.47 g (59%) of clear, colorless liquid, bp 71-72° (155 mm), whose spectral properties were identical to an authentic sample of 2-methylnorbornene. The optical rotation of the sample was $[\alpha]^{25}_D = +2.01 \pm 0.1^\circ$ (c 10.2, CHCl$_3$).

(+)-(1S)-2-Methylenenorbornane (160). A mixture of 29.0 g (81.3 mmol) of methyltriphenylphosphonium bromide in 300 ml of dry hexane was placed in a 500-ml, three-necked, round-bottomed flask equipped with a mechanical stirrer, serum cap, addition funnel, reflux condenser, and drying tube. Fifty milliliters (1.6 M, 80 mmol) of n-butyllithium in hexane was added via a syringe to the stirred mixture. After stirring at 25° for 4 hr, 6.35 g (57.8 mmol) of $15\beta^{100}$ in 20 ml of hexane was slowly added and the reaction mixture was refluxed for 16 hr. After cooling to 25°, water was slowly added to quench the mixture. The layers were separated and the aqueous layer was extracted with two 50-ml portions of hexane. The combined organic layers were washed with water and dried over anhydrous magnesium sulfate. The solution was filtered and the solvent was distilled at atmospheric pressure. Distillation of the residue at reduced pressure afforded 3.20 g (51%) of clear, colorless 160; bp 75-78°/45 mm (lit. bp 123°), $[\alpha]^{25}_D = +33 \pm 5^\circ$ (c 6.0, CHCl$_3$).
Hydrogenation of (±)-(1S)-2-Methylene norbornane (160). A solution of 1.75 g (16.1 mmol) of (±)-(1S)-2-methylene norbornane (160) in 20 ml of 95% ethanol was hydrogenated over 250 mg of 5% palladium on carbon at atmospheric pressure (5 hr). The solution was filtered through Celite and distilled through a 60 cm Teflon annular spinning band column. The product co-distilled with the ethanol and the fraction boiling from 75-78° was collected. Pure (−)-(1S,2R)-endo-2-methylnorbornane (161) (0.265 g, 15% yield) was obtained by preparative vpc at 115° on a 20 ft x 3/8 in 30% SE-30 on 45/60 Chromosorb W column and had infrared absorptions (CHCl₃ solution) at 6.89, 7.28, and 9.00 μ. The nmr spectrum of 161 was unresolved except for the methyl doublet (J = 6 Hz) at τ 9.05, and the optical rotation was [α]D²⁵ = −9.44 ± 0.2° (c 7.05, CHCl₃).

Hydrogenation of (+)-(1S)-2-Methylnorbornene (155). A 2.10 g (19.4 mmoles) sample of optically active 2-methylnorbornene from the reaction of (+)-(1S)-2-chloronorbornene (153) and methylithium was hydrogenated over 200 mg of 5% palladium-on-carbon in the manner presented for the hydrogenation of 160. Isolation of the product by preparative vpc afforded 248 mg (12%) of endo-2-methylnorbornane which was identical in all respects to authentic material and had [α]D²⁵ = −9.20 ± 0.2° (c 6.03, CHCl₃), indicating the structure to be 161.

Reaction of 2-Chloronorbornene (107) with n-Butyllithium. A solution of 5.00 g (39.0 mmol) of 2-chloronorbornene, 125 ml of anhydrous ether

and 125 ml of 1.6 M n-butyllithium (200 mmol) in hexane was stirred under nitrogen for 7 days. The reaction mixture was cautiously poured onto ca 300 g of ice. The layers were separated and the aqueous layer was extracted with 50 ml of ether. The combined organic layers were washed with saturated salt solution and dried over magnesium sulfate. After filtering the solution, the solvents were removed by distillation and the residue was fractionally distilled through a 10 cm Vigreux column. The fraction boiling from 78-88° (21 mm) was subjected to further purification by preparative vpc at 160° on a 20 ft x 3/8 in 30% SE-30 on 45/60 Chromosorb W column.

The first component to elute (2.34 g, 40% yield) was identified as 2-n-butynorbornene (162). The spectral properties of 163 were:

ir (neat) 6.18 μ; nmr (CCl4/TMS), τ 4.51 (1H, broad s), 7.24 (1H, m), 7.33 (1H, m), 7.93 (2H, m), 8.2-9.2 (13H, m); nD = 1.4724; near ir λmax = 1.675 μ (ε = 0.229).

Found: C, 88.05; H, 12.16.

The second component to elute (1.23 g, 21% yield) was identified as 2-n-butynortricyclene (163) on the basis of its spectral properties: ir (neat), 3.24, 12.5 doublet; nmr (CCl4/TMS) as unresolved multiplet from τ 8.1-9.2; nD = 1.4669; near ir (CCl4) λmax = 1.666 μ (ε = 1.280).

Found: C, 87.90; H, 12.25.
Hydrogenation of 2-n-Butylnorborne (162). A solution of 200 mg (1.33 mmol) of 162 in 10 ml of absolute ethanol was hydrogenated in an atmospheric hydrogenator using 100 mg of 5% palladium-on-carbon. After 1.5 hr the theoretical amount of hydrogen had been taken up and the catalyst was removed by filtration. The filtrate was diluted with water and extracted with three 15-ml portions of pentane. The combined extracts were washed with two 10-ml portions of water and were dried over anhydrous magnesium sulfate. After filtering the solution, the solvent was distilled. The product was distilled in a molecular still to give 152 mg (75%) of clear, colorless liquid, which was identical in all respects to an authentic sample of 164.

endo-2-n-Butylnorborne (164). A solution of 5.11 g (46.4 mmol) of norcamphor (149) in 10 ml of anhydrous ether was added via a syringe over 20 min to a magnetically stirred solution of 35 ml of 1.6 M n-butyllithium (56 mmol) in hexane so as to maintain a gentle reflux. After stirring at 25° for an additional 2.5 hr, the reaction mixture was cautiously poured onto ice. The layers were separated and the aqueous layer was extracted with three 50-ml portions of ether. The combined organic phases were washed with 50 ml each of water and saturated salt solution and were dried over anhydrous magnesium sulfate. After filtering the solution, the solvents were removed on a rotary evaporator to give 7.31 g (95%) of alcoholic product 165 which was used without further purification. The infrared spectrum of 165 showed absorptions at 3.01 and 9.91 μ.
A stirred mixture of 165 (7.31 g, 43.5 mmol), and 1 ml of 85% phosphoric acid was heated at 100° for 1 hr and then maintained at 25° overnight. The mixture was then diluted with 30 ml of water and 50 ml of ether, the layers were separated and the aqueous layer was extracted with 25 ml of ether. The combined organic layers were washed with 25 ml each of saturated sodium carbonate solution and saturated salt solution and dried over anhydrous magnesium sulfate. After filtering the solution, the solvent was removed by distillation. Distillation of the residue through a 10 cm Vigreux column gave 5.02 g (77%) of clear, colorless liquid, bp 69-70° (9 mm). The isomers of 166 were not separated at this point and had $\delta_{D}^{17} = 1.4792$.

A solution of 700 mg (4.76 mmol) of the olefin isomers in 15 ml of absolute ethanol was hydrogenated on an atmospheric hydrogenator using 200 mg of 5% palladium-on-carbon. After 1.5 hr, the theoretical amount of hydrogen had been taken up and the catalyst was removed by filtration. After work-up, as described in the hydrogenation of 162, distillation of the residue afforded 523 mg (74%) of clear, colorless liquid, bp 71-72° (10 mm), which was ca 90% endo-2-n-butylnorbornane (164). An analytical sample of 164 was obtained by preparative vpc at 160° on a 20 ft x 3/8 in 30% SE-30 on 45/60 Chromosorb W column and its spectral properties were:

1. Infrared (neat), 6.85 μ (quartet), 7.29, 7.59, and 8.54 μ;
2. NMR (CCl₄/TMS) δ 7.86 (m, 2H), and 8.0-0.2 (m, 18H); $\delta_{D}^{17} = 1.4593$.

**Anal.** Calcd for C₁₁H₂₀: C, 86.76; H, 13.24.

Found: C, 86.61; H, 13.49.
Reaction of 2-Chloronorbornene (107) with Methylithium in Hexane-Ether.

This reaction was carried out as previously described except that the reaction solution was diluted with an equal volume of hexane. After 8 days, only 107 and 103 were found in the reaction mixture.

Reaction of 2-Chloronorbornene (107) with tert-Butyllithium. Under a dry nitrogen atmosphere (dry box), 3.00 g (23 mmol) of 107 was added via a syringe to a stirred solution of 35 ml of 2.1 M tert-butyllithium (73.5 mmol). After stirring at 25° for 6 days, the reaction mixture was carefully hydrolyzed by pouring onto ice. The mixture was extracted with three 50-ml portions of pentane and the combined extracts were washed with 25 ml of water and dried over anhydrous magnesium sulfate. After filtering the solution, the solvent were removed by distillation and the residue was distilled through a 10 cm Vigreux column to give 1.44 g of clear, colorless liquid, bp 68-72° (23 mm). Analysis of the forerun and material in the dry ice trap afforded 0.70 g (38%) of norbornene and 0.50 g of starting material. The distillate was subjected to further purification by preparative vpc at 100° on a 10 ft x \( \frac{1}{4} \) in 5% SE-30 on 30/80 Chromosorb W column.

The first component to elute (0.146 g, 5% yield) was identified as 2-tert-butylnorbornene (169), on the basis of its spectral properties: ir (CCl₄ solution) 3.26 (w), 6.22, 7.40, and 7.83 μ; nmr (CCl₄/THF) τ 4.50 (1H, d, J = 3 Hz), 7.12 (1H, d), 7.22 (1H, d), 8.0-9.1 (15H, m, containing a sharp singlet at τ 8.92).

Anal. Calcd for C₁₁H₁₈: C, 87.92; H, 12.08.

Found: C, 87.66; H, 12.37.
The second, major, component (1.285 g, 44% yield) was identified as 2-tert-butynortricyclene (172) on the basis of its spectral properties: ir (CCl₄ solution) 3.25 and 7.36 μ; nmr (CCl₄/TMS) τ 8.16 (1H, m), 8.48 (1H, m), and 8.7-9.25 (16H, m, containing sharp singlet at τ 9.07); nD²⁰ = 1.4693; near ir (CCl₄) λmax = 1.667 μ (ε = 1.011).

Anal. Calcd for C₁₁H₁₈: C, 87.92; H, 12.08.

Found: C, 87.64; H, 12.20.

Reaction of 2-Chloronorbornene (107) and Phenyllithium. A stirred mixture of 5.01 g (39 mmol) of 107 and 91 ml (2.2 M, 200 mmol) of phenyllithium in 70:30 benzene-ether was refluxed for 24 hr. After cooling to 25°, the reaction mixture was poured onto ice and the layers were separated. The aqueous phase was extracted with three 50-ml portions of ether and the combined organic layers were washed with water and saturated salt solution, and dried over anhydrous magnesium sulfate. The solution was filtered and the solvents were removed on a rotary evaporator. The crude product was chromatographed on ca 600 g of activity I alumina. Elution with pentane afforded 465 mg (7%) of 3-phenynortricyclene (173), bp 90-92° (0.45 mm) and 4.12 g (62%) of 5-benzalbicyclo[2.1.1]hexane (175), bp 98-100° (1.45 mm).

The spectral properties of 173 were: ir (neat) 3.35, 3.42, 3.56, 6.24, 12.33, 13.54, and 14.89 μ; nmr (CCl₄/TMS) τ 2.81 (5H, s), 7.17 (1H, s), 8.03 (1H, s), 8.53 (2H, m), and 8.67-9.15 (4H, m); nD²⁰ = 1.5525; near ir (CCl₄) λmax = 1.665 μ.


Found: C, 91.52; H, 8.39.
The spectral properties of \( \text{I75} \) were ir (neat) 3.33, 3.44, 3.54, 5.90, 6.22, 13.15, and 14.33 \( \mu \); nmr (\( \text{CCl}_4/\text{TMS} \)) \( \tau \) 2.83 (5H, s), 4.22 (1H, s), 6.60 (1H, m), 7.07 (1H, m), 8.20 (5H, s), 8.78 (1H, d, \( J = 7 \) Hz), \( n^2_\text{D} = 1.5712 \).

**Anal.** Calcd for C\(_{13}\)H\(_{14}\): C, 91.71; H, 8.29.

Found: C, 91.69; H, 8.31.

2-Phenylnorbornene (\( \text{I74} \)). This compound was prepared according to the procedure of Kleinfelter, et al.

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**Reaction of 5-Benzalbicyclo[2.1.1]hexane (\( \text{I75} \)) with Osmium Tetroxide.**

A solution of 267 mg (1.57 mmole) of \( \text{I75} \), 8 ml of pyridine, and 399 mg (157 mmole) of osmium tetroxide was stirred at 25° for 2 hr. A solution of 700 mg of sodium bisulfite, in 10 ml of water and 5 ml of pyridine, was added, followed by two additional 100-mg portions of sodium bisulfite at 30 min intervals. The dark red reaction mixture was poured into 75 ml of water and extracted with four 25-ml portions of ether. The combined extracts were washed with four 50-ml portions of water, 50 ml of saturated salt solution, and dried over anhydrous magnesium sulfate. After filtering the solution, the solvent was removed at reduced pressure to give 300 mg (92%) of crude [exo-(5-hydroxy)-bicyclo[2.1.1]hex-5-yl]phenylcarbinol (\( \text{I77} \)). Recrystallization from hexane gave white needles, mp 126.4-127.8°. The spectral characteristics of \( \text{I77} \) were: ir (nujol) 3.10, 13.56, and 14.30 \( \mu \); nmr (\( \text{CCl}_4/\text{TMS} \)) \( \tau \) 2.70 (5H, m), 4.82 (1H, s), 7.13 (2H, s), 7.42 (1H, m), 7.9-8.8 (6H, m), 9.27 (1H, d, \( J = 7.8 \) Hz).
Anal. Calcd for C\textsubscript{13}H\textsubscript{16}O\textsubscript{2}: C, 76.44; H, 7.90.

Found: C, 76.37; H, 7.79.

Cleavage of \textit{177} with Periodic Acid. To a stirred solution of 199 mg (0.98 mmol) of \textit{177} in 5 ml of ether, 14 ml of a saturated ethereal solution of periodic acid (16 mg/ml) was added dropwise over 3 min a white precipitate was formed. After stirring for 15 min anhydrous magnesium sulfate was added. The solution was filtered and carefully concentrated by distillation at atmospheric pressure. Preparative vpc of the residue on a 10 ft x \(\frac{3}{4}\) in 25% XF-1150 on Chromosorb W column at 120\(^\circ\) afforded 63 mg (67\%) of bicyclo[2.1.1]hexan-5-one (\textit{176})\textsuperscript{110,111} and 71 mg (68\%) of benzaldehyde (\textit{178}). The spectral properties of \textit{176} were identical to the published spectrum.

7,7-Dimethoxy-2-chloronorbornene (\textit{184}). This compound was prepared according to the procedure of Patton.

Reaction of 7,7-Dimethoxy-2-chloronorbornene (\textit{184}) with Methyllithium.
A solution of 50 ml of 1.6 M methyllithium (80 mmol) in ether was added via a syringe to a stirred sample of 3.00 g (15.9 mmol) of \textit{184}. After stirring at 25\(^\circ\) for 28 hr, the reaction mixture was carefully poured onto ice and the layers were separated. The aqueous layer was extracted with two 50-ml portions of ether, the combined organic layers were washed with saturated salt solution, and dried over anhydrous magnesium

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sulfate. After filtering the solution, the solvent was removed by
distillation. Distillation of the residue afforded 2.13 g of clear,
colorless liquid, bp 53-55° (5 mm) which was subjected to final puri-
fication by preparative vpc at 160° on a 20 ft x \(3/8\) in 30% SE-30 on
\(45/50\) Chromosorb W column.

The first component to elute, 0.174 g (6.5% yield), was identified
as 7,7-dimethoxy-2-methylbornene (\(\text{187}\)) on the basis of its spectral
properties: ir (neat) 3.26, 6.13 (w), 8.13, and 9.35 μ; nmr (CCl₄/TMS) 
\(\tau\) 4.25 (1H, m), 6.92 (3H, s), 6.96 (3H, m), 7.45 (1H, m), 7.59 (1H,
m), 8.23 (2H, m), 8.28 (3H, d), and 9.18 (2H, m).

**Anal.** Calcd for C₁₀H₁₆O₂: C, 71.39; H, 9.59.

**Found:** C, 71.14; H, 9.46.

The second, major, component, 1.87 g (72%) was identified as 7,7-
dimethoxy-3-methylworldine (\(\text{188}\)) . Its spectral properties were:
ir (neat) 3.22, 7.54, 8.71, 8.85, 9.40, and 10.08 μ; nmr (CCl₄/TMS) 
\(\tau\) 6.85 (6H, m), 8.1-8.5 (3H, m), and 8.7-9.0 (7H, m, containing CH₃
doublet at \(\tau\) 8.85, \(J = 7 \text{ Hz}\)); \(\delta\) \(D\) = 1.4657; near ir (CCl₄) \(\lambda_{max} =
1.660 \mu\) and \(\lambda_{max} = 1.666 \mu\) (ε 0.903).

**Anal.** Calcd for C₁₀H₁₆O₂: C, 71.39; H, 9.59.

**Found:** C, 71.49; H, 9.56.

Reaction of 7,7-Dimethoxy-2-chloronombeline (\(\text{184}\)) with \(\text{n-Butyllithium}\).
A solution of 25 ml of 1.6 M \text{n-Butyllithium} (40 mmol) in hexane was
slowly added over 20 min via a syringe to an ice-cooled, stirred, 3.00
g (15.9 mmol) sample of \(\text{184}\) . After stirring at 0° for an additional
5 min and then at 25° for 5 min, the reaction mixture was poured onto ice and worked up in the previously described manner. After filtration, the solution was concentrated on a rotary evaporator. Distillation of the residue afforded 3.02 g of clear, colorless liquid, bp 63-66° (0.15 mm), which was subjected to further purification by preparative vpc at 160° on a 10 ft x ½ in 10% Carbowax 20M:KOH (4:1) on 60/80 Chromosorb W column.

The first component to elute (0.167 g, 5% yield) was identified as 7,7-dimethoxy-2-n-butylnorbornene (189) on the basis of its spectral properties: ir (neat) 3.25, 6.14 (w), 9.11, and 9.35 μ; nmr (CCl4/TMS) τ 4.48 (1H, m), 6.91 (3H, s), 6.96 (3H, s), 7.47 (2H, m), and 7.7-9.4 (13H, m); nD 17 = 1.4655.

**Anal.** Calcd for C13H22O2: C, 74.24; H, 10.54.

**Found:** C, 74.35; H, 10.49.

The major component (2.77 g, 83% yield), which eluted second, was identified as 7,7-dimethoxy-3-n-butylnortricyclene (190) on the basis of its spectral properties: ir (neat) 3.24, 7.55, 8.73, 8.90, and 9.40 μ; nmr (CCl4/TMS) τ 6.88 (6H, s), 8.0-9.3 (16H, m); nD 17 = 1.4651; near ir (CCl4) λmax = 1.660 μ (ε 1.009) and λmax = 1.667 μ (ε 1.038).

**Anal.** Calcd for C13H22O2: C, 74.24; H, 10.54.

**Found:** C, 74.59; H, 10.45.

Reaction of 7,7-Dimethoxy-2-chloronorbornene (184) with Phenyllithium.

A solution of 25 ml of 1.6 M phenyllithium (40 mmol) in 77% benzene in ether was slowly added via a syringe to an ice-cooled, stirred, 3.00
1.39 g (15.9 mmol) sample of $^{184}$ sample was stirred at 0° for 5 min and at
25° for 30 min, the reaction mixture was poured onto ice and water and
the layers were separated. The aqueous layer was extracted with two
25-ml portions of ether and the combined organic layers were washed
with 25 ml of saturated salt solution and dried over anhydrous mag-
nesium sulfate. The solution was filtered and concentrated on a ro-
tary evaporator. The residue was vacuum transferred to give, after
removal of most of the biphenyl, 3.00 g (82%) of 7,7-dimethoxy-3-
phenylnortricycle [bath temp 120-140° (0.45 mm)]. An analytical sam-
ple was obtained by preparative vpc at 170° on a 10 ft x ½ in 10% Car-
bowax 20M:KOH (4:1) on $^{60}/_{80}$ Chromosorb W column and had the following
spectral properties: ir (neat) 3.24, 6.24, 7.57, 8.74, 9.01, 9.40,
13.67, and 14.41 μ; nmr (CCl₄/TMS) δ 2.3-3.0 (5H, m), 6.86 (3H, s),
6.98 (1H, s), 7.52 (3H, s), 7.8-8.1 (2H, m), 8.3-8.7 (4H, m); $n_D^{17}$ =
1.5445; near ir (CCl₄) $λ_{max}$ = 1.666 μ ($ε$ 1.155).


Found: C, 78.21; H, 7.92.

2,2,5-Trichloronorbornane (196). A mixture of 48.0 g (0.174 mol, 90%
active chlorine) of iodobenzene dichloride, 300 ml of carbon tetrachloride and 20.00 g (0.155 mol) of 2-chloronorbornene was freeze-
degassed and placed under nitrogen. The stirred mixture was slowly
brought to reflux and an exothermic reaction initiated. After the
solid had dissolved, the solution was refluxed for an additional 15
min. The solution was cooled to 25° and stirred with 200 ml of satura-
ted sodium bicarbonate solution for 15 min. The layers were separated, the aqueous layer was extracted with 75 ml of carbon tetrachloride, and the combined organic phases were dried over anhydrous magnesium sulfate. The solution was filtered, the solvent was removed by distillation, and the residue was fractionally distilled through a 30 cm Vigreux column to give 33.61 g (95%) of iodobenzene, bp 65-68°C (5.5 mm) and 27.17 g (87%) of a waxy, red solid, bp 92-97°C (5.5 mm). Analytically pure 2,2,3-trichloronorbornane was obtained by preparative glc at 140°C on a 10 ft x $\frac{3}{4}$ in 5% SE-30 on 60/80 Chromosorb W and sublimation at 65°C (28 mm) as a waxy, white solid, mp 81-82°C. The spectral properties of 2,2,3-trichloronorbornane were: \textit{ir} (KBr) 11.62, 12.40, 12.74, and 14.10 μ; \textit{nmr} (CCl₄/TMS) τ 5.89 (1H, d, J = 3 Hz), 7.12 (1H, m), 7.58 (1H, m), and 7.7-8.7 (6H, m).

\textbf{Anal.} Calcd for C₇H₉Cl₃: C, 42.14; H, 4.55; Cl, 53.31.

Found: C, 42.12; H, 4.57; Cl, 53.49.

2,3-Dichloronorbornene (195). A solution of 22.50 g (0.113 mol) of 196 in 25 ml of anhydrous dimethyl sulfoxide was added dropwise to a stirred, ice-cooled solution of 14.0 g (0.125 mol) of potassium tert-butoxide in 100 ml of anhydrous dimethyl sulfoxide. After heating on the steam bath for 1 hr, the solution was poured onto ice and water and was extracted with three 200-ml portions of pentane. The combined extracts were washed twice with water and were dried over anhydrous magnesium sulfate. The solution was filtered and the solvents were distilled. Distillation of the residue afforded 15.58 g (85%) of clear,
colorless liquid, bp 62-64° (9 mm). An analytical sample of 195 was obtained by preparative vpc at 100° on a 10 ft x 1/4 in 5% SE-30 on 60/80 Chromosorb W column and had the following spectral properties: ir (neat) 6.24, 7.73, 9.19, 9.36, 11.75, 12.63, and 13.80 μ; nmr (CCl₄/TMS) τ 7.04 (2H, m), 8.0-9.2 (6H, m); ρD¹⁷ = 1.5108.

**Anal.** Calcd for C₇H₆Cl₂: C, 51.57; H, 4.95; Cl, 43.49.
Found: C, 51.65; H, 5.02; Cl, 43.35.

Reaction of 2,3-Dichloronorbornene (195) with Phenyllithium. A solution of 4.00 g (24.5 mmol) of 195 and 80 ml (1.6 M, 125 mmol, Matheson Coleman & Bell) of phenyllithium solution in 70:30 benzene-ether was stirred at reflux for 8 days. The cooled reaction mixture was cautiously poured onto ice and water. The layers were separated and the aqueous layer was extracted with two 50-ml portions of ether. The combined organic layers were washed with water and saturated salt solution and dried over anhydrous magnesium sulfate. The solution was filtered and concentrated on a rotary evaporator to give 6.88 g of brownish-red residue. The residue was chromatographed on 571 g of basic, activity I alumina. The isolated products in order of elution with pentane were: 376 mg of 195, 440 mg (17% yield based on unrecovered starting material) of 2-phenylnorbornene (174), 56 mg (1%) of a 2-chloro-3-phenylnorbornene (197) and 1.508 g (28%) of 2,3-diphenylnorbornene (198). When biphenyl began to elute, the solvent was gradually changed to pure ether. The biphenyl (1.95 g) eluted completely with 5% ether-pentane and elution with 10% ether-pentane to ether gave 1.247 g of crude brown oil which resisted all attempts at purification and identification.
The structures of 174, 197, and 198 were assigned on the basis of spectral comparisons to authentic samples.

**exo-3-Chloronorcamphor (199).** This compound was prepared according to the procedure of McDonald and Tabor in 94% yield.

**exo-3-Chloro-2-phenylnorbornan-2-ol (200).** A stirred solution of 10.00 g (69.2 mmol) of 199 in 50 ml of anhydrous ether at 0°C was treated with 50 ml (1.6 M, 80 mmol) of phenyllithium in 70:30 benzene-ether which was added via a syringe at a rate slow enough to prevent reflux. After stirring at 25°C for 1.5 hr, the solution was cautiously poured onto ice and water and the layers were separated. The aqueous phase was extracted with two 100-ml portions of ether. The combined organic layers were washed with 50 ml each of water and saturated salt solution, and dried over anhydrous magnesium sulfate. After filtering, the solution was concentrated on a rotary evaporator and the residue was distilled through a 15 cm Vigreux column to give 12.04 g (78%) of colorless liquid, bp 109-112°C (0.35 mm). The spectral properties of 200 were: ir (neat) 2.84 (O-H), 2.24 (aromatic H), 6.23 (C=C), 9.38, 9.72, 12.27, 12.93, 13.36, and 14.32 μ; nmr (CCl₄/TMS) τ 2.74 (5H, m), 5.60 (1H, d, J = 2 Hz), 7.2-7.7 (4H, m), and 8.2-8.9 (5H, m); nD = 1.5570.

*Anal. Calcd for C₁₃H₁₅ClO: C, 70.11; H, 6.79; Cl, 15.92.*
*Found: C, 70.42; H, 6.80; Cl, 15.60.*

**2-Chloro-3-phenylnorbornene (197).** A solution of 10.0 g (45.0 mmol) of 200, 20 ml of benzene, and 0.5 ml of 85% phosphoric acid was refluxed for 1 hr in a 50-ml round-bottomed flask, equipped with a Dean
Stark trap. After cooling, the mixture was diluted with an equal volume of ether and washed with 100 ml of water. The aqueous wash was back-extracted with 25 ml of ether and the combined organic layers were washed with 50 ml each of saturated sodium bicarbonate solution, saturated salt solution, and dried over anhydrous magnesium sulfate. After filtering, the solution was concentrated on a rotary evaporator and the infrared spectrum of the residue indicated some alcohol remained. Distillation of the residue from potassium acid sulfate afforded 3.57 g (93%) of clear, colorless liquid, bp 101-105° (0.3 mm). An analytical sample of pure 137 was obtained by chromatography on basic alumina, activity I, and redistillation, bp 74-75° (0.05 mm). The spectral properties of 137 were: ir (neat) 3.21, 6.23, 9.24, 13.04, and 14.50 μ; nmr (CCl₄ solution) τ 2.3-3.0 (5H, m), 6.72 (1H, m), 7.08 (1H, m), and 8.0-9.0 (6H, m); n_D = 1.5813.

Anal. Calcd for C₁₃H₁₃Cl: C, 76.28; H, 6.40; Cl, 17.32.

Found: C, 76.12; H, 6.44; Cl, 17.34.

Calcd m/e: 204.0706.

Found: 204.0704.

2,3-Diphenylnorbornene (198). A solution of 1.00 g (5.38 mmol) of endo-3-phenylnorcamphor (201) in 5 ml of anhydrous ether was cooled in an ice bath. Six milliliters (1.6 M, 9.6 mmol) of phenyllithium in 70:30 benzene-ether was added dropwise via a syringe. After stirring at 25° for 15 min, the reaction mixture was cautiously poured onto ice and water and the layers were separated. The aqueous layer
was extracted with 25 ml of ether and the combined organic layers were washed with saturated salt solution and dried over anhydrous magnesium sulfate. The solution was filtered and concentrated on a rotary evaporator to give the crude alcohol \( 202 \), which was used without further purification.

A stirred mixture of 1.60 g of crude \( 202 \), 20 ml of benzene and 0.5 ml of 85% phosphoric acid was placed in a 50-ml round-bottomed flask, equipped with a Dean Stark trap. After refluxing for 1 hr, the solution was diluted with an equal volume of ether and was washed successively with 35 ml of water, 50 ml of saturated sodium bicarbonate, and 25 ml of saturated salt solution, and dried over anhydrous magnesium sulfate. The solution was filtered, and concentrated on a rotary evaporator. Because the infrared spectrum of the crude product showed some alcohol still present, the residue was distilled from potassium acid sulfate to give 0.67 g (51%) of liquid, bp 125-130° (0.35 mm). An analytical sample of \( 198 \) was obtained by chromatography through basic alumina, activity I, and redistillation, bp 101-103° (0.05 mm). The spectral properties of \( 198 \) were: ir (neat) 3.24, 6.24, 13.20, 13.51, and 14.42 \( \mu \); nmr (CCl\(_4\)/TMS) \text{t} 2.91 (m, 10H), 6.79 (m, 2H), 7.9-8.9 (m, 6H); \( n_D^{17} = 1.6205 \).

**Anal.** Calcd for \( \text{C}_{13}\text{H}_{18} \): C, 92.64; H, 7.36.

**Found:** C, 92.50; H, 7.44.

Calcd m/e: 246.1408.

**Found:** 246.1405.
Reaction of 2-Chloro-3-phenylborborene (197) with Phenyllithium. A stirred solution of 3.00 g (14.7 mmol) of 197 and 50 ml (1.6 M, 80 mmol, Matheson Coleman & Bell) of phenyllithium in 70:30 benzene-ether was refluxed for 5 days. After cooling to room temperature, the reaction mixture was cautiously poured onto ice and water and the layers were separated. The aqueous phase was extracted with three 50-ml portions of ether. The combined organic layers were washed with water and saturated salt solution and dried over anhydrous magnesium sulfate. After filtering, the solution was concentrated on a rotary evaporator and the residue was chromatographed on basic alumina, activity I, to give 1.51 g (42%, pentane eluted) of 2,3-diphenylborborene (198) which was identical in all respects to an authentic sample.
APPENDIX

Table III
Comparative Chemical Shifts of Bridgehead Hydrogens of Some Norbornane Derivatives

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REFERENCES


27. Two methods are reported to give reduction of only the central bond of the bicyclo[1.1.0]butane moiety.28,29


34. Kindly provided by Mr. H. R. Drewes.


39. The structure was conclusively established by comparison with an authentic sample.

40. Kindly provided by Dr. William Sheppard of the duPont Co.


45. In some respects there is a similarity between the stepwise mechanism for the rearrangement of $^{15}$ proposed in Scheme III and that which has been suggested for the metal catalyzed rearrangement of tri-tert-butylprismane [K. L. Kaiser, R. F. Childs, and P. M. Maitlis, J. Amer. Chem. Soc., 93, 1270 (1971)]. Both mechanisms use the transition metal catalyst as an electron acceptor. For an additional discussion see J. E. Byrd, L. Cassar, P. E. Eaton, and J. Halpern, Chem. Commun., 40 (1971).


47. This is the pathway taken in the "normal" protic acid catalyzed reaction of $^{15}$. 
Control experiments demonstrated that the dimer could be recovered unchanged from methanol and that the addition of enough sodium methoxide to make the reaction mixture strongly basic did not stop the reaction. Hence, it would appear that the observed reaction was not due to the formation of some new catalyst from methanol and rhodium dicarbonyl chloride dimer nor by generation of a Brønsted acid in the solution.


51. Alternately, $\text{74}$ could be formed by homoallylic participation of the double bond in $\text{73}$. A multistep mechanism which involves initial cleavage of the central bond of $\text{31}$ could also be constructed to explain the origin of $\text{38}$.

52. An infrared spectrum of authentic $\text{72}$ was kindly provided by Professor W. Dauben.

53. Compound $\text{77}$ could also be obtained by treatment of the mixture of $\text{78}$ and $\text{79}$ with $\text{p}$-toluenesulfonyl chloride in pyridine followed by refluxing the crude product in methanol.


56. From one point of view this rearrangement can be classified as a cyclopropyl to allyl type isomerization. Although such transition metal complex promoted rearrangements are known, they generally do not occur readily at room temperature. For typical examples see ref. 18, 19b, 19e, 19g; K. G. Powell and F. J. McQuillen, *Chem. Commun.*, 931 (1971); D. M. Roundhill, D. N. Lawson, and G. Wilkinson, *J. Chem. Soc. (A)*, 845 (1968); and R. J. Ouellette and C. Levin, *J. Amer. Chem. Soc.*, 90, 6889 (1968).

57. The nature of the intermediate formed in the first step of the cleavage has not been determined. It seems likely that the transition metal must be strongly associated with the intermediate (whether $\text{81}$, $\text{86}$, or $\text{87}$ is the intermediate of importance). Hence, the structures shown for $\text{81}$, $\text{86}$, and $\text{87}$ are only meant to show which bonds were broken, not how they were broken nor the role of the transition metal complex.
58. W. Greenlee, personal communication.

59. This is essentially the procedure of W. Roth and M. Martin, Justus Liebig's Ann. Chem., 702, 1 (1967).


62. The nmr assignments are those of Roth and Martin (ref. 59).

63. Measurements of cyclopentene, cyclohexene, and cycloheptene gave ratios of 1:3.31, 1:4.49, and 1:5.72 (average of three determinations), respectively, on the nmr spectrometer used for these analyses. These values indicate that the ratio of 1:3.21 represents complete scrambling of the label.


66. If the reaction solution containing 3-methylenecyclohexene (28), and 24 was allowed to remain in contact with the rhodium dicarbonyl dimer for long periods of time, some changes were noted in the nmr spectrum of 24. However, this was most likely due to interactions of 28 and 24 and not due to an intermediate in the reaction of 15 and rhodium dicarbonyl chloride dimer. If the solution of 24 was vacuum transferred as soon as 15 had completely disappeared, no change in the nmr spectrum of 24 was observed.

67. Within the limits of analysis by vpc, no methyl ether could be detected from the reaction of 24 with rhodium dicarbonyl chloride dimer in methanol.

68. The postulate of the formation of a hydride intermediate in the isomerization of 24 was supported by recent observations from the laboratory of Prof. K. B. Wiberg. These workers observed that the use of methanol-0-d as solvent for this isomerization of 24 led to the incorporation of deuterium into the cyclopentene. K. B. Wiberg, personal communication.

70. For a recent proposal analogous to this addition see R. Noyori, T. Suzuki, and H. Takaya, J. Amer. Chem. Soc., 93, 5896 (1971).


73. For a recent sigma-rho study of silver ion promoted isomerizations of highly strained polycyclics, see G. F. Koser, Chem. Commun., 388 (1971).


98. H. Shechter, personal communication to P. G. Gassman.


102. The formation of optically active products in this reaction also adds additional evidence against the "norbornyne" mechanism. Presumably, norbornyne would be symmetrical and loss of optical activity would be expected if it were an intermediate.


105. The term "coupling product" will be used henceforth in order to expedite the explanation of product types. However, its use is strictly in the formal sense since no chemical evidence was obtained to eliminate the other mechanistic possibilities.

106. This is a common reaction of this type of bicyclic carbene. For typical examples see (a) J. Bredt and W. Holz, J. Prakt. Chem., 203, 133 (1917); (b) A. Angeli, Gazz. Chem. Ital., 24, II, 317 (1894); (c) J. W. Powell and M. C. Whiting, Tetrahedron, 7, 305 (1959); (d) P. Clarke, M. C. Whiting, G. Papenmeier, and W. Reusch, J. Org. Chem., 27, 3356 (1962).

107. Alfa Inorganics Inc., 2.2 M phenyllithium in 70:30 benzene-ether.
108. No ε could be accurately calculated due to overlap of an absorption presumably due to the aromatic hydrogens.


112. The tentative assignment of the stereochemistry of 177 was based on a comparison of its nmr spectrum with those of exo- and endo-5-hydroxybicyclo[2.1.1]hexane.


120. For a comparison of chemical shifts of methoxyl hydrogens for other 7,7-dimethoxynortricyclyl derivatives see J. L. Marshall, Ph.D. Thesis, The Ohio State University, 1966.


123. Kindly provided by Mr. J. Valcho.

124. Due to the nature of reactions of 125 and 127 with phenyllithium, several observations should be noted. Large amounts of biphenyl were produced in these reactions which complicated the isolation procedure. Fortunately, the products isolated eluted from basic alumina with pentane before the biphenyl. Continued elution with more polar solvents gave highly aromatic compound(s) as oils which could not be crystallized or purified by other means. Therefore, the low yields of 174, 197, and 193 do not preclude their instability under the reaction conditions. Furthermore, other products could initially be formed and be labile under the reaction conditions. These difficulties inherent in the reactions themselves and in the isolation techniques used, would severely restrict the use of an excellent trapping reagent, such as diphenylisobenzofuran.


127. The yield reported is an average of duplicate runs as determined by VPC at 25° on a 15 ft x 1/8 in 20% DC-Silicone 200, 1000 c.s. on 60/80 Columnpak column vs an internal standard.

128. A diazomethane solution, which was prepared from 20 g of nitroso-methylurea, 300 ml of ether and 60 ml of 45% potassium hydroxide solution, and dried over potassium hydroxide pellets overnight, was stirred over 8 ml of 1 N sodium deuterioxide in deuterium oxide and 6 ml of tetrahydrofuran for 3 hr at 0°. The solution was decanted and the process was repeated. The etheral solution was then dried over anhydrous potassium carbonate and found to be 0.30 M in dideuteriodiazomethane by standard titration. This procedure was based on an excellent new preparation of dideuteriodiazomethane, P. G. Gassman and W. Greenlee, procedure submitted to Org. Syn.

129. An 80% yield based on dideuteriodiazomethane gives 27.6 mmol of reagent 23.61


