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DISSERTATION

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

By

Thaliyil V. Rajan Babu, B.Sc (Special), M.Sc.

* * * * *

The Ohio State University
1976

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INTRODUCTION

The present research involves elaboration of the chemistry of bicyclo[4.2.1]nona-2,4,7-trien-9-yl and bicyclo[4.2.2]deca-2,4,9-trien-7-yl derivatives and subsequent intermediates.

Bicyclo[4.2.1]nona-2,4,7-trien-9-yl anion has been predicted to be bicycloaromatic and stabilized. Generation, capture and reactions of bicyclo[4.2.1]nona-2,4,7-trien-9-yl anion and the isomeric tricyclo[6.1.0.0^4,9]nona-2,6-dien-5-yl (homosemibullvalenyl) and tricyclo[3.3.1.0^4,6]nona-2,7-dien-9-yl (barbaraly) anions are thus to be investigated to establish the interrelationships of these species and their relevance to the concept of bicycloaromaticity. Bicyclo[4.2.1]nona-2,4,7-trien-9-yl halides and related derivatives are possible precursors to the above anions. Synthesis of these precursors via homolytic and heterolytic substitution reactions at C-9 of the bicyclo[4.2.1]nona-2,4,7-triene system might, in addition to the synthetic utility, also provide important information about the bicyclo[4.2.1]nona-2,4,7-trien-9-yl cation and
radical.

\[ \text{The chemistry of bicyclo[4.2.1]nona-2,4,7-trien-9-ylidene and bicyclo[4.2.2]deca-2,4,9-trien-7-ylidene is to be investigated in order to obtain detailed information about the interactions of their } \pi \text{-systems with carbenic centers and the effects of these and other transannular interactions on the rearrangements of these carbenes. Barbaralylidene is isomeric with bicyclo[4.2.1]nona-2,4,7-}\]

\[ \text{trien-9-ylidene and these carbenes may reveal an interesting degenerate relationship.} \]
Syntheses of bicyclo[4.2.1]nona-2,4,7-trien-9-yl derivatives were first reported in 1963. Thus lithium cyclo-octatetraenide reacts with acid chlorides to give 9-hydroxy-bicyclo[4.2.1]nona-2,4,7-triene and its derivatives (Equation 1) along with acylation products.¹


Analogously, reactions of cyclooctatetraene dianion with acetic and benzoic anhydrides yield syn-9-hydroxy-9-methylbicyclo[4.2.1]nona-2,4,7-triene and syn-9-hydroxy-9-phenylbicyclo[4.2.1]nona-2,4,7-triene, respectively²,³ (Equation 2).


\[
\text{\textcircled{2}Li}^\oplus \xrightarrow{\text{RCOCR}} \text{HO}
\]

\[
R = \text{CH}_3, \text{C}_6\text{H}_5
\]

Treatment of cyclooctatetraene dianion with dimethylcarbamoyl chloride in ether at 5°C yields, after hydrolysis, bicyclo[4.2.1]nona-2,4,7-trien-9-one⁴ (Equation 3).


\[
\text{\textcircled{2}Li}^\ominus + (\text{CH}_3)_2\text{NCOCl} \xrightarrow{1. -\text{2LiCl, 5°C}} \xrightarrow{2. \text{H}_2\text{SO}_4} \quad \text{E}^\ominus
\]
Bicyclo[4.2.1]nona-2,4,7-trien-9-yl cation and anion have evoked considerable interest in recent years because of the potential homoaromatic and bicycloaromatic interactions in these species.5

Thus using molecular orbital symmetry methods to extend the concept of homoaromaticity ($2\pi$-bridges) to bicycloaromaticity ($3\pi$-bridges), Goldstein and Hoffmann predicted that bicyclo[4.2.1]nona-2,4,7-trien-9-yl cation to be bicycloaromatic and stabilized.5a Several studies on the generation and rearrangement of this cation have since appeared.4,7,8 Two distinct paths of rearrangement have been described for the cation (Equations 4 and 5).

\[
\begin{align*}
(4) & \\
(5) & \\
Z & = D, H, C_6H_5, \text{and } CH_3
\end{align*}
\]
Mechanisms of the type in Equation 4 are presumed in (1) the reaction of bicyclo[4.2.1]nona-2,4,7-trien-9-one with boron trifluoride to give 1-indanone\(^4\) (Equation 6), (2) the displacement of syn-9-hydroxy-9-phenylbicyclo-[4.2.1]nona-2,4,7-triene by thionyl chloride\(^7\) in pyridine (Equation 7), and (3) cationic decomposition of 9-diazo-bicyclo[4.2.1]nona-2,4,7-triene\(^8\) (Equation 8) as derived from its precursor \(\text{p-tosylhydrazone} \).
Mechanisms analogous to that in Equation 5 are apparently involved in the conversions of syn- and anti-bicyclo[4.2.1]nona-2,4,7-trien-9-yl p-toluenesulphonates and of di-syn-bicyclo[4.2.1]nona-2,4,7-trien-9-yl sulfite to indene. This conclusion is based on the position of deuterium in the products when 9-deuterated substrates are employed for the reactions. Similarly, acid-catalyzed reactions of syn-9-hydroxy-9-phenylbicyclo[4.2.1]nona-2,4,7-triene and 9-methylenebicyclo[4.2.1]nona-2,4,7-triene give the corresponding 2-substituted indenes.

Syn-9-substituted bicyclo[4.2.1]nona-2,4,7-trienes resist nucleophilic displacement. Thus attempts to synthesize 9-substituted derivatives from bicyclo[4.2.1]nona-2,4,7-trien-9-yl tosylate give only indene (Equation 9). This reaction probably proceeds through the mechanism shown
in Equation 5.

\[
\text{TsO} \xrightarrow{I^-, Br^-, CN^- \text{ or } N_3^-} \text{Bicyclo}[4.2.1]nona-2,4,7-trien-9-yl anion}
\]

Bicyclo[4.2.1]nona-2,4,7-trien-9-yl anion is predicted to be bicycloaromatic.\(^5\) There is little information, however, with respect to the detailed properties of the bicyclic carbanion. Wolff-Kishner reduction of bicyclo[4.2.1]-nona-2,4,7-trien-9-one is reported to yield tricyclo-[6.1.0.0^4,9]nona-2,6-diene (homosemibullvalene) as the exclusive product\(^1\) (Equation 10).


In this reduction it is assumed that the initially formed bicyclo[4.2.1]nona-2,4,7-trien-9-yl anion rearranges to homosemibullvalenyl anion followed by proton capture.

Wolff-Kishner reduction of bicyclo[4.2.1]nona-2,4,7-trien-9-one hydrazone in the presence of potassium t-butoxide and t-butanol in dimethyl sulfoxide results in two different products: bicyclo[4.2.1]nona-2,4,7-triene and 2-methylbicyclo[4.2.1]nona-2,4,7-triene (Equation 11).\(^9\)
The difference in product distribution is thought to be due to the ability of dimethyl sulfoxide to stabilize the initially formed carbanion and make it available for proton capture. No such stabilization is available in diethylene glycol and the carbanion undergoes rearrangement to the isomeric homosemibullvalenyl anion.

\[
\text{(a) NH}_2\text{NH}_2 \xrightarrow{\text{diethylene glycol 210°}} \text{cyclic anion} \\
\text{or} \\
\text{(b) 1. NH}_2\text{NH}_2 \\
\text{2. KOBu}^+\text{/DMSO} \xrightarrow{\text{b) DMSO}} \text{isomeric anions} \quad \text{(11)}
\]

Bicyclo[4.2.1]nona-2,4,7-trien-9-one provides access to other polycyclic systems. Thus photolysis of the ketone in benzene sensitized by Michler's ketone gives barbaralone in 60-70% yield (Equation 12).

\[
\text{hv, benzene} \xrightarrow{\text{PS}^*} \text{keto} \quad \text{(12)}
\]
Diazomethane converts the ketone to the ring expansion product, bicyclo[4.2.2]deca-2,4,9-trien-7-one along with spiro-bicyclo[4.2.1]nona-2,4,7-trien-9,2'-oxirane (Equation 13).\(^{4,13}\)

\[ \text{CH}_2\text{N}_2\text{LiCl} \rightarrow \text{bicyclo[4.2.2]deca-2,4,9-trien-7-one} + \text{spiro-bicyclo[4.2.1]nona-2,4,7-trien-9,2'-oxirane} \ (13) \]

Many derivatives\(^{13,14}\) of bicyclo[4.2.2]deca-2,4,9-triene have been synthesized from bicyclo[4.2.2]deca-2,4,9-trien-7-one as summarized in Scheme I.


Scheme I

Reactions of bicyclo[4.2.2]deca-2,4,9-trien-7-one
Bicyclo[4.2.2]deca-2,4,7,9-tetraene is an important source of bishomoaromatic ions via electrophilic reactions. In super acid medium the tetraene shows nmr characteristics of a highly delocalized ion$^{15,16}$.

![Chemical structure](image)

---


Among other related longicyclic systems, none has been studied more extensively than the bicyclo[3.2.2]nonatrien-2-yl anion.$^{5b,17,18,19,20}$ The nmr spectrum of the anion immediately after preparation (Equation 14) shows no scrambling of deuterium. Deuterium scrambling through a nine carbon degenerate rearrangement is observed, however, on quenching the anion after 2 days (Equation 14). This degeneracy can be formulated as a series of 1,2-vinyl shifts.
or through the intermediacy of the barbaralyl anion.\textsuperscript{5b}


\[
\begin{align*}
\text{Na/K, DME} & \quad \xrightarrow{25^\circ C} \quad \text{D (14)} \\
\end{align*}
\]

The nmr spectrum of the anion indicates it to be a delocalized structure:

There is considerable disagreement whether homoaromatic or longicyclic interaction is responsible for the stability of bicyclo[3.2.2]nonatrien-2-yl anion.\textsuperscript{17,18}

Barbaralyl anion generated by the reactions of alkali metals
with 9-halobarbaralane (Br, Cl) undergoes quantitative conversion to the bicyclo[3.2.2]nona-3,6,8-trien-2-yl anion. The isomerization is especially interesting since the bicyclo[3.2.2]nona-3,6,8-trien-2-yl cation rearranges to the triply degenerate barbaralyl cation and these transformations provide the first examples of what has been termed "reversible charge control" in homoconjugated topologies (Equation 15).


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While there has been significant work on the interrelationships of carbanions and carbénium ions of the structural types discussed above, very little has been reported in the carbene area.

7-Norbornenylidene has been predicted to be homoallylically stabilized\textsuperscript{23} and the intramolecular chemistry of this specie is fairly well established.\textsuperscript{24} The proposed
mechanisms for isomerization of the carbene are summarized in Scheme II.


Vinyl migration is the major process in the reactions of 7-norbornenylidenes (R=H, 67%; R=CH₃, 77%). Mechanistically this can be explained by participation of the π-electrons of the double bond with the empty orbital of the carbene center (π-route) or by a direct migration of the vinyl group from C₁ to C₇ via a σ-route (Scheme II).

**Scheme II**

Rearrangements of 2-norbornen-7-yldienes

![Scheme II Diagram]

- Vinyl migration: R = CH₃, H
- ethano migration: R = CH₃, H
Bicyclo[4.2.1]nona-2,4,7-trien-9-ylidene has been presumed to be generated by thermolysis and photolysis of the sodium salt of the corresponding ketone tosylhydrazone. The major product of the decomposition is indene (Equation 16). This carbene is of particular interest in that it is potentially capable of undergoing carbene-carbene (degenerate) rearrangements (Equation 17).

\[
\begin{align*}
\text{Na} & \rightarrow & \text{Na} \\
\text{NNTs} & \rightarrow & \text{NNTs} \\
hv & \rightarrow & \text{hv} \\
(\Delta) & \rightarrow & (\Delta)
\end{align*}
\]

There are many interesting questions concerning the interrelationships of bicyclo[4.2.1]nona-2,4,7-trien-9-ylidene and its \( \text{C}_9\text{H}_8 \) isomeric carbenes, their degeneracy, and multiplicities, which however, remain to be answered (Equation 17).

\[
\begin{align*}
\pm & \rightarrow & \pm \\
\pm & \rightarrow & \pm \\
\pm & \rightarrow & \pm \\
(17)
\end{align*}
\]
RESULTS AND DISCUSSION

1. Study of the Wolff-Kishner Reduction of Bicyclo[4.2.1]nona-2,4,7-trien-9-one and Syntheses of Possible Precursors of Bicyclo[4.2.1]nona-2,4,7-trien-9-yl Anion (2)

Upon initiation of the present research, there was little information on the properties of bicyclo[4.2.1]nona-2,4,7-trien-9-yl anion (2). Attempts to prepare ready precursors such as syn and anti-9-halobicyclo[4.2.1]nona-2,4,7-trienes to 2 were unsuccessful.4,9 The only investigation related to anion 2 is a study of the Wolff-Kishner reduction of bicyclo[4.2.1]nona-2,4,7-trien-9-one (1).9,12 Thus ketone 1 on reaction with hydrazine hydrate and potassium hydroxide in diethylene glycol at 210° and distillation yields tricyclo[6.1.0.0^3]nona-2,6-diene (4, homosemibullvalene, Equation 19). In this reduction it is presumed that trienyl anion 2 isomerizes to the homosemibullvalenyl anion (3) which upon protonation

\[
\begin{align*}
1 \xrightarrow{\text{hydrazine hydrate, KOH, diethylene glycol}} & 2 \\
& \xrightarrow{\text{ROH}} 3 \\
& \xrightarrow{\text{H_2O, H_2N NH_2}} 4
\end{align*}
\]

(19)

gives homosemibullvalene (4).

In a subsequent study in this laboratory by Sanders9 the hydrazone of bicyclo[4.2.1]nona-2,4,7-trien-9-one
(5) was found to react with potassium \( t \)-butoxide and \( t \)-butanol in dimethyl sulfoxide to yield bicyclo[4.2.1]-nona-2,4,7-triene (6) and 2-methylbicyclo[4.2.1]nona-2,4,7-triene (7) in varying proportions depending on the reaction conditions (Equation 20, Table I).

\[
\text{N-NH}_2
\]

\[
\begin{align*}
\text{N-H}_2 & \quad \text{KOBu}^+ + \text{HOBut}^+ \\
\text{5} & \quad \text{DMSO} \\
\rightarrow & \quad \text{3} \\
\text{6} & \quad \text{9} \\
\text{7} & \quad \text{CH}_3
\end{align*}
\]

\text{(20)}

Table 1: Wolff-Kishner Reduction of Bicyclo[4.2.1]nona-2,4,7-trien-9-one (1).

<table>
<thead>
<tr>
<th>Experimental Conditions</th>
<th>4(%)</th>
<th>6(%)</th>
<th>7(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrazone 5, KOBu(^t), 25°C, DMSO</td>
<td>3.0</td>
<td>37.6</td>
<td>5.1</td>
</tr>
<tr>
<td>hydrazone 5, KOBu(^t), 2 equiv HOBut(^t), 25°C, DMSO</td>
<td>-</td>
<td>25.1</td>
<td>-</td>
</tr>
<tr>
<td>hydrazone 5, KOBu(^t), 74°C, DMSO</td>
<td>1</td>
<td>49.2</td>
<td>9.7</td>
</tr>
<tr>
<td>hydrazone 5, KOBu(^t), 2 equiv HOBut(^t), 74°C, DMSO</td>
<td>-</td>
<td>69.0</td>
<td>trace</td>
</tr>
<tr>
<td>Ketone 1, hydrazine hydrate, KOH, ethylene glycol</td>
<td>93%</td>
<td>6%</td>
<td>-</td>
</tr>
</tbody>
</table>

The different product distribution in the two Wolff-Kishner reductions is of considerable interest. This difference was thought to be due to the difference in the solvation of the carbanions (2 and 3) involved in the two reactions.
media. It was argued that dimethyl sulfoxide is very capable of solvating carbanions and thus stabilization of carbanion \( \text{2} \) would allow its capture by a proton from the solvent. Diethylene glycol on the other hand is not capable of such stabilization and hence initially formed \( \text{2} \) would rearrange to homosemibullvalenyl anion (3) followed by protonation to give homosemibullvalene (4).

As seen from Table I, the proportion of the methylated hydrocarbon \( \text{7} \) (Equation 20) increases with decreasing amounts of t-butanol in the medium. This is due to the fact that the concentration of dimsyl potassium essential for the formation of \( \text{7} \) increases with decreasing amounts of t-butanol.

The conversion to 2-methylbicyclo[4.2.1]nona-2,4,7-triene (7) was explained by addition of dimsyl potassium to the diene bridge of a Wolff-Kishner intermediate followed by elimination of methylsulfenol (CH\(_3\)SOH), subsequent rearrangement, and reduction such as shown in Equation 21.

A mechanism for formation of \( \text{7} \) involving methylation of bicyclo[4.2.1]nona-2,4,7-triene (6) is ruled out since the treatment of 6 with potassium t-butoxide and t-butanol in dimethyl sulfoxide under Wolff-Kishner conditions fails to yield 2-methylbicyclo[4.2.1]nona-2,4,7-triene (7).
The present research was initiated as a study of the mechanism of Wolff-Kishner reduction of 1. A particular objective was to explain further the difference in product distribution when the reaction is carried out in diethylene glycol and in dimethyl sulfoxide. It was also of interest to intercept by various methods one or more of the intermediates involved in the reduction. Reduction of 8 in media which allow deuterium capture might provide more definitive evidence concerning the intermediacy of the bicyclo[4.2.1]nona-2,4,7-trien-9-yl anion (2).
A study was thus made of deuterium exchange during Wolff-Kishner reduction of bicyclo[4.2.1]nona-2,4,7-trien-9-one hydrazone-N-d$_2$ (8). Deuterated hydrazone 8 is readily prepared from hydrazone 5 and excess deuterium oxide in methylene chloride. By repeated treatment ~80% deuterium incorporation into 5 is conveniently achieved. Hydrazono-N-d$_2$ 8 on reaction with potassium t-butoxide and two equivalents of t-butanol-0-d in dimethyl sulfoxide-d$_6$ at 74°C gives bicyclo[4.2.1]nona-2,4,7-triene and 2-methyl-bicyclo[4.2.1]nona-2,4,7-triene with extensive deuterium incorporation (Equation 22). The deuterium content of the trienes was determined by nmr methods. The bridgehead protons of the trienes were assumed to undergo little or no exchange at all and were used as standards.$^{25}$ It was

found that 6 forms with 80% exchange on its C_2-C_5 diene bridge, 0% on the C_7-C_8 monoene unit, and 100% at the apical C-9 positions. Similar results are obtained for 2-methylbicyclo[4.2.1]nona-2,4,7-triene (7) with the exception that exchange of the diene hydrogens is about 87% (Equation 22).

Treatment of bicyclo[4.2.1]nona-2,4,7-triene (6) with potassium t-butoxide (1 equiv) and t-butanol-O-d (1 equiv) at 74°C under conditions identical to the Wolff-Kishner reduction of hydrazone 8 fails to effect any deuterium exchange into the triene. Reaction, however, of hydrocarbon 6 in the much stronger base, lithium cyclohexylamide in cyclohexylamine-N-d_2, results in extremely low (<7%) recovery of triene 6 with 89% deuterium on the monoene, 55% on the diene and 0% at the C-9 positions (Equation 23).

\[
\begin{align*}
\text{KOBu}^t/\text{DOBu}^t & \quad \text{No Exchange (23)} \\
\text{DMSO-d}_6, 74^\circ &
\end{align*}
\]

89% D on C_7-C_8
55% D on C_2-C_5
Attempts to exchange the olefinic protons of hydrazone 5 in dimethyl sulfoxide-\textsubscript{d\textsubscript{6}} containing \textsubscript{t}-butanol-0-d and potassium \textsubscript{t}-butoxide proved unsuccessful due to problems in recovering hydrazone 5 from the medium.

Therefore, to evaluate the effects of the \textsubscript{ND\textsubscript{2}} moiety in hydrazone 8 on the exchange of the diene bridge, bicyclo[4.2.1]nona-2,4,7-trien-9-one dimethylhydrazone (9) was stirred with potassium \textsubscript{t}-butoxide and \textsubscript{t}-butanol-0-d in dimethyl sulfoxide at room temperature for several days. There was no incorporation of deuterium into 9 as revealed by the nmr spectra of various samples (Equation 24).

\textit{It thus became apparent that at least one intermediate in the Wolff-Kishner reduction of hydrazone 8 is responsible for the selective exchange of the protons of the C\textsubscript{2}-C\textsubscript{5} diene bridge during the formation of 6d and 7d.}

A possible mechanism for Wolff-Kishner reduction of the hydrazone (5) of bicyclo[4.2.1]nona-2,4,7-trien-9-one (1) is shown in Scheme III. One of the intermediates in
Scheme III

Mechanism of Wolff-Kishner Reduction of Bicyclo[4.2.1]-H
nona-2,4,7-trien-9-one (1)

\[ \text{ROH} \xrightarrow{\text{BH}} \text{ROH} \]
this mechanism is the monoalkyldiimide anion \( \overset{\sim}{11} \). Anion \( \overset{\sim}{11} \) could add to its diene system and then give pyrazoline \( \overset{\sim}{13} \) which might undergo further reactions and even be involved in the Wolff-Kishner reduction.

Establishment of the intermediacy and the chemistry of pyrazoline \( \overset{\sim}{13} \) might be significant in understanding the mechanism of Wolff-Kishner reduction of bicyclo[4.2.1]-nona-2,4,7-trien-9-one \( \overset{\sim}{1} \). Attempts were made to isolate such an intermediate by running the Wolff-Kishner reaction at lower temperatures and modifying the work up procedure. Indeed bicyclo[4.2.1]nona-2,4,7-trien-9-one \( \overset{\sim}{1} \) on treatment with hydrazine hydrate at 120° for 2 hr followed by extractive work up (not distillation!) with petroleum ether gives crystalline 2,3-diazatricyclo[6.3.0.0²⁴]undeca-2,5,9-triene \( \overset{\sim}{13} \), Equation 25) in excellent yields (75%). The structure of \( \overset{\sim}{13} \) is assigned from spectral data and from reactions to be described subsequently. Pyrazoline \( \overset{\sim}{13} \) gives a correct elemental analysis and an exact
mass for the molecular ion. Its spectral properties are:
ir, 1630 cm\(^{-1}\) (azo); uv (\(\chi_{\text{cyclohexane}}\)) 220, 340 nm, (E\(_{\text{max}}\) 4100, 360); nmr, \(\delta\) 5.92-5.12 (m, 5H, olefinic H on C-5, -6, -9, -10, H on C-4), 4.97 (m, 1H, H on C-1), 3.62-1.82 (m, 4H, H on C-7, -8, -11).

A similar reaction has been observed previously in Wolff-Kishner reduction of bicyclo[4.2.2]deca-2,4,9-trien-7-one (16, Equation 26) to yield 2,3-diazatricyclo-
[6.3.1.0\(^{1,4}\)]dodeca-2,5,9-triene.\(^{13a}\)

\[\text{Pyrazoline 13 undergoes thermal extrusion of nitrogen to give tricyclo[6.1.0.0\(^{4,9}\)]nona-2,6-diene (4) (homosemi-bullvalene) in near quantitative yield on heating in diethylene glycol at 200°C for 30 min. The product was collected by distillation and analyzed by gas chromatography and nmr spectroscopy. The structure was confirmed by comparison with an authentic sample. Pyrazoline 13 is stable to potassium hydroxide in diethylene glycol up to 180°C. These experiments show that formation of pyrazoline 13 followed by thermal extrusion of nitrogen may be the}
source of tricyclo[6.1.0.0^{4,9}]nona-2,6-diene (4, homosemi­
bullvalene) in the Sakai-Winstein experiment (Equation 19). Pyrazoline \( \sim 13 \) also loses nitrogen on photolysis in pentane using a Hanovia medium pressure lamp through pyrex to give homosemibullvalene (4) in quantitative yield (Equation 27).

\[
\begin{align*}
\text{N} & \quad \text{H} \\
\text{N} & \quad \text{N} \\
13 & \quad \Delta \text{ or hv} \\
-\text{N}_2 & \quad \rightarrow \\
\text{4} & \quad \rightarrow
\end{align*}
\]

The thermolysis and photolysis of \( \sim 13 \) to give \( \sim 4 \) as the exclusive product further support the assigned struc­
ture of \( \sim 13 \). An alternate structure of the pyrazoline would be 2,3-diazatricyclo[6.3.0.0^{4,11}]undeca-2,6,9-triene (\( \sim 13' \)) arising via proton capture of \( \sim 12 \) at a different carbon atom. Pyrazoline \( \sim 13' \) would, on nitrogen extrusion, give tricyclo[4.3.0.0^{2,9}]nona-3,6-diene (\( \sim 14 \)) which has characteristic nmr absorptions at \( \delta 6.85 \) (m, 2H). The absence of nmr signals below \( \delta 6.05 \) for products derived from the thermolysis or photolysis of the pyrazoline clearly rules out a structure \( \sim 13' \).
The intermediacy of pyrazoline 13 in Wolff-Kishner reductions of hydrazone 5 in dimethyl sulfoxide is indeed demonstrated by following the reaction system in its early stages by thin layer chromatography on silica gel. A major component, along with hydrazone 5, is easily identified as pyrazoline 13 by comparison of its Rf values with an authentic sample.

Further, though pyrazoline 13 is stable to potassium hydroxide in diethylene glycol, when treated with potassium t-butoxide in the presence of t-butanol in dimethyl sulfoxide, (which is a more basic medium), bicyclo[4.2.1]-nona-2,4,7-triene (6) and 2-methylbicyclo[4.2.1]nona-2,4,7-triene (7) are obtained (Equation 28). This result is identical to that previously observed in Wolff-Kishner reduction of bicyclo[4.2.1]nona-2,4,7-trien-9-one hydrazone (5) and supports the intermediacy of pyrazoline 13 in the Wolff-Kishner reduction. A possible mechanism for formation of 6 is shown in Equation 28. With potassium t-butoxide in dimethyl sulfoxide (pKa 27), pyrazoline 13 can undergo elimination to give monoalkyldiimide anion
which loses nitrogen in a fast step to yield bicyclo-[4.2.1]nona-2,4,7-trien-9-yl anion (2) and subsequently by protonation.

\[
\begin{align*}
\text{KOH/diethylene glycol} \quad \xrightarrow{\text{No reaction}} \\
\end{align*}
\]

Formation of 2-methylbicyclo[4.2.1]nona-2,4,7-triene (7) from pyrazoline 13 raises the possibility of a new mechanism (Equation 29) for formation of the methylated triene besides the one previously discussed (Equation 21). This mechanism involves formation of intermediate 15 via displacement of the azo moiety in 13 by dimsyl potassium. Reduction of 15 by loss of nitrogen and protonation of the intermediate carbanion followed by (or concurrent with) base-assisted loss of methylsulfenol (CH$_3$SOH) and further rearrangement completes a sequence of events that results in 7 (Equation 29).
The intermediacy of pyrazoline 13 also provides an attractive mechanistic rationale for the selective exchange of hydrogens on the C₂⁻C₅ diene moiety in Wolff-Kishner reduction of bicyclo[4.2.1]nona-2,4,7-trien-9-one hydrazone -N-d₂ (8). This aspect of the reaction mechanism is to be discussed later.

Pyrazoline 13, via reaction with potassium t-butoxide in dimethyl sulfoxide serves as a convenient precursor of bicyclo[4.2.1]nona-2,4,7-trien-9-yl anion (2) and anion 2 can be captured by deuterium if deuterated reagents are employed for reduction. Stereochemistries of the deuterated reduction products, bicyclo[4.2.1]nona-2,4,7-triene (21, Scheme IV) and 2-methylbicyclo[4.2.1]nona-2,4,7-triene (22), are unambiguously assigned by nmr methods. Bicyclo[4.2.1]nona-2,4,7-triene²⁶ (6), inter alia,
shows a doublet of a triplet for the anti-hydrogen (Ha at C-9) at δ 1.94, a broad doublet for syn-hydrogen at δ 1.32 and a broad triplet for C₁ and C₆ hydrogens (bridgehead) at 3.05.

The pmr spectrum of deuterated bicyclo[4.2.1]nona-2,4,7-trienes (21 and 22) isolated from reaction of pyrazoline 13 with potassium t-butoxide and t-butanol-O-d in dimethyl sulfoxide-d₆ reveals the following features: the doublet of triplets at δ 1.94 for the anti-9-H collapses into a broad triplet and the doublet at δ 1.32 due to syn-9-H collapses into a broad singlet; together the resonance integrates to a total of about one proton. The bridgehead protons which appear at δ 3.05 now become a broad singlet from an original triplet. This nmr spectrum
is consistent with the formation of bicyclo[4.2.1]nona-2,4,7-trien-9-yl anions 19 and 20, and capture of these anions at C-9, leading to a mixture of syn- and anti-9-deuterated bicyclo[4.2.1]nona-2,4,7-trienes (21 and 22, Schème IV). The ratios of syn to anti capture products are shown in Table II.
### TABLE II

Deuterium incorporation in Wolff-Kishner and related reactions of bicyclo[4.2.1]nona-2,4,7-triene-9-one hydrazone-N-d$_8$ (8) and 2,3-diazatricyclo[6.3.0.0$^4$11]undeca-2,5,9-triene (13).

<table>
<thead>
<tr>
<th>Reaction Conditions</th>
<th>Products</th>
<th>%</th>
<th>syn</th>
<th>anti</th>
<th>Total H at C-9 ($\pm 0.05$)</th>
<th>H on diene ($\pm 0.05$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13 KOBu$^+$, HOBu$^+$, DMSO, 74°C, 10hr</td>
<td>Triene 20</td>
<td>75</td>
<td>1.00</td>
<td>1.00</td>
<td>4.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Methyltriene 21</td>
<td>20</td>
<td>1.00</td>
<td>1.00</td>
<td>3.00</td>
<td></td>
</tr>
<tr>
<td>13 KOBu$^+$, DOBu$^+$, DMSO-d$_6$, 74°C, 10hr</td>
<td>Triene 20</td>
<td>50</td>
<td>0.50</td>
<td>0.50</td>
<td>1.80</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Methyltriene 21</td>
<td>45</td>
<td>0.50</td>
<td>0.50</td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td>13 KOBu$^+$, DOBu$^+$, DMSO-d$_6$, RT, 14hr</td>
<td>Triene 20</td>
<td>81</td>
<td>0.30</td>
<td>0.50</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Methyltriene 21</td>
<td>18</td>
<td>0.40</td>
<td>0.50</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>13 NaD$_2$CSOC$_3$, CD$_3$SOCD$_3$, 74°C</td>
<td>Triene 20</td>
<td>40</td>
<td>0.40</td>
<td>0.60</td>
<td>4.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Methyltriene 21</td>
<td>54</td>
<td>0.45</td>
<td>0.55</td>
<td>3.00</td>
<td></td>
</tr>
<tr>
<td>13 NaD$_2$CSOC$_3$, CD$_3$SOCD$_3$, RT, 20min</td>
<td>Triene 20</td>
<td>30</td>
<td>0.40</td>
<td>0.65</td>
<td>4.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Methyltriene 21</td>
<td>60</td>
<td>0.40</td>
<td>0.60</td>
<td>3.00</td>
<td></td>
</tr>
<tr>
<td>Hydrazone-N-d$_8$, KOBu$^+$, DOBu$^+$, DMSO-d$_6$, 74°C, 14hr</td>
<td>Triene 6d</td>
<td>70</td>
<td>trace</td>
<td>trace</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Methyltriene 7d</td>
<td>25</td>
<td>trace</td>
<td>trace</td>
<td>0.50</td>
<td></td>
</tr>
</tbody>
</table>
Scheme IV

Mechanism of Selective Deuterium Incorporation in Reduction of B and U

\[ \text{etc.} \]
The stereochemistry of proton transfer to carbanions generated from monoalkylidiimide anions depends on steric and electronic effects as well as reaction conditions.\(^\text{27,28,29}\) For example, generation of 2-norbornyl anions \(23\) and \(24\) by oxidation of isomeric 2-norbornylhydrazines with potassium periodate results predominantly in exo capture of deuterium. These results are explained on the basis of rapid equilibration of \(23\) and \(24\) and the steric accessibility of the face of anion \(23\) to the solvated electrophile\(^\text{28}\) (Equation 30).

\[
\begin{align*}
\text{KIO}_4/\text{KOH} & \quad \text{NHNH}_2 \\
\text{H} & \quad \Rightarrow \quad \text{H} \\
23 & \quad \text{D} \\
(97\%) \\
\text{H} & \quad \Rightarrow \quad \text{H} \\
24 & \quad \text{D} \\
(3\%) 
\end{align*}
\]
The importance of electronic effects is borne out by similar experiments with syn and anti-7-norbornenylhydrazines in which basic oxidative cleavage of either isomer with periodate results in anti and syn-7-d-norbornenes in approximately 94:6 ratio. These results are explained on the basis of antibishomoaromaticity in syn-carbanion making the intermediate unstable relative to anti-carbanion (Equation 31).

In these systems solvent effects on the stereochemistry of proton transfer are minimal.

In the pyrazoline system presently investigated, both steric and electronic effects may be important. Electronically, it can be argued that syn-9-bicyclo[4.2.1]-nona-2,4,7-trien-9-yl anion (19) has favorable bishomoaromatic (6\pi) interaction whereas isomer 20 suffers bishomoantiaromatic (4\pi) effects. Molecular models reveal that in 20 antibishomoaromaticity may not be very
significant because of geometric factors. The interacting orbitals are farther apart from each other at least as compared with 2-norbornenyl anion. Carbons 1,6,7,8,9 of the bicyclo[4.2.1]nona-2,4,7-trien-9-yl anion are essentially coplanar whereas the C₂-C₅ diene unit is almost perpendicular to this plane. This geometry is ideally suited, however, for bishomoaromatic overlap in 19. Another consequence of this geometry is that approach of the electrophile from the anti-side is much more favorable than from the syn-direction. Thus both electronic and steric effects may play roles in formation of the two different products 21 and 22. While it is not possible to dissect the steric and electronic effects in the capture processes of the bicyclo[4.2.1]nona-2,4,7-trien-9-yl anions (19 and 20), it is noted that under a variety of conditions the ratios of syn/anti capture products are comparable (Table II). The steric preference for anti-capture may be at least offset in part by syn-capture probably arising through the intermediacy of bishomoaromatic 20.

Treatment of pyrazoline 13 with potassium t-butoxide and t-butanol-0-d in dimethyl sulfoxide-d₆ results in extensive exchange of the C₂-C₅ diene protons during formation of bicyclo[4.2.1]nona-2,4,7-triene and 2-methyl-bicyclo[4.2.1]nona-2,4,7-triene. The selective exchange of diene protons is very similar to that previously observed in Wolff-Kishner reduction of
bicyclo[4.2.1]nona-2,4,7-trien-9-one hydrazone-N-d² in perdeuterated medium and further supports the intermediacy of pyrazoline 13 in the overall reaction process as summarized in Scheme IV.

Pyrazoline 13 reacts with sodium dimethyl sulfoxide in dimethyl sulfoxide even in the absence of hydroxylic solvents to give hydrocarbons 6 and 7 (Equation 32). Alcohols actually slow the decomposition of 13 by sodium dimsyl in dimethyl sulfoxide. Addition of 13 in dimethyl sulfoxide to sodium dimsyl at room temperature results in immediate evolution of nitrogen and the reaction is complete in approximately 20 minutes. When t-butoxide in dimethyl sulfoxide is used instead, nitrogen evolution is incomplete even after 10 hours at room temperature.

Another significant difference is the greater conversion of 13 to 2-methylbicyclo[4.2.1]nona-2,4,7-triene (7) by sodium dimsyl-dimethyl sulfoxide when a hydroxylic component in the solvent is absent. This result parallels the earlier observation that the conversion to methylated
triene \( \mathcal{J} \) decreases as the concentration of \( t \)-butanol in the medium is increased in Wolff-Kishner reduction of bicyclo[4.2.1]nona-2,4,7-trien-9-one hydrazone (5).

Exchange of deuterium into the \( C_2-C_5 \) diene bridge during reduction is minimized when the base is sodium dimethyl sulfoxide-\( d_6 \) rather than potassium \( t \)-butoxide in dimethyl sulfoxide and \( t \)-butanol-\( O-d \). A mechanism for this process is shown in Equation 33.

Since a ready deuterium source is unavailable, as for example, \( t \)-butanol-\( O-d \), this is not totally unexpected, since the reverse of the first step in Equation 33 becomes more difficult. This result is especially true considering the fact that loss of nitrogen from the monoalkyldiimide anion \( 11 \) is a fast reaction—probably faster than any deuterium exchange process that takes place between dimethyl sulfoxide-\( d_6 \) and pyrazoliny1 anion \( 12 \).
Treatment of pyrazoline $\sim 13$ with sodium dimethyl sulfoxide in dimethyl sulfoxide at room temperature followed by quenching with deuterium oxide does not give hydrocarbon products containing deuterium, suggesting that the bicyclo-[4.2.1]nona-2,4,7-trien-9-yl anion (2) thus generated readily captures a proton from dimethyl sulfoxide, and further that $\sim 6$ is much less acidic than dimethyl sulfoxide (pKa 27).
Tricyclo[6.1.0.0\(^2,7\)]nona-2,7-dien-5-yl anion (3) is isomeric with bicyclo[4.2.1]nona-2,4,7-trien-9-yl anion (2) and isomerization of 2 to 3 was initially thought to be involved in the formation of tricyclo[6.1.0.0\(^2,7\)]nona-2,6-diene (homosemibullvalene, 4) from Wolff-Kishner reduction of bicyclo[4.2.1]nona-2,4,7-trien-9-one (1, Equation 19). A study was then made of Wolff-Kishner reduction of tricyclo[6.1.0.0\(^2,7\)]nona-2,6-dien-5-one (27).

Anion 3, presumably as generated by reaction of tricyclo[6.1.0.0\(^2,7\)]nona-2,6-dien-5-one (homosemibullvalenone, 27) with potassium hydroxide and hydrazine in diethylene glycol yields only one capture product, tricyclo[6.1.0.0\(^2,7\)]nona-2,6-diene (4), with less than 5% of rearranged hydrocarbons. The structure of 4 is established by comparison of its spectral properties with an authentic sample. This experiment thus shows that under the given conditions 3 does not isomerize to the bicyclo[4.2.1]nona-2,4,7-trien-9-yl anion (2) an intermediate which is predicted to be bicycloaromatic and stabilized. It is emphasized that these conditions do allow
rearrangement of an initially formed anion to a more stable one.

Further, reaction of homosemibullvalene (4) with potassium t-butoxide and t-butanol in dimethyl sulfoxide under conditions identical to those of Wolff-Kishner reduction of bicyclo[4.2.1]nona-2,4,7-trien-9-one hydrazone (5) yields only indane (28). There is no bicyclo-[4.2.1]nona-2,4,7-triene (6), the major product from Wolff-Kishner reduction of 5. This study thus shows that homosemibullvalenyl anion (3) is not involved in Wolff-Kishner reduction of 5. The formation of indane from 4 probably involves the dihydroindanyl anion (29) as shown in Equation 35.

\[ \begin{align*}
4 & \xrightarrow{B^\ominus/BH} 3 \\
& \xrightarrow{(b)} \xrightarrow{BH} 28
\end{align*} \]

A recent report\(^{21}\) that barbaralyl anion (31) rearranges quantitatively to bicyclo[3.2.2]nona-3,6,8-trien-2-yl anion (32) prompted reexamination of the Wolff-Kishner reduction of barbaralone (30).\(^{30}\) Barbaralone was presently
synthesized by sensitized photolysis of bicyclo[4.2.1]-nona-2,4,7-trien-9-one (1).\(^4\) Ketone 30 reacts with hydrazine hydrate and potassium hydroxide in diethylene glycol to give bicyclo[3.2.2]nona-2,6,8-triene (33, 50%),\(^5\) tricyclo[3.3.1.0\(^2,8\)]nona-3,7-diene (barbaralane, 34, 30%)\(^3\) and bicyclo[3.2.2]nona-2,6-diene (35, 20%).\(^17,18\) In previous study of this reduction, only 34 was identified.\(^3\) It is now clear that barbaralyl anion (31) undergoes partial rearrangement to bicyclo[3.2.2]nonatrienyl anion (32) followed by protonation (Equation 36).

Bicyclo[3.2.2]nona-2,6-diene (35) probably arises via reduction of triene 33 by diimide as formed by air oxidation of hydrazine. The structure 35 is confirmed by comparison of its nmr spectrum with that of a sample prepared by diimide (generated from dipotassium azocarboxylate) reduction of bicyclo[3.2.2]nona-2,6,8-triene (33). The pertinent data leading to the assignment of 33 and 35 are: nmr: 33, δ 6.50 (m, 2H), 6.15 (m, 2H), 5.90 (m, 1H), 5.05 (m, 1H), 3.10 (m, 2H), 2.20 (q, 2H); 35, mp 52°C (lit., 53°C 18); nmr: δ 6.40 (t, 3.5 Hz, 1H), 5.90 (m, 2H), 5.30 (m, 1H), 2.80-1.50 (m, 8H).

Wolff-Kishner reduction of the hydrazone of barbaralone (36) takes a different path. When 36 is treated with potassium t-butoxide and t-butanol in dimethyl sulfoxide, the major hydrocarbon product is bicyclo[3.2.2]nona-2,6,8-triene (33, 80%, Equation 37). None of the expected reduction product 34 is obtained. Two minor hydrocarbons (~8%) were not identified. The present synthesis via Wolff-Kishner reduction is a marked improvement on the presently available one for the synthesis of 33 in nine steps. By the present method bicyclo[3.2.2]nona-2,6,8-triene (33) can be prepared in 30-35% yield from cyclooctatetraene in four steps (Equation 37).
1. \((CH_3)_2NCCl\)
2. hv, PS*

\[ \begin{align*}
\text{2Li}^+ & \quad \text{2Li}^+ \\
\text{NNH}_2 & \quad \text{KOBu}^+ / \text{HOBu}^+ \\
& \quad \text{DMSO} \\
\end{align*} \]

30

36

33

(37)
Since bicyclo[4.2.1]nona-2,4,7-trien-9-yl anion (2) as generated by treatment of either hydrazone 8 or pyrazoline 13 with potassium t-butoxide in dimethyl sulfoxide is invariably protonated under the reaction conditions, direct study of carbanion 2 was not possible. Independent generation of 2 as a possible long-lived intermediate by different methods and study of its spectral and chemical properties were thus objectives of the research to be described.

Bicyclo[4.2.1]nona-2,4,7-trien-9-yl halides (37) are of interest as possible sources of the bicyclo[4.2.1]-nona-2,4,7-trien-9-yl anion (2) and the bicyclo[4.2.1]nona-2,4,7-trien-9-yl radical (38). Syn-9-hydroxybicyclo[4.2.1]-nona-2,4,7-triene (39) and anti-9-hydroxybicyclo[4.2.1]-nona-2,4,7-triene (40), logical precursors of 37 and 38, are readily prepared by reduction of bicyclo[4.2.1]nona-2,4,7-trien-9-one 8 (1) with aluminum isopropoxide-isopropanol (Equation 38). Large quantities of pure 39 and 40 are obtainable from the reduction mixture by column
chromatography on alumina. Syn-alcohol 39 has absorptions, inter alia, at $\delta$ 4.40 (t, 1H, H on C-9, anti), 3.05 (t, br, 2H, H on C-1, -6), 1.80 (s, br, 1H, H on -OH). Anti-alcohol 40 is characterized by signals at $\delta$ 5.90 (m, 4H, H on C-2, -3, -4, -5), 5.35 (s, br, 2H, H on C-7, -8), 4.05 (s, H on C-9, syn), 3.00 (d, br, 2H, H on C-1, -6), 2.00 (s, 1H, H on -OH). The difference in coupling of the C$_9$-syn- and anti- protons (triplet in the former and singlet in the latter) is similar to that observed for bicyclo[4.2.1]nona-2,4,7-triene (6).

In the presence of lithium bromide and collidine, syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (39) reacts with phosphorus tribromide at 0°C to yield tris(bicyclo[4.2.1]nona-2,4,7-trien-9-yl)phosphate (41) of proper exact mass, elemental analysis and ir and nmr spectra. Formation of 41 is a substitution reaction on phosphorus to give a phosphite which undergoes oxidation in air to form phosphate 41. The reluctance of bicyclo[4.2.1]-nona-2,4,7-trien-9-yl derivatives to undergo displacement
has been observed previously. Alcohol 39, on refluxing in benzene with phosphorus tribromide in the presence of pyridine and lithium bromide, yields indene (43). Under these conditions no 9-bromobicyclo[4.2.1]nona-2,4,7-triene (37) is formed; the system undergoes cationic rearrangements rather than substitution. The mechanistic aspects of this process have been described in the second chapter (see page 5) of this dissertation.

\[\text{Tris(bicyclo[4.2.1]nona-2,4,7-trien-anti-9-yl) phosphate (42) is obtained on treatment of anti-9-hydroxybicyclo-[4.2.1]nona-2,4,7-triene with phosphorus tribromide in the presence of pyridine. None of the expected 9-bromobicyclo-[4.2.1]nona-2,4,7-triene (37, } X = \text{Br} \text{) is found. If the reaction is carried out under forcing conditions, for} \]
example, in refluxing benzene, indene is formed as the major product.

Reaction of alcohol $39$ with triphenylphosphine dibromide in acetonitrile also fails to yield any 9-bromobicyclo[4.2.1]nona-2,4,7-triene. At room temperature there is no reaction; on heating the reaction mixture to $70^\circ$, however, the alcohol $(39)$ indeed disappears as revealed by thin layer chromatography. The major product obtained after disappearance of $39$ is indene. The expected 9-bromobicyclo[4.2.1]nona-2,4,7-triene could not be found in these experiments (Equation 40). Reaction of anti-9-

$$\text{(major) } \overset{43}{\text{C}} \overset{43}{\text{H}}_5 \overset{43}{\text{P}} \overset{43}{\text{Br}} \overset{43}{\text{2}} \overset{43}{\text{CH}}_3 \overset{43}{\text{CN}}, 70^\circ \overset{43}{\text{No reaction}} \overset{43}{\text{CH}}_3 \overset{43}{\text{CN}}, 25^\circ$$

hydroxybicyclo[4.2.1]nona-2,4,7-triene with triphenylphosphine dibromide in acetonitrile at $70^\circ$C also gives indene $(43)$ as the major product.

Reaction of $39$ with thionyl chloride depends on the conditions. In the presence of pyridine in hexane at $0^\circ$C,
di-syn-bicyclo[4.2.1]nona-2,4,7-triene-9-yl sulfite (44) is obtained (Equation 41). When 39 is added to excess thionyl chloride at 0°C followed by removal of thionyl chloride under vacuum, bicyclo[4.2.1]nona-2,4,7-trien-9-yl chlorosulfite (45) is isolated. The structure of 45 is consistent with spectral data and reactions to be described.

Chlorosulfite 45 on thermolysis gives cis-7-chlorobicyclo[4.3.0]nona-2,4,8-triene (48) contaminated with traces of indene (Equation 42). The structure of 48 is confirmed by its nmr spectrum; nmr: $\delta$ 5.80 (m, 6H, H on C-2, -3, -4, -5, -8, -9), 4.80 (m, 1H, H on C-7), 3.80 (d, m, 10Hz, 1H, H on C-1), 3.35 (d, m, 10Hz, H on C-6).

The mechanism of this reaction is of considerable interest. Bicyclo[4.2.1]nona-2,4,7-trien-9-yl cation undergoes rearrangement via two distinct paths (Equations 4 and 5, page 5). In order to establish the mechanism of the formation of cis-7-chlorobicyclo[4.3.0]nona-2,4,8-triene (48) from chlorosulfite 45, syn-9-hydroxybicyclo-[4.2.1]nona-2,4,7-triene-9-d was treated with thionyl chloride and the resulting chlorosulfite (46) pyrolyzed.
The position of deuterium in the product was established by nmr spectroscopy (see Experimental) and the structure of the resulting chlorosulfite was assigned as 51. A mechanism consistent with the position of deuterium is shown in Equation 43. It is noted that this mechanism differs from that of reaction of 9-hydroxy-9-phenylbicyclo[4.2.1]nona-2,4,7-triene with thionyl chloride in which rearrangement proceeds via C2-C5 diene migration (Equation 7, page 6).

Anti-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (40) was treated with excess thionyl chloride in order to assess the effects of stereochemistry on the course of decomposition of intermediate chlorosulfites 45 and 47. Alcohol 40 readily forms chlorosulfite 47 as identified by its
nmr spectrum. Decomposition of 47 at 140° yields cis-7-chlorobicyclo[4.3.0]nona-2,4,8-triene (48); no other products were detected. Thus it is concluded that mechanistic details of thermolysis of syn- and anti- chlorosulfites 45 and 47 are essentially unchanged by stereochemistry (Equation 42).

Alcohols in general are converted to chlorides by triphenylphosphine in carbon tetrachloride.32 Alcohols 39 and 40, however, do not react with triphenylphosphine-carbon tetrachloride at room temperature. Under forcing conditions (50°C, 4 hr) indene is the major product; no other product is observed by TLC.

Efforts to convert 39 and 40 by S_N2 processes thus have been unsuccessful. Preparation of 9,9'-dichlorobicyclo[4.2.1]nona-2,4,7-triene was then attempted by treating ketone 1 with phosphorus pentachloride in methylene chloride. The only product obtained in these experiments is 1-chloroindene (52) identified by comparison of its nmr spectrum with that previously reported.33 It is noted that even traces of 3-chloroindene is not formed in this reaction. A gross mechanism for conversion of 1 to 52 is illustrated in Equation 44.

Bicyclo[4.2.1]nona-2,4,7-trien-9-yl radical (38) has been proposed as an intermediate in Raney Nickel desulfurization of bicyclo[4.2.1]nona-2,4,7-trien-9-one ethylene-dithioketal to give indene. Attempts to prepare 9-halo-bicyclo[4.2.1]nona-2,4,7-trienes (37) in the present study were then made via radical routes involving capture of 38.

Alcohols can be converted to halides via the decomposition of the corresponding alkyl tert-butylperoxyglyoxalates in the presence of carbon tetrachloride, bromotrichloromethane and similar halogen donors. The method was thus extended to 39. Alcohol 39 reacts with oxalyl
chloride at 0°C to give chloroglyoxalate 53 in 64% yield.


The structure of 53 is assigned from its spectral properties including carbonyl absorptions at 1785 and 1750 cm\(^{-1}\) and nmr absorptions at \(\delta\) 6.10 (m, 4H, H on C-2, -3, -4, -5), 5.35 (d, 2H, H on C-7, -8), 5.20 (m, 1H, H on C-9), 3.50 (t, 2H, H on C-1, -6). Chloroglyoxalate 53 on treatment with t-butyl hydroperoxide in the presence of pyridine in carbon tetrachloride readily yields peroxyester 54 as identified by its nmr spectrum; nmr: \(\delta\) 6.10 (m, 4H, H on C-2, -3, -4, -5), 5.30 (m, 3H, H on C-7, -8, -9), 3.50 (t, br, 2H, H on C-1, -6), 1.40 (s, 9H, t-butyl H). Thermal
decompositions of 54 in carbon tetrachloride and bromotrichloromethane in sealed tubes at 90° and 100°C and in refluxing solutions did not give 9-halobicyclo[4.2.1]-nona-2,4,7-trienes (37) or indene (43).

Carboxylic acids on photolysis in the presence of lead tetraacetate followed by addition of iodine give halides via intermediate acyloxy radicals, loss of carbon dioxide, and radical capture by iodine. A study was thus initiated of the possible conversion of bicyclo[4.2.1]-nona-2,4,7-trien-syn-9-carboxylic acid (55) to bicyclo[4.2.1]nona-2,4,7-trien-9-iodides (37, X = I). Carboxylic acid 55 was synthesized by oxidation of bicyclo[4.2.1]nona-2,4,7-trien-syn-9-carboxaldehyde. Photolysis of a mixture of lead tetraacetate and acid 55, addition of iodine in carbon-tetrachloride, removal of lead salts and product analysis did not yield bicyclo[4.2.1]nona-2,4,7-trien-9-yl iodides, however (37, Equation 46).

\[
\begin{align*}
55 \xrightarrow{\text{CrO}_3} & \xrightarrow{1.\text{Pb(OAc)}_4, \text{hv}} 37, \text{X=I} \\
& \xrightarrow{2.\text{I}_2}
\end{align*}
\]
Tricyclo[6.1.0.0^4,9]nona-2,6-dien-5-yl and bicyclo-[4.2.1]nona-2,4,7-trien-9-yl intermediates are isomeric and are of present interest in that they might be interconvertible. Indeed, tricyclo[6.1.0.0^4,9]nona-2,6-dien-5-yl (homosemibullvalenyl) anion (3) as derived from bicyclo[4.2.1]nona-2,4,7-trien-9-yl anion (2) was originally invoked in Wolff-Kishner reduction of bicyclo[4.2.1]-nona-2,4,7-trien-9-one (1, Equation 19). Homosemibullvalenyl anion (3) as generated by the Wolff-Kishner reduction of tricyclo[6.1.0.0^4,9]nona-2,6-dien-5-one (27) does not isomerize to bicyclo[4.2.1]nona-2,4,7-trien-9-yl anion (Equation 34). The only product isolated in the reduction is homosemibullvalene (4). It is thus relevant to the present study to investigate the behaviour of homosemibullvalenyl anion (3) prepared by methods other than Wolff-Kishner reduction of 27.

Reduction of ketone 27 to 5-hydroxytricyclo-[6.1.0.0^4,9]nona-2,6-diene with hydride reagents followed by conversion of this alcohol to the corresponding halide might provide a ready precursor to tricyclo[6.1.0.0^4,9]-nona-2,6-dien-5-yl anion (3).

Ketone 27 has been previously prepared by photosensitization (Michler's Ketone) of bicyclo[3.2.2]nona-3,6,8-trien-2-one (56). Bicyclo[3.2.2]nona-3,6,8-trien-2-one (56) was synthesized by the route shown in Scheme V.
Very pure ketone 56 (mp 44°, lit 44°) was conveniently obtained by column chromatography of the product mixture.

Scheme V

**Synthesis of bicyclo[3.2.2]nona-3,6,8-trien-2-one (56)**

In the present study sensitized photolysis of 56 was found to give a minor amount of 1-indanone in addition to 27 (Equation 47). Pure 27 was obtained by column chromatography and characterized by nmr spectroscopy. The structure of 27 was further confirmed by its conversion to tricyclo[6.1.0.0^4,9]nona-2,6-diene (4) by Wolff-Kishner reaction.
reduction as described earlier in this chapter (Equation 34).

Ketone 27 is reduced by sodium borohydride or Vitride to endo-tricyclo[6.1.0.0^4,9]nona-2,6-dien-5-ol (57, Equation 48), mp 84-85°C. Alcohol 57 is of correct exact mass and elemental analysis and its structural assignment is in agreement with its nmr: \( \delta \) 6-5.40 (m, 4H, olefinic), 4.80 (m, 1H, H at C-5), 3.10 (m, 1H, H at C-4), 2.20 (m, 2H, H at C-1, -8), 1.80 (s, 1H, hydroxyl H), 1.40 (m, 1H, H at C-9). The stereochemistry of the alcohol is presumed on the basis that approach of hydride to the carbonyl group is easier from the exo-side leading to formation of endo-alcohol (57). The chemical shift for hydrogen at C-5 indicates that the hydrogen is not as shielded as would be expected if it were endo, and hence it is assigned as of exo-stereochemistry. Similar logic has been used previously to assign the stereochemistry of endo- and exo-tricyclo[6.1.0.0^4,9]nona-2,5-dien-7-ol (58a and 58b). The difference in the chemical shifts
of exo- and endo- C-8 protons in tricyclo[4.3.0.0²,⁹]- nona-3,6-diene (58c) has also been explained similarly.²⁷b


Alcohol 57 was treated with triphenylphosphine dibromide in acetonitrile in an attempt to synthesize 5-bromotricyclo[6.1.0.0⁴,⁹]nona-2,6-diene, an important intermediate for preparation of homosemibullvalenyl anion (3). The major product of the reaction however, was identified as indene (43) by the nmr spectrum of the distilled product (Equation 49). The absence of high field protons (<δ 2.20) for a tricyclic system such as 57 or 58 clearly rules out the presence of any 5-bromotricyclo[6.1.0.0⁴,⁹]-nona-2,6-diene in the product.

A similar reaction giving indene as the only isolable product is observed on treating alcohol 57 with triphenylphosphine in carbon tetrachloride.

The formation of indene from alcohol 57 presumably proceeds via a cationic route. This reaction is, in certain respects, similar to that discussed for reactions
of 9-hydroxybicyclo[4.2.1]nona-2,4,7-trienes (39 and 40) with triphenylphosphine dibromide and triphenylphosphinecarbon tetrachloride and might involve similar intermediates. Formation of bishomoaromatic cation 59 from 57 is expected to be facile in the present case. Loss of a proton followed by aromatization via 1,5-sigmatropic rearrangement of a hydrogen gives indene (43, Equation 49).

\[
\begin{align*}
\text{57} & \xrightarrow{\text{P(C}_6\text{H}_5)_3\text{Br}_2, \text{CH}_3\text{CN}, -\text{HBr}} \text{59} \\
\text{50} & \xrightarrow{-\text{H}^+} \text{43}
\end{align*}
\]

Cation 59 has indeed been generated in super acid medium from exo-tricyclo[6.1.0.0^{4,9}]nona-2,5-dien-7-ol (58a) and its nmr spectrum recorded at low temperature\(^{38}\) (Equation 50).
Thus attempts to prepare halide precursors for the bicyclo[4.2.1]nona-2,4,7-trien-9-yl anion (2) and the homosemibullvalenyl anion (3) from the corresponding alcohols have not been successful. These alcohols and their derivatives resist displacement ($S_N1$ and $S_N2$) reactions and then undergo deep-seated rearrangements to aromatic products under a variety of forcing conditions. Future research involving synthesis of tricyclo[4.2.1.0$^{2,5}$]nona-3,7-dien-9-yl halides (60) from 9-hydroxybicyclo-[4.2.1.0$^{2,5}$]nona-3,7-dienes (Equation 51) may be of value since these halides can serve as precursors of carbanions isomeric with 2 and 3. It is conceivable that,
if 2 is as stable as predicted, 60 might give 2 on treatment with alkali metals (Equation 52).

\[
\begin{align*}
\text{MX} & \quad \text{MX} \\
60 & \quad \text{M}^+ \quad \text{H} \\
\end{align*}
\]

Tricyclo[6.1.0.0^{4,9}]nona-2,6-dien-9-yl (homosemi-bullvalenyl) anion (3) can, in principle, be generated from 5-methoxytricyclo[6.1.0.0^{4,9}]nona-2,6-diene via cleavage by sodium/potassium. Alcohol 57 is converted by methyl iodide in the presence of sodium hydride in glyme to endo-5-methoxytricyclo[6.1.0.0^{4,9}]nona-2,6-diene (61, Equation 53). It will be of considerable interest to investigate whether carbanion 3 generated under long life conditions rearranges to the bicyclo-[4.2.1]nona-2,4,7-trien-9-yl anion (2, bicycloatomatic^5) or cis-dihydroindenyl anion (29) and subsequently to
cyclononatetraenyl anion (62, aromatic)\(^{38a}\) as shown in Equation 54. These anionic transformations together with the results of the present study in which it is shown that the tricyclo[6.1.0.0\({4,9}\)]nona-2,6-dien-5-yl cation (59) presumably undergoes rearrangement to cis-dihydroindenyl cation, would represent interesting charge control in the rearrangements of tricyclo[6.1.0.0\({4,9}\)]nona-2,6-dien-5-yl intermediates (Equation 55).

2. Carbenic Rearrangement and Fragmentation Reactions of Bicyclo[4.2.2]deca-2,4,9-triene-7-ylidene (66) and Bicyclo[4.2.1]nona-2,4,7-triene-9-ylidene (84) and Related Carbenes.

Bicyclo[4.2.1]nona-2,4,7-triene-9-ylidene (84) and bicyclo[4.2.2]deca-2,4,9-triene-7-ylidene (66) are of interest because of their possible deep seated rearrangement processes and because of their potential for degenerate behaviour. The properties of these carbenes are expected to be affected by the interactions of their \( \pi \)-systems with their divalent centers.

Carbenes 84 and 66 were generated by pyrolysis of the sodium salts of their corresponding ketone tosylhydrazones. Bicyclo[4.2.2]deca-2,4,9-triene-7-one tosylhydrazone (63, Equation 56) was synthesized from 1 according to the procedure of J. B. Press. The sodium salts were generated by addition of sodium hydride to methylene chloride solutions of the tosylhydrazones at 0°C.
Isomerization of carbene 66 at 220°C, as generated from 7-diazobicyclo[4.2.2]deca-2,4,9-triene (65) by pyrolysis of the dry sodium salt of tosylhydrazone 64, yields bicyclo[4.3.1]deca-2,4,6,8-tetraene (69, 81%), tricyclo[4.3.1.0^1,6]deca-2,4,7-triene (71, 5%) and 1-propargyl-cyclohepta-2,4,6-triene (73, 14%). Although thermal migration of α-hydrogen to a carbenic center is usually a very facile reaction, the expected product, bicyclo[4.2.2]deca-2,4,7,9-tetraene (76) or its subsequent derivatives, are not observed.

Tetraene 69 is a strained bridgehead olefin. It is sensitive to heat and air and at present cannot be separated preparatively from 71 and 73. The mixture of 69, 71 and 73 can be kept at -78°C without rapid change (as revealed by nmr spectroscopy) and is a satisfactory source of 69 for direct study and use in synthesis. The isomeric products 71 and 73 are separable by gas chromatography and were identified by comparison with authentic samples. Cycloheptatriene 73 was synthesized


Scheme VI

Rearrangements of Bicyclo[4.2.2]deca-2,4,9-trien-7-ylidene (66).

\[ \text{H NNTs} \]

\[ \text{NaH/CH}_2\text{Cl}_2 \]

\[ 220^\circ, 0.1 \text{ mm} \]

\[ \text{Na NNTs} \]

\[ \text{N}_2 \]
according to a literature procedure.

Tetraene 69 is identified by spectral analysis and its chemical reactions to be described later. Though the nmr spectra of the mixture of 69, 71, and 73 is complex, it is possible with the aid of the standard spectra of the minor components (71 and 73) to arrive at the following data for 69: \(^1\text{H nmr (CDCl}_3\), } 2.2 (\text{m, 1H}), 2.7 (\text{m, 1H}), 2.9 (\text{m, 1H}), 5.6 (\text{m, 1H}), 5.9 (\text{m, 4H}) \text{ and 6.3 (m, 2H); } \(^{13}\text{C nmr (CDCl}_3\), } -40^\circ) 139.3, 138.7, 135.3, 128.0, 125.6 (2) 121.4, 36.4, \text{ and 32.8. It is difficult to identify the }^{13}\text{C-resonance of C}_6 \text{ in 69 because of its low intensity due to tetrasubstitution.}

Participation of the \(\pi\)-electron system appears to be important in the isomerizations of 66 to 69, 71 and 73. Formation of 69 involves the equivalent of a 1,2-shift of C5 of the diene to C7. This may possibly involve 67 and 68 in which use is made of the bishomotropylium character of the rearrangement process. A similar interaction has been previously invoked in explaining the reactivity of 7-norbornenylium (74). \(^{24}\)
Triene 71 presumably is formed from 70 and possibly 69; the mechanistic aspects of such a process are as yet unclear but are consistent with the properties of 69 to be described later.

Acetylene 73 may be derived from 72 as formed by cycloaddition of the C\textsubscript{2}-C\textsubscript{5} diene and the C\textsubscript{9}-C\textsubscript{10} monoene units, cyclopropylcarbinyl fragmentation\textsuperscript{41}, and reorganization. This mechanism assumes initial conversion of 65 to 66 which then yields 72. It cannot, however, be ruled out that the sodium salt of bicyclo[4.2.2]deca-2,4,9-trien-7-one p-tosylhydrazone or/and 65 undergo intramolecular cycloaddition of the C\textsubscript{2}-C\textsubscript{5} diene and C\textsubscript{9}-C\textsubscript{10} monoene bridges before conversion to 72.

An alternate, less likely mechanism for the formation of 1-propargylcyclohepta-2,4,6-triene (73) involves isomerization of bicyclo[4.2.2]deca-2,4,9-trien-7-ylidene (66) to bullvalenylidene (75) and then cyclopropylcarbinyl fragmentation (Equation 57).

Photolysis of 65 as generated by irradiation (Hanovia medium pressure mercury lamp through pyrex) of sodium bicyclo[4.2.2]deca-2,4,9-trien-7-one p-tosylhydrazone suspended in ethyl ether at 25° results in significant

hydrogen migration from C₈ to the carbenic center C₇ to yield \( 76 \) (Equation 58). The mixture of minor hydrocarbons obtained was not identified. None of the products obtained under thermolysis conditions (Scheme VI) are observed.

Thus the photochemical and thermal carbenic processes are decidedly different.

\[
\begin{align*}
\text{Na} & \quad \xrightarrow{\text{hv}} & \quad \text{ether, } 25^\circ & \quad \text{NNTs} \\
64 & \quad \rightarrow & \quad 66 & \quad \rightarrow & \quad 76
\end{align*}
\]

Thus the photochemical and thermal carbenic processes are decidedly different.

Bicyclo[4.2.2]deca-2,4,9-trien-7-yl cation (\( 78 \)) is of considerable theoretical interest. In the present
study the sodium salt of 63 photolyzes efficiently in methanol to exo-7-methoxybicyclo[4.3.1]deca-2,4,8-triene (79). In the protic environment diazonium ion 77 is presumably formed which undergoes loss of nitrogen, cationic carbon skeleton rearrangement to the bishomoaromatic bicyclo[4.3.1]decatrienyl cation (78) and then solvent capture (Equation 59). The structure of methyl ether 79

\[
\begin{align*}
\text{65} & \xrightarrow{\text{H}^+} \text{77} & \xrightarrow{\text{-N}_2} \text{78} & \xrightarrow{\text{HOCH}_3} \text{79}
\end{align*}
\]

is confirmed by comparison of its nmr spectrum with that reported previously. 42

As expected the bridgehead double bond in tetraene 69 is highly reactive. Diimide and dideuterodiimide reduce 69 selectively at $-40^\circ$ to bicyclo[4.3.1]deca-2,4,7-triene (80a) and 1,9-dideuterobicyclo[4.3.1]deca-2,4,7-triene (80b) respectively (Equation 60). An authentic sample of 80a was prepared by addition of hydrogen bromide to bicyclo[4.2.2]deca-2,4,7,9-tetraene (76) followed by reduction of the product, exo-7-bromobicyclo[4.3.1]deca-2,4,8-triene (81), with lithium triethylborohydride in tetrahydrofuran (Equation 61). The structure of 80a is consistent with its spectral properties: exact mass
calculated for \( \text{C}_{10}\text{H}_{12} \), 132.0939; observed, 132.0941; nmr
\( \text{CDCl}_3, \delta \): 1.69-2.10 (m, 4H, \( \text{H}_9 \) and \( \text{H}_{10} \)), 2.77 (br, m,
1H, \( \text{H}_1 \)), 3.13 (br, m, 1H, \( \text{H}_6 \)), and 5.80 (m, 6H, olefinic
H).

95, 1669 (1973).

1,9-Dideuterobicyclo[4.3.1]deca-2,4,7-triene (80b)
shows similar spectral patterns to 80a: exact mass cal-
culated for \( \text{C}_{10}\text{H}_{10}\text{D}_2 \): 134.1064; observed, 134.1066; nmr
\( \delta \) 1.69-2.10 (m, 3H, \( \text{H}_9 \) and \( \text{H}_{10} \), coupling simplified,
one of the \( \text{H}_9 \) s now replaced with D), and 3.13 (br, m,
1H, \( \text{H}_6 \)) 5.80 (m, 6H, olefinic H). As expected the absorp-
tion at \( \delta \) 2.77 attributed to \( \text{H}_1 \) in 80a now disappears in
80b because of D-substitution.

Attempts to trap bridgehead olefin 69 by Diels-
Alder reactions have been unsuccessful. Diphenylisobenzo-
furan and furan fail to react with tetraene 69 to
give 1:1 adducts. Only oligomeric products are recovered
from these experiments.

The potential of 69 for reaction as a 1,3-dipolaro-
phile at its \( \text{C}_6-\text{C}_7 \) double bond is revealed, however, by its
addition of phenyl azide at 0\(^\circ\)C to give a \( \text{N-phenyltriazoquiv} \) for which the position of the phenyl group is
not yet established. The gross structure of the adduct
is confirmed by its combustion analysis and by the following spectral data: m/e 221 (M^+ - N_2); ir: max (CHCl_3) cm^{-1} 3020, 1595, 1480, 1450, 1320, 1300, 1085, 1060, 1045, 1010, 830, 675, 640; nmr: δ 7.25 (m, 5H, aromatic), 6.00 (m, 6H, H at C-2, -3, -4, -5, -8, -9), 4.45 (dd, 1.5Hz, 1H, H at C-7), 3.15 (m, br, bridgehead H at C-1), 2.25 (d, 13 Hz, 1H, H at C-10, endo-), 1.6 (dd, 12 Hz, 5 Hz, 1H, H at C-10, exo-). Molecular models indicate that

\[ \text{[Diagram]} \]

H_{10}^{\text{endo}} (endo to the C_2-C_5 diene) in 81 or 81' is perpendicular to bridgehead H_1. Therefore, H_{10}^{\text{endo}} is coupled only to H_{10}^{\text{exo}} giving rise to a doublet at δ 2.25; H_{10}^{\text{exo}} is coupled both to H_{10}^{\text{endo}} and H_1 and thus appears as a doublet of doublets. H_7 is coupled only to H_8 and H_9 and thus appears as a doublet of doublets with a small
coupling constant of 1.5 Hz for allylic coupling.

Bicyclo[4.3.1]deca-2,4,6,8-tetraene (69) reacts quantitatively with dimesyl sodium in dimethyl sulfoxide to give the 10π-anion, 1,5-methanocyclononatetraenyl anion (82). Anion 82 is characterized by its unmistakable nmr spectrum: (CDCl₃, δ) 6.84 (dd, 2H, 5Hz, 2H), 5.77 (center of 9 lines, 5H), -0.72 (d, 7.2Hz, H on C-10), -1.20 (d, 7.2Hz, H on C-10). The chemical shifts are measured with reference to CD₂HSOCD₃ at δ 2.49. Anion 82 is easily converted into tricyclo[4.3.1.0²⁶]deca-2,4,7-triene (71) by protonation (Equation 63). Such an overall process might be the source of 71 from pyrolysis of 64 in a basic environment; a concerted 1,7 H-shift in 69 is forbidden by both geometric and orbital symmetry considerations. A further aspect of the present system is that vacuum pyrolysis of the sodium salt of bicyclo-

\[\text{[4.2.2]deca-2,4,9-trien-7-one p-tosylhydrazone and reaction}\]
of the condensate with sodium dimethyl at low temperatures followed by acidification of the product represent the final sequence of an efficient four-step synthesis of 71 from cyclooctatetraene (the yield based on tosylhydrazone 63 is above 55%) and might be of further use in synthesis of various C10-substituted derivatives of 71.

Bicyclo[4.2.1]nona-2,4,7-trien-9-ylidene (84), presumably generated by decomposition of 9-diazobicyclo[4.2.1]nona-2,4,7-triene (83) as derived from thermolysis of the dry sodium salt of the p-tosylhydrazone of bicyclo[4.2.1]nona-2,4,7-trien-9-one (3), has been reported to give indene (43, 95%). A simple path for conversion of 84 to 43 (and is analogous to that suggested for conversion of 66 to 69) is rearrangement to bicyclo[4.3.0]nona-2,4,6,8-tetraene (86) which undergoes a 1,5-sigmatropic hydrogen shift (Scheme VII).
It has now been found that 84 generated thermally also yields 1-ethynyl-2,4,6-cycloheptatriene (88, 5%). Thus acetylene 88 may result from cyclopropyl-carbinyl collapse of 89 as formed by cycloaddition of the C_2-C_5 diene and C_7-C_8 monoene moieties within 84 or its precursors. An alternate, more complicated,
mechanism involving rearrangement of 84 to barbaralylidene (87) and subsequent cyclopropylcarbinyl fragmentation similar to that described for bicyclo[4.2.2]deca-2,4,9-trien-7-ylidene (66) cannot be ruled out at present. Indeed it has been presently found that barbaralylidene (87) generated thermally via pyrolysis of the dry sodium salt of barbaralone p-tosylhydrazone (90) gives 1-ethynylcyclohepta-2,4,6-triene (88) in essentially quantitative yield (Equation 64). It is noted that the yield of acetylenic product 73 is higher in the [4.2.2] system (66) in which formation of the tetracyclic internal adduct 72 is relatively easier due to the lesser strain involved.

An earlier report 45 that 1-vinylcyclohepta-2,4,6-triene undergoes thermal rearrangement to dihydroindene prompted a present investigation of the thermal chemistry
of 1-ethynylcyclohepta-2,4,6-triene (88). A partial objective of this effort was to establish that indene (43) obtained from bicyclo[4.2.1]nona-2,4,7-trien-9-ylidene (84) is a primary product and not that arising from 88.

Pyrolysis of 1-ethynylcyclohepta-2,4,6-triene (88) at 250°C and above was found to give 3-ethynylcycloheptatriene (91) along with recovered 88 (Equation 65). The product of rearrangement, 91, was identified by its characteristic nmr spectrum: \( \delta \) 6.9 (d, 6.5Hz, 1H, H at C-4), 6.15 (m, 2H, H at C-2, -5), 5.4 (m, 2H, H at C-1, -6), 2.9 (s, 1H, acetylenic H), 2.2 (t, 6.5Hz, 2H, H at C-7). The nmr of 91 compares very well with that reported for other 3-substituted cycloheptatrienes.46


\[
\begin{align*}
\text{88} & \quad \begin{array}{c}
300^\circ \quad 10 \text{ mm}
\end{array} \\
\rightarrow & \\
\text{91 (68%)}
\end{align*}
\]
Acid-catalyzed rearrangement of \( \text{88} \) does give aromatic products. Refluxing a solution of 1-ethynylcyclohepta-2,4,6-triene (\( \text{88} \)) in benzene containing a trace amount of p-toluenesulfonic acid results in a low yield of phenylallene (\( \text{94} \)). The mechanism of such a process might involve the norcaradiene valence isomer \( \text{92} \), protonation, rearrangement and aromatization via loss of a proton (Equation 66). A similar process occurs in acid-catalyzed rearrangement of ethyl-\( \beta \)-(cyclohepta-2,4,6-trien-1-yl)-propynoate (\( \text{95} \), Equation 67).\(^{47}\)

\[ \begin{align*}
\text{88} & \rightleftharpoons \text{92} \\
\text{93} & \rightarrow \text{94}
\end{align*} \]

A carbene of related present interest, if it were to undergo transannular insertion, is \((\text{bicyclo}[4.2.1]\text{nona}-2,4,7\text{-trien}-9\text{-yl})\text{methylene}\) \((96)\). The corresponding aldehyde was prepared according to the procedure of Sanders\(^9\) (Equation 68). Pyrolysis of the sodium salt of the \(\text{p}\)-tosylhydrazone gives only \(9\text{-methylenebicyclo}[4.2.1]\text{nona}-2,4,7\text{-trien}\) \((97)\) in 96% yield, as identified by comparison with an authentic sample from bicyclo[4.2.1]-nona-2,4,7-trien-9-one and methylenetriphenylphosphorane.\(^9\)
Aldehyde 98 is of some value for synthesis. The corresponding oxime 100 is obtained in good yield by reaction with hydroxylamine hydrochloride (Equation 69).
EXPERIMENTAL

General Techniques:

Melting points were recorded on a Thomas Hoover capillary melting point apparatus and are uncorrected.

Infrared spectra were obtained on Perkin-Elmer Model 137 or 457 recording spectrometers. The spectra were calibrated against the polystyrene absorption peak at 1601 cm$^{-1}$.

Nuclear magnetic resonance spectra were determined using Varian Associates NMR Spectrometers: Models A-60, A-60-A and HA-100 and a Bruker Spectrometer HX-90. All samples except those noted otherwise were dissolved in chloroform-d and tetramethylsilane was used as an internal standard.

High resolution mass spectra were obtained on an AE-1 MS-9 mass spectrometer.

Elemental analyses were performed by Micro-Analysis, Inc., Wilmington, Delaware.

Gas chromatography was accomplished on a Varian Associates Gas Chromatograph, Model 920, with a thermal conductivity detector. Conditions of the analyses are recorded under each of the experiments.

Preparation of bicyclo[4.2.1]nona-2,4,7-trien-9-one (1).

Ketone 1 was prepared by the method described by T. A. Antkowiak in 60-70% overall yield from cyclooctatetraene.
Preparation of $2,3$-diazatricyclo$[6.3.0.0^4,11]$undeca-$2,5,9$-triene (13).

Ketone 1 (3 g) was heated with hydrazine hydrate (5 ml) and potassium hydroxide (4 g) in diethylene glycol to 100-120°C for 60 min. The mixture was then raised to 170-180°C and maintained at that temperature for 30 min. The reaction mixture was cooled, added to water (200 ml), and extracted with petroleum ether (7 x 150 ml). The petroleum ether extracts were combined, washed with water and dried over anhydrous sodium sulfate. Evaporation of the solvent yielded a white solid which on recrystallization from hexane gave crystalline $2,3$-diazatricyclo$[6.3.0.0^4,11]$undeca-$2,5,9$-triene (13) (2.46 g, 75%). An analytical sample was prepared by sublimation of the product at 10 mm pressure (bath temperature 70°C). The structure of 13 was confirmed by the following spectral data and reactions to be described later: mp 130-135°C; ir (CHCl$_3$): 3060, 3025, 2940, 2880, 1630, 1600, 1525, 1415, 1390, 1350, 1300, 1260, 1180, 1170, 1105, 1020, 950, 885, 855, 810, 760 cm$^{-1}$; nmr: $\delta$ 5.92-5.12 (m, 5H, olefinic H, H on C-4, -5, -6, -9, -10), 4.97 (m, 1H, H on C-1), and 3.62-1.82 (m, 4H, H on C-7, -8, -11); exact mass calculated for C$_9$H$_{10}$N$_2$: 146.0844, found 146.0848.

Anal. Calcd for C$_9$H$_{10}$N$_2$: C, 73.93; H, 6.89; N, 19.17.

Found: C, 73.85; H, 6.90; N, 19.39.
Thermolysis of 2,3-diazatricyclo[6.3.0.0^4,11]undeca-2,5,9-
triene (13).

A solution of pyrazoline (0.400 g) in diethylene
glycol was heated to 200°C for 30 min and then the product
was distilled. The distillate was poured into water and
extracted with pentane. The pentane extracts were combined,
dried and concentrated. Analysis on a carbowax 20M column
(20% on Chromosorb W, 20'-x4", 135°C) indicated the presence
of three hydrocarbons. The major hydrocarbon (~95%) was
identified as tricyclo[6.1.0.0^5,9]nona-2,6-diene (4). nmr:
(CDCl_3) δ 6.05-5.05 (m, 4H, H on C-2, -3, -6, -7), 3.10 (m
1H, H on C-4), and 2.6-1.1 (m, 5H, H on C-1, -5, -8, -9);
mass spectrum m/e 118. One of the minor hydrocarbons having
the lowest retention time was identified as bicyclo[4.2.1] -
nona-2,4,7-triene (6) by comparison of its retention time
with that of an authentic sample previously reported by
D. C. Sanders.

Photolysis of 2,3-diazatricyclo[6.3.0.0^4,11]undeca-2,5,9-
triene (13).

Pyrazoline (0.45 g) was dissolved in pentane (150 ml)
and the solution was then thoroughly degassed. The mixture
was photolyzed using a Hanovia Medium Pressure mercury lamp
through pyrex until evolution of nitrogen stopped (approx-
imately one hour). The pentane was evaporated off on a
rotary evaporator and the product analyzed by gas
chromatography. Analysis on the carbowax 20 M column indicated tricyclo[6.1.0.0^{4,9}]nona-2,6-diene (4, 0.38 g, 95%) as the major product with less than 3% other products. The NMR spectrum and retention time of 4 are indistinguishable from the sample obtained by thermolysis of 13.

Preparation of bicyclo[4.2.1]nona-2,4,7-trien-9-one hydrazone (5).

Hydrazone 5 was prepared from ketone \( \text{I} \) and anhydrous hydrazine in methylene chloride according to the method of D. C. Sanders. The structure of 5 was confirmed by the following spectral data; nmr: \( \delta \) 6.25-5.52 (m, 4H, H at C-2, -3, -4, and -5), 5.25 (m, 2H, H at C-7, -8), 4.95 (m, 2H, N-H hydrogens which disappear when shaken with deuterium oxide), 3.85 (m, 1H, bridgehead) and 3.35 (m, 1H, bridgehead).

Preparation of bicyclo[4.2.1]nona-2,4,7-trien-9-one hydrazone-N-d\( _2 \) (8).

Hydrazone 5 (3.4 g, 0.023 mole) was dissolved in methylene chloride (20 ml) and deuterium oxide (20 ml) and then a tiny piece of sodium added. The mixture was stirred for 90 min at room temperature and the aqueous layer was extracted with methylene chloride. The methylene chloride layers were combined and washed with D\( _2 \)O, dried, and concentrated. Analysis by NMR indicated 8 to be formed with 80% deuterium incorporation on nitrogen; nmr: \( \delta \) 6.25-5.52
(m, 4H, H at C-2, -3, -4, -5), 5.25 (m, 2H, H at C-7, -8),
4.95 (m, 0.4H, H on nitrogen), 3.85 (m, 1H, bridgehead H),
and 3.35 (m, 1H, bridgehead hydrogen).

Preparation of bicyclo[4.2.1]nona-2,4,7-triene (6) and
2-methylbicyclo[4.2.1]nona-2,4,7-triene (7).

The hydrazone (5) of bicyclo[4.2.1]nona-2,4,7-trien-9-one was treated with potassium t-butoxide and t-butanol
(2 equivalents) in dimethyl sulfoxide at 74°C for 12 hr,
according to the procedure of D. C. Sanders. A mixture
of hydrocarbons 6 and 7 was obtained in 65% and 8% yields
respectively. The structures were confirmed by nmr spec-
troscopy.

6: nmr: δ 5.90 (m, 4H, H at C-2, -3, -4, -5), 5.20 (d, 
2Hz, 2H, H at C-7, -8), 3.05 (t, 8Hz, 2H, H at C-1, -6),
1.94 (dt, 1H, H at C-9, anti), and 1.32 (d, 10Hz, 1H, H at
C-9, syn).

7: δ 5.86 (m, 4H, H at C-2, -3, -4, -5), 5.18 (d, 2Hz, 2H,
H at C-7, -8), 2.95 (m, 2H, H on C-1, -6), 1.94 (m, 4H,
H on C-9, anti; H on CH₃ ), and 1.40 (d, 12Hz, 1H, H on
C-9, syn).

A third hydrocarbon was identified as tricyclo-
[6.1.0.⁰⁴,⁹]nona-2,6-diene (4, ~2%) by comparison of its
gas chromatographic retention times with those of an authen-
tic sample prepared previously.
Reaction of 2,3-diazatricyclo[6.3.0.0^4,11]undeca-2,5,9-
triene (13) with potassium t-butoxide and two equivalents
of t-butanol at 74°C in dimethyl sulfoxide.

A solution of pyrazoline 13 (0.40 g, 0.0027 mole) in
dimethyl sulfoxide (5 ml) was added in 30 min to a mixture
of potassium t-butoxide (0.700 g, 0.006 mole) and t-butanol
(0.400 g, 0.0054 mole) in dimethyl sulfoxide (10 ml) at
74°C. The mixture was stirred for 12 hr at 74°C and worked
up by adding excess water (350 ml) and repeatedly extract­
ing with pentane (200 ml x 6). The pentane extracts were
combined, washed with water and dried over anhydrous sodium
sulfate. Concentration of the solution yielded a mixture
of hydrocarbons. Analysis on a 20% carbowax 20 M column
(20 x \(\frac{3}{4}\)", 130°C) indicated two major components identified
as bicyclo[4.2.1]nona-2,4,7-triene (6, 75%) and 2-methyl
bicyclo[4.2.1]nona-2,4,7-triene (7, 20%) by comparison of
retention times and spectral properties with those of
authentic samples. A trace of tricyclo[6.1.0.0^4,9]nona-
2,6-diene (4) was also detected. A minor component (~5%)
was not identified. The overall yield of decomposition
was 90%.

Reaction of 2,3-diazatricyclo[6.3.0.0^4,11]undeca-2,5,9-
triene (13) with potassium t-butoxide and two equivalents
of t-butanol-0-d at 74°C in dimethyl sulfoxide-d_6.

The procedure reported in the previous experiment was
used except that deuterated solvents were employed. The
volatile products were identified as bicyclo[4.2.1]nona-2,4,7-triene, (6, 50%), 2-methylbicyclo[4.2.1]nona-2,4,7-triene (7, 45%) and tricyclo[6.1.0.0^4,9]nona-2,6-diene (4, 3%).

Extensive deuterium incorporation into the products was noted. The deuterium content was measured by nmr spectroscopy and mass spectrometry.

In determining the isotope content at various positions in the olefins, it was assumed that the bridgehead protons did not undergo any exchange.\textsuperscript{25a} Intensity measurements of various peaks in the pmr spectrum of bicyclo[4.2.1]nona-2,4,7-triene (6) indicated 55% deuterium incorporation into the C\textsubscript{2}-C\textsubscript{5} diene bridge and 50% each at the \textit{syn} and \textit{anti} positions of C\textsubscript{9}. There was no deuterium at any other position. The nmr spectrum of deuterated 6 is \(\delta 5.90\) (m, 1.8H, H at C-2, -3, -4, -5), 5.20 (d, 2H, H at C-7, -8), 3.05 (s, br, 2H, H at C-1, -6), 1.94 (t, br, 0.5H, H at C-9, \textit{anti}) and 1.32 (s, br, 0.5H, H at C-9, \textit{syn}). Mass spectrometry indicated low concentrations of species with up to a maximum of six deuteriums. The distribution of \(d_1\), \(d_2\), \(d_3\), \(d_4\), \(d_5\) and \(d_6\) was not estimated.

Similar measurements showed 81% deuterium incorporation into the C\textsubscript{2}-C\textsubscript{5} diene bridge of 2-methylbicyclo[4.2.1]-nona-2,4,7-triene (7) with 50% each at the \textit{syn}- and \textit{anti}-positions at C-9. The nmr of deuterated 7 is: \(\delta 5.86\) (s, br, 0.60H, H at C-2, -3, -4, -5), 5.18 (s, 2H, H at
(C-7, C-9), 2.95 (s, br, 2H, H at C-1, C-6), 1.89 (t, br, 0.5H, H at C-9, anti), and 1.40 (s, br, 0.5H, H at C-9, syn). It is noted that the doublet of triplets due to the C-9 anti-proton in 6 and 7 has collapsed to a triplet and the doublet due to C-9 syn-H converted to a singlet. Also the triplet due to the bridgehead hydrogen is reduced to a broad singlet.

Reaction of 2,3-diazatricyclo[6.3.0.04,11]undeca-2,5,9-triene (13) with potassium t-butoxide and two equivalents of t-butanol-O-d at room temperature in dimethyl sulfoxide-d6.

Pyrazoline 13 (0.200 g, 0.0014 mole) dissolved in dimethyl sulfoxide-d6 (99.5 + %-d, 6 ml) was added to a solution of potassium t-butoxide (0.35 g, 0.003 mole) and t-butanol-O-d (0.20 g, 0.0027 mole) in dimethyl sulfoxide-d6 (4 ml) in 90 min. The mixture was stirred for 10 hr at room temperature and worked up as described in the previous experiment.

Analysis of the product on a carbowax 20 M column indicated the presence of two volatile products (~90%): bicyclo[4.2.1]nona-2,4,7-triene (6, 81%) and 2-methylbicyclo[4.2.1]nona-2,4,7-triene (7, 18%). The deuterium content of 6 and 7 was determined by nmr spectroscopy as described earlier.
The nmr of the deuterated bicyclo[4.2.1]nona-2,4,7-triene is: \( \delta \) 5.90 (m, 1.00H, H at C-2, -3, -4, -5), 5.20 (s, 2H, H at C-7, 8), 3.05 (s, br, 2H, H at C-1, -6), 1.94 (t, br, 0.50H, H at C-9, \text{anti}), and 1.32 (s, br, 0.30H, H at C-9, \text{syn}); that for 2-methylbicyclo[4.2.1]nona-2,4,7-triene-d\textsubscript{n} is: \( \delta \) 5.86 (s, br, 0.30H, H at C-2, -3, -4, -5), 5.18 (s, 2H, H at C-7, -8), 2.95 (s, br, 2H, H at C-1, -6), 1.89 (t, br, 0.50H, H at C-9, \text{anti}), 1.40 (s, br, 0.40H, H at C-9, \text{syn}).

Reaction of 2.3-diazatricyclo[6.3.0.0\textsuperscript{4,11}]undeca-2,5,9-triene (13) with sodium dimethyl sulfoxide in dimethyl sulfoxide at room temperature.

Dimsyl anion was prepared from dimethyl sulfoxide (2 ml) and sodium hydride (0.100 g, 57% dispersion in mineral oil) at 65°C and the solution was cooled to room temperature. Pyrazoline 13 in dimethyl sulfoxide (5 ml) was added to the solution of dimsyl anion. Immediate evolution of nitrogen occurred. The addition was completed in 20 min and the mixture was stirred at room temperature for 20 min. Excess deuterium oxide was added and the reaction was worked up as usual by extraction with pentane. Analysis of the product (90%) indicated the presence of bicyclo[4.2.1]nona-2,4,7-triene (6, 40%), 2-methylbicyclo[4.2.1]nona-2,4,7-triene (7, 54%), tricyclo[6.1.0.0\textsuperscript{4,9}]nona-2,6-diene (4, trace) and an unidentified hydrocarbon (\textasciitilde 4%). Examination of their
nmr spectra indicated no deuterium incorporation into the products.

Reaction of 2,3-diazatricyclo[6.3.0.0^4,11]undeca-2,5,9-
triene (13) with sodium dimethyl sulfoxide-d$_5$ in dimethyl-
sulfoxide-d$_6$ at room temperature.

The method used in the previous experiment was repeated
with deuterated solvents. The reaction mixture was added
to excess water and extracted with pentane. Analysis of
the product, (~90%) as separated by preparative gas chro­
matography, was done by nmr spectroscopy. Both bicyclo-
[4.2.1]nona-2,4,7-triene (6) and 2-methylbicyclo[4.2.1]-
nona-2,4,7-triene (7) showed no incorporation of deuterium
at the olefinic (C-2, -3, -4, -5, -7, -8) or the bridge­
head (C-1, -6) positions. Deuterium content at C-9 was
calculated from the following data: 6: $\delta$ 1.94 (t, br,
0.65H, H at C-9, anti) and 1.32 (s, br, 0.40H, H at C-9,
syn); 7: $\delta$ 1.89 (t, br, 0.60H, H at C-9, anti), 1.40
(s, br, 0.40H, H at C-9, syn).

Reaction of 2,3-diazatricyclo[6.3.0.0^4,11]undeca-2,5,9-
triene (13) with sodium dimethyl sulfoxide-d$_5$ in dimethyl-
sulfoxide-d$_6$ at 74°C.

Pyrazoline 13 (0.200 g, 0.0014 mole) dissolved in
dimethyl sulfoxide (4 ml) was added to a solution of
dimsyl sodium (generated from 0.100 g of 57% NaH in
mineral oil and 2 ml of dimethyl sulfoxide-d₆ at 74°C in 20 min. The evolution of nitrogen was instantaneous. The reaction mixture was cooled to room temperature and the product was worked up and analyzed by gas chromatography and nmr spectroscopy.

Here again as in the previous experiment no deuterium incorporation was noted at any of the bridgehead or olefinic positions. The distribution of deuterium at C-9 was calculated from the appropriate peak intensities: 6:

1.94 (t, br, 0.60H, H at C-9, anti), 1.32 (s, br, 0.40H, H at C-9, syn).

7:

1.89 (s, br, 0.55H, H at C-9, anti), 1.40 (s, br, 0.45H, H at C-9, syn).

Reaction of bicyclo[4.2.1]nona-2,4,7-triene (6) with potassium t-butoxide, t-butanol-0-d and dimethyl sulfoxide-d₆ at room temperature.

A mixture of triene 6 (0.08 g, 0.00068 mole), potassium t-butoxide (0.076 g, 0.00068 mole) and t-butanol-0-d (0.045 g, 0.00060 mole) in dimethyl sulfoxide-d₆ (1.5 ml) was stirred for 21 hr at room temperature. The mixture was poured into water (50 ml) and extracted with pentane (20 ml x 6). The pentane extracts were washed and dried. Concentration yielded 0.0625 g (78% recovery) of hydrocarbon which on G.C. analysis was found to contain about 95% bicyclo[4.2.1]nonatriene (6) and 5% 2-methylbicyclo[4.2.1]nona-2,4,7-triene (7). There was no incorporation
of deuterium into the recovered bicyclo[4.2.1]nonatriene (6) as determined by nmr spectroscopy.

Wolff-Kishner reduction of bicyclo[4.2.1]nona-2,4,7-trien-9-one hydrazone-N-d₂ (8) in dimethyl sulfoxide-d₆ in the presence of potassium t-butoxide and two equivalents of t-butanol-0-d at 74°C.

To a rapidly stirred solution of potassium t-butoxide (0.700 g, 0.006 mole), t-butanol-0-d (0.400 g, 0.0054 mole) in dimethyl sulfoxide-d₆ (10ml) at 74°C was added in 40 min hydrazone 8 (0.400 g, 0.0027 mole) dissolved in dimethyl sulfoxide-d₆ (5 ml). The solution turned black on addition of the hydrazone and evolution of nitrogen started almost immediately. The mixture was stirred for 12 hr at 74°C, added to excess (300 ml) water after cooling, and extracted with pentane (7 x 150 ml). The pentane extract was dried and concentrated to yield a mixture of hydrocarbons (0.240 g, 75%). The hydrocarbons were separated on a carbowax 20 M column (20% on chromasorb W, 20' x ½", 135°C) and identified as bicyclo[4.2.1]nona-2,4,7-triene (6, 70%), 2-methyl-bicyclo[4.2.1]nona-2,4,7-triene (7, 25%) and tricyclo-[6.1.0.0₄,₉]nona-2,6-diene (4, 3%).

Integration of the appropriate peak intensities of the nmr spectra revealed extensive incorporation of deuterium into the hydrocarbon products.
The major product, 6, showed the following spectral characteristics nmr: \( \delta 5.90 \ (m, 0.8H, H \text{ at } C-2, -3, -4, -5), 5.20 \ (s, 2H, H \text{ at } C-7, -8), 3.05 \ (s, \text{ br}, 2H, H \text{ at } C-1, -6) \). The peaks at \( \delta 1.94 \) and 1.32 had completely disappeared suggesting 100\% deuterium incorporation at C-9.

2-Methylbicyclo[4.2.1]nona-2,4,7-triene (7) isolated in this reaction has the following nmr absorptions: \( \delta 5.86 \ (s, \text{ br}, 0.5H, H \text{ at } C-2, -3, -4, -5), 5.18 \ (s, 2H, H \text{ at } C-7, -8), 2.95 \ (s, \text{ br}, 2H, H \text{ at } C-1, -6). \) No peaks due to C-9 protons were observed, again suggesting complete deuterium incorporation.

**Preparation of bicyclo[4.2.1]nona-2,4,7-trien-9-one dimethylhydrazone (9),**

Ketone 1 (1 g) was heated with 1,1-dimethylhydrazine (3 ml) at 86\(^\circ\)C for 30 hr. The mixture was diluted with water (20 ml) and extracted with methylene chloride (3 x 30 ml). The organic layer was dried with anhydrous potassium carbonate. Concentration of the methylene chloride extract gave crude 2 as an oily liquid (1.05 g, 80\%) which was used for the next reaction; nmr: \( \delta 5.9 \ (m, 4H, H \text{ at } C-2, -3, -4, -5), 5.5 \ (d, 2H, H \text{ at } C-7, -8), 4.0 \ (m, 1H, H \text{ at } C-1 \text{ or } C-6), 3.3 \ (m, 1H, H \text{ at } C-1 \text{ or } C-6) \) and 2.35 (s, 6H, H of methyl groups).
Attempted exchange of olefinic protons in bicyclo[4.2.1]-nona-2,4,7-trien-9-one dimethylhydrazone (9) using potassium t-butoxide and t-butanol-0-d in dimethyl sulfoxide at room temperature.

Hydrazone 9 (0.48 g, 0.0027 mole), potassium t-butoxide (0.70 g, 0.0060 mole) and t-butanol-0-d (0.40 g, 0.0054 mole) in dimethyl sulfoxide-d6 (1 ml) was stirred at room temperature for several days in a nmr tube. Analysis of the nmr spectrum of 9 at various intervals showed no deuterium incorporation into the olefinic protons.

Attempted reaction of bicyclo[4.2.1]nona-2,4,7-trien-9-one (1) with potassium t-butoxide in dimethyl sulfoxide.

To a solution of potassium t-butoxide (0.85 g, 0.0076 mole) in dimethyl sulfoxide (10 ml) at 74°C was added ketone 1 (0.50 g, 0.0038 mole) dissolved in dimethyl sulfoxide (2 ml). The mixture turned black almost instantaneously. The reaction was worked up after 2 hr by pouring into water, extracting with ether and recovering the product by concentration of the ether solution. The only recovered product (preparative gas chromatography) was unreacted ketone 1 (0.040 g, 8%).

Reaction of tricyclo[6.1.0.04,9]nona-2,6-diene with potassium t-butoxide and t-butanol in dimethyl sulfoxide.

Tricyclo[6.1.0.04,9]nona-2,6-diene 4 (0.40 g, 0.0034 mole) was treated with potassium t-butoxide (0.70 g, 0.006
mole) and \(^{\text{t}}\)-butanol (0.400 g, 0.0054 mole) at 74°C in
dimethyl sulfoxide (10 ml) for 11 hr. The mixture was
poured into water and extracted with pentane (6 x 150 ml).
Gas chromatographic analysis of the product indicated that
the major components were unreacted homosemibullvalene (4)
and indane. Bicyclo[4.2.1]nona-2,4,7-triene (5) was not
detected.

A similar experiment carried out at 165°C for 2 hr
gave only indane in low yield (\(~20\%\)).

**Synthesis of bicyclo[3.2.2]nona-3,6,8-trien-2-one (56).**

Ketone 56 was synthesized according to the procedure
by S. Winstein and J. B. Grutzner.\(^{5b}\) Very pure 56 was iso­
lated by column chromatography on silica gel using pentane/
ether as solvent (mp 44°C, lit. 44°C).

**Synthesis of tricyclo[6.1.0.0\(^{4,9}\)]nona-2,6-dien-5-one (27).**

A mixture of bicyclo[3.2.2]nona-3,6,8-trien-2-one
(56, 0.800 g) and Michler's ketone (0.400 g) in dry benzene
(430 ml) was irradiated through pyrex at room temperature
for 50 min using a Hanovia medium pressure lamp.\(^{36}\) The
solvent was evaporated and 1:1 ether/hexane (50 ml) was
added to the reaction mixture. The Michler's ketone which
precipitated was filtered and the filtrate was concentrated
and carefully chromatographed on silica gel. The various
fractions were analyzed by gas chromatography (5% QF-1 on
chromosorb-W, 7' x \(\frac{1}{4}\)", 125°C).
The initial component was starting material, bicyclo[3.2.2]nona-3,6,8-trien-2-one (56, 0.240 g).

The second component was identified as tricyclo[6.1.0.0\(^4\,9\)]nona-2,6-dien-5-one (27) from its nmr spectrum, which had been reported earlier.\(^{36a}\) nmr: \(\delta\) 6.55 (q, 4.5 Hz, 1H, H at C-7), 6.15 (d, 9 Hz, 1H, H at C-6), 5.85 (m, 1H, H at C-3), 5.50 (m, 1H, H at C-2), 3.60 (m, 1H, H at C-4), 3.10-2.40 (m, 2H, H at C-1, -9), and 2.10 (m, 1H, H at C-8).

The last fractions were combined to give a mixture of tricyclo[6.1.0.0\(^4\,9\)]nona-2,6-dien-5-one (27) and 1-indanone.

The yield of a typical run was 80-85% based on converted bicyclo[3.2.2]nona-3,6,8-trien-2-one (56).

Wolff-Kishner reduction of tricyclo[6.1.0.0\(^4\,9\)]nona-2,6-dien-5-one (27).

A mixture of tricyclo[6.1.0.0\(^4\,9\)]nona-2,6-dien-5-one (27, 0.400 g), hydrazine hydrate (1.5 ml) and potassium hydroxide (1 g) in diethylene glycol (0.5 ml) was heated for 1 hr at 110\(^\circ\)C and for another hr at 180\(^\circ\)C. The mixture was cooled and water (50 ml) was added. Extraction of the aqueous layer with pentane (6 x 40 ml) and evaporation of the solvent gave an oil which on gas chromatographic analysis (carbowax 20 M, 20% on chromosorb-W, 20' x \(\frac{1}{4}\)" 135\(^\circ\)C) indicated one major hydrocarbon (~95%) identified as tricyclo[6.1.0.0\(^4\,9\)]nona-2,6-diene (4) by comparison with previously synthesized material.
Preparation of tricyclo[3.3.1.0^4,6]nona-2,7-dien-9-one (30, Barbaralone).

Barbaralone (30) was synthesized in 60-75% yield by Michler's ketone sensitized irradiation of bicyclo[4.2.1]-nona-2,4,7-trien-9-one (1) in benzene by the procedure of T. A. Antkowiak^4. Pure 30 (mp 50-51°C) was isolated by sublimation.

Wolff-Kishner reduction of barbaralone (30).

The Wolff-Kishner reduction of 30 was carried out by the procedure of von E. Doering^30. Ketone 30 (400 mg) was heated with hydrazine hydrate (1.5 g, 85%) and potassium hydroxide (2 g) in diethylene glycol (3 ml) for 1 hr at 115°C and for 3 hr at 180-190°C. The product solidified in the condenser as a white solid which was collected (0.16 g, 46%) and analyzed by gas chromatography on a carbowax 20M column (20%, 20' x \( \frac{1}{4} \)', 140°C). The product consisted of three components.

The component with the longest retention time (30%) was tricyclo[3.3.1.0^2,8]nona-3,7-diene (barbaralane, 34).

The major product (50%) was identified as bicyclo-[3.2.2]nona-2,6,8-triene (33) from its spectral properties^1719: nmr: δ 6.50 (m, 2H), 6.15 (m, 2H), 5.90 (m, 1H), 5.05 (m, 1H), 3.10 (m, 2H), 2.20 (q, 2H); mass spectrum m/e 118.

The third component (20%, shortest retention time) was a reduction product of 33, bicyclo[3.2.2]nona-2,6-
diene (35); mp 52° (lit 53°18); nmr: δ 6.40 (t, 3.5 Hz, 1H), 5.90 (m, 2H), 5.30 (m, 1H), 2.8-1.5 (m, 8H); mass spectrum m/e 120.

An authentic sample of diene 35 was synthesized as described below.

**Synthesis of bicyclo[3.2.2]nona-2,6-diene (35).**

A sample of bicyclo[3.2.2]nona-2,6-diene (35) was prepared by diimide reduction of bicyclo[3.2.2]nona-2,6,8-triene (33).

Potassium azocarboxylate (970 mg, 0.005 mole) was dissolved in methanol (3 ml) and the solution was degassed and cooled to -20°C.

A mixture of acetic acid and methanol (2 ml) was degassed and cooled to -20°C. The bicyclo[3.2.2]nona-2,6,8-triene (33) (0.118 g, 0.001 mole) was dissolved in the acetic acid-methanol mixture and added to the potassium azocarboxylate solution about one tenth at a time with constant stirring. The mixture was warmed to room temperature and then stirred for 30 min. Water (20 ml) was added and the aqueous layer was extracted with pentane (4 x 25 ml). The pentane extracts were combined, washed with water, and dried over anhydrous magnesium sulphate.

Analysis on a carbowax 20M column (20% on chromosorb W, 20' x 1/4", 140°) showed three components. The third component showed the same retention time as that of the
hydrocarbon of shortest retention time obtained from the Wolff-Kishner reduction of barbaralone. This product (0.020 g, ~16%) was isolated by preparative gas chromatography and further identified as bicyclo[3.2.2]nona-2,6-diene (35) by nmr and ir spectroscopy; mp 54° (lit. 53°18); nmr: δ 6.40 (t, 3.5 Hz, 1H), 5.90 (m, 2H), 5.30 (m, 1H), 2.80-1.50 (m, 8H); mass spectrum m/e 120.

Preparation of tricyclo[3.3.1.04,6]nona-2,7-dien-9-one hydrazone (36).

Ketone 30 (0.300 g, 0.0025 mole) dissolved in methylene chloride (2 ml) was added dropwise to rapidly stirred anhydrous hydrazine (0.40 g, 0.125 mole). The solution was heated on a steam bath for one hour and then poured into water (10 ml) and extracted with methylene chloride (3 x 20 ml). The methylene chloride layers were combined, dried over anhydrous potassium carbonate and concentrated to give 36 a white amorphous solid (0.36 g, 97%); ir (CHCl₃): 3330 (m), 3200 (m) cm⁻¹; nmr (CD₃SOCD₃): δ 5.85-4.85 (m, 4H), 3.6 (m, 2H), 3.3.2.1 (m, 4H); mass calcd for C₉H₁₀N₂ 146.0844, found 146.0846; elemental analysis of hydrazone 36 was not attempted.
Wolff-Kishner reduction of tricyclo[3.3.1.0^4,6]nona-2,7-dien-9-one hydrazone (36) with potassium t-butoxide in the presence of two equivalents of t-butanol at 74°C in dimethyl sulfoxide.

To a rapidly stirred solution of potassium t-butoxide (0.700 g, 0.006 mole) and t-butanol (0.40 g, 0.0054 mole) in dimethyl sulfoxide (10 ml) was added (60 min) hydrazone 36 (0.40 g, 0.0027 mole) dissolved in dimethyl sulfoxide (5 ml). The solution slowly turned black. The mixture was stirred at 74°C for 12 hr. Excess water was added and the solution was extracted with pentane (5 x 150 ml). The organic extracts were combined, washed with water, and dried over magnesium sulphate. Concentration yielded an oil which on analysis on a carbowax 20M column (20% on chromosorb W, 20' x ¼", 110°C) indicated the presence of 3 hydrocarbons. The major component (90%) was identified as bicyclo[3.2.2]nonatriene (33) by comparison of its spectral properties with a sample prepared earlier. Two minor hydrocarbons (~ 10%; neither of them was tricyclo[3.3.1.0^4,6]nona-2,7-diene, 34) were not identified.


Alcohols 39 and 40 were prepared by the procedure of W. Kirmse et. al. 8

The mixture of alcohols was easily separated by chromatography on alumina (activity 3) using 10:1
petroleum ether/chloroform as the solvent. The purity of 39 and 40 was checked by gas chromatography (SF-96, 20% on chromosorb-W, 15' x ½", 125°C). Smaller amounts of 39 and 40 were separated more efficiently by thick layer chromatography on alumina using 1:1 petroleum ether/ether.

Alcohols 39 and 40 were identified by their nmr spectra: 39: δ 6.10 (m, 4H, H on C-2, -3, -4, -5), 5.25 (d, 2Hz, 2H, H on C-7, -8), 4.40 (m, 1H, H on C-9, anti); 3.10 (t, br, 6Hz, 2H, H on C-1, -6), and 1.80 (s, br, 1H, hydroxylic H); 40: δ 5.90 (m, 4H, H on C-2, -3, -4, -5), 5.35 (s, br, 2H, H on C-7, -8), 4.05 (s, br, H on C-9, syn), and 3.00 (d, br, 6Hz, H on C-1, -6), 1.95 (s, br, 1H, hydroxylic H).

Reaction of syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (39) with phosphorus tribromide in the presence of collidine and lithium bromide.

Phosphorus tribromide (2.02 g, 0.0076 mole) in ether (20 ml) was added dropwise to a solution of collidine (2 ml), anhydrous lithium bromide, and syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (1 g, 0.0076 mole) in ether (20 ml) at -30°C. The mixture was stirred at -30 to -10°C for 90 min. Excess ice was added and the mixture was extracted with ether. The combined extract was washed with dilute hydrochloric acid (3N), sodium bicarbonate solution and
water and then concentrated to an oil which was crystal-
lized from ether/hexane at -78°C.

The white crystalline solid isolated (mp 161-163°C, 55%) was identified as tris(bicyclo[4.2.1]nona-2,4,7-trien-
syn-9-yl)phosphate (41); exact mass calcd for C$_{27}$H$_{27}$O$_4$P 446.1647; found 446.1655; ir (KBr): $\gamma_{\text{max}}$ 1275, 990 cm$^{-1}$; nmr: $\delta$ 5.90 (m, 4H, H on C-2, -3, -4, -5), 5.15 (s, br, 2H, H on C-7, -8), 4.60 (m, 1H, H on C-9) and 3.10 (t, br, 2H, H on C-1, -6).

Anal: Calcd C, 71.38; H, 6.27.

Found C, 71.78; H, 6.12.

The reaction was repeated by refluxing alcohol 39 with 3 equivalents of phosphorus tribromide in the presence of pyridine and lithium bromide in benzene for 3 hr. The reaction was worked up as described earlier and the only product obtained was still triphosphate 41. However, on prolonged refluxing of the reaction mixture in benzene (26 hr) triphosphate 41 undergoes cationic rearrangement to give indene (43), as identified by its nmr spectrum and G.C. retention times.

Reaction of anti-9-hydroxybicyclo[4.2.1]nona-2,4,7-
triene (40) gave tris(bicyclo 4.2.1 nona-2,4,7-trien-anti-
9-yl)-phosphate (42) on treatment with phosphorus tribro-
mide under conditions described earlier; mp 140-143°C, mass spectrum, m/e 446).
Reaction of syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (39) with triphenylphosphine dibromide in acetonitrile.

A three necked flask fitted with a stirrer and dropping funnel and cooled in an ice bath was charged with acetonitrile (10 ml, distilled from phosphorus pentoxide) and triphenylphosphine (2.62 g, 0.01 mole). Bromine (1.6 g, 0.01 mole) was added slowly (15 min). The excess bromine was decolorized by adding trace amounts of triphenylphosphine. The ice bath was removed and alcohol 39 (1.34 g, 0.01 mole) dissolved in acetonitrile (10 ml) was slowly added in 15 min. The mixture was warmed to 60°C to dissolve the solid triphenylphosphine dibromide and then stirred at 60°C for 25 min. The reaction was quenched by adding water (200 ml) and then the product was extracted with ether (4 x 200 ml). The ether extracts were combined, washed with sodium bicarbonate and then water, dried, concentrated and distilled under vacuum. Analysis of the product by gas chromatography and nmr spectroscopy revealed the presence of only unreacted alcohol 39 and traces of indene (43).

The reaction was repeated at higher temperatures. When heating was continued at 70°C until all of the alcohol 39 disappeared (as revealed by thin layer chromatography), and the reaction worked up, one product was found to be major. This product was separated by thick layer chromatography (alumina, 1:5 ether/petroleum ether) and was
identified as indene (43). Two minor products (~15% combined) were not identified though it was clear from the nmr spectra that neither was the expected 9-bromobicyclo[4.2.1]nona-2,4,7-triene.

**Reaction of bicyclo[4.2.1]nona-2,4,7-trien-9-one (1) with phosphorus pentachloride.**

A solution of ketone 1 (0.528 g, 0.004 mole) in methylene chloride (10 ml) was added to a suspension of phosphorus pentachloride (0.917 g, 0.0044 mole) in methylene chloride stirred at room temperature. The reaction was followed by thin layer chromatography (silica gel, 1:1 benzene/petroleum ether). After 6 hr ketone 1 was still present. The mixture was refluxed for 30 min. Excess water was added and the product extracted with methylene chloride. The methylene chloride layer was washed with 10% sodium bicarbonate, saturated sodium chloride and water. The organic layer was dried and concentrated. Column chromatography (silica gel, 2:1 petroleum ether/chloroform) yielded only one product, 1-chloroindene (33, 52); nmr: δ 7.20 (m, 4H, aromatic H), 6.75 (d, 6Hz, 1H, H on C-3), 6.30 (q, 6.0Hz, 2Hz, 1H, H on C-2), and 5.25 (s, br, 1H, H on C-1).
Reaction of syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (39) with thionyl chloride.

Alcohol 39 (0.264 g, 0.002 mole) was added to thionyl chloride (3 ml) cooled to 0°C. The mixture was stirred at 0°C for 2 hr and then warmed to room temperature and further stirred for 10 hr. Excess thionyl chloride was removed on a rotary evaporator. Analysis of the product (0.400 g, 92%) by thin layer chromatography indicated the presence of two components (silica gel, benzene/hexane 1:1). The minor component was identified as di-syn-bicyclo[4.2.1]nona-2,4,7-trien-9-yl sulfite (44) which had been previously synthesized by D.C. Sanders.

The major component was identified as syn-bicyclo[4.2.1]nona-2,4,7-trien-9-yl chlorosulfite (45) based on the reaction to be described in the next section and on its spectra; ir (CHCl₃): 3060, 3025, 1390, 1200, 1070, 1040, 1005, 970, 918, 892, 882 cm⁻¹; nmr δ 5.90 (m, 4H, H on C-2, -3, -4, -5), 5.20 (d, 2H, H on C-7, -8), 4.85 (t, 1H, H on C-9, anti), and 3.15 (t, 2H, H on C-1, -6).

Thermolysis of syn-bicyclo[4.2.1]nona-2,4,7-trien-9-yl chlorosulfite (45).

Chlorosulfite 45 from the previous reaction was distilled under vacuum using a short path distillation head (140°C, bath temp, 0.2 mm pressure). The distillate (typically 85-90% yield based on 45) was collected in a
well-cooled receiver. Careful examination of the nmr spectrum indicated the presence of \textit{cis}-7-chlorobicyclo[4.3.0]nona-2,4,8-triene\textsuperscript{38a} (48) contaminated with indene (43, 8%). 48 nmr: \(\delta 5.80\) (m, 6H, olefinic H), 4.80 (m, 1H, H on C-7), 3.80 (d, m, 10Hz, 1H, H on C-1), and 3.35 (d, m, 10Hz, 1H, H on C-6).

\textbf{Reaction of syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene-9-d (39d) with thionyl chloride.}

Treatment of \textit{syn}-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene-9-d (39d) with thionyl chloride as described in the previous section followed by distillation under vacuum yielded (70% based on alcohol 39d) \textit{cis}-7-chlorobicyclo[4.3.0]nona-2,4,8-triene-8-d (51) as evident from the nmr spectrum. \(\delta 5.80\) (m, 5H, olefinic H), 4.80 (m, 1H, H on C-7, coupling simplified), 3.80 (d, m, 10Hz, 1H on C-1), and 3.35 (d, m, 10Hz, 1H, H on C-6).

\textbf{Reaction of anti-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (40) with thionyl chloride.}

Reaction of 40 with thionyl chloride was carried out exactly as described in the previous sections. The only product isolated on vacuum distillation of the chlorosulphite was identified as \textit{cis}-7-chlorobicyclo[4.3.0]nona-2,4,8-triene\textsuperscript{38a} (48) from its nmr spectrum.
Reaction of syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (39) with oxalyl chloride.

Alcohol 39 (0.67 g, 0.005 mole) was added in small lots to well-stirred oxalyl chloride (2 ml) at 0°C. After addition was completed, the ice bath was removed and the mixture stirred for 30 min. Excess oxalyl chloride was removed on a rotary evaporator. The product was distilled under vacuum (82°C, 1 mm Hg pressure) to yield syn-9-chloroglyoxalylbicyclo[4.2.1]nona-2,4,7-triene (53, 0.72 g, 64%); ir (neat): $\gamma_{\text{max}}$ 3025, 2950, 1785, 1750, 1270, 1070, 1025, 980, 910, 890; nmr: $\delta$ 6.10 (m, 4H, H on C-2, -3, -4, -5), 5.35 (d, 2H, H on C-7, -8), 5.20 (m, 1H, H on C-9) and 3.50 (t, 2H, H on C-1, -6).

Reaction of syn-9-chloroglyoxalylbicyclo[4.2.1]nona-2,4,7-triene (53) with t-butyl hydroperoxide in the presence of pyridine.

To a mixture of t-butyl hydroperoxide (0.261 g, 0.0029 mole) and pyridine (0.23 g, 0.0029 mole) in carbon tetrachloride (3 ml) at 0°C was added a solution of chloroglyoxalate 53 (0.65 g, 0.0029 mole) in carbon tetrachloride (3 ml) over 10 min. Pyridine hydrochloride separated. The ice bath was removed and the mixture was stirred for 25 min. The precipitated hydrochloride was removed, washed with carbon tetrachloride and the carbon tetrachloride solution was used for the next step without further
purification. The product was identified as syn-9-bicyclo[4.2.1]nona-2,4,7-trien-yl t-butylperoxyglyoxalate (54); nmr: δ 6.10 (m, 4H, H on C-2, -3, -4, -5), 5.30 (m, 3H, H on C-7, -8, -9), 3.50 (t, br, 2H, H on C-1, -6), 1.40 (s, 9H, t-butyl H).

Thermolysis of syn-9-bicyclo[4.2.1]nona-2,4,7-trienyl-t-butylperoxyglyoxalate (54).

Thermolyses of peroxy ester 54 were carried out in carbon tetrachloride or in bromotrichloromethane under a variety of conditions. Typically a 0.20-0.25 molar solution of 54 was used.

A solution of 54 in carbon tetrachloride in a sealed ampule was heated for 10 min at 96°C. The mixture was cooled, concentrated and the gummy solid obtained was analyzed by nmr spectroscopy. Even traces of bicyclo-[4.2.1]nona-2,4,7-trien-9-yl chloride were not present in this product.

The reaction was repeated by refluxing peroxy ester 54 in carbon tetrachloride for 60 min. Only intracetable materials were obtained. Similar reactions in bromotrichloromethane (1. sealed ampule, 100°C, 10 min; 2. reflux, 10 min) also failed to yield any of the expected 9-bromobicyclo[4.2.1]nona-2,4,7-triene.

Photolyses of the carbon tetrachloride solutions using a Hanovia medium pressure lamp through pyrex were
carried out without success in generating 9-chlorobicyclo-4.2.1] nona-2,4,7-triene. No gas was evolved even after several hours of irradiation.

Reaction of syn-9-hydroxybicyclo[4.2.1] nona-2,4,7-triene (39) with triphenylphosphine in carbon tetrachloride.

A solution of alcohol 39 (0.264 g, 0.002 mole) in carbon tetrachloride (5 ml) was added to triphenylphosphine (0.94 g, 0.002 mole) in carbon tetrachloride (5 ml) at 0°C. The ice bath was removed and the mixture was stirred at room temperature. The reaction was followed by thin layer chromatography (1:1 chloroform/hexane, alumina). After 6 hr alcohol 39 was still present. The reaction mixture was warmed to 50°C and then stirred at that temperature for 4 hr.

The solution was concentrated and the product, as analyzed by thin layer chromatography (silica gel, hexane) and gas chromatography (OV-1) 3% on chromosorb W, 8' x ½", 110°C), revealed the presence of indene (43) and alcohol 39. Vacuum distillation and analysis of the product by nmr spectroscopy confirmed the presence of indene (43) and alcohol 39.

Reaction of anti-9-hydroxybicyclo[4.2.1] nona-2,4,7-triene (40) with triphenylphosphine in carbon tetrachloride also failed to yield bicyclo[4.2.1] nona-2,4,7-trien-9-yl chloride under conditions described in the previous experiment.
Photolysis of syn-9-bicyclo[4.2.1]nona-2,4,7-triene carboxylic acid (55) in the presence of lead tetraacetate and subsequent reaction with iodine.

Carboxylic acid 55 was synthesized by the procedure of D. C. Sanders. A solution of 55 (0.81 g, 0.005 mole) and lead tetraacetate (2.40 g, 0.0055 mole) in benzene (75 ml) was irradiated with a 275 watt tungsten lamp for 15 min. A solution of iodine (0.63 g, 0.005 mole) in carbon tetrachloride was added and the irradiation continued for 20 min. The lead salts were filtered and the organic layer was washed with sodium thiosulphate and then with water. Column chromatography on silica gel using petroleum ether/ether (10:1) as solvent yielded only intratable materials.

Preparation of endo-tricyclo[6.1.0.0^4,9]nona-2,6-dien-5-ol (57).

A solution of tricyclo[6.1.0.0^4,9]nona-2,6-dien-5-one (27, 0.300 g) in methanol (15 ml) was added to a stirred solution of sodium borohydride (0.800 g) in methanol (15 ml) at room temperature. After the mixture was stirred for 2 hr the sodium borohydride was destroyed by addition of 20% potassium hydroxide (10 ml). The aqueous layer was extracted with ether and the combined ether extracts were washed with water. The dried solution of the product in ether was concentrated, pentane (10 ml)
was added, and the mixture was kept in a freezer. The white crystals were collected, recrystallized from hexane (0.130 g, 41%, mp 84-85°C), and identified as endo-tricyclo[6.1.0.0⁴,⁹]nona-2,6-dien-5-ol (57) based on the following data: nmr: δ 6-5.4 (m, 4H, olefinic H), 4.80 (m, 1H, H at C-5), 3.10 (m, 1H, H at C-4), 2.20 (m, 2H, H at C-1, -8), 1.80 (s, 1H, hydroxyllic H), and 1.40 (m, 1H, H at C-9); exact mass calcd for C₁₁H₁₀O: 134.0731; found: 134.0733.

Analysis Calcd for C₁₁H₁₀O: C, 80.56; H, 7.51.

Found: C, 80.48; H, 7.51.

Preparation of endo-5-methoxytricyclo[6.1.0.0⁴,⁹]nona-2,6-diene (61).

To a solution of alcohol 57 (0.190 g, 0.0014 mole) and methyl iodide (0.14 g) in dry glyme was added (10 min) sodium hydride (0.070 g, 57% in mineral oil, 0.0017 mole). The mixture was stirred for 30 min and additional methyl iodide (0.15 g) was added. Stirring was continued for another 7 hr. Excess glyme and methyl iodide were removed on a rotary evaporator. Anhydrous ether was added to the residue and the sodium iodide precipitated was filtered. Vacuum distillation of the product yielded pure 61 (0.170 g, 85%). The structure was confirmed by spectral analysis: exact mass calcd for C₁₀H₁₂O: 148.0888; found: 148.0890; nmr: δ 5.70 (m, 3H, olefinic), 5.25 (m, 1H, olefinic), 4.25 (m, br, 1H, H on C-5), 3.30 (s,
3H, methoxyl H), 3.20 (m, 1H, H on C-4), 2.20 (m, 2H, H on C-1, -8), and 1.35 (m, 1H, H on C-9).

Analysis Calcd for C_{10}H_{12}O: C, 81.04; H, 8.15
Found: C, 80.71; H, 8.15

Reaction of endo-tricyclo[6.1.0.0^{4,9}]nona-2,6-dien-5-ol (57) with triphenylphosphine dibromide in acetonitrile.

Triphenylphosphine dibromide was prepared from triphenylphosphine (0.28 g, 0.001 mole) and bromine (0.17 g, 0.001 mole) in acetonitrile (3 ml). The mixture was cooled to 0°C and alcohol 57 (0.134 g, 0.001 mole) dissolved in acetonitrile (3 ml) was slowly added. The solution was stirred at room temperature for an hour and then warmed to 60°C. The reaction was followed by thin layer chromatography for the disappearance of 57. After 60 min the mixture was cooled and acetonitrile removed on a rotary evaporator. The product was distilled and analyzed by nmr spectroscopy. Absence of high field protons (< δ 2.2) indicated the absence of the expected product, 5-bromo-tricyclo[6.1.0.0^{4,9}]nona-2,6-diene. The major product (~70%) was identified as indene by nmr and ir spectroscopy and gas chromatography.

Reaction of endo-tricyclo[6.1.0.0^{4,9}]nona-2,6-dien-5-ol (57) with triphenylphosphine and carbon tetrachloride.

To a solution of alcohol 57 (0.134 g, 0.001 mole) in carbon tetrachloride (2 ml) was added triphenylphosphine
(0.393 g, 0.0015 mole). The mixture was stirred at room temperature and the reaction was followed by thin layer (silica gel, 10% ether in hexane) and gas chromatography (10% OV-1 on chromosorb-W, 6' x 3/8", 120°C). The only two components present were easily identified as unreacted 58 and indene (43).

**Synthesis of bicyclo[4.2.2]deca-2,4,9-trien-7-one (16).**

Ketone 16 was prepared in 50-60% yields by diazomethane ring expansion of bicyclo[4.2.1]nona-2,4,7-trien-9-one (1).

**Preparation of bicyclo[4.2.2]deca-2,4,9-trien-7-one p-tosylhydrazone (63).**

Ketone 16 (2 g, 0.014 mole) in ethanol (25 ml) was mixed with a solution of tosylhydrazide (3.60 g, 0.02 mole) in ethanol (25 ml) containing a drop of concentrated hydrochloric acid and the mixture was stirred for 12 hr at room temperature. The solution was concentrated and cooled in a freezer. The bicyclo[4.2.2]deca-2,4,9-trien-7-one tosylhydrazone (63) formed was filtered and recrystallized from ethanol. The material was identical to the sample previously reported 13a.
Reaction of bicyclo[4.2.2]deca-2,4,9-trien-7-one tosylhydrazone (63) with sodium hydride.

Tosylhydrazone 63 (0.1 g, 0.003 mole) in dry methylene chloride (10 ml) was cooled to 0°C. Sodium hydride free of mineral oil (from 0.15 g, 57%, 0.0037 mole) was then added slowly (10 min). The solution was stirred until the evolution of hydrogen ceased. The solvent was evaporated on a rotary evaporator. The last traces of the solvent were removed by a high vacuum pump. The white amorphous solid was used for the reactions described in the following sections. A fresh sample of the sodium salt 64 was prepared for each of the experiments.

Pyrolysis of the sodium salt (64) of bicyclo[4.2.2]deca-2,4,9-trien-7-one p-tosylhydrazone at 220°C.

A 50 ml round bottom flask containing salt 64 was connected via an adapter (partially packed with glass wool to prevent spattering) to 2 traps cooled in dry ice/acetone baths and then to a vacuum pump. The system was evacuated to 0.1 mm mercury pressure. A high temperature silicone oil bath at 220°C was raised and immersed the pyrolysis flask. Evolution of nitrogen was almost instantaneous and the product distilled (0.41 g, ~100%) into the traps.

The reaction product was extremely sensitive to heat and oxygen (?) and extensive polymerization to a white amorphous solid occurred when the temperature was raised.
The product could, however, be kept at -78°C in a freezer for a few days without much change as determined by nmr spectroscopy.

Gas chromatographic analysis of the product on a carbowax 20M column (20% on chromosorb W, 10' x 1/8", 145°C) showed three components to be present.

The first component was identified as tricyclo-[4.3.1.0^1,6]deca-2,4,7-triene (71) by comparison of its spectral properties and G. C. retention times with those of an authentic sample. 39

The third component, also isolated by gas chromatography, was identified as 1-propargylcyclohepta-2,4,6-triene (73) by comparison with an authentic sample prepared by the procedure of Pauson et. al. 40

The major component of the reaction mixture could not be isolated pure because of its instability and the high losses on chromatography. Reaction mixtures containing up to 80% of this product were subjected to extensive nmr spectral studies and trapping experiments to be described later. The structure of this product is assigned as bicyclo[4.3.1]deca-2,4,6,8-tetraene (69); pmr: δ 6.3 (m, 2H), 5.9 (m, 4H), 5.6 (m, 1H), 2.9 (m,
\( \delta 139.3, 138.7, 135.3, 128.0, 125.6 \) (2), 121.4, 36.4 and 32.8. The \( ^{13}C \)- resonance of C-6 is of too low intensity compared with the others and can not be identified.

**Reduction of the mixture of hydrocarbons 69, 71 and 73 with diimide generated from potassium azocarboxylate and acetic acid.**

A mixture of water (5 ml), methanol (20 ml) and dipotassium azocarboxylate in a 50 ml round bottom flask equipped with magnetic stirrer was thoroughly degassed with argon and then cooled to a barely stirrable paste in an acetone-dry ice bath. A solution of acetic acid (3.90 g) in methanol (10 ml) was similarly degassed and cooled.

The pyrolysis product from tosylhydrazone 63 (1 g) and sodium hydride (0.16 g, 57%) in mineral oil was dissolved in the acetic acid at \(-78^\circ C\) and then added to the solution of dipotassium azocarboxylate about \( \frac{1}{4} \) at a time. The solution was slowly allowed to warm to room temperature and stirred for 2.5 hr. Water (50 ml) was added and the aqueous layer was extracted with pentane (6 x 50 ml). The pentane extracts were combined, washed with water, dried over anhydrous magnesium sulphate, and evaporated. The hydrocarbon product (0.220 g, 42%) was analyzed on a carbowax 20M column (20% chromosorb W, 20' x \( \frac{1}{4}'' \)) at \( 152^\circ C \).
The first component (~10%) was assigned as tricyclo-[4.3.1.0\(^1,6\)]deca-2,4,7-triene (73) from its nmr and ir spectra.

The second (and the major) component was identified as bicyclo[4.3.1]deca-2,4,7-triene (80a) by comparison of its properties with those of an authentic sample prepared as described below. The structure was confirmed by nmr: \(\delta 5.80 (m, 6H, \text{olefinic } H), 3.13 (m, br, 1H, H \text{ at C-6}), 2.77 (m, br 1H, H \text{ at C-1}) \text{ and } 1.69-2.10 (m, 4H, H \text{ at C-9, -10}); \text{ exact mass calcd 132.0939; found 132.0942.}

The third component (~15%) was identified as 1-propargylcycloheptatriene (73) by comparison with an authentic sample.

**Reduction of the mixture of hydrocarbons 69, 71 and 73 as obtained from the pyrolysis of bicyclo[4.2.2]deca-2,4,9-trien-9-one p-tosylhydrazone sodium salt, with dideutero-diimide.**

The reduction was carried out according to the procedure described in the previous section.

The pyrolysis product from 1 g of tosylhydrazone 63 was dissolved in degassed acetic acid-\(d_1\) (3.90 ml)/methanol-\(d\) (10 ml) solution at \(-78^\circ\text{C.}\) This mixture was added to a solution of dipotassium azocarboxylate (6.2 g) in methanol-\(d\) (50 ml) and \(D_2O(5 \text{ ml})\) at about \(-40^\circ\text{C.}\) The
solution was allowed to warm to room temperature and stirred for 2½ hr. The product was worked up by adding to excess water (50 ml) and extracting with pentane (6 x 50 ml). Concentration of the dried pentane extract followed by gas chromatographic analysis revealed the presence of one major hydrocarbon which was identified by nmr and mass spectrometry as 1,9-dideuterobicyclo[4.3.1]deca-2,4,7-triene (80b, 53%); nmr: δ 5.80 (m, 6H, olefinic H), 3.13 (m, br, 1H, H at C-6), and 1.69-2.10 (m, 3H, H at C-9, -10, coupling simplified). It is noted that the absorption at δ 2.77 originally attributed to H on C-1 in 80a has disappeared and the intensity of the signals due to hydrogens on C_9 and C_10 decreases to three exact mass calc'd for D_{10}H_{10}D_2: 134.1064, found 134.1066.

Reduction of exo-7-bromobicyclo[4.3.1]deca-2,4,8-triene (81); preparation of bicyclo[4.3.1]deca-2,4,7-triene (80a).

To a solution of exo-7-bromobicyclo[4.3.1]deca-2,4,8-triene (81, 220 mgm, 0.001 mole, prepared according to the procedure of G. Schröder\(^1\)) in dry tetrahydrofuran (5 ml) was added lithium triethylborohydride (5 ml of 1 M solution, 0.005 mole) in 30 min. The mixture was stirred at room temperature for 5 hr. Excess water (20 ml) was added and the mixture was extracted with hexane (4 x 25 ml). The combined organic layer was washed with brine and water and dried over anhydrous calcium chloride. Evaporation of the solvent yielded an oily liquid which on analysis
on an OV-1 column at 120°C showed two volatile products.

The major product (90%) was identified as bicyclo-[4.3.1]deca-2,4,7-triene (80a, 0.0501 g, 36%); nmr: δ 5.80 (m, 6H, olefinic H), 3.13 (m, br, 1H, H at C-6), 2.77 (m, br, 1H, H at C-1), and 1.69-2.10 (m, 4H, H at C-9, -10); mass spectrum, m/e 132.

The minor component (~10%) was not identified.

Reaction of bicyclo[4.3.1]deca-2,4,6,8-tetraene (89) with sodiodimethyl sulfoxide-d₆ in dimethyl sulfoxide-d₆.

Sodium hydride (0.040 g, 57% in mineral oil) was placed in a nmr tube and washed with pentane (3 times). The last traces of pentane were removed under vacuum. Dimethyl sulfoxide-d₆ (0.5 ml) was added and the mixture was heated at 75°C for 30 min. The nmr tube was fitted inside a cold trap such that when connected to a tosylhydrazone pyrolysis set up, the product would directly distil into the tube.

The hydrocarbon mixture generated from decomposition of tosylhydrazone 64 (0.270 g) was collected inside the nmr tube at -78°C. The mixture was then warmed to room temperature and the pmr spectrum recorded on a Brucker HX-90 spectrometer.

The spectrum was identical in all respects to that of 1,5-methanononatetraenyl sodium (82) as reported by P. Radlick; nmr: δ 6.84 (dd, 2 and
5Hz, 2H), 5.77 (center of nine lines, 5H), -0.72 (d, 7.2Hz, H on C-10) and -1.20 (d, 7.2Hz, H on C-10). The chemical shifts were measured with reference to HCD<sub>2</sub>SOCD<sub>3</sub> at δ 2.49.

Under these conditions none of the other hydrocarbons or products derived from them were detectable by nmr.

**Preparation of tricyclo[4.3.1.0<sup>1,6</sup>]deca-2,4,7-triene (71) from bicyclo[4.3.1]deca-2,4,6,8-tetraene (69).**

Dimethyl sulfoxide (1 ml) was stored with sodium hydride (0.09 g, 57% in mineral oil) at 75°C until evolution of hydrogen ceased. The mixture was cooled to -78°C and the hydrocarbon mixture generated from pyrolysis of the sodium salt of bicyclo[4.2.2]deca-2,4,9-trien-7-one tosylhydrazone (64, 0.66g) was added using the set up described in the previous section. The mixture was warmed to room temperature, stirred for 30 min and water (1 ml) was added. After the mixture was stirred for another 15 min, excess water was added and the mixture extracted with hexane (3 x 30 ml). The hexane extracts were washed with water and dried over anhydrous magnesium sulphate. Analysis of the product on a OV-1 column (10% on chromosorb W, 6' x 3/8'', 80°C) showed the presence of tricyclo-[4.3.1.0<sup>1,6</sup>]deca-2,4,7-triene (71, 90%) and 1-propargylcyclohepta-2,4,6-triene (73, 10%).
Reaction of bicyclo[4.3.1]deca-2,4,6,8-tetraene (69) with phenyl azide.

The pyrolysis product from the sodium salt of the tosylhydrazone of bicyclo[4.2.2]deca-2,4,9-trien-7-one (64, 0.660 g) was condensed into a trap at -78°C containing phenyl azide (0.25 g). The hydrocarbon condensed on the wall of the trap was washed down with cold pentane. The mixture was stirred overnight; a white solid precipitated. After cooling the mixture in a freezer (-20°C), the solid was filtered, recrystallized from hexane and the structure was assigned as triazole 81 in which the position of the phenyl group is not yet established (0.050 g, 10%); mp 92-94°C (dec.); nmr: δ 7.25 (m, 5H, aromatic), 6.00 (m, 6H, H at C-2, -3, -4, -5, -8, -9), 4.45 (dd, 1.5Hz, 1H, H at C-7), 3.15 (m, br, bridgehead H at C-1), 2.25 (d, 13Hz, 1H, H at C-10, endo), 1.60 (dd, 12Hz, 5Hz, 1H, H at C-10, exo); mass spectrum m/e 221 (M-N₂); ir (CDCl₃): 3020, 1595, 1480, 1450, 1320, 1300, 1085, 1060, 1045, 1010, 830, 675, 640 cm⁻¹.

Anal calcd for C₆₆H₅₅N₂: C, 76.80; H, 6.04; N, 16.79.

Found: C, 76.96; H, 6.17; N, 16.35.

Attempted reaction of bicyclo[4.3.1]deca-2,4,6,8-tetraene (69) with diphenylisobenzofuran.

The hydrocarbon product, principally 69, as generated by pyrolysis of the sodium salt of the tosylhydrazone of
bicyclo[4.2.2]deca-2,4,9-trien-7-one (64) was condensed into a trap containing diphenylisobenzofuran in chloroform (5 ml) at -78°C. The mixture was stirred for 30 min and then warmed to room temperature. The color slowly disappeared on stirring the mixture for 24 hr at room temperature. The solvent was rotary evaporated and the product chromatographed on silica gel (50 g) using 1:4 petroleum ether/chloroform. The only isolable solid (0.060 g) was recrystallized from ether and analyzed by nmr spectroscopy and mass spectrometry. The nmr spectrum of the product revealed only aromatic protons; the mass spectrum indicated m/e 332. Neither result is consistent with the capture product of the strained double bond by diphenylisobenzofuran.

Photolysis of the sodium salt of bicyclo[4.2.2]deca-2,4,9-
trien-7-one tosylhydrazone (64) in ether.

The sodium salt generated from tosylhydrazone 63,
(1 g, 0.0032 mole) and sodium hydride (0.15 g, 57% in mineral oil, 0.0037 mole) was dispersed in dry ether. Nitrogen was bubbled through the solution and then the mixture was irradiated with a Hanovia medium pressure lamp through pyrex until evolution of nitrogen stopped (~2 hr). The mixture was filtered and the residue collected by concentrating the ether solution was passed through a short column of silica gel as eluted with pentane. The pentane
fractions were collected and the product analyzed by gas chromatography (20% carbowax on chromosorb W, 20' x \( \frac{1}{4} \), 110°C). The major peak was identified as bicyclo[4.2.2]-deca-2,4,7-9-tetraene (76, \( \sim 20\% \)) by comparison with an authentic sample. Two minor peaks (combined less than 10%) were not identified. The minor products did not contain either tricyclo[4.3.1.0^1,6]deca-2,4,7-triene (71) or 1-propargylcyclohepta-2,4,6-triene (73).

**Photolysis of the sodium salt of bicyclo[4.2.2]deca-2,4,9-trien-9-one tosylhydrazone (64) in methanol.**

The sodium salt generated from bicyclo[4.2.2]deca-2,4,9-trien-7-one tosylhydrazone (64, 1 g) was photolyzed in methanol (175 ml) until gas evolution stopped. The product was isolated by concentrating the methanolic solution followed by column chromatography on silica gel using 10% ether/hexane as solvent. The major component of the isolable product (90%) was identified as **exo-7-methoxy-bicyclo[4.3.1]deca-2,4,8-triene (79)** previously reported by G. Schröder.\(^{42}\) nmr: \( \delta \) 5.80 (m, 6H, H at C-2, -3, -4, -5, -8, -9), 3.34 (s, m, 4H, H on C-7, -OCH\(_3\)), 3.16 (m, 1H, H at C-1), 2.92 (m, 1H, H at C-6), 2.24 (m, 1H, H at C-10, _anti_), and 1.46 (m, 1H, H at C-10, _syn_).

A complex mixture of four hydrocarbons (combined less than 10%) was not identified.
Preparation of tricyclo[3.3.1.0^4,6]nona-2,7-dien-9-one p-tosylhydrazone (90).  

Tosylhydrazone 90 was prepared in 95% yield according to the procedure by von Doering. 30

Pyrolysis of sodium salt of tricyclo[3.3.1.0^4,6]nona-2,7-dien-9-one p-tosylhydrazone (90).  

Tosylhydrazone 90 (0.83 g, 0.0028 mole) was dissolved in methylene chloride (10 ml) and sodium hydride (0.132 g, 57% mineral oil, 0.0038 mole) was added over 10 min. The mixture was stirred for 30 min and the solvent removed on a rotary evaporator. The remaining traces of the solvent were removed at high vacuum.

The flask containing the tosylhydrazone salt was connected via an adapter (partially packed with glass wool to avoid spattering) to 2 traps cooled in dry ice/acetone baths, the entire system was connected to a vacuum pump. The setup was evacuated to 1 mm mercury pressure. The flask containing the sodium salt was then immersed into an oil bath at 195°. The product distilled into the trap. The red color initially formed, presumably due to the intermediate diazo compound, slowly faded. Analysis of the product (~95%) by gas chromatography indicated the presence of a major and a minor (~3%) component. The minor component was identified as toluene by comparison of retention times on a number of gas
chromatography columns and presumably arises from decom-
position of sodium p-toluenesulfinic.

The major component (~95%) was separated by gas
chromatography (carbowax 20M, 20% on chromosorb W, 20' x
{\frac{1}{4}}", 132°) and identified as 1-ethynylcyclohepta-2,4,6-
triene (88); ir: 3293, 2105 cm^{-1}; nmr: 6 6.6 (t, 2H, H at C-4, -5), 6.10 (m, 2H, H at C-3, -6), 5.25 (q, 2H, H at C-2, -7), 2.50 (m, 1H, H at C-1) and 2.10 (d, 1H, acetylenic H).

Product 88 was identical with an authentic sample
synthesized by the reaction of ethynyl magnesium bromide
and 1-methoxycyclohepta-2,4,6-triene.

Pyrolysis of 1-ethynylcyclohepta-2,4,6-triene (88) at
300°C.

A solution of 1-ethynylcyclohepta-2,4,6-triene (88)
in benzene was passed through a pyrex column (2' long
filled with glass beads) at 300°C at a pressure of 1 mm
(Hg). The product was collected quantitatively in a
trap cooled in dry ice/acetone and analyzed on a SE-30
column (20% on chromosorb P, 10' x {\frac{1}{4}}", 140°C). The
product contained one component (68%) other than 1-ethynyl-
cyclohepta-2,4,6-triene (32%) which was identified as
3-ethynylcyclohepta-2,4,6-triene (91) on the following
basis: 46 ir (neat) 3297, 2100 cm^{-1}; nmr: 6 6.90 (d, 6.5Hz, 1H, H at C-4), 6.15 (m, 2H, H at C-2, -5), 5.40
(m, 2H, H at C-1, -6), 2.90 (s, 1H, acetylenic H), and 2.20 (t, 6.5Hz, 2H, H at C-7).

Acid-catalyzed rearrangement of 1-ethynylcyclohepta-2,4,6-triene (88).

To a solution of 1-ethynylcyclohepta-2,4,6-triene (88, 0.300 mg) in benzene (10 ml) was added p-toluene-sulfonic acid (40 mg) and the mixture was refluxed for 12 hr. The solvent was removed on a rotary evaporator and resulting product chromatographed on silica gel using pentane as the solvent. The pentane fractions were combined and concentrated. The product (0.05 g, 16%) was isolated and then identified as phenylallene (94) by nmr, ir and mass spectrometry: nmr: $\delta$ 7.25 (s, br, 5H, aromatic H), 6.15 (t, 6.5 Hz, 1H, H at C-1), 5.1 (d, 6.5 Hz, 2H, H at C-3); ir: 3020, 3060, 3080, 1940, 860 cm$^{-1}$; mass spectrum m/e 116.

Thermolysis of the sodium salt of bicyclo[4.2.1]nona-2,4,7-trien-9-one tosylhydrazone (83).

The sodium salt of the tosylhydrazone was prepared according to the procedure described by D. C. Sanders. The thermolysis of the dry sodium salt was carried out as described for the pyrolysis of bicyclo[4.2.2]deca-2,4,9-trien-7-one tosylhydrazone (64). Analysis of the product by gas chromatography established the presence of a minor hydrocarbon (~5%) in addition to indene (43,}
95%) which had previously been identified. Comparison of the retention time and infrared spectrum with those of an authentic sample allowed identification of the minor product as 1-ethynylcyclohepta-2,4,6-triene (88).

**Synthesis of bicyclo[4.2.1]nona-2,4,7-triene-syn-9-carboxaldehyde p-tosylhydrazone (99).**

Aldehyde 98 was prepared as described by D. C. Sanders.

A mixture of aldehyde 98 (0.182 g, 0.0012 mole) and tosylhydrazine (0.300 g, 0.0016 mole) in absolute ethanol (30 ml) containing a drop of hydrochloric acid was stirred at room temperature for 6 hr. The solution was then reduced to a volume of 20 ml and cooled to -20°C. Tosylhydrazone 99 (0.300 g, 77%) was recrystallized from absolute ethanol; mp 160-161°C, nmr: δ 7.40 (m, 4H, aromatic H), 6.80 (d, 1H, aldehydic H), 5.80 (m, br, 4H, H on C-2, -3, -4, -5), 5.10 (d, br, 2H, H on C-7, -8), 3.10 (m, br, 2H, H on C-1, -6), 2.80 (m, 1H, H on C-9) and 2.40 (s, 3H, methyl H); mass spectrum m/e 314.

Anal Calcd for C_{16}H_{18}N_{2}O_{2}S: C, 64.94; H, 5.77; N, 8.91.

Found: C, 64.60; H, 5.74; N, 8.89.

**Pyrolysis of the sodium salt of bicyclo[4.2.1]nona-2,4,7-triene-syn-9-carboxaldehyde tosylhydrazone (99).**

To tosylhydrazone 99 (0.230 g, 0.0007 mole) dissolved in dry methylene chloride at 0°C was added sodium hydride
(0.030 g, 57% dispersed in mineral oil). The methylene chloride was evaporated after evolution of hydrogen ceased (30 min). The last trace of solvent was removed under high vacuum. The sodium salt was pyrolyzed at 210°C and 1 mm pressure (Hg) using the set up as described earlier for the decomposition of bicyclo[4.2.2]deca-2,4,9-trien-7-one tosylhydrazone salt. The product distilled over as a neat liquid (0.090 g, 94%) and was analyzed by gas chromatography (SF-96, 20% on chromosorb W, 15' x 1/8", 145°C).

The major hydrocarbon (~96%) was isolated by preparative gas chromatography and identified as 9-methylenebicyclo[4.2.1]nona-2,4,7-triene (97) by comparison of its retention times and nmr spectrum with those of an authentic sample prepared from methylenetriphenylphosphorane and bicyclo[4.2.1]nona-2,4,7-trien-9-one (1).

Preparation of syn-bicyclo[4.2.1]nona-2,4,7-triene-9-carboxaldehyde oxime (100).

Aldehyde 98 (0.50 g, 0.0035 mole) and hydroxylamine hydrochloride (0.70 g, 0.01 mole) were dissolved in methanol (10 ml). A solution of potassium carbonate (0.70 g, 0.005 mole) dissolved in water was added and the mixture stirred for 24 hr at room temperature. Water (40 ml) was added and the aqueous layer extracted with ether (3 x 100 ml). The ethereal layer was washed with sodium chloride solution, dried, and concentrated to a
white solid which was recrystallized from hexane/ether. The product was identified as syn-bicyclo[4.2.1]nona-
2,4,7-triene-9-carboxaldehyde oxime (100); m/e 161, ir
(KBr): 3300, 1660 cm⁻¹, nmr: δ 8.24 (s, br, 1H, -OH),
7.04 (d, 7Hz, 1H, aldehydic H), 6.00 (m, 4H, H on C-2, -3,
-4, -5), 5.2 (s, br, 2H, H on C-7, -8), and 3.34 (m, 3H,
H on C-1, -6, -9, anti).
Anal Calcd for C₁₀H₁₁NO: C, 74.51; H, 6.88; N, 8.68.
    Found: C, 74.31; H, 7.06; N, 8.75.
BIBLIOGRAPHY


