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THE CHEMISTRY OF BICYCLO[4.2.1]NONA-2,4,7-TRIEN-9-ONE,
BICYCLO[4.2.1]NONA-2,4,7-TRIEN-9-YL INTERMEDIATES AND THEIR DERIVATIVES

DISSERTATION

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

By
David Carroll Sanders, B.Sc., M.Sc.

The Ohio State University
1972

Approved by

[Signature]
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STATEMENT OF PROBLEM

Bicyclo[4.2.1]nona-2,4,7-trien-9-one (1) is obtained by reaction of dimethylcarbamoyl chloride and cyclooctatetraene dianion.

The present research involves exploration of the chemistry of bicyclo[4.2.1]nona-2,4,7-trien-9-one (1), the chemistry of bicyclo-[4.2.1]nona-2,4,7-trien-9-yl cation, carbene, and carbanion, and the stability of these intermediates with respect to theoretical predictions. The chemistry of specific products of interest derived from bicyclo-[4.2.1]nona-2,4,7-trien-9-one (1) will also be investigated.
HISTORICAL

Synthesis of bicyclo[4.2.1]nona-2,4,7-triene derivatives was first reported in 1963. Thus reaction of cyclooctatetraene dianion and acetyl chloride produces 9-acetoxy-9-methylbicyclo[4.2.1]nona-2,4,7-triene (13%) and 9-methylbicyclo[4.2.1]nona-2,4,7-trien-9-ol (19%, Equation 1) along with other acetylation products. Analogously, 9-benzoyloxy-

\[
\text{O} \quad \text{R-C-O-R} \\
\text{R} = \text{CH}_3^- \\
= \text{C}_6\text{H}_5^- \\
\]

9-phenylbicyclo[4.2.1]nona-2,4,7-triene (62%) is obtained from cyclooctatetraene dianion and benzoyl chloride.

The parent hydrocarbon, bicyclo[4.2.1]nona-2,4,7-triene was first prepared along with cyclopentadiene by pyrolysis of the exo-trans-endo-norbornadiene dimer (Equation 2). Decomposition of the sodium salt of

\[
2 \text{Li}^+ + 2 \text{RCOCl} \rightarrow 2 \text{LiCl} \\
\]

tropolacetaldehyde tosylhydrazone \(^{3,4}\) in dioxane also gives bicyclo[4.2.1]-

nona-2,4,7-triene (18\%) along with tricyclo[3.3.1.0^{4,6}]nona-2,7-diene (2\%, Equation 3). **Anti-9-phenylbicyclo[4.2.1]nona-2,4,7-triene** (30\%)

is obtained by pyrolysis of the sodium salt of \(\alpha\)-phenyl-\(\alpha\)(7-tropyl)-acetaldehyde tosylhydrazone.
Thermal decomposition of the sodium salt of bicyclo[5.1.0]octa-2,4-dien-8-al tosylhydrazone (Equation 4) has also been found to yield

(5) M. Jones, Jr., and S. D. Reich, ibid., 82, 3935 (1967).

\[ \text{bicyclo[4.2.1]nona-2,4,7-triene (13%), along with bicyclo[3.2.2]nona-2,6,8-triene (42%), bicyclo[5.2.0]nona-2,4,8-triene (9.5%), and tropylidene (6.6%).} \]

Thermal rearrangement of cis-bicyclo[6.1.0]nona-2,4,7-triene molybdenum tricarbonyl at 125° followed by decomposition of the bicyclo[4.2.1]-

(6) W. Grimme, Ber., 100, 113 (1967).
nona-2,4,7-triene molybdenum tricarbonyl complex thus formed with di-
ethylenetriamine has also been reported as a synthesis of bicyclo[4.2.1]-
nona-2,4,7-triene (35%, Equation 5).

\[ \text{Mo(CO)}_3 \stackrel{125^\circ}{\longrightarrow} \text{Mo(CO)}_3 \]

Syn-9-hydroxy-9-phenylbicyclo[4.2.1]nona-2,4,7-triene (74%) and syn-
9-hydroxy-9-methylbicyclo[4.2.1]nona-2,4,7-triene (77%) are also produced
by treatment of cyclooctatetraene dianion with benzoic anhydride and
acetic anhydride respectively \(^7,8\) (Equation 6). The corresponding products

\[ \text{(6)} \]

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

\[ \text{R}' = \text{CH}_3 \quad \text{R}' = \text{CH}_2\text{CH}_3 \]

---

\(^7\) T. A. Antkowiak, Ph.D. Dissertation, The Ohio State University,
Columbus, Ohio (1968).

are also formed, albeit in lower yield, from the dianion upon reaction with methyl benzoate and ethyl acetate. Cyclooctatetraene dianion and phenylacetyl chloride condense with cyclization to syn-9-benzoyl-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (60%).

Cyclooctatetraene dianion upon treatment with dimethylcarbamoyl chloride in ether at 5° yields, after hydrolysis with 3N sulfuric acid, bicyclo[4.2.1]nona-2,4,7-trien-9-one (75.7%, Equation 7). The facile synthesis of bicyclo[4.2.1]nona-2,4,7-trien-9-one in high yield is of particular importance in the present work in that it serves as an excellent entry for study of the parent bicyclo[4.2.1]nona-2,4,7-trienyl-9-cation, anion, and related intermediates.

Addition of dicyanocarbene to cyclooctatetraene affords 9,9-dicyanobicyclo[4.2.1]nona-2,4,7-triene (Equation 8).
Heterobicyclo[4.2.1]nona-2,4,7-triene systems are also known. Phenylphosphabicyclo[4.2.1]nona-2,4,7-triene has been prepared by reaction of dichlorophenylphosphine and cyclooctatetraene dianion in tetrahydrofuran to give 9-phenylphosphabicyclo[6.1.0]nona-2,4,6-triene which isomerizes on heating at 70° (Equation 9).

\[
2 K^+ + \text{C}_6\text{H}_5\text{PCl}_2 \xrightarrow{\text{THF}} \rightarrow 70^\circ
\]
9-Cyano-9-azabicyclo[4.2.1]nona-2,4,7-triene is a product of reaction of triplet cyanonitrene and cyclooctatetraene.

Bicyclo[4.2.1]nona-2,4,7-trienes have had limited study. Cannell reports (2) photolysis of bicyclo[4.2.1]nona-2,4,7-triene in acetone to a mixture of exo and endo-tricyclo[4.2.1.0^{2,5}]nona-3,7-dienes (Equation 11). Kurabayashi and co-workers report that this same photolysis as

Sensitized by benzophenone yields barbaralane (Equation 12).

\[
\text{Bicyclo[4.2.1]nona-2,4,7-triene pyrolyzes at 290}^{\circ}\text{C in either the gas phase or dodecane solution to bicyclo[4.3.0]nona-2,4,7-triene (cis-8,9-dihydroindenene). A "hydrogen rebound" mechanism (Equation 13),}
\]

essentially two successive 1,5-homodiencyl hydrogen shifts $a \rightarrow b \rightarrow c$, is proposed to account for the transformation since the two possible types of concerted transition state possible are "forbidden" by orbital symmetry.


Pyrolysis of 9-benzoyloxy-9-phenylbicyclo[4.2.1]nona-2,4,7-triene and 9-acetoxy-9-methylbicyclo[4.2.1]nona-2,4,7-triene in $\sigma$-dichlorobenzene (184°) affords 2-phenylindene (67%) and 2-methylindene (62%), respectively. One possible mechanism for formation of indenes by pyrolysis of bicyclo[4.2.1]nonatrienes involves valence isomerization, loss of the carboxylic acid, and electronic and molecular rearrangement as in Equation 14.

Syn-9-hydroxy-9-phenylbicyclo[4.2.1]nona-2,4,7-triene prepared by alkaline hydrolysis of its benzoate (1), is converted by two equivalents of thionyl chloride and one equivalent of pyridine to 1-chloro-9-phenyl-cis-8,9-dihydroindene (Equation 15) in high yield. The rearrangement


R = Cells
R = CH₃

(14)

(15)

(16)
has been proposed to proceed through the carbonium ion (Sequence of Equation 16). To verify the suggested mechanism, the starting alcohol was labeled with deuterium at C-2, -3, -4, and -5 and reacted with thionyl chloride. The chlorodihydroindene was obtained in which there was no deuterium scrambling (Equation 17).

\[
\text{Syn-9-hydroxy-9-phenylbicyclo[4.2.1]nona-2,4,7-triene reacts quantitatively with p-toluenesulfonic acid in chloroform to give 2-phenylindene (Equation 18). Completely different mechanisms must be operating in the thionyl chloride and acid-induced rearrangements of syn-9-hydroxy-9-phenylbicyclo[4.2.1]nona-2,4,7-triene.}
\]

Direct photolysis of bicyclo[4.2.1]nona-2,4,7-trien-9-one in Pyrex with a 450 watt Hanovia high pressure mercury lamp at room temperature affords cyclooctatetraene (80%), and carbon monoxide along with tricyclo-[4.2.1.02,5]nona-3,7-dien-9-one (3.5%) and tricyclo[3.3.1.04,6]nona-2,7-
diene-9-one (Equation 19). Sensitized photolysis of bicyclo[4.2.1]nona-

\[
\begin{align*}
\text{hv} & \quad \text{ether} \\
\text{R-C-R} & \quad \text{hv} \\
\end{align*}
\]

2,4,7-trien-9-one using benzophenone (in ether), acetone (neat), or
Michler's ketone (benzene), yields tricyclo[3.3.1.0^4,6]nona-2,7-dien-9-
one as the major product. The following illustration shows one possible
mechanism for this conversion (Equation 20). Using acetone, barbaralone

\[
\begin{align*}
\text{hv} & \quad \text{hv} \\
\text{R-C-R} & \quad \text{R-C-R} \\
\end{align*}
\]

is produced in 20% yield; benzophenone sensitization gives barbaralone
in 40% yield; and Michler's ketone as sensitizer results in advantageous
synthesis of barbaralane (68%).

The previously described photolytic work was later repeated by Kurabayashi and Mukai with similar results.

Reduction of bicyclo[4.2.1]nona-2,4,7-trien-9-one with sodium borohydride in this laboratory has been initially described to give a mixture of syn and anti-9-hydroxybicyclo[4.2.1]nona-2,4,7-trienes (Equation 21). The alcohols upon reaction with acetic anhydride and pyridine produce the indicated acetates (Equation 21). Attempted pyrolysis of the acetates at 210° for 35 hr and at 300° in a gas chromatography proved fruitless since only unreacted acetates were recovered.

Photolysis of syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene in pentane using Pyrex optics yields syn-9-hydroxytricyclo[4.2.1.0^2,5]nona-3,7-diene

---


(60%, Equation 22).

\[
\begin{align*}
\text{Direct photolysis of } &9\text{-thiabicyclo[4.2.1]nona-2,4,7-triene (13)} \text{ results in } 9\text{-thiabicyclo[6.1.0]nona-2,4,7-triene, a reaction which is reversed by thermolysis (Equation 23). 9-Thiatricyclo[3.3.1.0^2,3]nona-3,6-diene is obtained by sensitized photolysis of 9-thiabicyclo[4.2.1]-nona-2,4,7-triene (Equation 24).}
\end{align*}
\]

\[
\text{(23) Theoretical predictions concerning the bicyclo[4.2.1]nona-2,4,7-trien-9-yl cation and anion have been made. The bicyclo[4.2.1]nona-}
\]

\[
\text{2,4,7-trien-9-yl cation is predicted to be destabilized and antibicycloaromatic while the bicyclo[4.2.1]nona-2,4,7-trien-9-yl anion is predicted to be stabilized and bicycloaromatic.}
\]

Additional interest in C₉H₉ cations and anions was kindled by von Schleyer and Leone in a paper entitled "Degenerate Carbonium Ions".

Questions were raised concerning interrelationships, and possible degeneracy of various C₉H₉ species.
RESULTS AND DISCUSSION

The present investigation involves study of the chemistry and synthetic utility of bicyclo[4.2.1]nona-2,4,7-trien-9-one, bicyclo[4.2.1]-nona-2,4,7-trien-9-yl intermediates and their derivatives. Access to bicyclo[4.2.1]nona-2,4,7-trien-9-yl system is provided by prior observation of this laboratory that bicyclo[4.2.1]nona-2,4,7-trien-9-one (Equation 25) may be prepared simply and in high yield. Cyclooctatetraene dianion thus reacts with dimethylcarbamoyl chloride in ether at 5° to yield, after hydrolysis with 3N sulfuric acid and work-up, bicyclo[4.2.1]nona-2,4,7-trien-9-one (1, 75.7%, bp 46-47°/0.3 mm). The physical properties of 1 include infrared absorption at 1800 cm⁻¹ indicative of a bridged carbonyl group, ultraviolet absorption maxima (λmax) at 216, 269, 277, and 325 μm (ε = 3080, 4010, 3820, and 567 respectively), and nmr absorptions at 4.12 (m, 6H, H at C-2, -3, -4, -5, -7, and -8), and at 6.91 (m, 2H, at C-5 and -6).
(24) Another method which could have been used to prepare ketone 1 as reported to us in a private communication by S. Weinstein, Chemistry Department, University of California at Los Angeles, involves reaction of cyclooctatetraene dianion with phosgene. This procedure was not attempted because of the much lower yield and less convenient overall workup.

Bicyclo[4.2.1]nona-2,4,7-triene, its 9-substituted, and its 9,9-disubstituted derivatives all show nmr absorptions at 3.80-4.10 τ for 4-olefinic hydrogens (C-2, -3, -4 and -5), and at 4.6-4.9 τ for 2-olefinic hydrogens (C-7 and -8) along with the absorption at 6.77-7.27 for their bridgehead protons (C-1 and -6) (Table I). The deshielding of the C-7 and -8 protons in 1 resulting in their absorption in the 4.1 τ region is thus noted. It is not clear whether the downfield shift for the nmr of the C-7 and -8 protons in 1 is the result of ring current effects derived from the carbonyl group or whether there is major interaction of the bishomocyclopropenyl type (25,26) in 1 involving its C-7 and -8 double bond and its carbonyl group.

(25) (a) S. Weinstein in "Aromaticity," Chemical Society Special Publication No. 21, London, p 5 ff. (b) Independent delocalization of the carbonyl group with the C-2, -3, -4 and -5 diene unit is
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<th>τ of C-7, -8</th>
<th>τ of C-1, -6</th>
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<td>Bicyclo[4.2.1]nona-2,4,7-trien-9-one</td>
<td>4.1</td>
<td>4.1</td>
<td>6.91</td>
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<td>Syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene</td>
<td>4.0</td>
<td>4.80</td>
<td>7.08</td>
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<td>Bicyclo[4.2.1]nona-2,4,7-triene</td>
<td>4.0</td>
<td>4.75</td>
<td>6.85</td>
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<td>4.0</td>
<td>4.80</td>
<td>6.95</td>
</tr>
<tr>
<td>Syn-9-methoxybicyclo[4.2.1]nona-2,4,7-triene</td>
<td>4.0</td>
<td>4.85</td>
<td>6.90</td>
</tr>
<tr>
<td>Syn-9-acetoxy-9-methylbicyclo-[4.2.1]nona-2,4,7-triene</td>
<td>3.98</td>
<td>4.74</td>
<td>6.77</td>
</tr>
<tr>
<td>Syn-9-hydroxy-9-methylbicyclo-[4.2.1]nona-2,4,7-triene</td>
<td>3.84</td>
<td>4.75</td>
<td>7.27</td>
</tr>
<tr>
<td>Syn-9-benzoyloxy-9-phenylbicyclo-[4.2.1]nona-2,4,7-triene</td>
<td>3.89</td>
<td>4.69</td>
<td>6.16</td>
</tr>
</tbody>
</table>
expected to be unfavored because it is of the bishomocyclopenta-

(26) Molecular models reveal that 1 is a highly strained rigid ketone
in which the C-7 and -8 double bond is nearly coplanar with C-1,
C-6, and the C=0 group; the plane of C-1, C-6, and the C=0 group
is \( \sim 60^\circ \) out of the plane of the strained planar C-2, -3, -4, and
-5 diene moiety in which its C-C bond angles are \( \sim 135^\circ \).

The ultraviolet spectrum of 1 also supports the existence of some
interaction of the triene system with its carbonyl group at C-9 (Table
II). The absorptions at 269 and 277 m\( \text{\AA} \) (\( \varepsilon = 4010 \) and 3820 respectively)
are \( \sim 100 \) times stronger than that of 7-norbornenone at 272 m\( \text{\AA} \) (\( \varepsilon = 
38.9 \)), and \( \sim 10 \) times stronger than the absorption at 278 m\( \text{\AA} \) (\( \varepsilon = 602 \))
in 3,5-cycloheptadienone. The ultraviolet properties of 1 may be
indicative of delocalization effects as in 2 or/and 3.

\[ \begin{array}{c}
\delta^-
\quad 0
\quad \delta^+
\end{array} \]

Reaction of ketone 1 with sodium borohydride at 5\( ^\circ \) in methanol pro-
duces syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (4, 74\%, m.p. 51.0-52.5\( ^\circ \),
Equation 26). This reaction was originally run by Antkowiak who claimed
to have obtained a syn,anti mixture of alcohols. Inspection of the
molecular model of bicyclo[4.2.1]nona-2,4,7-trien-9-one reveals that
### Table II

Comparative Ultraviolet Absorption Data of
Bicyclo[4.2.1]nona-2,4,7-trien-9-one and Similar Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ(_{\text{max}}), (\text{nm})</th>
<th>(\epsilon)</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bicyclo[4.2.1]nona-2,4,7-trien-9-one</td>
<td>216, 269, 277, 325</td>
<td>3080, 4010, 3820, 557</td>
<td>7, 19</td>
</tr>
<tr>
<td>Bicyclo[4.2.1]nona-2,4,7-triene</td>
<td>257</td>
<td>4740</td>
<td>27a</td>
</tr>
<tr>
<td>hexane</td>
<td>190, 258-300, 325</td>
<td>4100, 6-11, 7</td>
<td>27b</td>
</tr>
<tr>
<td>3-cyclopentenone</td>
<td>213, 278</td>
<td>5495, 602</td>
<td>27b</td>
</tr>
<tr>
<td>EtOH</td>
<td>248</td>
<td>7400</td>
<td>27c</td>
</tr>
<tr>
<td>7-ketononorbornene</td>
<td>272</td>
<td>38.4</td>
<td>27d</td>
</tr>
</tbody>
</table>

the side of the carbonyl group facing the two-carbon bridge is considerably less hindered than the side facing the four-carbon bridge. Approach of a reagent from the side of the carbonyl syn to the four-carbon bridge is blocked because the plane of the four carbon bridge is at an angle of \( \sim 60^\circ \) to the plane of the bridgehead carbon and the carbonyl, whereas approach of a reagent from the side anti to the four-carbon bridge is virtually unobstructed as C-7 and -8 are coplanar with the bridgeheads (C-1 and -6) and the carbonyl group. This type of reasoning predicts that the approach of sodium borohydride should occur preferentially if not singularly from the side of the carbonyl anti to the four carbon bridge, thus producing syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene. The stereochemistry of alcohol \( \text{1} \) can be assigned unambiguously upon comparison of its nmr with that of bicyclo[4.2.1]nona-2,4,7-triene. Alcohol \( \text{1} \) exhibits a multiplet for 4 diene hydrogens (C-2, -3, -4, and -5) at 4.11 \( \tau \), a multiplet for 2 olefinic hydrogens (C-7 and -8) at 4.97 \( \tau \), a doublet of a triplet for a single hydrogen (H on C-9) at 5.74 \( \tau \), a broad triplet for the 2 bridgehead hydrogens at 7.08 \( \tau \), and a doublet for the hydroxyl hydrogen at 8.36 \( \tau \). The nmr of bicyclotriene \( \text{2a} \) shows a doublet of a triplet for the anti hydrogen (Ha at C-9) at 8.08 \( \tau \).
and a broad doublet for the syn hydrogen (Hb at C-9) at 8.70 τ. In 5 there is no resonance for a syn hydrogen at C-9; there is a doublet of a triplet for the anti hydrogen at C-9 which is shifted downfield from that of 5

(29) In 5 Hc is orthogonal to Ha and parallel to Hb. Hence, the nmr of Hb, split only by Hb, appears as a doublet whereas that of Hb, split by Hc and Hb, occurs as a doublet of triplets. Replacement of Hb by hydroxyl will result in disappearance of the Hb doublet.

Syn-bicyclo[4.2.1]nona-2,4,7-trien-9-yl tosylate is of interest as a possible entry to the bicyclo[4.2.1]nona-2,4,7-trien-9-yl cation and as a possible route to bicyclo[4.2.1]nona-2,4,7-triene. Treatment of alcohol 4 with tosyl chloride in pyridine at 0° afforded the tosylate (6, 86%, mp 83-85°, Equation 27) as a white solid. The nmr of the tosylate: τ 2.4 (m, 4H, aromatic H), 4.0 (m, 4H, H at C-2, -3, -4, and -5), 4.85 (m, 2H, H at C-7 and -8), 5.1 (broad t, 1H, H at C-9), 6.95
(broad t, 2H, bridgehead), and 7.55 (s, 3H, CH₃), indicates that the tosylate is of unrearranged structure. The tosylate is unstable and is stored advantageously at -20°.

In an attempt to study the displacement of p-toluenesulfonate anion, 6 was reacted with sodium iodide in refluxing acetone for 10 hr. No iodine containing compound was detected. The major product was identified as indene (59%, Equation 28) from its nmr and glc retention time.

In an attempt to increase the possibility of nucleophilic displacement of tosylate by external nucleophile, dimethylsulfoxide was employed as
solvent. Reaction of tosylate 6 with sodium iodide at 74° in dimethyl-
sulfoxide for 3 hr again resulted in formation of indene (75%) as did
reaction of 6 with sodium cyanide in dimethylsulfoxide at 74° (85%) and
reaction of 6 with sodium azide under the same conditions (70% indene
produced). It appears that the faster S_N1 ionization and rearrangement
precludes nucleophilic displacement of p-toluenesulfonate anion by
iodide, cyanide or azide. In fact, pyrolysis of tosylate 6 in dimethyl-
sulfoxide at 74° or acetone at reflux results in formation of indene.

Formation of 13 from 6 might arise (Equation 29) by ionization of
6 to 7 or its delocalized analog 6 by migration of C-2 or C-5 of the
four-carbon bridge to cationic site C-9 to yield, via 11, the 8,9-di-

(30) This mechanism is consistent with the observation that 2,3,4,5-
tetradecutero-syn-9-hydroxy-9-phenylbicyclo[4.2.1]nona-2,4,7-triene
reacts with thionyl chloride (2 equiv) and pyridine (1 equiv) to
give 1-chloro-5,6,7,8-tetradecutero-9-phenyl-cis-8,9-dihydroindene. 18

hydro-1-indenyl cation, and then 12 which undergoes sigmatropic isomeriza-
tion to indene (13). Another possible mechanism involves internal Diels-
Alder reaction of cation 7 to bishomotropylium ion 2 followed by mole-
cular rearrangement to 13.

In an attempt to trap carbonium ion 7 (forming bicyclo[4.2.1]nona-
2,4,7-triene) before rearrangement, tosylate 6 was reacted with lithium
aluminum hydride in tetrahydrofuran-ether at reflux for 96 hr. The major
product was identified as cis-8,9-dihydroindene (85%), while no bicyclo-
[4.2.1]nona-2,4,7-triene was detected among the minor products. The
formation of cis-8,9-dihydroindene \( \text{II} \) can be rationalized as arising from trapping of the cis-8,9-dihydro-1-indenyl cation (\( \text{II} \)) by hydride (Equation 30). The structure of \( \text{III} \) was deduced from the following data.

\[
\begin{align*}
\text{II} & \xrightarrow{\text{LiAlH}_4} \text{III} \\
\end{align*}
\]

On standing in air, or bubbling of oxygen into the compound, indene is produced. The mass spectrum of the hydrocarbon shows a parent ion at \( m/e = 118 \); the nmr absorptions are centered at \( \tau 4.0 \) (m, 6H, olefinic H) and at 6.7 (broad m, 4H, methylene and methyne H). Reaction of \( \text{III} \) with tetracyanoethylene in tetrahydrofuran at 85° for 1 hr gives white crystals of the 1:1 adduct (mp 231-233°, lit, mp 231.0-231.5°, Equation 31).

In an attempt to force the system to undergo S<sub>N</sub>2 reaction and prepare 9-chlorobicyclo[4.2.1]nona-2,4,7-triene, alcohol 1 was reacted with thionyl chloride in pyridine and hexane at 0° for 1 hr or upon reflux for several hours. The only isolable product is di-syn-bicyclo-

\[
\text{[4.2.1]nona-2,4,7-trien-9-yl sulfite (15, 93%, mp 117-118°, Equations 32 and 33). No chlorine containing derivative of 15 is detected.}
\]

\[
\begin{align*}
\text{HO} & \quad \text{Cl} \\
\text{C}_9\text{H}_{12}N & \quad \text{SOCl}_2 \\
\text{C}_9\text{H}_{12}N & \quad \text{SOCl}_2
\end{align*}
\]

Again the system shows resistance to S<sub>N</sub>2 reaction, preferring to form sulfite ester 15 which resists further nucleophilic attack under the conditions studied. The structure of 15 is assigned on the basis of its mass spectrum, m/e = 314; its nmr with τ 3.95 (m, 8H, H at each C-2, -3, -4, and -5), 4.75 (m, 4H, H at each C-7 and -8), 5.08 (broad t, 2H, H at each C-9), and 6.85 (broad t, 4H, H at each bridgehead), and its proper micro-analysis.
Pyrolysis of \( \text{15} \) in dimethylsulfoxide, as does injection of the sulfite ester into a gas chromatograph at 200\(^\circ\), results in the formation of indene (54\%).

In order to study the properties of the 9-hydroxybicyclo[4.2.1]-nona-2,4,7-trien-9-yl cation, ketone \( \text{1} \) was reacted with boron trifluoride etherate at 25-30\(^\circ\). Acid-catalyzed isomerization of the ketone (1) occurred to give 1-indanone (20, 59\%) after hydrolysis of the reaction mixture. The 1-indanone was identified by comparing its infrared, nmr spectra, and \( R_F \) values to those of the authentic compound. The conversion of 1 to 20 may be rationalized simply (Equation 34) among
many possibilities, by migration of C-2 or -5 of the diene bridge to the cationic center of 16 to give 17 which loses boron trifluoride forming 18 which enolizes to 19 which tautomerizes to 20. In a related mechanistic sequence it has been proposed that 19 is a stepwise pro-


duct in the sulfuric acid catalyzed rearrangement of bicyclo[3.2.2]-nona-2,6,8-trien-1-one to 1-indanone. The details of the structure of 16 and its conversion to 20 are unknown. However, the isomerization path pictured is analogous to the cationic rearrangement process indicated in Equation 30. It is clear that when the bicyclo[4.2.1]nona-2,4,7-trien-9-yl cation is formed it rapidly rearranges to the 8,9-dihydro-1-indenyl cation.

It became of interest to prepare 9-methylenebicyclo[4.2.1]nona-2,4,7-triene as a precursor for the study of the 9-methylbicyclo[4.2.1]-nona-2,4,7-trien-9-yl cation. Reaction of ketone 1 with methylenetriphenylphosphorane in dimethylsulfoxide at 74° produces 9-methylenebicyclo[4.2.1]nona-2,4,7-triene (21, 77%, 43-44°/1 mm, Equation 35). The

\[
\begin{align*}
\text{\(\Phi_3\text{P}=\text{CH}_2\)} & \quad \xrightarrow{\text{DMSO, 74°}} \\
\text{21} & \quad \text{(35)}
\end{align*}
\]
tetraene polymerizes slowly at room temperature and even at $-20^\circ$. The structure is verified by the following data: the mass spectrum shows m/e at 130, and the nmr has absorptions at $\tau 3.75-4.40$ (m, $4\text{H}$, H at C-2, -3, -4, and -5), $4.74$ (m, $2\text{H}$, H at C-7 and -8), $5.34$ (s, $2\text{H}$, methylene hydrogens), and $6.64$ (d, $2\text{H}$, bridgehead hydrogens).

In an effort to generate the 9-methylbicyclo[4.2.1]nona-2,4,7-trien-9-yl cation, $\text{2}_1$ was heated with catalytic quantities of p-toluene-sulfonic acid in benzene. After 3 hr at $74^\circ$ it was determined that $\text{2}_1$ had isomerized to 2-methylindene in near-quantitative yield. The structure assignment of the product is based on comparison of its nmr to that of 2-methylindene prepared from methyl magnesium bromide and 2-indanone and dehydration of the resulting alcohol with p-toluenesulfonic acid.

---


---

The number of possible mechanisms for this transformation is reduced from those previously discussed because of the required positioning of the methyl substituent in the 2-methylindene produced. One possible mechanism (Equation 36) involves protonation of the methylene function forming $\text{2}_2$ which undergoes an internal Diels-Alder reaction (33) followed by molecular rearrangement to $\text{2}_5$.

An ionic stepwise mechanism (Equation 37) can be envisaged which proceeds via a cyclononatetraenyl intermediate; however, both 2 and 3 substituted indenes are likely to be derived from such species and the
absence of 3-methylindene in the reaction mixture leads this author to favor a directed process as shown in Equation 36. In either case, a driving force for the rearrangement is the stabilization provided by formation of the indenyl aromatic system.

In order to obtain additional information concerning the stereochemistry of addition to its carbonyl group, ketone 1 was reacted with methylmagnesium bromide. The alcohol formed, \(\text{syn-9-hydroxy-9-methylbicyclo[4.2.1]nona-2,4,7-triene (28)}\) is identified by comparison of its nmr with that of this alcohol as prepared from acetyl chloride and cyclooctatetraene dianion. Just as in reaction of ketone 1 with sodium borohydride, attack of methylmagnesium bromide occurs exclusively from the less hindered anti-side of the carbonyl group.

Protonation of the hydroxyl function and loss of water should produce the 9-methylbicyclo[4.2.1]nona-2,4,7-trien-9-yl cation or its related analogs that are postulated in reaction of 9-methylenebicyclo[4.2.1]nona-2,4,7-triene and \(p\)-toluenesulfonic acid; therefore, it is predicted that reaction of \(\text{syn-9-hydroxy-9-methylbicyclo[4.2.1]nona-2,4,7-triene with } p\text{-toluenesulfonic acid will produce 2-methylindene. In fact, treatment of 28 with } p\text{-toluenesulfonic acid (Equation 38) affords 2-methylindene (80%).}

Bicyclo[4.2.1]nona-2,4,7-trien-9-ylidene (32) is of interest with respect to its possible interrelationships, degeneracy, and intramolecular chemistry. Reaction of ketone 1 with tosylhydrazide in methanol affords bicyclo[4.2.1]nona-2,4,7-trien-9-one tosylhydrazone (29, 85%,}
mp 177-179°, Equation 39) as white crystals. The nmr of 29 has absorptions at \( \tau \) 2.4 (m, 4H, aromatic H), 4.15 (m, 4H at C-2, -3, -4, and -5), 4.81 (m, 2H, H at C-7 and -8), 6.15 (m, 1H, bridgehead H), 6.50 (m, 1H, bridgehead H), and 7.55 (s, 3H, CH\(_3\)). Reaction of tosylhydrazone 29 with sodium hydride produces the sodium salt (30) of the tosylhydrazone. Decomposition of 30 is effected by pyrolysis of the dry salt (30) at 190° or photolysis of the salt in methylene chloride with a Hanovia medium pressure lamp. Bicyclo[4.2.1]nona-2,4,7-trien-9-ylidene (32),
the carbene presumably generated by decomposition of 9-diazobicyclo-
[4.2.1]nona-2,4,7-triene (31) as derived from 32, isomerizes to give
indene (13, 42 to 63%) as the major hydrocarbon product. Conversion of
32 to 13 must involve carbon skeleton rearrangement and hydrogen migra-
tion. A relatively simple path (Equation 40) for isomerization of 32,
which might be considerably delocalized (33) or isomerize to bishomo-
tropyldiene (34) or other intermediates, involves the equivalent of a
1,2-shift of C-2 or -5 of its diene bridge to carbenic center C-9 to

\[
(34) \quad 35 \text{ might be highly delocalized through its olefinic and cyclo-
propyl moieties.}
\]

give bicyclo[4.3.0]nona-2,4,6,8-tetraene (12) which undergoes 1,5-sigma-
tropic rearrangement to 13. Other C9H8 species such as tricyclo-
[3.3.1.02,8]nona-3,6-dien-9-yldene (36, barbaralidene), bicyclo-
[4.3.0]nona-2,4,8-trien-8-yldene (37), cyclononatetraenylidene (38),
bicyclo[5.2.0]nona-2,4,6,8-tetraene (39), and bicyclo[3.2.2]nona-2,5,7-
trien-3-yldene (40), among others, may play roles in transformation(s)
of 32 to 13. The many important questions of the interrelationships,
(a) Intermediates $36-40$ may be involved via isomerization of $32$, $33$, or $34$. (b) For related discussion of the structures, degeneracy, and intramolecular chemistry of various $C_9H_9$ cations, see reference 23. (c) The intermediates: $32-35$ and $36-39$ might be triplets rather than singlets.

The multiplicities, and the possible degeneracy of various $C_9H_9$ species await resolution.

The Wolff-Kishner reduction of ketone 1 was studied in an effort to find a better synthesis of bicyclo[$4.2.1$]nona-$2,4,7$-triene (41) and as a means of studying the chemistry of the bicyclo[$4.2.1$]nona-$2,4,7$-trien-9-yl anion (43). Ketone 1 was refluxed with hydrazine hydrate and potassium hydroxide in ethylene glycol for two hr followed by distillation (up to $130^\circ$). Three compounds were detected upon glc analysis of the hydrocarbon products (Equation 41). The first component of the mixture is identified as the unrearranged hydrocarbon, bicyclo[$4.2.1$]-
nona-2,4,7-triene (41, 6.4%) by comparison of its retention time and nmr with those of a sample prepared by decomposition of the sodium salt of tropylacetaldehyde tosylhydrazone as reported by Tsuruta, et al. The hydrocarbon has a parent peak at m/e = 118 and the following nmr:

\[ \tau 3.57 \text{ to } 4.37 (m, 4H, hydrogens at C-2, -3, -4, and -5), \tau 5.20 (m, 2H, hydrogens at C-7, -8), \tau 2.92 (t, 2H, bridgehead hydrogens), \tau 1.95 (d of t, 1H, H at C-9), \tau 1.32 (d, 1H, H at C-9). \]

The second and major component of the mixture is identified as tricyclo[6.1.0.0^4,9]nona-2,6-diene (76.6%, 42) on the basis of the following data. The mass spectrum of 42 shows its molecular weight to be 118, and the nmr has absorptions at \[ \tau 3.95 \text{ to } 4.95 (m, 4H, vinyl hydrogens), \tau 6.90 (m, 1H, bridgehead), \tau 7.4-8.9 (m, 5H, cyclopropyl and methylene hydrogens). \] The structure of 42 is further verified by comparison of its nmr to that of tricyclo[6.1.0.0^4,9]nona-2,6-diene as prepared by Petrowski by photolysis of cis-bicyclo[6.1.0]nona-2,4,6-triene. 

(37) Private communication from S. Weinstein indicates that his group has also obtained 42 as the major product of this reduction and has verified its structure by comparison to 42 as prepared by Petrowski.
One possible mechanism for formation of $h_2$ in this reaction (Equation 42) involves reduction of $l$ via its hydrazone and base to $h_3$, which

$$
\text{H$_2$N-NH$_2$H$_2$O}
\xrightarrow{\text{KOH}}
\text{H}
\rightarrow
\text{43}
\xrightarrow{(42)}
\text{42}
$$

is the anionic analog of cation $l$ and carbene $32$, followed by proton abstraction from the environment. It appears that under these conditions carbanion $44$ is involved rather than $h_3$, thus leading to $h_2$ as the major product. The third component (3.9%) has not been identified.

Since a major objective is development of a satisfactory procedure for converting ketone $l$ to the unrearranged hydrocarbon $h_1$, a low temperature Wolff-Kishner procedure was tried.

---

Ketone 1 upon heating with excess anhydrous hydrazine produces bicyclo[4.2.1]nona-2,4,7-trien-9-one hydrazone (45, Equation 43), amorphous yellow solid. The unrearranged structure of the hydrazone is verified by its nmr absorptions at \( \tau 3.75-4.48 \) (m, 4H, H at C-2, -3, -4, and -5), 4.75 (m, 2H, H at C-7 and -8), 5.05 (m, 2H, N-H hydrogens), 6.15 (m, 1H, bridgehead hydrogen), and 6.65 (m, 1H, bridgehead hydrogen).

Wolff-Kishner reduction of 45 was effected upon its slow addition to a solution of potassium t-butoxide and dimethylsulfoxide at room temperature. The mixture obtained after work up was column chromatographed on silica gel to separate bicyclo[4.2.1]nona-2,4,7-trien-9-one azine (46) from the hydrocarbon product. Azine 46 (12.6%) is identified by comparison of its tlc, \( R_f \) value, mp, and infrared spectrum to those of a sample prepared from ketone 1 and a half equivalent of hydrazine.

Analysis of the hydrocarbon products by glc on Column A at 132° indicated the presence of 3 components. The first and major component
is identified as bicyclo[4.2.1]nona-2,4,7-triene (47, 37.6%) from its retention time and the nmr of a preparative sample. The second component is found to be tricyclo[6.1.0.0^{4,9}]nona-2,6-diene (3%, 42) from its retention time and upon comparison with a previously obtained sample. The third component is assigned as 2-methylbicyclo[4.2.1]nona-2,4,7-triene (47, 5.1%) from the following data. The mass spectrum of 47 shows a parent ion at m/e = 132, and nmr of the following absorptions: τ 3.86-4.40 (m, 3H, H at C-3, -4, and -5), 4.75 (m, 2H, H at C-7 and -8), 6.95 (broad unsymmetrical triplet, 2H, bridgehead hydrogens), 8.06 (d of t, 1H, H at C-9), 7.99 (s, 3H, methyl), 8.61 (d, 1H, H at C-9).

Two structures were considered on the basis of the above data, 47 and 48.

Structure 47 is chosen because of the variation in the structure of its bridgehead proton resonance which normally appears as a symmetrical triplet in the unsubstituted bicyclo[4.2.1]nona-2,4,7-triene system, but appears as a partially collapsed triplet in 47. Replacement of the hydrogen at C-2 by a methyl group would be expected to cause a change in the splitting pattern of the bridgehead hydrogens, while a methyl group at C-3 is not expected to cause such a change.
It has been reported that butadiene can be alkylated to 1,3-pentadiene by potassium tert-butoxide in dimethylsulfoxide. In the cases reported, alkylation occurs at the terminal as opposed to internal olefinic positions, a finding that is understandable since attack of an anion at the external position of a diene system produces a resonance stabilized allylic anion while internal attack produces a simple primary or secondary carbanion. These findings also substantiate the assignment of the present alkylation product as 2-methylbicyclo[4.2.1]nona-2,4,7-triene.

(a) Other examples of alkylation products resulting from reaction of methylsulfinyl carbanion with olefinic or aromatic systems have been reported by Nozaki et al.\(^{40b}\) and Russell and Weiner.\(^{40c}\) (b) H. Nozaki, Y. Yamamoto, and R. Noyori, Tetrahedron Letters, 1123 (1966). (c) G. Russell, and S. Weiner, J. Org. Chem., 31, 248 (1966).

Attempts to alkylate bicyclo[4.2.1]nona-2,4,7-triene with dimethylsulfoxide and potassium tert-butoxide at 74\(^\circ\) for 2 hr and at 130\(^\circ\) for 1 hr results only in recovery of starting hydrocarbon; therefore, hydrazone 45 or a nitrogen containing derivative thereof must be undergoing alkylation during Wolff-Kishner reduction. Two of the possible paths for formation of 47 from 45 are visualized in Equation 44.
In path A, $\text{42}$ is formed by addition of methylsulfinyl carbanion followed by hydride migration and elimination of methylsulfonate anion forming $\text{50}$ which undergoes the normal reduction process yielding $\text{47}$. Path B proceeds by protonation of $\text{42}$ which produces $\text{51}$ which eliminates the elements of methylsulfenic acid, thus forming $\text{42}$ which tautomerizes to $\text{50}$ followed by normal reduction to $\text{47}$. No attempt was made to illu-
citate the actual mechanism, although Nozalki et al. suggest that path B is more likely on the basis of their methylation of 9-deuterio-phenanthrene in which 50% of the deuterium is lost.

Formation of tricyclo[6.1.0.0^3,9]nona-2,6-diene as the major product of Wolff-Kishner reduction on ethylene glycol and bicyclo[4.2.1]nona-2,4,7-triene as the major product in dimethylsulfoxide is a subject of real interest. Initially it was suspected that $h_2$ is the product of thermodynamic control and $h_1$ the kinetic product. The reduction was then run in dimethylsulfoxide at higher temperatures in order to observe the variation in product ratio. The various percentages of products formed by reduction at different temperatures are reported in Table III along with the results of reduction in the presence of two equivalents of t-butyl alcohol. It is noted that the ratio of bicyclo[4.2.1]nona-2,4,7-triene ($h_1$) to tricyclo[6.1.0.0^3,9]nona-2,6-diene ($h_2$) does not vary significantly as the temperature is raised. These data along with the fact that $h_1$ and $h_2$ are not interconvertible under the reaction conditions removes the possibility that the ratio of $h_1$ to $h_2$ is seriously temperature dependent. Since a temperature effect is ruled out as an explanation of the change in major products, solvent effects must predominate. The strong solvating power of dimethylsulfoxide might stabilize carbanion $h_3$ to the extent that it can undergo the normal reduction procedure producing bicyclo[4.2.1]nona-2,4,7-triene; whereas the weaker solvating power of ethylene glycol might force $h_2$ to rearrange to $h_4$ which produces $h_2$ upon protonation. Table III reveals that the ratio of bicyclo[4.2.1]nona-2,4,7-triene ($h_1$) and 2-methylbicyclo[4.2.1]-
### Table III
Products of Wolff-Kishner Reduction of 1

<table>
<thead>
<tr>
<th>Experimental Conditions</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene glycol, KOH, reflux 2 hr</td>
<td>6.4%</td>
</tr>
<tr>
<td>Dimethylsulfoxide, potassium t-butoxide, 25°C</td>
<td>37.6%</td>
</tr>
<tr>
<td>Dimethylsulfoxide, potassium t-butoxide, 2 equiv. of t-BuOH, 25°C</td>
<td>25.1%</td>
</tr>
<tr>
<td>Dimethylsulfoxide, potassium t-butoxide, 74°C</td>
<td>49.2%</td>
</tr>
<tr>
<td>Dimethylsulfoxide, potassium t-butoxide, 2 equiv. t-BuOH, 74°C</td>
<td>69.0%</td>
</tr>
<tr>
<td>Dimethylsulfoxide, potassium t-butoxide, 130°C</td>
<td>24.4%</td>
</tr>
<tr>
<td>Dimethylsulfoxide, potassium t-butoxide, 2 equiv. t-BuOH, 130°C</td>
<td>35.0%</td>
</tr>
</tbody>
</table>
nona-2,4,7-triene (47) is in fact temperature dependent. As the reaction temperature is raised, the percentage of 47 rises whereas that of 41 decreases.

Since the formation of 47 depends on the concentration of the methylsulfinyl carbanion, addition of hydroxylic solvent to the reaction mixture should retard formation of 47 because of hydrogen bonding of the t-butoxide, thus reducing its basicity. In fact, when the reaction is run in 2 equivalents of t-buty1 alcohol, formation of 47 is drastically reduced (Table III). At 74° in the presence of 2 equivalents of t-buty1 alcohol, the sole hydrocarbon product is 41, while at 130° suppression of 47 is noted but not complete. At 25°, 2 equivalents of alcohol slows the reactions to the extent that nitrogen evolution is still detected after several days.

Ketone 4 was treated with potassium t-butoxide in dimethylsulfoxide in an attempt to effect alkylation of the diene moiety as found in the Wolff-Kishner experiment (Equation 45). Large quantities of intractables
are produced and a very small amount of unreacted ketone (1) is recoverable, but no alkylation products were detected.

The previously noted tendency of the bicycloheptatrienone system to undergo nucleophilic attack on its diene moiety prompted study of reactions of metal hydrides and 1.

Reaction of 1 with excess sodium bis(methoxyethoxy)aluminum hydride and hydrolysis affords a waxy solid mixture containing two components in a ratio of 2:3 as shown by glc analysis (Equation 46). The first

![Equation 46]

component is identified as syn-9-hydroxybicyclo[4.2.1]nona-2,7-diene (53, 33.8%) from the following data: nmr at \( \tau \) 3.95 (m, 2H, H at C-2 and -3), 4.44 (m, 2H, H at C-7 and -8), 5.75 (t, 1H, H at C-9), 6.83 (m, 1H, bridgehead hydrogen), 7.33 (m, 1H, bridgehead hydrogen), 7.75 to 8.50 (m, 4H, H at C-4 and -5), and 7.97 (s, 1H, hydroxyl hydrogen); the mass spectrum shows a parent peak at m/e = 136. The second component is syn-9-hydroxybicyclo[4.2.1]nona-3,7-diene (54, 50.8%) on the basis of a mass spectral parent ion at m/e = 136, and nmr absorptions at \( \tau \) 4.24 (m, 2H, H at C-7 and -8), 4.53 (m, 2H, H at C-3 and -4), 5.54 (t, 1H, H at C-9), 7.24 (m, 2H, bridgehead hydrogens), 7.69 (m, 4H, H at C-2 and -5), and 8.24 (s, 1H, hydroxyl hydrogen). Nmr analysis makes 53 and
easily distinguishable since alcohol 53 is unsymmetrical with respect to its bridgehead hydrogens and thus 53 has two different bridgehead absorptions, whereas 54 is symmetrical with respect to the bridgeheads and displays only a single bridgehead hydrogen absorption. To establish the stereochemistry of the hydroxyl group in 53 and 54, a mixture of the two alcohols in ethanol was catalytically hydrogenated (10% Pd on C), and the resulting 9-hydroxybicyclo[4.2.1]nonane (55) was compared to the catalytic reduction product of syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (Equation 47). The mp (173-175°) and infrared spectra of the products are identical, and there is no depression in the mp of a mixture of the separately derived saturated alcohols.

Treatment of syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene with sodium bis(methoxyethoxy)aluminum hydride under the same conditions as
for 1 results in formation of two alcohols (53 and 54) as obtained from reduction of 1. The fact that reduction occurs only on the diene moiety can be explained by initial reduction of the ketone function and formation of complex 56 which positions the aluminum hydride function over the 4-carbon bridge followed by attack on the diene moiety (Equation 48).

In an effort to find another nucleophile that will add to the diene and to study the possibility of cleavage of the ketone to a methyl cyclo-octatrienecarboxylate, ketone 1 was refluxed with lithium methoxide in anhydrous methanol for 10 hr. Workup affords a yellow solid which upon glc analyzes as two components in a ratio of 9 to 1. The major product is identified as syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (5, 81%, Equation 49) by comparison of its nmr and infrared spectra and glc.
retention time with those of the alcohol prepared previously in this study. The rationalization for formation of 2 from $\frac{1}{2}$ in this reaction is analogous to that for Meerwein-Ponndorf-Verley reduction for ketones.


In the present case, lithium methoxide replaces aluminum isopropoxide as the reducing agent as it is oxidized to formaldehyde while reducing the bicyclic ketone. Formaldehyde was found in the reaction product by formation of the expected 2,4-dinitrophenylhydrazone, mp 166°. Equation 50 shows a possible mechanism for the conversion. Substitution

\[
\text{Li}^+ + \text{C} = \text{H} \quad \iff \quad \text{O}-\text{Li}^+ + \text{C} = \text{H} + \text{H} \quad \text{(50)}
\]

of sodium methoxide for lithium methoxide results in much slower and less efficient conversion of $\frac{1}{2}$ to $\frac{1}{2}$, possibly because of sodium ion's lesser ability, as compared to lithium ion's, to coordinate with the ketone oxygen. The observed reduction seems to present an outstanding example in which lithium methoxide in methanol acts as a reducing media.

The second component of the reduction has not been identified.
The oxime (57) of 1 was prepared so that is Beckmann rearrangement could be studied. Treatment of ketone 1 with hydroxylamine hydrochloride and sodium carbonate in methanol-water affords bicyclo[4.2.1]nona-2,4,7-trien-9-one oxime (57, 79%). The infrared spectrum of the oxime has a strong O-H stretching band (3180 cm\(^{-1}\)) and the nmr shows the following absorptions: \(\tau\ 0.65\ (s, 1H, OH), 4.05\ (m, 4H, H at C-2, -3, -4, and -5), 4.55\ (m, 2H, H at C-7 and -8), 5.75\ (m, 1H, bridgehead hydrogen), and 6.45\ (m, 1H, bridgehead hydrogen).

Reaction of ketoxime 57 with tosyl chloride in pyridine results in Beckmann fragmentation (Equation 51) to give cyano-1,3,5,7-cyclooctatetraene (58, 57%); conversion of 57 to 7-azabicyclo[4.2.2]deca-2,4,9-trien-8-one (59, Equation 52) or its structural isomers is not observed.

Analysis, mass spectroscopy (m/e = 129), infrared absorption at 2240 cm\(^{-1}\) for the nitrile group, and the nmr spectrum which reveals only the presence of olefinic hydrogens (broad singlet at 4.05 \(\tau\)) affirms the structure of 58. The product (58) is produced by an abnormal Beckmann reaction (Equation 53) in which the driving force is formation of stabilized carbonium ion 61 as derived by carbon-carbon bond breakage.


In order to generate and study the chemistry of carbene \( \text{62} \) via pyrolytic decomposition of the sodium salt of cyclooctatetraene-9-carbox-
aldehyde tosylhydrazone, the following sequence of reactions was completed.

Reaction of nitrile 58 with diisobutyl aluminum hydride at -78° results in a brown oil which after column chromatography on silica gel yields 1,3,5,7-cyclooctatetraenecarboxaldehyde (63, 79%, Equation 54). 44

(44) Continued elution affords a small amount of tarry material which shows a N-H infrared stretch at this probably contains 1,3,5,7-cyclooctatetraenylmethylamine.

\[
\begin{align*}
\text{CN} & \quad 1) \quad [(\text{CH}_3)_2\text{CHCH}_2]_2\text{AlH} \\
& \quad 2) \quad 10\% \text{H}_2\text{SO}_4 \\
\text{H} & \quad \text{C=O} \\
\end{align*}
\]

Aldehyde 63 is unstable at room temperature but is storable at -78°. The mass spectrum of 63 reveals a parent peak at m/e = 132; the nmr exhibits absorptions at \( \tau \) 0.60 (s, H, aldehydic hydrogen), and 3.5-4.5 (m, 7H, vinyl hydrogens). The infrared spectrum of 63 has carbonyl absorption at 5.91 \( \mu \) as expected, and aldehydic C-H stretching bands at 3.52 and 3.67 \( \mu \). Reaction of 63 with 2,4-dinitrophenylhydrazine produces its 2,4-dinitrophenylhydrazone, orange crystals, mp 218-219°.

1,3,5,7-Cyclooctatetraenecarboxaldehyde tosylhydrazone 64 was prepared from 1,3,5,7-cyclooctatetraenecarboxaldehyde (63) and tosylhydrazone in methanol. The product obtained was purified by column chromato-
graphy on silica gel and crystallization from methylene chloride-hexane at -10°, thus yielding 1,3,5,7-cyclooctatetraenecarboxaldehyde tosylhydrazone (64), yellow crystals, mp 114-116°. The nmr of 64 displays the following absorptions: \( \tau 1.58 \) (s, 1H, H at C-9), 2.06-2.83 (m, 5H, aromatic and N-H hydrogens), 3.90-4.36 (m, 7H, vinyl hydrogens), and 7.60 (s, 3H, methyl).

Tosylhydrazone 64 is converted to its sodium salt 65 by reaction with sodium hydride in methylene chloride (Equation 55). Pyrolysis of the dry salt (65) at 280° (0.3 mm) gives no hydrocarbon products; a volatile liquid is obtained which crystallizes from methylene-chloride-hexane as fine yellow needles, mp 103-105°. The experimentally determined exact mass of the solid is 144.0687 which compares with a calculated value of 144.0688 for C9H8N2. The infrared spectrum of the product has a N-H stretch at 3350 cm\(^{-1}\), the ultraviolet spectrum has maxima at 207, 226, 264, 271, and a shoulder at 283 \( \mu \) with \( \epsilon \) of 6046, 9760, 14180, 13960, and 7750 respectively. Nmr absorptions occur at \( \tau 1.6 \) (s, 1H, NH, washed out with D2O), 2.8 (s, 1H, H at C-9), and 3.80-4.24 (m, 6H, vinyl hydrogens).
Considering the above data, possible structures for the product may be narrowed to 66 and 67.

\[ \text{66} \]

\[ \text{67} \]

Previously reported compounds with structures similar to 67\(^{45,46}\)

\(\text{(45) E. LeGoff and R. B. LaCount, Tetrahedron Letters, 2787 (1965).}\)


such as cycloocta[c]furan \(\text{(68)}\), 7,8-dimethylene-1,3,5-cyclooctatetraene \(\text{(69)}\), and 7-methylene-8-halomethylene-1,3,5-cyclooctatriene \(\text{(70)}\) are all extremely unstable and form oxygen containing polymers very rapidly when exposed to air. The compound obtained in the present study is stable in air (no special storage requirement) and is stable at 400\(^\circ\)F for short periods. On the basis of the present data, the structure of
pyrolysis product is tentatively 66. The formation of 66 is visualized in Equation 56.

\[ 65 \xrightarrow{\Delta} \text{C}_{7}H_{7}SO_{2}Na \rightarrow \]

Bicyclo[4.2.1]nona-2,4,7-trien-syn-9-carboxaldehyde \( (71) \) and bicyclo[4.2.1]nona-2,4,7-trien-syn-9-carboxylic acid \( (72) \) are of interest as precursors to the bicyclo[4.2.1]nona-2,4,7-trien-9-yl radical \( (73) \) possibly by photolysis or pyrolysis of aldehyde \( 71 \), and pyrolysis of the t-buty1 perester of acid \( 72 \).
As a precursor to aldehyde \( \text{L}_1 \), 9-methoxymethylenebicyclo[4.2.1]-nona-2,4,7-triene (\( \text{L}_4 \)) was prepared by reaction of ketone \( \text{L}_2 \) with (methoxymethylene)triphenylphosphorane in dimethylsulfoxide at \( 74^\circ \). Workup afforded \( \text{L}_4 \) as a water clear liquid (70%, bp 67-68°/1.1 mm, Equation 57).

\[
\begin{align*}
\text{L}_2 & \xrightarrow{\phi_3P = \text{CHOCH}_3} \text{L}_4 \\
\text{DMF} & \quad (57)
\end{align*}
\]

The physical properties of \( \text{L}_4 \) include: a parent molecular ion peak at \( m/e = 160 \); and nmr absorptions at \( \tau 3.60-4.34 \) (m, 5H, H at C-2, -3, -4, and -5 and methylene H), 4.70 (m, 2H, H at C-7 and -8), 6.1 (m, 1H, bridgehead hydrogen), 6.41-6.70 (m, 4H, bridgehead and methyl hydrogens).

Using a modification of a procedure developed by Levine, \( \text{L}_4 \) was hydrolyzed with aqueous trifluoroacetic acid at 25° to bicyclo[4.2.1]-nona-2,4,7-trien-9-carboxaldehyde (\( \text{L}_1 \), 82.7%, bp 67°/1.1 mm, Equation 58). Reaction of \( \text{L}_1 \) with 2,4-dinitrophenylhydrazine in ethanol yields

\[
\begin{align*}
\text{L}_1 & \xrightarrow{\text{CF}_3\text{COOH}} \text{L}_2 \\
\text{CHCl}_3 & \quad (58)
\end{align*}
\]

its 2,4-dinitrophenylhydrazone, yellow crystals, mp 184-185°. The infrared spectrum of aldehyde \[\text{71}\] displays a carbonyl stretch at 5.76 \(\mu\) and moderately intense bands of the aldehydic hydrogen at 3.54 and 3.69 \(\mu\). The nmr consists of absorptions at \(\tau 0.58\) (s, 1H, aldehydic H), 3.53-4.27 (m, 4H, H at C-2, -3, -4, and -5), 6.57 (t, 2H, bridgehead hydrogen), 7.17 (t, 1H, H at C-9). The fact that the C-9 hydrogen appears as a triplet allows assignment of the stereochemistry of the aldehyde function as \text{syn} to the 4-carbon diene bridge.

A hydrogen \text{anti} to the 4 carbon bridge is parallel to the two bridgehead hydrogens and should be split into a triplet, while a hydrogen \text{syn} to the 4 carbon bridge is perpendicular to the bridgehead hydrogens, and in accordance with the Karplus relationships, \(49\) should not be split by them, therefore appearing as a singlet.

\text{Anti}-9-phenylbicyclo[4.2.1]nona-2,4,7-triene has been prepared, \(49\) and its \text{syn} apical hydrogen is, in fact, a singlet as predicted. The


The fact that all of the compounds in the present work which have been proven to have a C-9 hydrogen \text{anti} to the 4-carbon bridge show a triplet for the C-9 hydrogen also supports this assignment.
Bicyclo[4.2.1]nona-2,4,7-trien-syn-9-carboxylic acid (72) is produced by chromic acid oxidation of aldehyde 71 (Equation 59). Acid 72 is isolated as white crystals (57%, mp 173-174°). The infrared absorption of 72 displays a >C=0 stretch at 5.78 μ and broad O-H stretching absorption from 2.8 to 3.5 μ. The ultraviolet absorptions at 217, 248, 256, 265, and 275 (ε = 4590, 3620, 4760, 4670, and 2750, respectively) are similar to the spectra of other bicyclo[4.2.1]nona-2,4,7-trienes.

The nmr of 72 consists of absorptions at τ 1.32 (s, 1H, acid H), 3.86 (m, 4H, H at C-2, -3, -4, and -5), 4.76 (m, 2H, H at C-7 and -8), 6.66 (m, 3H, H at C-1, -6, and -9). The abnormally high proton absorption for the carboxylic proton (1.32 τ) can be the result of hydrogen bonding to the π-cloud of the diene bridge.


As another approach to preparation of bicyclo[4.2.1]nona-2,4,7-triene, desulfurization of bicyclo[4.2.1]nona-2,4,7-trien-9-one ethyllenedithioketal was studied. Reaction of ketone 4 with 1,2-ethanedithiol and boron trifluoride etherate at 0° and column chromatography
of the product affords bicyclo[4.2.1]nona-2,4,7-trien-9-one ethylene-dithioketal (75, 79%, Equation 60), white crystals, mp 83-85°. The nmr

\[
\text{CH}_2 - \text{CH}_2
\]

of 75 shows absorptions at \(\tau\) 4.05 (m, 4H, H at C-2, -3, -4, and -5), 4.65 (m, 2H, H at C-7 and -8), 6.65 (m, 2H, bridgehead hydrogens), and 6.80 (s, 4H, methylene hydrogens).

Treatment of dithioketal 75 with Raney Nickel in ethanol yields a mixture of 9 products, none of which is major. Identification of these products was not attempted. Treatment of dithioketal 75 with dehydrogenated Raney Nickel results in no reaction; only starting material is isolated. Reaction of 75 with Raney Nickel in benzene, however, affords indene (13, 82%, Equation 61) as the major product. A minor product

\[
\text{CH}_2 - \text{CH}_2
\]

(3% <) was not identified. Raney Nickel desulfurizations, especially with less active nickel in non-polar solvents such as benzene, are known
to give unusual or abnormal products. These desulfurizations are common thought to occur by free radical processes. One possible rationalization for formation of indene in the desulfurization of I5 is illustrated in Equation 62. The process proceeds by loss of sulfur.
producing diradical $76$ which abstracts a hydrogen forming $77$. Elimination of ethylene and sulfur from $77$ produces $72$ or $79$ which rearranges to $80$ which loses a hydrogen radical forming $12$ which isomerizes to $13$.

The chemistry of radical $72$ is of interest and should be studied by unambiguous generation such as pyrolysis of the $t$-butyl perester of acid $72$ or by decarbonylation of aldehyde $71$.

Sensitized photolysis of ketone $1$, bicyclo[4.2.1]nona-2,4,7-triene $14$ or 9-thiabicyclo[4.2.1]nona-2,4,7-triene $19$ yields a tricyclo[3.3.1.0$^{4,6}$]nona-2,7-diene derivative in each case. It is of interest to study the photolysis of 9-methylenebicyclo[4.2.1]nona-2,4,7-triene because of its structural similarity to these compounds. Sensitized photolysis of 9-methylenebicyclo[4.2.1]nona-2,4,7-triene in acetone using a medium pressure 450 watt Hanovia mercury vapor lamp yields a single volatile hydrocarbon product (85%) and an amorphous solid (15%). The hydrocarbon product is 9-methylene tricyclo[3.3.1.0$^{4,6}$]nona-2,7-diene ($81$, 9-methylene barbaralone, 85%). One possible mechanism for the transformation is shown below (Equation 63). Analysis of $81$ shows a

\begin{equation}
54
\end{equation}

This mechanism is analogous to the one proposed by Antkowiak for conversion of ketone $1$ to barbaralone.

Mass spectral parent ion m/e = 130, and nmr absorptions at $\tau$ 4.27 (t, 2H, vinyl H at C-3 and -7), 5.28 (s, 2H, methylene hydrogens), 5.83 (t, 4H, averaging H at C-2, -4, -6, and -8), 3.16 (t, 2H, averaging H at C-1 and -5). The chemical shifts of each group of signals are similar
to those of barbaralone, dihydrobullvalene, and semibullvalene, Table IV, except for the C-9 protons, thus suggesting that 81 is 9-methylenetricyclo[3.3.1.0\(^{3,6}\)]nona-2,7-diene.

\[(\text{54a,b}) \quad \text{(a) W. von Doering and W. R. Roth, Angew. Chem., 75, 27 (1963); (b) J. B. Lambert, Tetrahedron Letters, 1901 (1963); (c) G. Schroder, Chem. Ber., 97, 3140, 3150 (1964); (d) H. E. Zimmerman and G. L. Grumwald, J. Amer. Chem. Soc., 88, 183 (1966).}\]

Compound 81 is expected to show fluxional behavior \(^{54a,b}\) (Equation (64))
This expectation is born out by its nmr in which there is a central triplet (4H) resulting from averaging of the resonances of the vinyl protons (H₂ and H₃) and of the allylic cyclopropane protons (H₄ and H₅). The intensity of the low field peak shows that only two protons retain vinylic character (H₃ and H₇). The high field peak results from the average of the resonances of bridgehead protons H₁ and H₅. As the temperature is decreased the rate of rearrangement is slowed. At -60° the

### Table IV

<table>
<thead>
<tr>
<th></th>
<th>Hₐ</th>
<th>Hₖ</th>
<th>Hₐ</th>
<th>-CO- or -{(CH₂)ₙ- or &gt;C=CH₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>barbaralane</td>
<td>4.3</td>
<td>5.8</td>
<td>7.3</td>
<td>&gt;C=0</td>
</tr>
<tr>
<td>semibullvalene</td>
<td>4.92</td>
<td>5.83</td>
<td>7.03</td>
<td>n=0</td>
</tr>
<tr>
<td>81</td>
<td>4.27</td>
<td>5.28</td>
<td>6.84</td>
<td>&gt;C=CH₂ 5.28</td>
</tr>
<tr>
<td>dihydrobullvalene</td>
<td>4.37</td>
<td>6.32</td>
<td>8.1</td>
<td>-CH₂-CH₂- ~ 8.1</td>
</tr>
</tbody>
</table>

[Diagram of the compound with labeled protons (Hₐ, Hₖ, Hₐ, Hₖ, Hₖ, X, Hₐ, Hₖ, Hₖ)]
central 4 hydrogen triplet is reduced in intensity while the intensity of the vinyl triplet is increased. At -90° the central triplet is a broad bump while the other protons all have resonances which fall from 100 to 200 cps. The infrared spectrum of 81 has moderate to strong C=C stretching bands at 6.03 and 6.08 μ.


Another area of future interest is preparation of a 9-halobicyclo-
[4.2.1]nona-2,4,7-triene which may be used as a precursor for study of the bicyclo[4.2.1]nona-2,4,7-trien-9-yl anion and for preparation of bicyclo[4.2.1]nona-2,4,7-triene and 9-deuteriobicyclo[4.2.1]nona-2,4,7-trienes via the corresponding Grignard reagent. Access to the 9-halobicyclo[4.2.1]nona-2,4,7-triene system is available by subjecting acid 72 to Hunsdiecker conditions, which also provides a means of studying the chemistry of the bicyclo[4.2.1]nona-2,4,7-trien-9-yl radical. A number of other reactions of the 9-halo system would also generate the radical. Pyrolysis of photolysis of aldehyde 71 and pyrolysis of the t-butyl perester of 72 may also provide a means of studying radical 72.
EXPERIMENTAL

General Procedures and Techniques

Melting Points. Melting points were determined with a Thomas Hoover Capillary Melting Point Apparatus. All melting points are uncorrected.

Boiling Points. Boiling points were obtained at atmospheric pressure unless otherwise noted. Thermometer corrections were not made.

Elemental Analysis. Elemental analyses were performed by Chemalytics, Inc., Tempe, Arizona, by Micro-Analysis Inc., Wilmington, Delaware, and by Galbraith Laboratories, Inc., Nashville, Tennessee.

Infrared Spectra. Infrared spectra were obtained on a Perkin Elmer Infracord Spectrophotometer. The spectra of solid compounds were obtained from potassium bromide wafers, and the spectra of liquid compounds were obtained from liquid films.

Ultraviolet Spectra. Ultraviolet spectra were measured on a Perkin Elmer 202 Spectrophotometer. The solvent used was 95% ethanol.

Nuclear Magnetic Resonance Spectra. Nuclear magnetic resonance spectra were determined with a Varian A-60 or A-60A instrument using carbon tetrachloride, deuterated chloroform, or deuterated dimethylsulfoxide as the solvent. Tetramethyldisilane was used as an internal solvent.
Column Chromatography. Column chromatography was frequently used in the separation and purification of products. The alumina was Woelm Alumina Activity Grade 1. The silica gel was EM (70-325 mesh) for column chromatography. Thin layer plates were Eastman Chromtogram Sheets (alumina or silica coated).

Gas Chromatography. Gas chromatography analyses were performed on a F and M, Model 720 Programmed Dual Column instrument equipped with a thermal conductivity detector.

Two columns were used most frequently, they were: Column A which was 10 ft of 30% SE 30 on 60/80 Chromosorb P, and Column B which was 14 ft of 20% Carbowax 20M on 60/80 Chromosorb P.

Quantitative measurements were made by comparison of peak areas of products to the peak areas of measured standards. Relative peak areas were obtained using the method of multiplying the peak height times the width at half-height.

Photolyses. Photolyses were carried out using a 450 watt medium pressure Hanovia lamp, 679A36.
Synthesis of Bicyclo[4.2.1]nona-2,4,7-trien-9-one (1).

Dry ether (300 ml) was placed in a 1 liter, 3-neck flask equipped with a stirrer, thermometer, condenser, and a nitrogen line. Small pieces of lithium (1.6 g, 0.23 mole) were cut and hammered into sheets on glassine powder paper moist with paraffin. The thin sheets were held in a stream of nitrogen and cut directly into the flask with scissors.

The lithium-ether mixture was cooled to -70° and cyclooctatetraene (10.4 g, 0.010 mole) was added all at once. The mixture was stirred at -70° for 4 hr under constant nitrogen purge. The Dry-Ice acetone bath was then removed and the mixture stirred 10-12 hr under nitrogen. Sufficient dry ether was added to dissolve all of the dilithium cyclooctatetraenide.

Dimethylcarbamoyl chloride (11.9 g, 0.11 mole) in dry ether (70 ml) was added dropwise (40 min) to the stirred solution of cyclooctatetraene dianion under nitrogen at 0°. The mixture was stirred for 2 hr and warmed to 15°. Dilute sulfuric acid (3N, 100 ml) was added to the stirred reaction mixture at 0°. The mixture was separated and the aqueous layer extracted with ether. The combined ether extracts were washed with water, saturated sodium bicarbonate, water, dried over anhydrous magnesium sulfate, filtered, and concentrated (50 ml) under reduced pressure. On storage, a yellow solid (0.25 g, unidentified) precipitated. Distillation of the liquid residue yielded \( \frac{1}{2} \) (7.1 g, bp 46-47°/0.3 mm) as a colorless liquid. The conversion cyclooctatetraene to \( \frac{1}{2} \) is 54%; the yield of \( \frac{1}{2} \) from dimethylcarbamoyl chloride and cyclo-
octatetraene dianion is considerably higher in that the latter reagent is usually formed in 60-70% efficiency from cyclooctatetraene. Ketone \( \text{I} \) solidifies and is conveniently stored in a freezer compartment at \( \sim -5^\circ \).

**Anal. Calcd for C\(_9\)H\(_8\)O: C, 81.04; H, 6.11.**

**Found: C, 81.00; H, 6.00.**

After a few weeks solid \( \text{I} \) turns yellow; however, simple vacuum distillation results in effective repurification of \( \text{I} \).

The infrared spectrum of \( \text{I} \) has a strong band at 1800 cm\(^{-1}\) indicative of a strained carbonyl group. The ultraviolet spectrum exhibits maxima at 216, 269, 277, and 525 m\(\mu\) (\(\epsilon = 3080, 4010, 3820, \) and 567). The nmr spectrum consists of a multiplet centered at 4.12 \(\tau\) (6H, H at C-2, -3, -4, -5, -7, and -8) and a multiplet centered at 6.91 \(\tau\) (2H, bridgehead hydrogens).

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**Preparation of Syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (4).**

To a solution of \( \text{I} \) (2.6 g, 0.02 mole) in methanol (18 ml) at 5\(^\circ\) was added sodium borohydride (0.236 g, 0.00624 mole) in 2N sodium hydroxide (0.25 ml) diluted with water (1.8 ml). After the mixture had been stirred for 0.25 hr at 5\(^\circ\), the methanol was evaporated and the residue was diluted with water (20 ml). The suspension produced was extracted with ether and the combined ether portion was washed with water, dried over anhydrous magnesium sulfate, filtered, and evaporated at reduced pressure. The solid remaining was crystallized from hexane to yield syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (4,
2.0 g, 74%) as white plates, mp 51.0-52.5°.

**Anal. Calcd for C₉H₁₃O: C, 80.60; H, 7.46.**

**Found: C, 80.38; H, 7.48.**

The ultraviolet spectrum of \( \frac{1}{4} \) exhibits maxima at 220 and 262 μm (\( ε = 3,300 \) and 4,360). The nmr spectrum consists of a multiplet at 4.11 τ (4H, H at C-2, -3, -4, and -5), a doublet at 4.79 τ (2H, hydrogens at C-7 and C-8), a complex multiplet at 5.74 τ (1H, hydrogen at C-9), a broad triplet at 7.08 τ (2H, bridgehead hydrogens), and a doublet at 8.36 τ (1H, hydroxyl hydrogen).

**Preparation of Syn-bicyclo[4.2.1]nona-2,4,7-trien-9-yl Tosylate (6).**

A mixture of syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-tiene (\( \frac{1}{4} \), 2.0 g, 0.015 mole), tosyl chloride (5.64 g, 0.030 mole), and pyridine (20 ml) was stored at -20° for 2 days, poured on ice, and extracted with ether. The ethereal layer was washed with cold 6N hydrochloric acid, saturated sodium bicarbonate solution, saturated sodium chloride, dried (MgSO₄), and the solvent was removed at reduced pressure. The resulting white solid (6, 3.61 g, 86%), mp 83-85°, was crystallized at -78° from hexane containing sufficient chloroform to clear the solution at room temperature; nmr τ 2.4 (m, 4H, aromatic H), 4.0 (m, 4H, H at C-2, -3, -4, and -5), 4.85 (d, 2H, H at C-7 and C-8), 5.1 (broad t, 1H, H at C-9), 6.95 (broad t, 2H, bridgehead C-H), and 7.55 (s, 3H, CH₃).

**Anal. Calcd for C₁₆H₁₆SO₃: C, 66.65; H, 5.60.**

**Found: C, 66.77; H, 5.63.**
Reaction of Syn-bicyclo[4.2.1]nona-2,4,7-trien-9-yl Tosylate (6) with Sodium Iodide in Acetone.

A mixture of 6 (1.0 g, 0.0034 mole) and sodium iodide (3.0 g, 0.020 mole) in acetone (25 ml) was refluxed 12 hr and poured into water (15 ml). Sodium thiosulfate was added a crystal at a time until the iodine color disappeared and the aqueous layer was extracted with ether (3 x 7 ml). Analysis by glc revealed the presence of indene (13, 0.118 g, 59%; identified by its retention time and its nmr); the two volatile minor products were not identified. No iodine-containing compound was detected.

Reaction of Syn-bicyclo[4.2.1]nona-2,4,7-trien-9-yl Tosylate (6) with Sodium Iodide in Dimethylsulfoxide.

A mixture of 6 (0.5 g, 0.0017 mole) and sodium iodide (1.0 g, 0.0067 mole) in dimethylsulfoxide (3 ml) was heated at 74° for 4 hr and poured into water (15 ml). Sodium thiosulfate was added a crystal at a time until the iodine color disappeared and the aqueous layer was extracted with ether. Analysis by glc revealed indene (13, 0.15 g, 75%) to be the only volatile product. No iodine-containing compound was detected.

Reaction of Syn-bicyclo[4.2.1]nona-2,4,7-trien-9-yl Tosylate (6) with Sodium Cyanide in Dimethylsulfoxide.

A mixture of 6 (0.50 g, 0.0017 mole) and sodium cyanide (0.42 g, 0.0085 mole) in dimethylsulfoxide (5 ml) was heated at 74° for 4 hr and poured into water (15 ml). Extraction of the aqueous mixture with
ether was followed by washing the ethereal extracts with water, drying over anhydrous magnesium sulfate and stripping the solvent at reduced pressure. Analysis of the residue by glc showed indene (0.17 g, 85%) as the sole hydrocarbon product. No nitrogen containing product was detected.

Reaction of Syn-bicyclo[4.2.1]nona-2,4,7-trien-9-yl Tosylate (6) with Sodium Azide in Dimethylsulfoxide.

A mixture of 6 (0.5 g, 0.0017 mole) and sodium azide (0.55 g, 0.0085 mole) in dimethylsulf oxide (5 ml) was heated at 74° for 4 hr and poured into water (15 ml). Work-up produced indene (0.14 g, 0.0012 mole, 70%) as the sole hydrocarbon product. No nitrogen-containing compound was detected.

Pyrolysis of Syn-bicyclo[4.2.1]nona-2,4,7-trien-9-yl Tosylate (6) in Dimethylsulfoxide.

Syn-bicyclo[4.2.1]nona-2,4,7-trien-9-yl Tosylate (0.50 g, 0.0017 mole) was dissolved in dimethylsulfoxide (5 ml) and heated at 74° for 4 hr. Isolation afforded indene (0.15 g, 0.0013 mole, 75%) as the sole hydrocarbon product.

Preparation of Di-syn-bicyclo[4.2.1]nona-2,4,7-trien-9-yl Sulfite (15).

To syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (2.0 g, 0.015 mole) in pyridine (10 ml) and hexane (20 ml) was added thionyl chloride (1.8 g, 0.015 mole) at 0°. A white precipitate formed immediately which remained while the mixture was refluxed 1 hr. Water (15 ml) was added to the mixture and the aqueous solution was extracted with ether. The
ether solution was washed with 5\% hydrochloric acid, saturated sodium bicarbonate, dried over anhydrous magnesium sulfate, and the ether was removed at reduced pressure to afford a white solid. Crystallization from hexane yielded 15 (2.17 g, 93\%) as a white solid, mp 117-118°; 

$\delta^{1} H$ 3.95 (m, 8H, H at C-2, -3, -4, and -5), 4.75 (m, 4H, H at C-7 and -8), 5.08 (broad t, 2H, H at C-9), and 6.85 (broad t, 4H, H at each bridgehead), mass spectrum m/e = 314.

**Anal. Calcd for C_{16}H_{18}SO_{3}: C, 68.76; H, 5.77.**

**Found: C, 68.70; H, 5.77.**

**Pyrolysis of Di-syn-bicyclo[4.2.1]nona-2,4,7-trien-9-yl sulfite (15).**

Di-syn-bicyclo[4.2.1]nona-2,4,7-triene-9-yl sulfite (15, 0.50 g, 0.0016 mole) in dimethylsulfoxide (5 ml) was heated at 105° for 10 hr. The yellow solution was poured into water (20 ml) and extracted with ether. The ether extracts were combined, washed with water, dried over anhydrous magnesium sulfate then evaporated at reduced pressure, leaving a yellow liquid which was identified as indene (0.26 g, 54\%) by g1c analysis.

**Reaction of Syn-bicyclo[4.2.1]nona-2,4,7-trien-9-yl Tosylate with Lithium Aluminum Hydride.**

The tosylate (6, 8.1 g, 0.028 mole) in tetrahydrofuran (35 ml) and ether (6 ml) was refluxed with lithium aluminum hydride (27 ml of 4.4 M reagent in ether) for 96 hr, cooled to 0° and hydrolyzed with 3N sodium hydroxide. Extraction with ether followed by washing of the extracts with saturated sodium chloride, drying over anhydrous magne-
sium sulfate and removal of the ether yielded a liquid product which was shown to be 90% one component and various minor contaminants. This product upon distillation gave a near-colorless liquid identified as bicyclo[4.3.0]nona-2,4,7-triene (14, cis-8,9-dihydroindene; 2.30 g, 85%), bp 65° (50 mm), mass spectrum m/e = 118, nmr spectrum at τ 4.0 (m, 6H, olefinic H) and 6.7 (broad m, 4H, methylene and methyne H’s). The triene (14) was oxidized by air in several days to indene (13). A solution of (0.20 g, 0.0017 mole) and tetracyanoethylene (0.22 g, 0.0017 mole) in tetrahydrofuran (1 ml) was heated at 85° for 1 hr. Recrystallization of the product from benzene gave the white 1:1 adduct, mp 231-233°, lit 231.0-231.5°.


Reaction of Bicyclo[4.2.1]nona-2,4,7-trien-9-one with Boron Trifluoride.

A mixture of 1 (2.0 g, 0.015 mole) and boron trifluoride etherate (15 ml, 4%) was stirred at room temperature for 48 hr. Water was added and the mixture was extracted with ether, the organic extracts were combined, washed with saturated sodium bicarbonate, brine, dried (MgSO₄), filtered, and evaporated at reduced pressure leaving a semi-solid. Column chromatography of the residue on silica gel using hexane-benzene gave, after recovery of 1 (0.71 g, 0.0052 mole), 1-indanone (20, 0.76 g, 59%), mp 39-41°, as identified by its mixed mp, ir spectrum, and Rf values on tlc.

A mixture of sodium hydride (1.58 g, 57% dispersion in mineral oil, 0.0375 mole) in dimethylsulfoxide (40 ml) was heated at 74° until hydrogen evolution stopped. The solution was cooled to 10° and triphenylmethylphosphonium bromide (13.4 g, 0.0375 mole) was added slowly after which the mixture was stirred 15 min. Ketone 1 (4.0 g, 0.030 mole) was added in 15 min at 10° and then the mixture stirred at 74° for 2 hr. The black mixture was poured into water (150 ml) and extracted with pentane. The organic extracts were washed with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The pentane was removed at reduced pressure leaving a faintly yellow liquid which was distilled (43-44°/1 mm) to yield water-clear 9-methylenebicyclo[4.2.1]nona-2,4,7-triene (3.0 g, 0.023 mole, 77%).

Anal. Calcd for C_{10}H_{10}: C, 92.26; H, 7.74.

Found: C, 92.02; H, 7.59.

The infrared spectrum exhibits $\nu_{\text{max}}$ ($\mu$) at: 3.26, 3.36, 6.02, 6.34, 7.29, 10.38, 10.91, 11.31, 11.55, 13.35, and 14.45. The nmr spectrum of 21 consists of a multiplet at 3.75-4.40 $\tau$ (4H, C-2, -3, -4, and -5 hydrogens) a narrow multiplet at 4.74 $\tau$ (2H, hydrogens at C-7 and -8), a singlet at 5.34 $\tau$ (2H, methylene hydrogens), and a broad doublet at 6.64 $\tau$ (2H, bridgehead hydrogens). The mass spectrum of 21 showed m/e = 130; the uv spectrum showed absorption maxima at 219, 254, 261, 271 and 280 m$\mu$ ($\epsilon$ = 3750, 2800, 3260, 3220, and 2100).
Reaction of 9-Methylenebicyclo[4.2.1]nona-2,4,7-triene with p-Toluenesulfonic Acid.

A mixture of 9-methylenebicyclo[4.2.1]nona-2,4,7-triene (0.260 g, 0.002 mole) and p-toluenesulfonic acid (25 mg) in benzene (3 ml) was heated at 74° for 3 hr. The black reaction mixture was poured into ether (10 ml) and the resulting solution was extracted with saturated sodium bicarbonate, dried over anhydrous magnesium sulfate, and the solvent was stripped. The very odorous liquid which remained was examined by glc on column A at 200° and proved to be 2-methylindene (0.240 g, 93%). Pure 25 was obtained by glc on column A at 200° has the same retention time, nmr, and ir, as a sample prepared from 2-indanone and methylmagnesium bromide followed by dehydration of the alcohol formed using p-toluenesulfonic acid.57


A solution of 1 (1.0 g, 0.0075 mole) in ether (5 ml) was added at 0° to stirred methylmagnesium bromide (8 ml of 1.9 M reagent, 0.015 mole). The mixture was refluxed for 30 min and then hydrolyzed with dilute hydrochloric acid. The aqueous layer was extracted with ether, dried over anhydrous magnesium sulfate and the solvent was removed at reduced pressure. Distillation afforded syn-9-hydroxy-9-methylbicyclo[4.2.1]nona-2,4,7-triene (26, 0.95 g, 86%) with nmr and ir spectra
identical to those of the same compound prepared by Cantrell\(^\text{58}\) from cyclooctatetraene dianion and acetyl chloride.


A solution of syn-9-hydroxy-9-methylbicyclo[4.2.1]nona-2,4,7-triene (0.296 g, 0.002 mole) and p-toluenesulfonic acid (25 mg) in benzene was refluxed until glc analysis on column A at 200\(^\circ\) indicated that all of the starting material had reacted. The mixture was poured into ether and the organic layer was washed with saturated sodium bicarbonate solution, dried over anhydrous magnesium sulfate, filtered, and evaporated. Glc analysis of the product on Column A at 200\(^\circ\) showed that the product to be 2-methylindene (0.21 g, 80\%) by comparison of retention time, ir, and nmr of this product with those of 2-methylindene prepared from 2-indanone and methylmagnesium bromide followed by dehydration.

Preparation of Bicyclo[4.2.1]nona-2,4,7-trien-9-one Tosylhydrazone.

Ketone \(\frac{1}{2} (5.0 \text{ g}, 0.038 \text{ mole})\) was added to a refluxing solution of tosylhydrazine (7.4 g, 0.040 mole) in methanol (40 ml) and heating was discontinued. After 0.5 hr the mixture was concentrated and the product crystallized upon cooling. Recrystallization from methanol gave \(\frac{22}{22} (9.60 \text{ g}, 85\%)\) as a near white solid, mp 177-179\(^\circ\); nmr \(\tau 2.4\)
(m, 4H, aromatic H), 4.15 (m, 4H, H at C-2, -3, -4, and -5), 4.81 (m, 2H, H at C-7 and -8), 6.15 (m, 1H bridgehead C-H), 6.50 (m, 1H, bridgehead C-11), and 7.55 (s, 3H, CH₃).


Found: C, 63.87; H, 5.11; N, 9.36.

Pyrolytic Decomposition of the Sodium Salt of Bicyclo[4.2.1]nona-2,4,7-trien-9-one Tosylhydrazone.

Sodium hydride (0.272 g, 59% mineral oil dispersion, 0.0068 mole) was slowly added to 29 (2.0 g, 0.0067 mole) in methylene chloride (30 ml) at 0°. After evolution of hydrogen ceased the solvent was stripped at reduced pressure leaving the sodium salt (30) as a white powder coated on the flask walls. The flask was attached via an adapter (partially packed with glass wool to prevent spatter entrainment) to a series of traps and a vacuum system. Upon decomposing salt of 30 at 190° (0.3 mm), a liquid was trapped which was shown to be 95% indene (13, 0.32 g, 42%) by glc analysis (comparative retention times) and by the nmr of a preparative sample. The single minor (< 5%) volatile product has not been identified.

Photolytic Decomposition of the Sodium Salt of Bicyclo[4.2.1]nona-2,4,7-trien-9-one Tosylhydrazone.

Sodium hydride (0.136 g of 59% mineral oil dispersion, 0.0034 mole) was added slowly to 29 (1.0 g, 0.0033 mole) in methylene chloride (30 ml) at 0°. After evolution of hydrogen ceased, the solvent was stripped
at reduced pressure leaving the salt \( \text{(20)} \) as a white powder coated on
the flask walls. The solid was then redissolved in nitrogen purged
methylene chloride \( (300 \text{ ml}) \) and irradiated in a Pyrex cell at room tem-
perature with a 450-watt Hanovia medium-pressure mercury lamp until
evolution of nitrogen, as monitored with a bubbler, ceased. The mix-
ture was then filtered and the methylene chloride was removed at
reduced pressure leaving 0.25 g of liquid which proved to be > 95%
indene \( (0.24 \text{ g}, 63\%) \) by glc retention time on Column A at 200° and the

**Wolff-Kishner Reduction of Bicyclo[4.2.1]nona-2,4,7-trien-9-one Using
the Huang-Minlon Procedure.**

A solution of potassium hydroxide \( (2.0 \text{ g}, 0.036 \text{ mole}) \), hydrazine
hydrate \( (3.0 \text{ g}) \), and ketone \( \frac{1}{2} \) \( (0.80 \text{ g}, 0.0061 \text{ mole}) \) in diethyleneglycol
\( (20 \text{ ml}) \) was refluxed for 2 hr during which time the bath temperature
rose to 200°. The flask was fitted with a short path distillation
head and the distillate was collected \( (\text{bp 120-130}^\circ) \). The distillate
was poured into water \( (8 \text{ ml}) \) and extracted with pentane. The pentane
extracts were washed with brine, dried over anhydrous magnesium sulfate,
filtered, and concentrated at reduced pressure. Glc analysis of the
residual liquid \( (0.63 \text{ g}) \) on column A at 132° showed three components,
two minor and one major. The product was analyzed by weight by adding
known weights of allylbenzene as a standard. The first component \( (0.045
\text{ g}, 6.4\%) \) was identified as bicyclo[4.2.1]nona-2,4,7-triene by comparison
of its retention time with that of a sample prepared by decomposition of
the sodium salt of tropylium acetaldehyde tosylhydrazone as reported by
Tsuruta et al. The nmr of the product showed \( \tau \, 3.57-4.37 \) (m, \( 4H \),

(1967).

hydrogens at C-2, -3, -4, and -5), \( \tau \, 5.20 \) (m, \( 2H \), hydrogens at C-7, -8),
2.92 (t, \( 2H \), hydrogens at bridgehead), 1.95 (d of t, \( 1H \), hydrogen at
C-9), 1.32 (d, \( 1H \), hydrogen at C-9) which is the same as the reported
nmr. The mass spectrum of the hydrocarbon showed \( m/e = 118 \); its ultra-
violet spectrum exhibited a maximum 257 (\( e = 4740 \)).

The major component (0.536 g, 75.6%) was identified as tricyclo-
[6.1.0.0^{4,9}]nona-2,6-diene from the following data. The mass spectrum
reveals the parent peak \( m/e = 118 \): ir, \( \nu_{max} (\mu) \): 3.92, 3.42, 3.53,
6.11 (w), 7.97, 10.63, 11.73, 13.71, and 14.35; nmr absorption occurs
at \( \tau \, 3.95-4.95 \) (m, \( 4H \), vinyl hydrogens), 6.90 (m, \( 1H \), bridgehead), 7.4-
8.9 (m, \( 5H \), cyclopropyl and methylene hydrogens). The structure was
further verified by comparison with the nmr of a sample of the hydro-
carbon prepared by photolysis of cis-bicyclo[6.1.0]nona-2,4,6-triene.

(60) G. Petrowski, Ph.D. Dissertation, University of California, Los
Angeles, 1969.

Anal. Calcd for C\(_{6}\)H\(_{10}\): C, 91.47; H, 8.53.

Found: C, 91.22; H, 8.78.

The third component (0.030 g, 3.9%) has not been identified al-
though the mass spectrum exhibits \( m/e = 118 \).
Preparation of Bicyclo[4.2.1]nona-2,4,7-trien-9-one Hydrazone.

Ketone 1 (3.0 g, 0.023 mole) was added dropwise to rapidly stirred anhydrous hydrazine (4.0 g, 0.125 mole). The solution was heated on a steam bath for 1 hr and then poured into methylene chloride. The methylene chloride layer was removed and additional methylene chloride was added. The methylene chloride layers were combined and washed quickly with a small amount of water, dried over potassium carbonate, filtered, and evaporated. The thick yellow oil solidified to bicyclo-
[4.2.1]nona-2,4,7-trien-9-one hydrazone.

The hydrazone has the following nmr: \( T 3.75-4.48 \) (m, 4H, hydrogens at C-2, -3, -4, and -5), 4.75 (m, 2H, hydrogens at C-7 and -8), 5.05 (m, 2H, N-H hydrogens which disappear when shaken with D\(_2\)O), 6.15 (m, 1H, bridgehead hydrogen), 6.65 (m, 1H, bridgehead hydrogen). Micro-analysis of the hydrazone was not attempted. The hydrazone was converted to the known tosylhydrazone by reaction with p-toluenesulfonyl chloride in pyridine. The hydrazone was stored at -78° until used.

Reaction of Bicyclo[4.2.1]nona-2,4,7-trien-9-one Hydrazone with Potassium t-butoxide in Dimethylsulfoxide at room temperature.

To a rapidly stirred solution of potassium t-butoxide (0.700 g, 0.006 mole) and dimethylsulfoxide (10 ml) was added dropwise, hydrazone 45 (0.400 g, 0.0027 mole) in dimethylsulfoxide. The solution turned black instantly and nitrogen evolution began. Addition was continued over a 2 hr period. After nitrogen evolution ceased, the reaction mixture was added to water and extracted with pentane. The organic extracts were combined, washed with water, dried over anhydrous magnesium sulfate, filtered, and
evaporated at reduced pressure to a light yellow liquid (0.21 g).

TLC analysis showed the presence of a compound with the same Rf value as the azine of 1. The mixture upon chromatography on silica gel separated to a liquid hydrocarbon fraction (0.16 g) using pentane, and a white solid residue (0.045 g) with 50/50 pentane-benzene. Glc analysis of the liquid on Column A at 132° indicated the presence of 3 volatile components. The first component was identified as bicyclo[4.2.1]nona-2,4,7-triene (0.12 g, 37.6%) by the retention time and the nmr analysis of a preparative sample. The second component was identified as tricyclo[6.1.0.03]nona-2,6-diene (0.004 g, 3%) by comparison of its retention time and nmr with those of this same compound as obtained in a previous reaction.

The third component was identified as 2-methylbicyclo[4.2.1]nona-2,4,7-triene (0.016 g, 5.1%) from the following data: mass spectrum, m/e = 132; nmr τ 3.86-4.40 (m, 3H, H at C-3, -4, and -5), 4.75 (m, 2H, H at C-7 and -8), 6.95 (broad t, 2H, bridgehead II), 8.06 (dt, 1H, H at C-9), 7.99 (s, 3H, methyl), 8.61 (d, 1H, H at C-9); uv absorption maxima in 95% ethanol at 215 and 265 µm (ε = 5790 and 2390). The azine (0.045 g, 12.6%) was identified by comparison of its Rf value, ir absorption and mp with those of an original sample.

Found: C, 90.71; H, 9.03.

Preparation of Bicyclo[4.2.1]nona-2,4,7-trien-9-one Azine.

To ketone 1 (0.5 g, 0.0038 mole) was added anhydrous hydrazine (0.061 g, 0.0019 mole). A vigorous reaction occurred which left a light yellow solid. Charcoal treatment and crystallization from methanol afforded bicyclo[4.2.1]nona-2,4,7-trien-9-one azine (0.42 g, 85%) as small white crystals (mp 185-187°).
Wolff-Kishner Reduction of Bicyclo[4.2.1]nona-2,4,7-trien-9-one Hydrazone in Dimethylsulfoxide with Potassium t-Butoxide at Room Temperature in the Presence of Two Equivalents of t-Butyl Alcohol.

To a rapidly stirred solution of potassium t-butoxide (0.700 g, 0.006 mole), t-butyl alcohol (0.40 g, 0.0054 mole), and dimethylsulfoxide (10 ml), hydrazone 45, (0.40 g, 0.0027 mole) in dimethylsulfoxide was added all at once. The black color developed much more slowly than usual; nitrogen evolution occurred extremely slowly, continuing for more than one week. Work up as described previously afforded a residue (0.12) which analyzed as bicyclo[4.2.1]nona-2,4,7-triene (0.080 g, 25.1%) and azine 46 (0.039 g, 10.8%). A trace of tricyclo[6.1.0.0²⁸]nona-2,6-diene was observed as a tail on the major peak.

Wolff-Kishner Reduction of Bicyclo[4.2.1]nona-2,4,7-trien-9-one Hydrazone in Dimethylsulfoxide with Potassium t-Butoxide at 74°.

Hydrazone 45 (0.040 g, 0.0027 mole) in dimethylsulfoxide was added dropwise to a rapidly stirred solution of potassium t-butoxide (0.070 g, 0.006 mole) in dimethylsulfoxide (10 ml). The solution turned black instantly and nitrogen evolution was very rapid. The addition was complete in one hour. After nitrogen evolution ceased, the reaction mixture was worked up as usual. Analysis of the residue in the usual manner gave the following results: bicyclo[4.2.1]nona-2,4,7-triene (0.157 g, 49.2%), tricyclo[6.1.0.0²⁸]nona-2,6-diene (0.004 g, 1%), 2-methylbicyclo[4.2.1]nona-2,4,7-triene (0.031 g, 9.7%) and azine 46 (0.040 g, 11.2%).
Wolff Kishner Reduction of Bicyclo[4.2.1]nona-2,4,7-trien-9-one
Hydrazone in Dimethylsulfoxide with Potassium t-Butoxide at 74° in the Presence of Two Equivalents of t-Butyl Alcohol.

To a rapidly stirred solution of potassium t-butoxide (0.700 g, 0.006 mole), t-butanol (0.40 g, 0.0054 mole) and dimethylsulfoxide (10 ml) was added hydrazone 45 (0.40 g, 0.002 mole) in dimethylsulfoxide dropwise. The solution turned black slowly; nitrogen evolution was slower than for reaction at 74° without alcohol, but many times faster than the reaction at room temperature. The addition was complete in 2 hr. When nitrogen evolution ceased, the reaction was worked up as usual. The products were bicyclo[4.2.1]nona-2,4,7-triene (0.22 g, 69%) and azine 46 (0.030 g, 8.4%).

Wolff Kishner Reduction of Bicyclo[4.2.1]nona-2,4,7-trien-9-one Hydrazone in Dimethylsulfoxide with Potassium t-Butoxide.

Hydrazone 45 (0.040 g, 0.0027 mole) in dimethylsulfoxide was added dropwise to a rapidly stirred solution of potassium t-butoxide (0.700 g, 0.006 mole) in dimethylsulfoxide (10 ml). The solution turned black instantly and nitrogen evolution was nearly instantaneous. Addition and nitrogen evolution were complete in 30 min. The usual workup afforded the following products: bicyclo[4.2.1]nona-2,4,7-triene (0.078 g, 24.4%), 2-methylbicyclo[4.2.1]nona-2,4,7-triene (0.072 g, 20.2%), and azine 46 (0.042 g, 11.8%).
Wolff-Kishner Reduction of Bicyclo[4.2.1]nona-2,4,7-triene-9-one

Hydrazone in Dimethylsulfoxide at 130° with Potassium t-Butoxide
in the Presence of Two Equivalents of t-Butyl Alcohol.

Hydrazone 45 (0.400 g, 0.002 mole) in dimethylsulfoxide (5 ml) was added dropwise 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 dimethylsulfoxide (10 ml). The solution turned black; nitrogen evolution was extremely rapid. Addition and nitrogen evolution were over in 0.5 hr. Work up afforded the following products: bicyclo[4.2.1]nona-2,4,7-triene (0.11 g, 55%), 2-methylbicyclo[4.2.1]nona-2,4,7-triene (0.04 g, 11.1%), and azine 46 (0.039 g, 10.8%).

Attempted Reaction of Bicyclo[4.2.1]nona-2,4,7-triene with Dimsyl Potassium.

To a rapidly stirred solution of potassium t-butoxide (0.38 g, 0.0034 mole) in dimethylsulfoxide (10 ml) at 74° was added bicyclo[4.2.1]nona-2,4,7-triene (0.200 g, 0.0017 mole) in dimethylsulfoxide (1 ml). The solution turned black immediately; after 4 hr the solution was poured into water and extracted with pentane. The extracts were combined, washed with water, dried over magnesium sulfate, filtered and evaporated at reduced pressure. The liquid residue (0.11 g) proved to be pure starting material.

A similar experiment was performed at 130° for 0.5 hr; again only starting material (0.08 g) was isolated.
Attempted Reaction of Bicyclo[4.2.1]nona-2,4,7-trien-9-one with Dimsyl Potassium.

To a rapidly stirred solution of potassium t-butoxide (0.85 g, 0.0076 mole) in dimethylsulfoxide (10 ml) at 74° was added ketone 1 (0.5 g, 0.0038 mole). The mixture turned black and stirring was continued for 2 hr. The tarry mixture was poured into water, extracted with ether, washed with water, dried over magnesium sulfate, filtered, and evaporated. The only product (0.030 g) was starting ketone.

Reaction of Ketone 1 with Sodium Bis(methoxyethoxy)aluminum Hydride

A solution of ketone 1 (1.0 g, 0.0078 mole) in ether (10 ml) was added in 5 min to a stirred solution of sodium bis(methoxyethoxy)-aluminum hydride (3.0 g of 70% benzene solution, 0.022 mole) at 0-5°. The mixture was refluxed for 2 hr and then hydrolyzed with 10% sulfuric acid. Extraction with ether followed by washing the combined extracts with brine, drying over anhydrous magnesium sulfate, and removal of the solvent at reduced pressure afforded a waxy colorless solid (0.90 g).

Glc analysis of this solid on Column B at 220° indicated the presence of two components in a ratio of 2:3. The first component (33.8%, 0.36 g) was identified as syn-9-hydroxybicyclo[4.2.1]nona-2,7-diene (53) from the following data: nmr at $\tau$ 3.95 (m, 2H, hydrogens at C-2 and -3), 4.44 (m, 2H, hydrogens at C-7 and -8), 5.75 (t, 1H, hydrogen at C-9), 6.83 (m, 1H, bridgehead hydrogen), 7.33 (m, 1H, bridgehead hydrogen), 7.75 to 8.50 (m, 4H, hydrogens at C-4 and -5), 7.97 (s, 1H,
hydroxyl hydrogen); uv maxima at 213 μm (ε = 4850); and mass spectrum for m/e = 136.


Found: C, 79.21; H, 8.59.

The second component (0.5 g, 50.8%) was identified as syn-9-hydroxybicyclo[4.2.1]nona-3,7-diene (5) from the following data: mass spectra for m/e = 136; nmr at 7 4.24 (m, 2H, hydrogens at C-7 and -8), 4.53 (m, 2H, hydrogens at C-3 and -4), 5.54 (t, 1H, hydrogen at C-9), 7.24 (m, 2H, bridgehead hydrogens), 7.69 (m, 4H, hydrogens at C-2 and -5), and 8.24 (s, 1H, hydroxyl hydrogen); uv maxima at 205 μm (ε = 2220).


Found: C, 79.53; H, 8.95.

Reaction of Syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene with Sodium Bis(methoxyethoxy)aluminum Hydride.

A solution of alcohol ½ (1.0 g, 0.0074 mole) in ether (10 ml) was added to a stirred solution of sodium bis(methoxyethoxy)aluminum hydride (3.0 g of 70% benzene solution, 0.022 mole) at 0° in 5 min and the mixture was refluxed for 2 hr. The mixture was hydrolyzed with 10% sulfuric acid solution. Extraction with ether followed by washing of the combined extracts with brine, drying over anhydrous magnesium sulfate and removal of the solvent at reduced pressure afforded waxy colorless solid (0.92 g). Glc analysis of the residue on Column B at 220° showed the presence of syn-9-hydroxybicyclo[4.2.1]nona-2,7-diene (0.37 g, 36.8%) and syn-9-hydroxybicyclo[4.2.1]nona-3,7-diene (0.55 g, 53.8%).

A solution of $\frac{1}{4}$ (100 mg) in ethanol was shaken with 10% Pd-C (10 mg) under hydrogen at 2 atm until absorption of hydrogen ceased. The mixture was filtered and evaporated leaving syn-9-hydroxybicyclo[4.2.1]nonane $\frac{55}{55}$ which was recrystallized from pentane affording white crystals, mp 175-177°C. The mass spectrum exhibits a parent ion at m/e = 140.

Catalytic Hydrogenation of a Mixture of Syn-9-hydroxybicyclo[4.2.1]-nona-2,7-diene ($\frac{53}{53}$) and Syn-9-hydroxybicyclo[4.2.1]nona-3,7-diene ($\frac{54}{54}$).

A mixture of alcohols $\frac{53}{53}$ and $\frac{54}{54}$ (40% $\frac{53}{53}$ and 60% $\frac{54}{54}$) in ethanol (10 ml) was shaken with 10% Pd-C (10 mg) under hydrogen (2 atm) until absorption of hydrogen ceased. After filtration, condensation, and recrystallization from pentane, syn-9-hydroxybicyclo[4.2.1]nonane $\frac{55}{55}$ was isolated as white crystals (mp 175-177°C). Glc analysis of the crude reduction product showed it to be one component with the same retention time as the reduction product from syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (4). A mixed mp of the two separately obtained alcohol samples shows no depression.

Reaction of Ketone $\frac{1}{4}$ with Lithium Methoxide.

To a stirring solution of lithium methoxide (0.5 g, 0.013 mole) in absolute methanol (10 ml) was added ketone $\frac{1}{4}$ (1.0 g, 0.0075 mole) and the solution was refluxed for 12 hr. The dark brown mixture was poured into water and extracted with ether. The ether extracts were combined and washed with brine, dried over anhydrous magnesium sulfate, filtered, and evaporated to a light yellow solid (0.90 g) which solidified on standing.
Glc analysis at 220° on Column B indicated the presence of two components. The first component (0.81 g, 81%) was identified as syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (l) by comparison of its infrared and nmr spectra to those of alcohol (l) as obtained by sodium borohydride reduction. The second component (9%) was not identified.

**Preparation of Bicyclo[4.2.1]nona-2,4,7-trien-9-one Oxime (57).**

To a rapidly stirred mixture of 1 (2.0 g, 0.015 mole), hydroxylamine hydrochloride (3.0 g, 0.043 mole), water (20 ml), and methanol (10 ml) at 0° was added anhydrous sodium carbonate (5.0 g, 0.028 mole) in portions. The mixture was stirred for 1 hr, water was added, and the mixture was extracted with ether. The organic portion was washed with brine, dried over anhydrous magnesium sulfate, and concentrated at reduced pressure to a white solid. Crystallization of the product from methylene chloride and hexane yielded bicyclo[4.2.1]nona-2,4,7-trien-9-one oxime (57) (1.61 g, 79%), white crystals, mp 112-113°.

The nmr of 57 showed \( \delta 0.65 (s, 1H, OH), 4.05 (m, 4H, H at C-2, -3, -4, and -5), 4.55 (m, 2H, H at C-7 and -8), 5.75 (m, 1H, bridgehead C-H), and 6.45 (m, 1H, bridgehead C-H).\)

**Beckmann Fragmentation of Bicyclo[4.2.1]nona-2,4,7-trien-9-one Oxime (57).**

Tosyl chloride (5.14 g, 0.027 mole) was added in 0.5 hr to oxime 57 (2.0 g, 0.014 mole) in pyridine (20 ml) at 0°. The mixture turned black on storage. After 2 days at -20°, the mixture was poured on ice and extracted with ether. The organic layer was washed with cold 6N hydrochloric acid, saturated sodium bicarbonate, and brine, dried over magnesium sulfate, and vacuum evaporated.
Column chromatography of the residual brown oil on alumina (Woelm, neutral grade 1) with benzene-hexane (1:1) afforded cyano-1,3,5,7-cyclooctatetraene ($\text{C}_8\text{H}_7\text{N}$, 1.02 g, 57%) as a yellow liquid after distillation, bp 66° (1.5 mm). The mass spectrum showed m/e = 129, IR absorption of the nitrile occurred strongly at 2230 (C=N), and the nmr had a broad singlet at $\tau$ 4.0.

**Anal. Calcd for C$_8$H$_7$N:** C, 83.69; H, 5.46; N, 10.89.

**Found:** C, 83.46; H, 5.27; N, 10.58.

**Preparation of Cyclooctatetraenecarboxaldehyde (62).**

Diisobutyl aluminum hydride (17.6 g, 25% in hexane, 0.033 mole) was injected into a rapidly stirred solution of nitrile 58 (2.0 g, 0.016 mole) in ether (40 ml) at -78° under nitrogen. The solution darkened as injection was made. After having been stirred for 3 hr the mixture was hydrolyzed with methanol (2 ml) followed by 10% sulfuric acid (2 ml) and then dumped into water. The mixture was then extracted with ether, the organic extracts were combined, washed with brine, dried over magnesium sulfate, filtered, and evaporated at reduced pressure. The yellow brown liquid residue, after chromatography on silica, afforded 1,3,5,7-cyclooctatetraenaldehyde (1.68 g, 79.5%). The aldehyde was fairly unstable and thus was stored at -78° until used.

The infrared spectrum displayed a $>$C=O stretching absorption at 5.94 $\mu$ and the expected aldehydic C-H stretching at 3.52 and 3.68 $\mu$; the mass spectrum reveals a parent peak at m/e = 132. The nmr showed $\tau$ 0.60 (singlet, H, aldehydic proton), and 3.5-4.5 (m, 7H, vinyl hydrogens).
Reaction of 1,3,5,7-Cyclooctatetraenecarboxaldehyde with 2,4-Dinitrophenylhydrazine.

1,3,5,7-Cyclooctatetraenecarboxaldehyde (0.1 g) in ethanol (1 ml) was added to 2,4-dinitrophenylhydrazine (0.1 g) dissolved in a solution of water (0.75 ml), concentrated sulfuric acid (0.5 ml), and 95% ethanol (2.5 ml). The orange precipitate which formed immediately was filtered and recrystallized twice from methylene chloride-hexane to yield orange crystals (0.123 g, 52%), mp 218-219°.

Anal. Calcd for C_{15}H_{12}N_{4}O_{4}: C, 57.70; H, 3.87.
Found: C, 57.42; H, 3.63.

Preparation of 1,3,5,7-Cyclooctatetraenecarboxaldehyde Tosylhydrazone.

1,3,5,7-Cyclooctatetraenecarboxaldehyde (1.22 g, 0.0092 mole) in methanol (3 ml) was added to tosylhydrazide (1.73 g, 0.0093 mole) dissolved in methanol (5 ml). The solution was then stored at room temperature for 2 hr. Cooling failed to cause crystallization; the volume of the mixture was reduced one-half but cooling again gave negative results. The remainder of methanol was removed at reduced pressure leaving a thick brown syrup. Chromatography on silica gel using 1:1 chloroform-benzene allowed purification of the tosylhydrazone (2.21 g, 80%) which after repeated recrystallization from methylene chloride-hexane gave light yellow crystals (mp 114-116°).

Anal. Calcd for C_{16}H_{14}N_{6}SO_{2}: C, 63.97; H, 5.37; N, 9.32.
Found: C, 64.30; H, 5.46; N, 9.45.
The nmr of the tosylhydrazone showed the following absorptions:

\[ \tau 1.58 \text{ (s, } 1\text{H, } H \text{ at } C-9), \ 2.06-2.83 \text{ (m, } 5\text{H, aromatic hydrogens and } N-H), \ 3.90-4.36 \text{ (m, } 7\text{H, vinyl hydrogens), and } 7.60 \text{ (s, } 3\text{H, methyl).} \]

**Preparation of the Sodium Salt of 1,3,5,7-Cyclooctatetraenecarboxaldehyde Tosylhydrazone and its Pyrolytic Decomposition.**

Sodium hydride (0.127 g of 57% NaH in mineral oil, 0.0032 mole) was added slowly to tosylhydrazone (0.87 g, 0.0029 mole) in methylene chloride (20 ml) at 0°. After evolution of hydrogen ceased, the solvent was stripped at reduced pressure leaving the salt, as a white powder coated on the flask walls. The flask was attached via an adapter (partially packed with glass wool to prevent spatter entrainment) to a series of traps and a vacuum system. Upon decomposing the salt at 280° (0.3 mm), a yellow liquid collected in the adapter and on the glass wool; the traps contained no products. The yellow liquid in the adapter solidified on cooling and was collected by dissolution in methylene chloride. The solid was recrystallized from methylene chloride-hexane to yield yellow needles (0.32 g, 76.2%), mp 103-105° with mass spectrum showing m/e = 144.

**Anal. Calcd for C₉H₆N₂:** C, 74.97; H, 5.91.

**Found:** C, 74.97; H, 5.80.

The ir spectrum of shows a N-H stretch at 3.06 μ. Nmr absorptions occur at \( \tau 1.6 \text{ (s, } 1\text{H, } N-H \text{, washed out of spectrum with } D₂O), \ 2.8 \text{ (s, } 1\text{H, } H \text{ at } C-9), \text{ and } 3.80 \text{ to } 4.24 \text{ (m, } 6\text{H, vinyl hydrogens). The uv spectrum of } \text{ exhibits maxima at } 209, 226, 264, 271, \text{ and } 283 \text{ μμμ (ε = 6046, } 9760, 14180, 13960, \text{ and } 7750).} \)
Preparation of 9 (Methoxymethylene)bicyclo[4.2.1]nona-2,4,7-triene (\(\text{74}\)).

A mixture of sodium hydride (0.95 g, 0.023 mole) in dimethylsulfoxide (30 ml) under nitrogen was heated at 74° until hydrogen evolution stopped. The black solution was cooled to 5° and 9-(methoxymethylene)triphenylphosphonium chloride (7.75 g, 0.023 mole) was added in ~5 min. The black solution turned dark red and was then stirred for 20 min. Ketone \(\text{1}\) (4.0 g, 0.030 mole) was added in 0.5 hr and the solution was heated at 74° for 3 hr. The black mixture was poured into water and extracted with pentane. The extracts were combined, washed with water, dried over anhydrous magnesium sulfate, filtered, and concentrated at reduced pressure to a thick orange liquid. Some phosphorus salts precipitated from the liquid at this point. Glc analysis on column A at 180° showed that one product had been formed. Distillation through a short path distilling head at 67-68° at 1.1 mm afforded 9-(methoxymethylene)bicyclo[4.2.1]nona-2,4,7-triene (3.37 g, 70.0%) as a near colorless liquid.

The mass spectrum of \(\text{74}\) showed m/e = 160 and has the following nmr absorptions: \(\tau\) 3.60-4.34 (m, 5H, H at C-2, -3, -4, -5, and methylene H), 4.70 (m, 2H, H at C-7 and -8), 6.1 (m, 1H, bridgehead H), 6.41-6.70 (m, 4H, bridgehead H and methyl hydrogens).

**Anal. Calcd for C\(_{11}\)H\(_{12}\)O: C, 82.46; H, 7.55.**

**Found: C, 82.73; H, 7.68.**

The uv absorption of \(\text{74}\) has maxima at 213, 265, and 278 m\(\mu\) (\(\epsilon = 12500, 3750, \text{and} 2600\)).
Preparation of Bicyclo[4.2.1]nona-2,4,7-triene-syn-9-carboxaldehyde (71).

A solution of 9-methoxymethylenebicyclo[4.2.1]nona-2,4,7-triene (2.0 g, 0.012 mole) in chloroform (15 ml) was added to a mixture of water (5 ml) and trifluoroacetic anhydride and the heterogeneous mixture was vigorously stirred overnight. The layers were separated and the aqueous layer was extracted with chloroform. The organic layers were combined and washed with saturated sodium bicarbonate, dried over anhydrous magnesium sulfate, filtered, and the chloroform was removed at reduced pressure. Glc analysis of the orange liquid residue on Column A at 180° indicated that the vinyl ether had been totally converted to a new compound. Distillation of this liquid through a short path distilling head (67° at 1.1 mm) afforded aldehyde 71 (1.59 g, 82.7%) as a colorless liquid which solidified in the freezer. The mass spectrum of 71 gave a proper parent ion: m/e = 146; the infrared spectrum is consistent with the assigned structure. The nmr of 71 has the following absorptions: 7 0.58 (s, 1H, aldehydic H), 3.53-4.27 (m, 4H, H at C-2, -3, -4, and -5), 6.57 (t, 2H, bridgehead H), 7.17 (t, 1H, H at C-9). The ultraviolet spectrum of 71 has absorption maxima at 214, 252, 258, 265, and 277 μ (ε = 3625, 3625, 3960, 3830, and 2100.


Found: C, 82.44; H, 6.76.

Reaction of Bicyclo[4.2.1]nona-2,4,7-triene-syn-9-carboxaldehyde with 2,4-Dinitrophenylhydrazine.

Aldehyde 71 (0.1 g) in 95% ethanol (1 ml) was added to 2,4-dinitrophenylhydrazine (0.1 g) dissolved in water (0.75 ml), concentrated
sulfuric acid (0.5 ml) and 95% ethanol (2.5 ml). The yellow precipitate which formed instantly was recrystallized twice from methylene chloride-hexane as yellow crystals (0.115 g, 53%), mp 184-185°.

**Anal.** Calcd for C_{15}H_{12}N_{4}O_{4}: C, 58.89; H, 4.32.

Found: C, 58.61; H, 4.49.

Chromic Acid Oxidation of Bicyclo[4.2.1]nona-2,4,7-trien-syn-9-carboxaldehyde (72).

A solution of chromium trioxide (1.0 g, 0.01 mole) in water (13 ml) and concentrated sulfuric acid (1 ml) was added dropwise to a rapidly stirred solution of aldehyde 71 (1.0 g, 0.0068 mole) and acetone (20 ml). The green mixture was stirred 30 min after addition was complete. The heavy chromium salt layer was removed, and then the remaining acetone layer was evaporated at reduced pressure. The remaining aqueous mixture was made basic with potassium hydroxide and extracted with ether. The aqueous layer was then acidified with 6N sulfuric acid and extracted with ether. The extracts were combined, dried over magnesium sulfate, and evaporated at reduced pressure leaving a green white solid. Decolorization with charcoal in acetone, and recrystallization from acetone-water afforded bicyclo[4.2.1]nona-2,4,7-trien-syn-9-carboxylic acid (72, 0.63 g, 57.1%) as white crystals, mp 173-174°.

**Anal.** Calcd for C_{10}H_{10}O_{2}: C, 74.05; H, 6.22.

Found: C, 74.21; H, 6.32.

The mass spectrum exhibits a parent ion at m/e = 162; the infrared spectrum shows the expected >C=O stretch at 5.78 μ, and a broad OH stretch
2.8 to 3.5 μ. The nmr spectrum of \( \mathcal{L} \) consists of absorptions at \( \tau \) 1.32 (s, 1H, acid II), 3.86 (m, 4H, H at C-2, -3, -4, and -5), 4.76 (m, 2H, H at C-7 and -8), 6.66 (m, 3H, H at C-1, -6, and -9).

**Preparation of Bicyclo[4.2.1]nona-2,4,7-triene-9-one Ethylenedithiocetal 75.**

Boron trifluoride etherate (1 ml, 45%) was added in 10 min to a stirred mixture of I (2.0 g, 0.015 mole) and 1,2-ethanedithiol (1.41 g, 0.015 mole) at 0°. A yellow viscous material formed to which methanol (15 ml) was added. The mixture partly solidified in a freezer and the liquid was decanted. Upon column chromatography of the semisolid on silica gel with hexane-benzene as eluent, bicyclo[4.2.1]nona-2,4,7-triene-9-one ethylenedithiocetal (75, 2.45 g, 0.012 mole, 79%) was isolated as white crystals, mp 83-85°, upon recrystallization from methylene chloride-hexane. The mass spectrum of 75 showed a parent ion at \( m/e = 208 \) and nmr absorptions at \( \tau \) 4.05 (m, 4H, H at C-2, -3, -4, and -5), 4.65 (m, 2H, H at C-7 and -8), 6.65 (m, 2H, bridgehead hydrogen), and 6.80 (s, 4H, methylene hydrogens).

**Anal. Calcd for \( \text{C}_{11}\text{H}_{12}\text{S}_{2} \): C, 63.41; H, 5.86.**

**Found: C, 63.15; H, 5.64.**

**Treatment of Bicyclo[4.2.1]nona-2,4,7-triene-9-one Dithiolketal 75 with Raney Nickel.**

Raney Nickel (1 teaspoon, Grace No. 28 Raney Active Nickel) was washed with water until no alkalinity was detected in the washings, several times with anhydrous ethanol and finally several times with benzene.
To a rapidly stirred suspension of this Raney Nickel in benzene (50 ml) was added dithioketal 75 (2.0 g, 0.0096 mole) and the mixture was refluxed for 6 hr and filtered hot. The filtered catalyst was washed with hot benzene which was added to the initial filtrate and removed at reduced pressure. The liquid residue was examined on Column A at 180° and found to be indene (0.91 g, 82%) with one trace minor component which was not identified.


9-Methylenebicyclo[4.2.1]nona-2,4,7-triene (0.100 g, 0.00077 mole) was dissolved in dry, nitrogen-purged acetone and photolyzed with a 450 watt Hanovia medium pressure lamp for 2 hr in a Pyrex tube. A tan powder (0.015 g) was filtered from the solution and the acetone was removed at reduced pressure. The highly odorous oil remaining was found to contain only one component by glc analysis at 132° on Column A.

The product was identified as 9-methylenetricyclo[3.3.1.0^4,6]nona-2,7-diene (0.085 g, 85%) from the following data.

Analysis showed a mass spectral parent ion m/e = 130°, nmr absorptions at δ 6.27 (t, 2H, vinyl H at C-3 and -7), 5.28 (s, 2H, methylene H), 5.83 (t, 4H, averaging H at C-2, -4, -6, and -8), 3.16 (t, 2H, averaging H at C-1 and -5). As the temperature is decreased, the rate of rearrangement of S1 is slowed. At -60° the central 4 hydrogen triplet has decreased in intensity. At -90° the central 4H triplet is virtually gone and the vinyl triplet is a broad hump and the other protons all
have resonances which fall from 100 to 200 cps. This pattern is similar to that of tricyclo[3.3.1.0^4,8]nona-2,7-diene-9-one (barbaralone) as discussed by J. B. Lambert.


Anal. Calcd for C_{10}H_{10}: C, 92.25; H, 7.75.
Found: C, 92.14; H, 7.81.

The infrared spectrum exhibits $\nu_{\text{max}}$ (\(\mu\)) at: 3.29, 3.39, 6.08, 6.18, 7.27, 7.43, 7.65, 7.99, 10.75, 11.22, 11.39, 11.71, 12.88, 13.37, and 13.64, and the ultraviolet spectrum shows a maximum at 213 (\(\epsilon = 8000\)).