An exploration of the C9H8O energy surface in the vicinity of bicyclo[5.2.0]nona-2,5,8-trien-4-one

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AN EXPLORATION OF THE 1,2-BENZOPYRAN ENERGY SURFACE IN THE VICINITY OF BICYCLO(5,2,0)NONA-2,5,8-TRIEN-4-ONE.

IOWA STATE UNIVERSITY, PH.D., 1978
An exploration of the C₉H₆O energy surface in the vicinity of bicyclo[5.2.0]nona-2,5,8-trien-4-one

by

David Michael Lokensgard

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of The Requirements for the Degree of DOCTOR OF PHILOSOPHY

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INTRODUCTION

Bicyclo[5.2.0]nona-2,5,8-trien-4-one might prove to be a versatile substrate for the examination of current organic structural theory. The molecule would consist of a cross-conjugated cycloheptadienone fused to a cyclobutene ring, displaying a folded geometry with a plane of symmetry.

The two isolated π-electron systems lie in close proximity on one face of the molecule. Overlap between the termini of these systems accompanied by localization of the carbonyl π electrons on oxygen would produce a cyclic array of atomic orbitals containing six electrons, an electronically stabilized, aromatic system according to recent extensions of the Hückel rule. Through-space interaction of this type has been observed in similar systems, and is known as bis-homoaromaticity. Physical manifestations of this effect can include enhanced thermodynamic stability relative to appropriate model systems, substantial charge delocalization, and a magnetic field-induced diamagnetic ring current. The best opportunity for observation of this phenomenon in the bicyclo[5.2.0]nona-2,5,8-trienyl system would lie in the formation of the unsubstituted cation, which is not directly accessible from the target ketone. The presence of the
carbonyl functionality with its strongly polarized double bond should place some fractional positive charge on the pentadienyl segment of the molecule, however, and any stabilization derived from aromaticity in the ketone might tend to reinforce this polarization. Operation of this effect would relate the ketone to its monocyclic counterpart, cycloheptatrienone, and should be reflected in a high dipole moment and a deshielded vinyl hydrogen absorption position in the nuclear magnetic resonance spectrum.

Protonation of the basic carbonyl oxygen should increase the cationic nature of the pentadienyl system, and thus the likelihood of observing bis-homoconjugative stabilization. Partial bond formation between the π systems would be expected to result in a shortening of the distance between the terminal nuclei, which might provide a mechanism for interchanging the connectivity of the two sets of cyclobutene carbon atoms, or for the production of an unusual ion containing two planes of symmetry and a coordinated cyclobutadiene.

One-electron reduction of the ketone should provide the radical anion, or ketyl, of the system. The presence and magnitude of any through-space interaction in the seven-π-electron system could be inferred from the hyperfine splitting constant due to the olefinic
cyclobutene hydrogen nuclei in the electron spin resonance spectrum of the radical.

The strain of the cyclobutene moiety and the high degree of unsaturation present in the trienone should combine to promote electrocyclic reactivity. Cleavage of the bridging single bond could occur thermally in three symmetry-allowed ways. Disrotatory opening, allowed with respect to the pentadienyl cation-like dienone system, would lead to $Z^4$- or $Z,E,E,Z$-cyclononatetraenone, vinylogs of cycloheptatrienone, which would be expected to possess antiaromatic character if planar. Conrotatory opening, governed by the symmetry of the cyclobutene, would produce $Z,E,Z,Z$-cyclononatetraenone. The single trans double bond of this eight-$\pi$-electron monocyclic ketone introduces a "twist" into the conjugated system, so that the molecule
might display Möbius aromaticity. Cope rearrangement would lead to a cyclopropanone in the bicyclo[6.1.0] nonatriene system, which is itself known to be a rich source of molecular rearrangement.

The photochemistry of the ketone might involve cleavage of the bridging single bond by electrocyclic, radical or sigmatropic mechanisms, cis-trans double bond isomerization or dimer formation.

The synthesis of the ketone can be approached via the Robinson-Schöpf condensation of 3-oxoglutaric acid, methylamine and a vicinal dialdehyde. This procedure is an elegant and general method for the construction of tropinone derivatives, which contain the required seven membered carbocyclic ring and plane of symmetry. Hofmann degradation of this system is known to lead to cycloheptadienones in good yield and provides the means of introducing the desired degree of unsaturation into the larger ring. The synthetic challenge may thus be reduced to the preparation of the unknown cis-cyclobutene-3,4-dicarboxaldehyde. This intermediate might be accessible by modification of the procedure used to prepare the known cis-cyclobutene-3,4-dicarboxylic acid.
Reduction of the olefinic bond of the dialdehyde or its equivalent would provide an independent route to bicyclo[5.2.0]nona-1(7),2,5-trien-4-one, a C₁₀H₈O isomer which may produce 4,5-bis(methylene)cyclohepta-2,6-dien-1-one on pyrolysis. This ring-opened product is of interest as an analog of 9-xylylene in the tropone system.
The conclusion reached by Winstein (1-4) during the early post-war years concerning the solvolytic behavior of the cholesteryl-i-cholesteryl system was an important stimulus to the development of the theory of the chemical bond. In order to explain the rapid rate of solvolysis, the first-order kinetics, and the structure and stereo-specific formation of the products, he proposed that a strong interaction between the formally trivalent cationic center and the non-conjugated double bond (or the cyclopropane moiety in the i-cholesteryl system) must occur during the ionization process to form a more stable, charge-delocalized homoallyl cation.

The term homoconjugation was applied to this phenomenon, and was defined as overlap between orbitals on atoms separated by and bound to one or more saturated centers. Bonding between the non-adjacent nuclei was suggested to be intermediate in type between $\sigma$ and $\pi$. 
The ensuing intensive investigation into this phenomenon, and into through-space orbital interaction generally, has served to stimulate the sophistication of mechanistic theory and synthetic methodology, the refinement of mathematical models of molecular structure and reactivity, and the development of the technology of physical organic chemistry.

A heated debate took place during the twenty years following Winstein's elaboration of Shoppee's (5) initial suggestion of anchimeric assistance during the solvolysis of cholesteryl chloride concerning the detailed electronic and structural nature of non-classical cations of several types, a few of which are depicted here.
The arguments used were based upon a staggering amount of classical mechanistic experimentation involving relative rate determinations, label scrambling, skeletal rearrangement, and product distributions during solvolysis of precursors to such ions, and centered about the question of whether such delocalized structures were energetic minima or simply represented transition states separating rapidly equilibrating "classical" ions (6). The scope of the discussion broadened considerably in 1959 with Winstein's designation (7) of the cation produced upon solvolysis of cis-bicyclo[3.1.0]hex-3-yl toluene-p-sulfonate (8) as a tris-homocyclopropenyl cation, after Woods et al. (9), and with his introduction of the term homoaromaticity. Homoaromatic species were related to classical aromatic species as homoallyl was to allyl, by the substitution of a through-space overlap for $\pi$-bonding between adjacent atoms. Although he expected the magnitude of the delocalization energy to be reduced in homoaromatic systems because of the less efficient orbital overlap of the homoconjugate linkage relative to the olefinic double bond, Winstein predicted special stability for homoaromatic structures, and went so far as to propose the heptahomotropylium cation as an experimental goal.
Extension of the concept of aromaticity to cyclic, electrically charged homoconjugated systems raised interpretive problems, since classical reactivity criteria such as the ability to undergo electrophilic substitution reactions could not be expected to apply to such species. While the theoretical basis for the electronic stabilization of molecules which satisfy the "4N+2 rule" was established during the early application of quantum mechanics to chemical structure (10, 11), that theory did not designate a universally applicable, macroscopically observable property of such systems. The solution to this problem of classification has been found to lie in the magnetic properties of orbital systems satisfying Hückel's rule.

The electrons occupying an atomic or molecular orbital respond to the application of an external magnetic field by "circulating" within that orbital, producing a microscopic induced magnetic field. When the electrons are contained within a cyclic overlapping system of atomic orbitals which obey the Hückel rule this circulation takes place around the periphery of the orbital system, and is known as an induced diamagnetic ring current. Elvidge and Jackman (12) have proposed that an aromatic molecule be defined as one which will sustain such a ring current. The value of this definition results from the fact that
an induced ring current produces effects measurable on a macroscopic scale. The presence and magnitude of the induced field of an aromatic molecule can be determined by measurement of the magnetic susceptibility of the substance, or by observation of its nuclear magnetic resonance spectrum.

The presence of a ring current is indicated by the sign and magnitude of the exaltation, \( \Lambda \), in susceptibility studies. This value is the difference between the measured susceptibility of a substance and the value obtained by summing the contributions of its component atoms and bonds as obtained from model systems, and is large and positive for an aromatic substrate (13). The experimental procedure is complex, the purity of the substrate is important, and the corrections necessary to arrive at a value for the calculated susceptibility in the presence of a charged molecule and its counterion limit the precision of the technique.

The introduction of commercial high resolution nuclear magnetic resonance spectrometers in the late 1950's simplified the detection of diamagnetism in organic molecules enormously. The ring current of an aromatic molecule creates a toroidal magnetic field which is anti-parallel to the external applied field within the right cylinder defined by the cyclic orbital system, and parallel to the applied field outside of that cylinder. The nuclei under observation during the n.m.r. experiment experience the sum of the applied and induced fields, and their apparent spin transition energies will be displaced from the values expected on the basis of other electronic and struc-
tural influences. Nuclei inside or outside of the aromatic ring will thus resonate at higher or lower fields, respectively, than expected, providing simple and direct information about the presence and magnitude of any induced ring current.

The position of resonance of a nucleus is also a sensitive, approximately linear function of the electron density surrounding it, so that proximal electric fields also shift the observed spin transition energy. A hydrogen nucleus bonded to sp²-hybridized carbon will exhibit a downfield shift of approximately ten parts per million (14, 15) for a unit positive charge accommodated by the p orbital on carbon, while the carbon atom itself, if nmr-observable (¹³C), will be deshielded by about one hundred sixty p.p.m. (16, 17). Both charge and ring current effects reduce the field at which a hydrogen nucleus on the perimeter of an aromatic cation resonates, so that it is necessary to assess the individual contribution of each of the two effects to the total ¹H deshielding which is observed. Fortunately, the carbon nuclei of an aromatic ring lie in a nodal surface of the induced field and consequently are not significantly deshielded by the presence of a ring current (16). The high sensitivity of the ¹³C absorption position to electron density thus provides an excellent measure of the charge distribution within an ion and allows charge correction of the ¹H spectrum to reveal ring current effects more clearly. The sensitivity of the nuclear magnetic resonance spectrum to the presence of ring currents and to electron distribution in organic ions, the simplicity of the experimental technique, and the
ability to measure these quantities at low temperatures combined to provide a powerful tool for the detection of aromaticity in charged molecules.

The majority of homoaromatic ions which have been directly observed have utilized the cycloheptatrienyl, or tropylium, cation as the parent aromatic system. Tropylium bromide, an ionic salt, was first prepared in 1891 (18), but its structure was unknown until the work of Doering and Knox was reported in 1954 (19). Since that time nearly fifty salts containing the tropylium ion have been prepared (20). The ion has been shown to possess D$_{7h}$ symmetry (21, 22), as expected for an aromatic seven-carbon six-$\pi$-electron system, and the exaltation of the diamagnetic susceptibility has been shown to be greater than that of benzene (23, 24).

\[
\begin{align*}
H_{1-6} & \delta 7.24 \\
C_{1-6} & \delta 128.7 \\
\Lambda & = 13.7
\end{align*}
\hspace{1cm}
\begin{align*}
H_{1-7} & \delta 9.31 \\
C_{1-7} & \delta 156.3 \\
\Lambda & = 16
\end{align*}
\]
Proton magnetic resonance of the tropylium ion occurred at 9.31 p.p.m. (δ) lower field than that of tetramethylsilane (20), while the carbon-13 resonance was 156.3 p.p.m. downfield from the corresponding absorption of TMS (17). The stability, substantial ring current and relatively unstrained perimeter of the cycloheptatrienyl cation suggested that incorporation of a homoconjugate linkage into this system might provide a means for testing the validity of Winstein's proposal.

In 1962 von Rosenberg, Jr. et al. (25) reported that protonation of cyclooctatetraene produced a cation which was isolable as the chloro-pentafluoroantimonate salt, and which displayed an nmr spectrum in 96% sulfuric acid which might be compatible with a homotropylium structure.
This ion and several ring-substituted derivatives were extensively studied by Keller and Pettit (26, 27) and by Winstein and co-workers (24, 28, 29), and were shown to be the first directly observable homoaromatic species. The n.m.r. spectra of the cation were particularly informative. The uniformity of chemical shift displayed by ring hydrogens 2-6 was indicative of substantial charge delocalization, and this feature was also reflected in the carbon-13 spectrum of the ion (30). The striking difference in the resonance positions of the methylene hydrogens, 5.7 p.p.m., demonstrated the non-planarity of the homoconjugate bridge and the presence of a substantial ring current. This difference, $\Delta$, in chemical shift between the methylene hydrogens in homotropylium cations has been taken as a measure of the magnitude of the induced field, and thus the degree of aromatic character, of such ions. The exaltation, $\Lambda$, of the homotropylium ion has been determined to be 15 (24), only slightly less than that of the parent tropylium ion.

\[
X = D, \Delta G^\ddagger = 22.3 \quad X = Cl, \Delta G^\ddagger = 23.3
\]
Treatment of cyclooctatetraene with dideuterosulfuric acid at -10°C produced about 80% of the 8-endo-deuterated ion. Equilibration of the epimers took place on warming, with a free energy of activation of 22.3 Kcal/mole (29).

The 8-chloro epimers underwent the same interconversion with a free energy of activation of 23.3 Kcal/mole (31, 32). These figures have been taken as a rough estimate of the delocalization energy of the homotropylium cation on the assumption that the planar cyclooctatrienyl cation represents the transition state of the reaction.

An x-ray diffraction study of the cation has not been reported, but several detailed quantum mechanical calculations of the geometry and electronic structure of the system have been carried out. Early work (33, 34) restricted the seven ring carbon atoms to a plane and arrived at a 1,7 internuclear distance compatible with a structure containing a normal cyclopropane moiety, as suggested by Deno (35). Haddon (36) has recently applied MINDO/3 together with a geometry optimisation program to the problem, which predicted the lowest energy structure to have an "open" cyclopropane ring with a C1-C7 distance of 1.62 Å. The methylene carbon was found to be inclined at an angle of 117.9° to the plane defined by its four nearest neighbor carbon atoms, and the ring formed by the seven unsaturated carbons was found to be slightly puckered toward the bridging methylene. This geometry was earlier suggested by Winstein and co-workers on the basis of a detailed study of the proton-proton coupling constants displayed by the ion (37). An HMO calculation (24) of the resonance integrals in homo-
tropylium based on its ultraviolet absorption spectrum led to a 1,7-bond order of 0.56, and values of 0.69, 0.69 and 0.65 for the 1,2-, 2,3-, and 3,4-bond orders, respectively.

The aromatic nature of the homotropylium structure was retained even when substituents which should have stabilized the classical cyclooctatrienyl cation were introduced.

\[
\begin{align*}
\text{pK}_{\text{BH}^+} & = -4.7 \\
\Delta & = 3.1 \\
\end{align*}
\]
Protonation of cycloocta-2,4,6-trien-1-one (38), bicyclo[5.1.0]octa-3,5-
dien-2-one (39), and bicyclo[5.1.0]octa-2,5-dien-4-one (40) led to the
1-, 2-, and 4-hydroxyhomotropylium cations, respectively. The aromati-
city of these ions was demonstrated by their n.m.r. and ultraviolet
spectra, and by the relatively high basicity of the parent ketones.

Provision for delocalization of charge into other aromatic systems
has also failed to eliminate homoconjugative interaction in the ion.
Phenyl (24), monobenzo (41, 42) and dibenzo (43, 44) derivatives have
been prepared, and each displayed a $\Delta$ value consistent with the presence
of a ring current in the homotropylium moiety.

![Diagram of protonation reactions](image-url)
\[ \text{OH} \quad \xrightarrow{H^+} \quad \Delta = 5.34 \]

\[ \text{OH} \quad \xrightarrow{H^+} \quad \Delta = 4.7 \]

\[ \quad \xrightarrow{H^+} \quad \Delta = 3.2 \]
This enormously successful realization of Winstein's concept of homoaromaticity in the tropylium series quite naturally generated interest in the limitations of homoconjugative participation in aromatic systems. The incorporation of two cyclopropyl groups into the cycloheptatrienyl system might lead to the 1,1-, 1,2-, 1,3-, or 1,4-bishomotropylium cations. Bonding in the 1,1- and 1,2-ions could not be adequately described by the simple homoconjugative model, and they have remained theoretical curiosities thus far.

Ahlberg and co-workers (45) reported the first direct observation of a 1,4-bishomotropylium cation in 1970 shortly after the intermediacy of a similar ion was suggested by Barborak et al. (46) in the rearrangements of the barbaralyl system. Extraction of 9-methyltricyclo[3.3.1.0^2,8]nona-3,6-dien-9-ol from dideuteromethylene chloride into a 1:3 mixture of fluoro sulfuric acid and fluoro sulfinyl chloride (super acid) at -135° led to the 9-methyl-9-barbaralyl cation. Warming of this solution to -118° promoted a rearrangement to the 1-methylbicyclo[4.3.0] nona-2,4,7-trien-9-ylum ion, which was identified by its n.m.r. spectrum.
The same ion has been produced by protonation of 2-methylbicyclo-[3.2.2]nona-3,6,8-trien-2-ol (47), 9-methylenebarbaralane, 5-methylene-tricyclo[6.1.0.0^3]nona-2,6-diene, and 2-methylenebicyclo[3.2.2]nona-3,6,8-triene (48).
The proton (45) and carbon-13 (47) n.m.r. spectra of the ion indicated that approximately 0.5 unit of positive charge was accepted by the butadienyl system, and that a diamagnetic ring current was present. The ion was assigned a bishomoaromatic structure on this basis, although it decomposed at -50° (45) and addition of nucleophiles to solutions of the cation failed to produce products derived from its capture.

The unsubstituted bicyclo[4.3.0]nonatrienyl cation has been prepared by rearrangement of the degenerate 9-barbaralyl cation (49) produced upon super acid treatment of bicyclo[3.2.2]nona-3,6,8-trien-2-ol, and directly, from both \textit{exo}-tricyclo[4.3.0.0_{2,9}]nona-4,7-dien-3-ol and \textit{exo-cis}-bicyclo[4.3.0]nona-2,4,8-trien-7-ol (50).
The carbon-13 n.m.r. spectrum of this ion has not been reported, but the similarity of its proton spectrum to that of the 1-methyl ion indicated that approximately the same degree of charge delocalization took place, and was again suggestive of the presence of a ring current. The chemical shift of the bridgehead hydrogens appeared to be unaffected by that current, and were suggested to lie in a nodal surface of the induced field (50).

Solvolytic studies involving derivatives of cis-bicyclo[4.3.0]nona-2,4,8-trien-7-ol (51) have resulted in negligible exo/endo rate ratios, and the solvolysis rates of both epimeric p-nitrobenzoates were found to be lower than that of a model system, 3-cyclopentenyl p-nitrobenzoate.

A more compelling case for aromaticity in the 1,4-bishomotropylium system has been found in the properties of the bicyclo[4.3.1]deca-2,4,7-tri enyl cation, obtained on protonation of bicyclo[4.2.2]deca-2,4,7,9-tetraene (52-54).
The p.m.r. spectrum of this ion clearly reflected the presence of a diamagnetic ring current, in that the bridging methylene hydrogens were found to absorb at unusually high fields, while the peripheral ring hydrogens were shifted to lower fields than those of the [4.3.0] cation. Charge distribution in the ion also appeared to be more uniform, as shown by the relative constancy of chemical shift among the ring hydrogen nuclei. Roberts et al. (53) estimated that 0.7 unit of positive charge had been accommodated by the butadienyl system of the [4.3.1] cation. The absorption position of the bridgehead hydrogens remained relatively unaffected by the induced field, tending to support the rationale applied to the spectrum of the [4.3.0] cation (50).

The methylene bridge of the [4.3.1] system resulted in improved homoconjugative efficiency relative to that of the [4.3.0] cation, possibly because of a more favorable angle of inclination of the three-carbon homoconjugate linkages to the plane of the seven-carbon delocalized system. The ion was thermally stable to 80° in non-nucleophilic media, and its intermediacy has been demonstrated under nucleophilic conditions. An exo/endo rate ratio of 33000 has been reported in the solvolysis of the epimeric bicyclo[4.3.1]nona-2,4,8-trien-7-yl p-nitrobenzoates (50), and Schröder and co-workers (54) have observed the intermediacy of 10-substituted bicyclo[4.3.1]nonatrienyl cations during the addition of several electrophiles to bicyclo[4.2.2]-deca-2,4,7,9-tetraene.
Corver and Childs (42) have prepared the syn- and anti-"4,5-benzo-2,4:6,7-bishomotropones" as possible precursors to syn- and anti-hydroxy-1,4-bishomotropylium cations.

\[ \Delta = 0.68 \quad \Delta = 0.10 \]
They concluded, on the basis of the \( \Delta \) values and the shielding expected to result from interaction of the inner methylene hydrogens in the syn ion, that the syn isomer was bishomoaromatic and that the spectrum of the anti ion was best explained by rapid equilibration of simple cyclopropyl carbynol cations. No syn/anti interconversion was observed.

Warner and Winstein (55) found that protonation of cis-bicyclo-[6.1.0]nona-2,4,6-triene in super acid media at -125° produced the parent 1,3-bishomotropylium cation.

\[
\begin{align*}
C_1,5 & \delta 137.0 \\
C_2,4 & \delta 167.9 \\
C_3 & \delta 183.4 \\
C_6,7 & \delta 141.4 \\
C_8,9 & \delta 31.5 \\
H_1,5 & \delta 7.18 \\
H_{2,4} & \delta 7.98 \\
H_3 & \delta 9.04 \\
H_{6,7} & \delta 7.00 \\
H_a & \delta 3.82 \\
H_b & \delta 1.91
\end{align*}
\]
The proton and carbon-13 (30) n.m.r. spectra provided evidence for the presence of a ring current and for the acceptance of about 0.3 unit of positive charge by the isolated ethylenic moiety. It has been suggested that protonation of the triene occurs from a folded conformation to produce a non-aromatic transoid ion which could undergo a ring flip to produce the more stable syn isomer, the only species observed (30, 55).

Paquette and co-workers (56-58) have suggested the intermediacy of such a transoid ion, which they have termed a "double-Möbius 1,3-bis-homotropylium" ion, in a direct addition of fluoro- and chlorosulfonyl isocyanates and of tetracyanoethylene to cis-bicyclo[6.1.0]nona-2,4,6-triene. Recent reports concerning the behavior of the [6.1.0] triene system have shown that a modification of this position is required.

The Rearrangements of Bicyclo[6.1.0]nona-2,4,6-triene and its Derivatives

Bicyclo[5.2.0]nona-2,5,8-trien-4-one would be formally related to the bicyclo[6.1.0]nona-2,4,6-triene system by the Cope rearrangement.
The latter system is known to be an unusually rich source of unimolecular reactions, some of which are believed to involve such a Cope rearrangement and the intermediacy of a [5.2.0] skeleton. A familiarity with the known details of the energy surface upon which the transformations of the bicyclo[6.1.0]nonatriene system occur, and with the effects of structural and electronic modifications of the parent system upon the shape of that surface, can be expected to aid in understanding the reactivity of this new C₈H₈O isomer.

Entry into the bicyclo[6.1.0]nonatriene system was first gained by Akiyosha and Matsuda (59), who reported in 1955 the copper-catalyzed reaction of ethyl diazoacetate with 1,3,5,7-cyclooctatetraene to give 9-carboethoxybicyclo[6.1.0]nona-2,4,6-triene. Phillips (60) published the same observation later during that year, together with the incorrect conclusion that the alcohol obtained by lithium aluminum hydride reduction of the ester followed by distillation retained the [6.1.0] skeleton. Not until 1961, then, were rearrangements of the system reported by Vogel and co-workers (61-63) as a result of a study of carbene additions to cyclooctatetraene.
The unsubstituted triene was found to produce predominately cis-fused 3a,7a-dihydroindene on thermolysis at 90°, together with a smaller quantity of an air-sensitive isomer. Both dihalo compounds rearranged at 90° to the respective 8,9-dihalo-cis-bicyclo[4.3.0]nona-2,4,7-trienes. The methyl ester required a much higher temperature for rearrangement, and gave 9-carbomethoxy-cis-bicyclo[4.3.0]nona-2,4,7-triene as the major product. Vogel proposed that rearrangement of the dihalo derivatives proceeded through valence isomerization to a tricyclo[4.3.0.0\textsuperscript{7,9}]nona-2,4-diene, a synchronous cleavage of the carbon-halogen and internal cyclopropane bonds, and collapse of the resulting ion pair to the observed products.
Diels-Alder adducts of the proposed tricyclic intermediate have been identified as products of the reaction of dimethyl acetylene-dicarboxylate (64-66), N-phenyl maleimide, hexafluoro-2-butyne, and benzyne (67) with the unsubstituted [6.1.0] triene, and an iron complex of the tricyclic diene has been isolated as the major product of the reaction between benzylideneacetoneiron tricarbonyl and the triene (68). The hydrocarbon was liberated by treatment of the complex with ceric ion at -20°, and the free energy of activation of its cycloreversion to bicyclo[6.1.0]nonatriene was determined to be 22.9 Kcal/mole. The value of the equilibrium constant for this reaction was estimated to be approximately 4500 at 50°.
Barborak et al. (69) have prepared the epimeric 9-chloro-9-deutero-bicyclo[6.1.0]nonatrienes and has examined the solvolysis and rearrangement rates and products of the two compounds. The rearrangement rates of the epimers in carbon tetrachloride at 75° were nearly identical, but the products were different.

\[ \Delta G^\ddagger = 22.9 \quad \Delta G^\ddagger_{\text{est.}} = 27.5 \]

\[ K_{\text{est.}} = 4500 \]

\[ \Delta G^\ddagger = 26 \quad \Delta H^\ddagger = 23, \quad \Delta S^\ddagger = -8.7 \]
The rates of solvolysis of the epimers in aqueous acetone were also similar, and both gave cis-bicyclo[4.3.0]nona-2,4,7-trien-9-ol products. A fundamental difference in mechanism was again apparent from the deuterium distribution in the products.

The alcohol produced on solvolysis of the syn-chloro compound was found to be deuterated exclusively at the 8 position, while the label was randomly distributed in the alcohol derived from the anti isomer. The authors proposed the intermediacy of a cyclononatetraenylium cation to account for the scrambling observed in the latter product. Support for such a mechanism has been provided by Anastassiou and Yakali (70) who found that dissolution of 9-chloro-9-deuterocyclonona-1,3,5,7-tetraene in liquid sulfur dioxide at -66°C led rapidly to the formation
of randomly labeled 9-chloro-cis-bicyclo[4.3.0]nona-2,4,7-triene.

These results tended to confirm the operation of Vogel's mechanism in the rearrangement of 9,9-dihalo- and syn-9-halobicyclo[6.1.0]nonatrienes, but demanded a separate route to the cis-fused dihydroindene thermolysis products in the absence of a syn-halocyclopropane moiety.

Bangert and Boeckelheide (71, 72) determined that the ester prepared by Akiyosha and Matsuda was predominately anti-9-carboethoxy-bicyclo[6.1.0]nonatriene by n.m.r. analysis. They reported that thermolysis of this ester at 150° produced rearrangement to a cis-fused dihydroindene ester and a minor amount of an air-sensitive isomer. The stable product was suggested to arise from ring closure of a Z₃,Z₃,Z₃-cyclononatetraene ester.
Similar results were obtained on thermolysis of the related acid and alcohol (73), and Burkoth (74) noted that the alcohol which had been reported by Phillips was in fact a rearranged isomer. The intermediacy of a symmetrical species, presumably a $^4\alpha$-cyclononatetraene, in the formation of the cis-fused [4.3.0] products was supported by Radlick and Fenical (75), who prepared and rearranged the syn- and anti-9-methylbicyclo[6.1.0]nonatrienes. They proposed that the similarity of the exo/endo ratios in the mixture of cis-bicyclo[4.3.0]nonatrienes produced upon pyrolysis of the [6.1.0] epimers reflected a simple stereochemical preference during ring closure of the intermediate monocycle, and precluded the operation of any stereospecific mechanism.
The principles of orbital symmetry control of concerted electrocyclic reactions were developed by several theoreticians during the early 1960's, and were clearly presented by Woodward and Hoffmann in the form of a set of rules which were shown to be remarkably powerful in explaining and predicting the stereochemical outcome of such reactions (76). Application of these rules to the thermal conversion of cis-bicyclo[6.1.0]nona-2,4,6-triene to a bicyclo[4.3.0]nona-2,4,7-triene via topologically reasonable processes involving cleavage of only one $\sigma$ bond resulted in the prediction that the transition state for production of a trans-fused dihydroindene should be less energetic than
that for formation of the cis isomer. The observation of "symmetry-forbidden" cis-dihydroindenes as the major pyrolysis products in this system was an apparent violation of orbital symmetry control, and served as a stimulus to detailed investigation of the reaction. Two concerted, symmetry-allowed mechanisms for the rearrangement consistent with a loss of stereochemistry at C-9 were proposed and tested by Baldwin et al. (77). Each mechanism involved the cleavage of two $\sigma$ bonds, and would have resulted in a change in perimeter connectivity during the reaction.
Baldwin and co-workers prepared and rearranged two appropriately labeled bicyclo[6.1.0]nonatrienes, each of which produced only one cis-fused dihydroindene. This information, when combined with the results of Grimme's study of the rearrangement of 9,9-dideuterobicyclo[6.1.0]nonatriene (78), excluded both proposed allowed mechanisms and any other route which involved a hydrogen shift or interchange of connectivity among the ring carbons.
Rearrangement of the [6.1.0] triene to the dihydroindene system did not produce the cis isomer exclusively, as noted in Vogel's original work (61). Radlick and Fenical (75) analyzed the product mixture obtained by thermolysis of the parent triene and found that the air-sensitive minor product fraction reported by the earlier workers was composed of the "symmetry-allowed" thermolysis product, trans-bicyclo[4.3.0]nona-2,4,7-triene, and isomers formed by hydrogen shifts within that system.

\[
\begin{align*}
\text{(9)} & \quad \text{(1)}
\end{align*}
\]

Anastassiou and Griffith (79) reinvestigated the thermal response of the 9-methylbicyclo[6.1.0]nonatriene epimers which had been pyrolyzed at rather high temperatures by Radlick and Fenical (75). The anti isomer was found to rearrange rapidly at 76° to the same product mixture reported by the earlier workers. The syn isomer, however, required temperatures on the order of 170° to produce a comparable reaction rate, and, while cis-dihydroindenes accounted for seventy percent of the product, the remainder was identified as a mixture of isomers derived from and including the 9-methyl-trans-bicyclo[4.3.0]nonatrienes. Anastassiou also measured the free energies of activation for the disappearance
of the unsubstituted, 9-methyl, and 9,9-dimethyl [6.1.0] systems. 9,9-dimethylbicyclo[6.1.0]nona-2,4,6-triene had been reported by Staley to rearrange predominately to 9,9-dimethyl-trans-bicyclo[4.3.0]nona-2,4,7-triene at 151° (80).
The activation energies and product distributions indicated that the rearrangements to cis and trans [4.3.0] systems were fundamentally different reactions, and that the course of rearrangement was somehow related to substitution at C-9 of the starting triene.

Staley (81) prepared the E- and Z-9-ethyl-9-methylbicyclo[6.1.0] nonatrienes and found that the major product of thermolysis of each isomer was a 1.8:1 mixture of E- and Z-9-ethyl-9-methyl-trans-bicyclo [4.3.0]nonatrienes, and that epimerization of the starting material at C-9 did not occur under the reaction conditions. The loss of stereo-

chemistry and the invariance of product distribution observed in these reactions indicated that production of the trans-fused [4.3.0] system also involved a symmetrical intermediate, which was supposed to be the symmetry-allowed product of thermal ring opening, an E,Z,Z,Z-cyclononatetraene. Staley and Henry (80) were the first to recognize that the influence of substituents at C-9 of the [6.1.0] triene on the course of rearrangement might be due to a restriction of the conformational
He suggested that bulky 9-syn substituents should raise the free energy of the folded conformer because of steric crowding, lowering its population and favoring symmetry controlled reaction from the extended conformation to produce trans-fused [4.3.0] products. The folded conformation of the starting triene was suggested to be the ultimate precursor to cis-dihydroindenes. Staley rationalized the predominate production of non-allowed products on thermolysis of
**syn-9-methylbicyclo[6.1.0]nonatriene** by the assignment of a smaller effective size to the **syn**-methyl group of this molecule than to the same functionality in the 9,9-dimethyl triene.

Anastassiou and Griffith (82) clearly demonstrated the operation of such a conformational effect with the preparation and rearrangement of both **syn**- and **anti-9-tert**-butylbicyclo[6.1.0]nona-2,4,6-trienes. The **syn** isomer was converted almost exclusively into a 2:1 mixture of dihydro-indenes which were shown to be derived from the **trans**-bicyclo[4.3.0]-nona-2,4,7-triene skeleton. The **anti** isomer produced predominantly the **cis**-fused product.
Rearrangement of the extended conformer of cis-bicyclo[6.1.0]-
nonatriene to trans-bicyclo[4.3.0]nonatriene through the intermediacy
of $E,Z,Z,Z$-cyclononatetraene could be understood as a straightforward
symmetry-allowed series of electrocyclic reactions. The details of
the lower energy path leading from the folded conformation to cis-
dihydroindene, presumably via $Z^4$-cyclononatetraene, were less obvious.
Winstein and co-workers (83) prepared trans-bicyclo[6.1.0]nona-2,4,6-
triene by irradiation of the cis isomer and found the molecule to be
thermally stable at 76°, a temperature at which the cis isomer rapidly
rearranged. Higher temperatures promoted polymer formation rather than
unimolecular rearrangement involving symmetry-allowed opening to $Z^4$-
cyclononatetraene. This result has been taken to imply that the cis-
fused [6.1.0] triene must not be a direct precursor to the monocyclic
tetraene.

Radlick and Fenical (75) suggested an alternative to direct ring
opening of the folded conformation of the [6.1.0] triene to $Z^4$-cyclononona-
tetraene which involved Cope rearrangement of the starting material to cis-
bicyclo[5.2.0]nona-2,5,8-triene. The all-cis monocycle was suggested
to arise either directly from the [5.2.0] skeleton or by trans+cis isomerization of \(Z,E,Z,Z\)-cyclononatetraene, a thermal symmetry-allowed product of the [5.2.0] triene system.

Staley (81) pointed out that such a Cope rearrangement could only occur from the folded conformation of the [6.1.0] triene, and would thus be consistent with the observed conformational influence on the course of the reaction. Baldwin et al. (77) reported the results of simple molecular orbital calculations which suggested that the symmetry-forbidden conversion of the [5.2.0] triene into \(Z^4\)-CNT was more favorable than a trans+cis isomerization of \(Z,E,Z,Z\)-cyclononatetraene.

Grimme (84) has demonstrated the feasibility of Cope rearrangement in the system with a study of the thermal response of several cis-
bicyclo[6.1.0]nona-2,6-dienes. The results indicated that 9-syn substitution did indeed raise the activation energy of the reaction and that even the 9,9-dimethyl diene could attain the required folded conformation. Further, Paquette and Epstein (85) have prepared 2,6-diphenylbicyclo[5.2.0]nona-2,4,8-triene at low temperatures and have observed its rapid rearrangement to the more stable [6.1.0] triene, which in turn rearranged to a dihydroindene of undetermined stereochemistry at higher temperatures. The high reactivity of the [5.2.0] triene
suggested that if it was formed during the rearrangement of bicyclo-
[6.1.0]nonatriene its concentration would be fixed at a low steady-
state or equilibrium value and its presence might be difficult to
detect in the reaction mixture. The scheme proposed by Radlick in-
cluded the possibility of electrocyclic opening of the [5.2.0] triene
to \( Z,E,Z,Z \)-cyclononatetraene, however, and the strained trans double
bond of this monocycle was expected to be highly reactive toward cyclo-
additive trapping reagents. Efforts were made to detect the mono-
trans tetraene, then, since its existence in the reaction mixture would strongly implicate the involvement of a Cope rearrangement and the intermediacy of bicyclo[5.2.0]nona-2,5,8-triene. Katz and Garratt (86) had reported the preparation of a 1:1 adduct of tetracyanoethylene with bicyclo[6.1.0]nonatriene in 1964. Okamura and Osborn (65) and Baxter and Garratt (66, 67) identified this molecule as 10,10,11,11-tetracyanobicyclo[7.2.0]undeca-2,4,7-triene, and demonstrated that hydrogen shifts were not involved in its formation. The structure of the adduct corresponded to that expected to result from a 2+2 cycloaddition of TCNE with the trans double bond of Z,E,Z,Z-CNT. Application of the Woodward-Hoffmann rules to such a thermal reaction resulted in the prediction that addition take place antarafacially with respect to one of the components. A cis ring fusion in the adduct would have resulted if the trans double bond participated in an antarafacial manner. These workers were unable to
determine the relevant stereochemistry by spectroscopic methods since proton-proton coupling constants in the n.m.r. spectra of tetra-cyanocyclobutanes were known to show considerable variation.

Several Diels-Alder adducts apparently resulting from capture of $Z,E,Z,Z$-cyclononatetraene with a diene have been prepared. Anastassiou and Griffith (87) reported that treatment of the bicyclic triene with 2,5-dimethyl-3,4-diphenylcyclopentadienone in boiling benzene led to the production of three 1:1 adducts, one of which was derived from cis-dihydroindene. The two remaining isomers were characterized as products of addition of the dienone to the 3,4 double bond of a cyclononatetraene. The bridgehead stereochemistry in both cases was established as trans by examination of the 220 MHz n.m.r. spectrum. Again, incorporation of deuterium into the methylene of the [6.1.0] triene led to exclusive retention of the label at the methylene of the adduct, so that a hydrogen shift could not be responsible for the observed structure or stereochemistry.
Analogous trans-fused adducts have been obtained by addition of diphenylisobenzofuran (88), α-pyrone (89), and 3,6-diphenyl-sym-tetrazine (90) to solutions of the [6.1.0] triene at temperatures which otherwise promoted rearrangement. The formation of these compounds was taken to be a result of Diels-Alder addition of the dienes to the trans double bond of an intermediate Z,E,Z,Z-cyclononatetraene, supporting the series of symmetry-allowed isomerizations proposed by Radlick.
The situation with regard to the origin of the adduct obtained from reaction of TCNE with the [6.1.0] triene was less clear. If the reaction did indeed proceed through the intermediacy of a Z,E,Z,Z-cyclononatetraene, and if the symmetry rules were obeyed, the adduct could have been expected to contain a cis ring fusion. The report of the gross structure of the TCNE adduct was contemporaneous with the first direct observations of bishomotropylium ions and with Paquette's interest in the reactivity of "uniparticulate electrophiles" (91). Paquette and co-workers presented evidence in a number of reports (56-58, 92, 93) which was interpreted to indicate that the TCNE adduct had not been formed via a cyclononatetraene.

The addition of TCNE or of chlorosulfonyl isocyanate to the [6.1.0] triene was found to occur at 30° in tetrahydrofuran, conditions under which rearrangement of the starting material to bicyclo-[4.3.0]nonatriene was very slow. The adducts were found to be trans-fused by x-ray diffraction analysis, and only one γ-lactam was isolated from reaction of the [6.1.0] triene with the isocyanate.

\[
\begin{align*}
\text{[6.1.0] triene} & \quad + \quad \text{isocyanate} \\
\text{THF/7 days} & \quad \xrightarrow{30^\circ} \\
\text{adduct} & \quad \text{63.5% (only product)}
\end{align*}
\]
Reaction of either reagent with anti-9-methyl- or anti-9-chloro-bicyclo[6.1.0]nonatriene again produced only one isolable product in each case, while both of the syn isomers and the 9,9-dimethyl triene failed to react under the same conditions. Paquette also prepared the 1-, 2-, 3-, and 4-methylbicyclo[6.1.0]nona-2,4,6-trienes and treated them with CSI in refluxing dichloromethane. Only one product isomer was isolated from the reaction mixture in each case.
1) CCl₄, CH₂Cl₂ reflux
2) ϕSH, pyridine

53%

54%

5%
+ polymer

6%
+ polymer
The observation of a trans ring fusion in these adducts was reconcilable with the involvement of $Z_E Z_Z$-CNT, since the same stereochemistry resulted from reactions of either TCNE or CSI with trans-cyclononene. The other features of the reactions seemed to mitigate against the intermediacy of a monocyclic tetraene, however.

There was no evidence to indicate that the $[6.1.0] + [5.2.0] \rightarrow Z_E Z_Z$-CNT isomerizations took place at the temperatures used in this work since the Diels-Alder adducts which had been reported, and acknowledged to be products of the mono-trans tetraene, had been prepared at temperatures high enough to effect rearrangement of the starting triene. The stereo- and regiospecificity observed was difficult to explain, since at least two and in some cases as many as eight stereoisomers might have been formed from a monocyclic intermediate. The failure of syn-9-methyl, syn-9-chloro-, and 9,9-dimethyl $[6.1.0]$ trienes to undergo addition implicated the folded conformation of the triene as a determining factor in the reaction.
Paquette supported a mechanism involving electrophilic attack on the folded conformation of the triene to produce an intermediate transoid bishomotropylium ion, followed by ring closure to give a product with the observed stereochemistry.

A non-aromatic zwitterionic structure was considered for the intermediate but was dismissed when bicyclo[6.2.0]deca-2,4,6-triene failed to react in an analogous manner, although it was noted that this might be due to conformational influences. This work attracted some attention because of the unusual ionic intermediate proposed and because of the divergence of Paquette's mechanism from the known chemistry of the [6.1.0] system, and led to experiments by other
workers which greatly clarified the nature of the processes which occur in that system.

Baldwin and Bryan (94) studied the kinetics of the reaction of chloro- and fluoroamino-functionalized isocyanates with bicyclo[6.1.0]nona-2,4,6-triene and concluded that rate-determining electrophilic attack on the folded form of the triene was untenable unless the rate of conformational equilibration was far slower than could reasonably be expected. The rate-determining step was suggested to be valence isomerization of the triene to \(Z,E,Z-Z\)-cyclononatetraene. Boche and co-workers (95) reported that at high concentrations of TCNE in acetonitrile or tetrahydrofuran the reaction with the \([6.1.0]\) triene became independent of the concentration of the electrophile, and suggested that the limiting reaction rate observed, \(9 \times 10^{-5}\, \text{sec}^{-1}\) at 31.3°C, represented the rate of formation of \(Z,E,Z,Z\)-cyclononatetraene. These experiments supported the existence of an equilibrium between the \([6.1.0]\) triene and the monocyclic tetraene, and presumably the \([5.2.0]\) isomer, and at relatively low temperatures. A complete explanation of the other aspects of this reaction has not yet been presented, but Paquette's work has provided a good deal of information on the subject.

The determination of a rate of formation of \(Z,E,Z,Z\)-cyclononatetraene by Boche also became important in the study of another aspect of \([6.1.0]\) triene chemistry, thermal epimerization at C-9. This phenomenon was first observed by Sohn and co-workers (96) who found that \(\text{syn-9-carbomethoxybicyclo[6.1.0]nona-2,4,6-triene}\) rearranged quite cleanly in solution or in the gas phase at 100°C to the \(\text{anti}\) isomer.
Enolization of the ester was eliminated as a mechanistic alternative by the retention of a deuterium label at C-9 during the reaction, and by the similar epimerization of the α-methyl ester.

Jones proposed a mechanism involving cleavage of the 1-9 bond to a diradical, rotation of C-9, and reclosure, pointing out that the external cyclopropane bonds should be weakened relative to those of the unsubstituted triene by the π-acceptor strength of the ester moiety (97-99). He also suggested that epimerization might explain the high yield of cis-fused methyldihydroindenenes from syn-9-methylbicyclo[6.1.0]nonatriene reported earlier by Anastassiou.

Anastassiou and Griffith (100) prepared syn- and anti-9-cyano-bicyclo[6.1.0]nonatriene and identified the products of partial thermolysis of each isomer at 139°. The increased ΔG‡ for rearrangement of the anti isomer compared to that of the unsubstituted triene (ΔG‡ = 27.5) was attributed to the strengthening influence of the 9-cyano group on the bridging cyclopropane bond. The free energy of activation for thermolysis of the syn isomer was taken to be the value required for its epimerization, since the similarity in the endo/exo ratio of cis-fused [4.3.0] products obtained from either starting material suggested that they were produced from the anti isomer.
exclusively. The parallel to the behavior of the epimeric 9-methyl trienes was unmistakeable, and Anastassiou agreed with Jones' suggestion of epimerization in that system, calculating that the concentration of anti isomer present during rearrangement of syn-9-methylbicyclo[6.1.0]nona-2,4,6-triene would be undetectably low.

Brown and Ogilvey (101) found that syn-9-flouro- and -methoxy-bicyclo[6.1.0]nonatrienes underwent rapid epimerization at room temperature, and that the syn-9-dimethylamino compound appeared to
epimerize prior to further thermal rearrangement. They observed that the order of reactivity of the known epimerizable [6.1.0] trienes was not related to the radical stabilizing efficiencies of the various C-9 substitutents, and so proposed an alternative to Jones' mechanism.

\[
\begin{array}{cc}
R & \Delta G_{\text{epim.}}^+ \\
F & 23.5 \\
OC\text{H}_3 & 26 \\
N\left(\text{CH}_3\right)_2 & 29 \\
CO_2\text{CH}_3 & 29.5 \\
CN & 32
\end{array}
\]

Their scheme involved initial electrocyclic closure of the triene to a tricyclo[4.3.0.0^{7,9}]nona-2,4-diene, followed by inversion of the cyclopropane via a 1,3-diradical.
Lewis and Brookhart (102) challenged Brown's diradical mechanism on thermodynamic grounds, noting that a good estimate of $\Delta G^\ddagger$ for closure of the [6.1.0] triene to the tricyclic isomer was 27.5 Kcal/mole, and that activation energies for inversion of known bicyclopentanes lay in the range of 37 to 45 Kcal/mole. They prepared syn-9-deuterobicyclo[6.1.0]nona-2,4,6-triene and found that the molecule readily underwent epimerization. The rate of this process, measured in acetonitrile at 31.3°C, was found to be $4.5 \pm 0.2 \times 10^{-5} \, \text{sec}^{-1}$, within experimental error of one-half the rate of formation of $Z,E,Z,Z$-cyclononatetraene as determined under the same conditions by Boche, et al. (95). The clear implication of this work was that the same intermediate was involved in both the epimerization and cycloadditive trapping processes, and that this species was $Z,E,Z,Z$-cyclononatetraene.
The diradical epimerization mechanism suggested by Jones was consi­dered by the authors to be a viable alternative in some special cases, and some support for that view was available from an examination of the rearrangement products of a few electronically perturbed [6.1.0] trienes.

The anti-9-flouro- and anti-9-dimethylaminobicyclo[6.1.0]nona­triene reported by Brown and Ogilvey (101) were each found to rearrange to a mixture of 9-substituted dihydroindenenes and a syn-9-substituted bicyclo­[4.2.1]nona-2,4,7-triene. The rate of formation of these products was
only slightly lower than the rates of epimerization of the syn isomers, so that partitioning of Jones' diradical intermediate might have accounted for both epimerization and the formation of the [4,2,1] isomers. The stereospecificity of the latter reaction, however, suggested that a symmetry-allowed thermal 1,5 sigmatropic shift was involved.
The first example of such a [6.1.0] to [4.2.1] conversion was discovered by Ciganek (103), who later reinvestigated the system with Anastassiou (104). The product of addition of singlet dicyanocarbene to cyclooctatetraene was found to rearrange exclusively to 9,9-dicyano-bicyclo[4.2.1]nona-2,4,7-triene upon heating at 190°. No mechanism was proposed for this process, although the reaction of triplet dicyanocarbene with COT produced the [4.2.1] skeleton directly, suggesting that a radical mechanism might also be feasible for the thermal process.

Klärner (105) prepared and rearranged both 9-cyano-9-methyl-bicyclo[6.1.0]nonatrienes. Both of the epimers produced a small amount of a dihydroindene which was not identified, but the major product was a mixture of 9-substituted bicyclo[4.2.1]nona-2,4,7-trienes. Recovered starting material in each reaction was found to be
stereochemically pure. The partial loss of stereochemistry at C-9 during the rearrangement, the high ΔG‡ and the difference in product distribution from each epimer prompted Klärner to suggest a diradical mechanism, with product stereochemistry controlled by the least-motion principle. He reasoned that the lack of epimerization was consistent with this scheme, since least-motion principles governing a formal 1,7 shift via a diradical would favor regeneration of the starting epimer. Accordingly, he prepared the epimeric 9-cyano-4,9-dimethylbicyclo[6.1.0]nonatrienes and studied their thermal behavior (106).

These compounds were heated to 102.5° in an n.m.r. spectrometer and a series of 1,7 shifts of C-9 was observed, effectively distributing the vinyl methyl among the four possible ring positions. While Klärner had anticipated the existence of this process, the low activation energy and the degree of stereospecificity observed were
concluded to be incompatible with a diradical mechanism. The equilibrating system derived from either starting isomer could be heated for days at 102.5° without epimerization, and higher temperatures led only to rearrangement to the \([4.2.1]\) system. The mechanism was suggested to be a concerted 1,7 sigmatropic shift with inversion at the migrating center, although the possibility of a polar, homotropylium-like transition state was noted.

Epiotis and Shaik (107) have suggested that the stereochemical results obtained on rearrangement of Klärner's nitrile to the \([4.2.1]\) system can also be reconciled with a concerted mechanism. Their analysis demonstrated that the stereochemical outcome of sigmatropic shifts may be different from that demanded by simple orbital symmetry considerations if the migrating center and the olefinic substrate have widely differing polarities.

The adducts of cyclopentadienyldiene (108) and of florenylidene (109) with COT have also been shown to rearrange thermally to the \([4.2.1]\) system. The questions of the possible involvement of charge-separated species and the importance of enhanced \(p\) character of the cyclopropane bonds at the quaternary carbon of the adducts during these reactions have not been addressed (110).
A final example of this "abnormal" reaction path of the \([6.1.0]\) series has been provided by Grimme (78) who found that the molybdenum tricarbonyl complex of the parent triene rearranged at 125° to a complex of the \([4.2.1]\) triene.

A similar degree of catalytic selectivity has been observed using rhodium-(I) (111), except that the product was a cis-bicyclo-[4.3.0]nonatriene. Even 9,9-dimethylbicyclo[6.1.0]nonatriene rearranged predominately to the cis-fused product under these conditions, suggesting that these reactions do not proceed by the same mechanism as the uncatalyzed process. In contrast, thermolysis of the unsubstituted triene in the presence of tricarbonyl(benzylideneacetone)iron (112) provided some useful information about the unperturbed rearrangement.
in the form of a low yield of a Z\textsuperscript{4}-cyclononatetraeneiron tricarbonyl complex (68). This complex had been prepared previously from diiron nonacarbonyl and the [6.1.0] triene (113, 114), and was known to rearrange

\[
\begin{align*}
10 & : 5 : 1 \\
\text{BDAFe(CO)}_3 & \text{Fe(CO)}_3 & \text{Fe(CO)}_3
\end{align*}
\]

\[
\begin{align*}
\text{BDAFe(CO)}_3 & \xrightarrow{55^\circ, 3 \text{h.}} \text{Fe(CO)}_3 + \text{Fe(CO)}_3 + \text{Fe(CO)}_3
\end{align*}
\]

to the dihydroindene complex at 100\textsuperscript{0}. The greater selectivity of BDAFe(CO)\textsubscript{3} toward planar dienes, however, supported the view that the monocyclic tetraene had been trapped as a free species in the solution. No other direct evidence for the presence of the all-cis monocycle during the rearrangement has been presented.

Bangert and Boeckelheide's suggestion (71) that Z\textsuperscript{4}-CNT might be the precursor to cis-fused dihydroindenes during the rearrangement of the [6.1.0] system coincided with the work of Katz and Garratt (115, 116) and LaLancette and Benson (117, 118), who investigated the production and quenching of the cyclononatetraenide anion. Treatment of syn-9-chlorobicyclo[6.1.0]nonatriene with lithium metal, or of the anti-9-methoxy derivative with potassium at -20\textsuperscript{0} was reported to give a
solution of the all-cis cyclononatetraenide anion, which was shown to be a stable, planar, aromatic species by its n.m.r. spectra and by the isolation of a solid tetraethylammonium salt.

Quenching of the anion with deuterium oxide or carbon dioxide followed by warming of the solution to room temperature led to the isolation of 9-substituted dihydroindenes of unestablished stereochemistry. Boche and co-workers (119) managed to isolate the all-cis tetraene as a pale yellow oil at 0°, and found that it rearranged quantitatively to cis-dihydroindene at higher temperatures with a free energy of activation of about 23 Kcal/mole.
Anastassiou et al. (120) found that $Z^4$-cyclononatetraene could also be produced by sensitized irradiation of the [6.1.0]triene, and confirmed the cis stereochemistry of its kinetically preferred ring-closure product. Direct irradiation of the monocycle through pyrex was reported to regenerate the starting material quantitatively.

Radlick and co-workers (75, 121) reported that treatment of cyclononatetraenide with iodomethane followed by warming produced a mixture of epimeric 9-methyldihydroindenes which was identical to the product mixture obtained on thermolysis of anti-9-methylbicyclo[6.1.0]-nona-2,4,6-triene, strongly implicating the intermediacy of $Z^4$-cyclononatetraenes in the symmetry-forbidden rearrangement.

The Diels-Alder reactivity of the tetraene in the presence of tetracyanoethylene at $0^\circ$ had been investigated by Katz and Garratt (116), who reported that the only isolable product was identical with that obtained from cis-dihydroindene. Normal dienic behavior was observed by Anastassiou and Cellura (122) however, in its addition to the more reactive 4-phenyl-1,2,4-triazoline-3,5-dione.
Masamune et al. (123) reported that irradiation of the cis-[6.1.0], trans-[6.1.0], or cis-[4.3.0] nonatrienes, or of Z\textsuperscript{4}-CNT itself at -50° using an unfiltered mercury arc led to similar photostationary states, from which E,Z,Z,Z-cyclononatetraene could be isolated. This molecule was found to rearrange rapidly and quantitatively at room temperature to trans-bicyclo[4.3.0]nona-2,4,7-triene. The plausibility of the intermediacy of such species in the rearrangement of those [6.1.0] trienes restricted to the extended conformation was thus supported.
Boche and co-workers (124) reexamined the reduction of anti-9-methoxybicyclo[6.1.0]nonatriene by alkali metals at -40°C, and found the product to be the trans-cyclononatetraenide anion rather than the previously reported all-cis ion (115-118). Conversion of this symmetry-allowed product to the cis isomer was reported to be catalyzed by excess potassium or cesium, by light, and by protic solvents (125). In the absence of these catalysts the trans anion was found to be stable to 120°C in solution. Analysis of the temperature-dependent n.m.r. spectrum of the anion revealed that it was planar and aromatic, the highly shielded internal hydrogen absorbing at \( \delta -3.52 \) (125, 126), and that it underwent an interesting and facile topomerization reaction involving a rotation of the three-carbon transoid moiety. Thus, reduction of syn-9-deutero-anti-9-chlorobicyclo[6.1.0]nona-2,4,6-triene at low temperatures produced the trans anion with deuterium predominantly \( \alpha \) to the internal hydrogen, which appeared as a doublet in the n.m.r. spectrum. The solution was warmed and a triplet appeared at the resonance position of the internal hydrogen while the intensity of the doublet decreased. After equilibrium had been reached, the intensity ratio of triplet to doublet was measured as 3:1, demonstrating that the deuterium atom had been distributed equally among all nine ring positions. Conversion of the trans anion to the cis isomer took place at 150°C, with an apparent activation energy of 34.8 Kcal/mole. This value was taken as a lower limit, however, since catalysis of the reaction could not be excluded. In contrast to the behavior of the unsubstituted anion, the \( \text{Z}^4 \)-benzocyclononatetraenyl anion
prepared by Anastassiou and Reichmanis (127) was reported to undergo cis → trans isomerization quite readily, with a much lower activation energy of 26.2 Kcal/mole.
Protonation of the parent trans anion at $-40^\circ$ was reported by Boche et al. (95) to produce a mixture of $E,Z,Z,Z$- and $Z,E,Z,Z$-cyclononatetraenes, which were observed to rearrange independently to trans-bicyclo[4.3.0]nona-2,4,7-triene and cis-bicyclo[6.1.0]nona-2,4,6-triene, respectively. The latter conversion, assumed to proceed via cis-bicyclo[5.2.0]nona-2,5,8-triene, confirmed the reversibility of the $[6.1.0] + [5.2.0] + Z,E,Z,Z$-CNT pathway proposed as the mechanism for epimerization of the $[6.1.0]$ system. $Z,E,Z,Z$-cyclononatetraene was also found to react rapidly with tetracyanoethylene at $-50^\circ$ to give an adduct identical to that previously obtained by reaction of that electrophilic olefin with the $[6.1.0]$ triene. Treatment of the trans anion with methyl iodide at $-40^\circ$ and reaction of the $Z,E,Z,Z$ product with TCNE also gave a product identical to that prepared from syn-9-methylbicyclo[6.1.0]nonatriene by Paquette (93), indicating that the product stereochemistry in such reactions is determined by factors other than the conformation of the starting triene.
The general topology of the energy surface upon which the rearrangements of the bicyclo[6.1.0]nona-2,4,6-triene system take place, and the effect of 9-substitution upon that surface, has been quite successfully mapped by the extensive work in this field. The unsubstituted triene has been shown to exist in two conformations, the folded and extended forms. When the conformational mobility of the
system is unrestricted, three isomers of the triene have been shown to be present in low equilibrium concentrations, namely tricyclo-
$[4.3.0.0^7,9^9]$nona-2,4-diene, $Z,E,Z,Z$-cyclonona-1,3,5,7-tetraene, and bicyclo$[5.2.0]$nona-2,5,8-triene. The last isomer mentioned has not been directly observed or trapped during uncatalyzed rearrangement of the system, although its tetracarbonyliron complex has been reported (114). The presence of a good leaving group in the syn-9 position has been shown to facilitate opening of the cyclopropane ring of the tricyclic isomer, leading to cis-fused dihydroindenes in which the substituent had undergone a 1,2 shift. Epimerization at C-9 has been shown to proceed via $Z,E,Z,Z$-CNT in some cases. Higher temperatures were demonstrated to produce $E,Z,Z,Z$-cyclononatetraenes from the folded conformation by an unknown, symmetry-forbidden mechanism, which then close to cis-dihydroindenes. Restriction of the system to the extended conformation led to a higher-energy rearrangement involving symmetry-allowed ring opening to $E,Z,Z,Z$-cyclononatetraenes and subsequent closure to trans-dihydroindenes. 9-substituents which interact electronically with the cyclopropane ring of the $[5.1.0]$ system have been shown to induce concerted 1,7 sigmatropic shifts of C-9 with inversion at the migrating center, and 1,5 shifts to the $[4.2.1]$ system.
The Effects of Structural and Electronic Modification on the Reactivity of the Bicyclo[6.1.0]nonatriene System

The subject molecule, bicyclo[5.2.0]nona-2,5,8-trien-4-one, will differ from the related isomer of bicyclo[6.1.0]nonatriene both by the hybridization at C-4 and by the availability of a high energy orbital on that atom for interaction with the remainder of the \( \pi \) system. Several molecules which incorporate one or both of these features and which are related to the [6.1.0] triene or its isomers have been prepared, and their thermal rearrangements have been studied in some detail.

Radlick and co-workers (128) prepared and pyrolyzed 9-((dimethylamino)methyl)bicyclo[6.1.0]nonatriene N-oxide as a possible route to the 9-methylene [6.1.0] triene. The only products isolated were identified as 4-methylene-cis-bicyclo[5.2.0]nona-2,5,8-triene and 9-methylene-cis-bicyclo[4.3.0]nona-2,4,7-triene in a ratio of 2:3. The relative yield of the [5.2.0] isomer was found to decrease as the pyrolysis time was increased, and both tetraenes were reported to polymerize even at
9-methylenebicyclo[6.1.0]nonatriene was presumed to be an intermediate because of the presence of its Cope rearrangement product and because the starting amine oxide was found to be stable with respect to rearrangement just below its decomposition point. The dihydroindene was proposed to arise from the [6.1.0] skeleton through the intermediacy of an all-cis nonafulvene, since pyrolysis of the bicyclo[6.1.0]nonene N-oxide led to a methylenecyclononadiene directly, presumably via the vinyl methylenecyclopropane. Nonafulvene
(Z\textsuperscript{4}-methyleneclononatetraene) was subsequently prepared at low temperatures by Neuenschwander and Frey (129-131) and was found to rearrange to 9-methylene-cis-bicyclo[4.3.0]nona-2,4,7-triene at 10\textdegree, as predicted by Radlick, et al. The \textsuperscript{1}H and \textsuperscript{13}C n.m.r. spectra of the monocycle were found to be unchanged between -110\textdegree and 10\textdegree, and analysis of the spectra indicated that the molecule either possessed a C\textsubscript{2} axis of symmetry or underwent interconversion of two tub-like conformers with an energy of activation of less than 7 Kcal/mole.

\begin{center}
\begin{align*}
\text{AcO} &\rightarrow \text{KOTBu} \rightarrow \text{10\textdegree} \rightarrow \text{t}_{1/2} \rightarrow \text{60\textdegree} \\
\end{align*}
\end{center}

A more stable "push-pull" nonafulvene, bis(dimethylamino)methyl-ethylenecyclononatetraene, was prepared by Hafner and Tappe (132) and isolated as a crystalline solid. A temperature of 60\textdegree was required to convert the yellow monocycle to an air-sensitive dihydroindene derivative of unestablished stereochemistry. The reaction of p-toluenesulfonyl azide with cyclononatetraenide anion has been reported to give diazocyclononatetraene, together with a small amount of indene (133).

A substantial amount of effort has been devoted to the study of molecules incorporating nitrogen at the nine position of the [6.1.0] system, and an unfortunate controversy has developed with regard to the thermal rearrangements of such systems.
Masamune and Castellucci (134) prepared the first 9-azabicyclo[6.1.0]nona-2,4,6-triene by addition of carboethoxynitrene to cyclo-octatetraene. He reported that the urethane underwent a rapid Cope rearrangement at 80°, and that this product isomerized to a cis-dihydroindole at 100° (135).

Anastassiou and co-workers have studied the thermal response of several compounds in this system with very different results. 9-carbomethoxy-9-azabicyclo[6.1.0]nona-2,4,6-triene was reported (136) to rearrange "quantitatively" to 4-carbomethoxy-4-azabicyclo[5.2.0]nona-2,5,8-triene at 56°. Column chromatography of the product at -15°, however, resulted in the isolation of a small amount (ca. 10%) of the
related trans-dihydroindole, the major [5.2.0] product, and no [6.1.0] isomer. The pure [5.2.0] Cope rearrangement product was heated at 56° and an equilibrium was reported to be established, consisting of the [5.2.0] and [6.1.0] isomers in a ratio of 19:1 (n.m.r.). No chromatography was performed on this mixture, which was then heated to 76°.

\[
\begin{align*}
\text{NCO}_{2}\text{CH}_3 & \quad \xrightarrow{56^\circ} \quad \text{CO}_2\text{CH}_3 \\
\text{COfiH}_2 & \quad \xrightarrow{t_{1/2}=73'} \quad \text{CO}_2\text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{NCO}_{2}\text{CH}_3 & \quad \xrightarrow{56^\circ} \quad \text{CO}_2\text{CH}_3 \\
\text{CO}_2\text{CH}_3 & \quad \xrightarrow{t_{1/2}=8h} \quad \text{CO}_2\text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{NCO}_{2}\text{CH}_3 & \quad \xrightarrow{56^\circ} \quad \text{CO}_2\text{CH}_3 \\
\text{CO}_2\text{CH}_3 & \quad \xrightarrow{t_{1/2}=76^\circ} \quad \text{CO}_2\text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{NCO}_{2}\text{CH}_3 & \quad \xrightarrow{76^\circ} \quad \text{CO}_2\text{CH}_3
\end{align*}
\]
Further slow, irreversible rearrangement took place at the higher temperature to a mixture which was separated on alumina and found to be composed of the corresponding cis-dihydroindole (27%), 2-carbomethoxy-2-azabicyclo[5.2.0]nona-3,5,8-triene (11%), and a total of 62% of two [4.3.0] products which were shown to be derived from a trans-dihydroindole, which could be isolated from the reaction mixture during the early stages of the thermolysis. Anastassiou suggested that the trans-dihydroindole arose directly from the [6.1.0] skeleton and that the 4-aza [5.2.0] isomer was involved in the production of both the cis-fused dihydroindole and the unsymmetrical [5.2.0] urethane.

No C9H10 isomer analogous to the 2-azabicyclo[5.2.0]nona-3,5,8-triene has been observed during the rearrangement of bicyclo[6.1.0]-nona-2,4,6-triene. However, Jones and Reich (137) have identified bicyclo[5.2.0]nona-2,4,8-triene as one product of rearrangement of bicyclo[5.1.0]octa-2,4-dien-8-yl carbene. The [5.2.0] triene was pyrolyzed at 360° in a flow of nitrogen to give cis-dihydroindene as the major product.

The ethyl urethane which had been prepared by Masamune was also studied by Anastassiou et al. (138). Thermolysis of 9-carboethoxy-0-aza-bicyclo[5.1.0]nona-2,4,6-triene at 56° was reported to produce, after chromatography, the Cope rearrangement product (71%), 9-carboethoxy-9-aza-trans-bicyclo[4.3.0]nona-2,4,7-triene (23%), and 9-carboethoxy-9-aza-cis-bicyclo[4.3.0]nona-2,4,7-triene (6%). Thermolysis of the pure Cope rearrangement product again gave only a [5.2.0] - [6.1.0] equili-
brium by n.m.r. analysis. This pair rearranged principally to a trans-dihydroindole at 76° in Anastassiou's laboratory. Masamune and Jones (139) have challenged the use of column chromatography in the determination of relative yields and product identity, citing the possibility of adsorbent-induced isomerization and incomplete sample recovery. Anastassiou has responded by denying the occurrence of such processes, labeling Masamune's work in the field "peripheral and largely confirmatory" (140, 141).

The behavior of N-acetyl-9-azabicyclo[6.1.0]nona-2,4,6-triene (138, 142) contrasted sharply with that of the two urethanes. An equilibrium mixture consisting of 95% of the [5.2.0] and 5% of the [6.1.0] isomers could be obtained from either pure isomer at 56°.
Dihydroindole formation was not observable by n.m.r. at 56°, and the mixture was not subjected to chromatography. Upon heating to 76° the sample rapidly rearranged to a 1.2:1 mixture of N-acetyl-9-aza-cis-bicyclo[4.3.0]nona-2,4,7-triene and N-acetyl-2-azabicyclo[5.2.0]nona-3,5,8-triene. The latter product was isolated and found to rearrange at 110° to a 1:2 mixture of the cis-dihydroindole and a hydrogen-shifted product of the trans isomer.
Addition of 2,5-dimethyl-3,4-diphenylcyclopentadienone to a refluxing benzene solution of the two equilibrating starting materials led to the isolation of two 1:1 adducts, one of which was identified as the product of Diels-Alder addition of the dienone to the trans double bond of N-acetyl-1-aza-Z,E,Z,Z-cyclonona-2,4,6,8-tetraene. The remaining adduct was assumed to be diastereomeric with the first on the basis of similarity of the spectral features of the two isomers.
Treatment of 2-acetyl-2-azabicyclo[5.2.0]nona-3,5,8-triene with the dienone under the same conditions led only to slow addition of the trapping agent to the cyclobutene double bond.

Anastassiou suggested that the mode of rearrangement of each of the three [6.1.0] molecules studied was governed by the availability of the nitrogen lone pair for participation in the ring opening process. Symmetry-allowed opening of the aziridine ring was expected to lead to an $E,Z,Z,Z$-azacyclononatetraene and ultimately to a trans-fused dihydroindole, and this mechanism was proposed to be operative during rearrangement of the urethanes. \textit{Trans$\rightarrow$cis} isomerization of the allowed
ring-opening product aided by nitrogen or a competitive, non-allowed isomerization of the [6.1.0] system to an all-cis monocyclic tetraene was invoked to explain the formation of cis-fused dihydroindoles. The tightly bound nitrogen lone pair of the acetamide was thought to be less prone to participate in the ring-opening process, enabling the familiar non-allowed electrocyclic reaction of the [6.1.0] triene system. A Dreiding model of Z,E,Z,Z-azacyclononatetraene was constructed, and two conformations differing in the disposition of the trans double bond of the monocycle were shown to be possible. Anastassiou reasoned that the two conformers might be expected to form different [5.2.0] molecules upon electrocyclic closure and proposed that the 2-aza [5.2.0] triene might arise from the 4-aza isomer by ring opening to Z,E,Z,Z-azacyclononatetraene followed by a conformational change and reclosure to form the cyclobutene ring of the new isomer.
Anastassiou found that lithium aluminum hydride reduction of the [6.1.0] (142) and [5.2.0] (143) urethanes provided the unsubstituted amines. Low temperature alkylation of the amines via the amide anion provided a dimethyl urea, a phenylsulfonylamine and a chloramine in the [6.1.0] series, and N-methyl and dimethyl urea derivatives of the [5.2.0] system. Of these compounds, only the [5.2.0] dimethyl urea displayed electrocyclic reactivity, rearranging rapidly to the [6.1.0] skeleton. The unsubstituted amines and the other derivatives were reported to decompose to unidentified products at temperatures above 100°.

N-cyano-9-azabicyclo[6.1.0]nona-2,4,6-triene has been reported as a minor product of the addition of cyanonitrene to cyclooctatetraene, and there appears to be some evidence for its thermal rearrangement to 9-cyano-9-azabicyclo[4.2.1]nona-2,4,7-triene (144-146). Tustin and co-workers (147) have observed the only definite example of a [6.1.0] to [4.2.1] conversion in the 9-aza system. Oxidation of N-aminophthalimide with lead tetraacetate in the presence of cyclooctatetraene produced 9-phthalimido-9-azabicyclo[6.1.0]nona-2,4,6-triene, which rearranged in low yield to the [4.2.1] isomer at 115°. Hydrolysis of the [6.1.0] phthalimide led to the isolation of 9-amino-9-azabicyclo-[4.2.1]nona-2,4,7-triene as the only product.
1-azacyclonona-2,4,6,8-tetraenes (azonins) have been studied as possible aromatic species and as intermediates in the thermal transformations of the related bicylic isomers. Both Masamune and co-workers (148) and Anastassiou and Gebrian (149, 150) have reported that irradiation of N-carboethoxy-9-azabicyclo[5.1.0]nona-2,4,6-triene at low temperatures produced N-carboethoxy-1,3,5,7-azonin, which displayed no evidence of aromaticity in its spectroscopic behavior or its reactivity. A temperature dependence of its n.m.r. spectrum has been ascribed to inversion at nitrogen by Anastassiou et al. (151), and to hindered rotation of the urethane moiety by Masamune and Darby (135). The monocycle was found to rearrange when warmed to a cis-dihydroindole derivative, consistent with its intermediacy in the formation of that product during thermolysis of the [6.1.0] isomer. Masamune et al. (148) found that irradiation with 2537 angstrom light of N-carboethoxy-4-azabicyclo[5.2.0]nona-2,5,8-triene...
also led to the all-cis azonin, while Anastassiou reported that direct irradiation of the azonin regenerated the [6.1.0] isomer quantitatively (149).

Treatment of N-carboethoxy azonin with potassium-t-butoxide at low temperatures was found by Anastassiou to produce the strongly diatropic azonide anion (152), which was quenched with t-butanol, iodomethane, iodoethane, benzyl bromide, acetyl chloride, and N-p-bromophenylcarbamoyl chloride to give the corresponding azonins. Of these, only the parent amine was classified as aromatic on the basis of n.m.r. and optical absorption spectroscopy.
Azonin itself was reported to be stable at 50° under an inert atmosphere for at least forty hours and to decompose to uncharacterized products at higher temperatures, as did the N-alkyl derivatives. The corresponding amide and urea both rearranged to cis-bicyclo[4.3.0] skeletons at room temperature.

The transient existence of Z,E,Z,Z-azonins during the rearrangement of some 9-azabicyclo[6.1.0]nonatrienes has been inferred from trapping experiments, one of which has already been mentioned. Adducts corresponding to those expected from Diels-Alder addition to the trans double bond of such species have also been prepared from N-acetyl-9-azabicyclo[6.1.0]nona-2,4,6-triene using α-pyrone (153) at a reaction temperature of 65° and 1,4-diphenyl-sym-tetrazine at 25° (154). Anastassiou has suggested that the latter reaction takes place by direct addition to the [6.1.0] amide, since the Cope-rearranged [5.2.0] isomer does not react as rapidly under the same conditions. A reaction of the [6.1.0] triene system similar to that proposed by Paquette (56) may thus have been realized in the aza series.

9-oxabicyclo[6.1.0]nona-2,4,6-triene was prepared by Reppe and co-workers (155) in 1948 by peracid oxidation of cyclooctatetraene. The structure of this "cyclooctatetraene oxide" was a subject of debate until 1964, due in part to the presence of an equilibrium concentration of the isomeric 8-oxatricyclo[4.3.0.0^7,9]nona-2,4-diene in samples of the purified epoxide (156-158). This tricyclic isomer has been trapped in Diels-Alder fashion with maleic anhydride (159). Pyrolysis of the epoxide at 260° has been found to produce cyclo-
hepta-1,3,5-triene-3-carboxaldehyde (160). The mechanism of this process was suggested to involve scission of two single bonds of the [6.1.0] isomer to produce cyclohepta-1,3,5-triene-7-carboxaldehyde followed by rearrangement to the observed product.

\[
\text{Cyclohepta-1,3,5-triene-7-carboxaldehyde} \xrightarrow{260^\circ} \text{Cyclohepta-1,3,5-triene-3-carboxaldehyde}
\]

Irradiation of the epoxide has been used as a route to oxacyclononatetraene, or oxonin, another possibly aromatic species. Holovka and co-workers (161) reported that Pyrex-filtered irradiation of cyclooctatetraene oxide at room temperature gave four isolable products. These were identified as trans-9-oxabicyclo[4.3.0]nona-2,4,7-triene, 9-oxabicyclo[5.2.0]nona-1(8),2,4-triene, cis-2-oxabicyclo[5.2.0]nona-3,5,8-triene, and cycloheptatriene. The authors suggested that the trans-fused dihydrobenzofuran was produced via on electronically excited state of oxonin, since its formation from the ground state all-cis monocycle was symmetry forbidden.
Anastassiou and Cellura (162) carried out a benzophenone-sensitized irradiation of the [6.1.0] epoxide at 0° and were able to isolate pure \(^4\)oxonin from the reaction mixture. The monocycle displayed an ordinary olefinic n.m.r. spectrum, and was assigned a C\(_2\) axis of symmetry passing through the oxygen atom on the basis of that spectrum. The consequent lack of a planar butadiene moiety in \(^4\)oxonin was demonstrated by its reaction with 4-phenyl-1,2,4-triazoline-3,5-dione at -78° (163). Addition of the dienophile was formulated as proceeding via a \(\pi^2S + \pi^8S\) cycloaddition followed by electrocyclic closure to a cyclohexadiene upon warming.
$\text{Z}^4$-oxonin was found to rearrange at 40° even more rapidly than $\text{Z}^4$-cyclononatetraene itself, to a single product which was initially characterized as trans-dihydrobenzofuran. The assignment of trans stereochemistry to this product was found to be a result of inadvertent mislabeling of the spectra of the cis and trans isomers of the molecule in a doctoral thesis, and the assignment was reversed by Anastassiou in a later communication (164). In addition, Pyrex filtered irradiation of $\text{Z}^4$-oxonin was reported to yield only the [6.1.0] isomer, and the appearance of cycloheptatriene as a photoproduct of cyclooctatetraene in the original report of Holovka, et al. was found to be a result of photolysis of the thermal rearrangement product of $\text{Z}^4$-oxonin, cis-9-oxabicyclo[4.3.0]nona-2,4,7-triene (165).

Masamune and co-workers (135, 166) have studied the response of 9-oxabicyclo[6.1.0]nonatriene to 2537 Å radiation at -80°. A steady state was attained, consisting of the starting epoxide, cis- and trans-dihydrobenzofurans, $\text{Z}^4$-oxonin and a monocycle proposed to be $\text{E},\text{Z},\text{Z},\text{Z}$-oxonin. The latter tetraene was found to rearrange thermally at -15° to trans-dihydrobenzofuran, which was found to be identical to the oxetene claimed by Holovka and co-workers. The remaining [5.2.0]
isomer reported in the original work on the photolysis of the [6.1.0] epoxide has not been observed by Masamune or Anastassiou, but it might have been expected to arise from electrocyclic closure of \( Z,E,Z,Z \)-oxonin, as yet unobserved. Interestingly, an adduct corresponding to that expected from Diels-Alder addition of 1,4-diphenyl-sym-tetrazine to that unknown isomer has recently been obtained by Anastassiou from reaction of the tetrazine with cyclooctatetraene oxide at 105\(^\circ\) (167).
Hess and Schaad (168, 169) have carried out calculations of the electronic properties of three heteronins. The calculated \( \pi \)-electron resonance energies of oxonin (0.000), azonin (0.014) and thionin (0.012) reproduced the trend observed in the six-\( \pi \)-electron systems, furan (0.007), pyrrole (0.039), and thiophene (0.032). The expectation that thionin (thiacyclononatetraene) might be an aromatic species has prompted synthetic efforts in that direction. Anastassiou and Chao (170, 171) have prepared 9-thiabicyclo[4.2.1]nona-2,4,7-triene-syn-9-oxide by treatment of cyclooctatetraene with thiirane-S-oxide at 140°. Irradiation of the product sulfoxide led only to expulsion of sulfur monoxide and recovery of cyclooctatetraene. Reduction of the oxide gave 9-thiabicyclo[4.2.1]nona-2,4,7-triene which was also prepared directly by Masamune and Darby (135) by means of photoinduced decomposition of carbonyl sulfide in the presence of cyclooctatetraene. Pyrex-filtered irradiation was found to produce isomerization of the [4.2.1] sulfide to 9-thiabicyclo[6.1.0]nona-2,4,6-triene, a reasonable precursor to thionin. Thermolysis of the [6.1.0] episulfide, however, led only to the [4.2.1] isomer, with a half life of sixty minutes at 56°. Oxidation of the [6.1.0] episulfide with m-chloroperbenzoic acid or periodate ion at temperatures as low as -30° gave the original [4.2.1] sulfoxide as the only product (172). Anastassiou found that sensitized irradiation of either the [6.1.0] or [4.2.1] sulfides also failed to generate a monocyclic species, leading instead to 9-thiabarbaralane. Conversion of the [4.2.1] isomer to the tricyclic, fluxional product was shown to proceed \textit{via} the intermediacy of the [6.1.0] episulfide.
Three annelated thionins have been prepared by Bindra et al. (173) and Garrat and co-workers (174) by means of Wittig condensations. All of these heterocycles were shown to have puckered ring systems and to lack aromatic character. No electrocyclic reactions of the system have been observed.
9-phenyl-9-phosphabicyclo[6.1.0]nona-2,4,6-triene has been prepared by Katz and co-workers (175) by addition of the cyclooctatetraene dianion to a solution of dichlorophenylphospine. The compound rearranged at 70° to syn-9-phenyl-9-phosphabicyclo[4.2.1]nona-2,4,7-triene. Irradiation of the [4.2.1] phosphine in acetone solution through Pyrex produced predominately 9-phenyl-9-phosphabarbaralane (176, 177). Oxidation of the [4.2.1] isomer led to the corresponding phosphine oxide, which took a different photochemical course in
rearranging to a phospha-homocubane derivative upon irradiation. The photochemistry of 9-phenyl-9-phosphabicyclo[6.1.0]nona-2,4,6-triene has not been reported.

The unusual synthesis of a phosphonin has been reported by Waite and Tebby (178). Reaction of 1,2,5-triphenyl-1-phospha-cyclopenta-2,4-diene with two equivalents of dimethyl acetylene-dicarboxylate was reported to give a tricyclic adduct, which rearranged in refluxing chloroform to the monocycle. The non-planar phosphonin was said to be stable to 245°, and lacked any sign of aromaticity in its n.m.r. spectrum.
Barton and Juvet (179) have proposed the transient existence of 9,9-dimethyl-9-silabicyclo[6.1.0]nona-2,4,6-triene. Copyrolysis of 1,2-dimethoxytetramethylidisilane and cyclooctatetraene at 450\(^{\circ}\) in a nitrogen flow resulted in the formation of a small amount of 9,9-dimethyl-9-silaindene. At a reaction temperature of 550\(^{\circ}\) the yield of this product increased, and an additional [4.3.0] isomer, the silaindane, was isolated. The authors pointed out that although the usual products of silylene addition to dienes are 1,4 adducts, these are known to arise through the intermediacy of vinyl silacyclopropanes (180). The suggested scheme for formation of the observed products, then, involved 1,2 addition of dimethylsilylene to the tetraene followed by rearrangement to the [4.3.0] system and subsequent aromatization or oxidation. The 1,4 adduct, 9,9-dimethyl-9-silabicyclo[4.2.1]nona-2,4,7-triene, was prepared by an independent route.
(181) and subjected to pyrolysis to test for its possible intermediacy in the reaction. The [4.2.1] silane rearranged exclusively to

\[ \text{[4.2.1] silane} \rightarrow \text{[6.1.0] silane} \]

9,9-dimethyl-9-silabarbaralane at 450° under the same conditions, but did produce some of the silaindene at 550°. Formation of the silaindene from the silylene reaction at 450° was thus concluded to support the formation of a [6.1.0] silane and its rearrangement in a manner similar to that observed in the carbocyclic system.
RESULTS AND DISCUSSION

The Synthesis of Bicyclo[5.2.0]nona-2,5,8-trien-4-one

The presence of a plane of symmetry and a cross-conjugated cycloheptadienone in the target molecule suggested the use of the Robinson-Schöpf tropinone synthesis for construction of the carbocyclic skeleton. This reaction, which was discovered by Sir Robert Robinson in 1917 (182) and subsequently refined by Schöpf and Lehmann (183), involves the reaction of 3-oxoglutaric acid with methylamine and a vicinal dialdehyde in aqueous solution at pH 5.5. Decarboxylation of the intermediate β-keto acids is spontaneous under these conditions, so that tropinone derivatives can be prepared in one step and in good yield.
The tropinone system includes the requisite seven-membered ring, and the reaction can be carried out using substituted dialdehydes in order to functionalize the two-carbon bridge. Elimination of the bridging nitrogen with the simultaneous introduction of two double bonds can be accomplished by quaternization of the amino ketone, followed by Hofmann elimination of the resulting ammonium salt, as demonstrated by Meinwald and co-workers (184). While the double bond distribution obtained upon degradation of tropinone methiodide itself is not that desired in the present case, incorporation of a strained ring syn to the nitrogen bridge into the system has been shown to favor the production of cross-conjugated dienones. Both cyclopropane- and cyclobutane-cis-1,2-dicarboxaldehydes have been subjected to the Robinson-Schöpf conditions, and the tropinone derivatives obtained could be transformed cleanly to the desired 2,5-dien-4-ones (185, 186).
The application of this series of reactions to the present synthesis required the preparation of the unknown cis-cyclobut-3-ene-1,2-dicarboxaldehyde. A route to the related dimethyl ester has been described by Vogel (187), and was adapted to provide a reasonable precursor to the desired dialdehyde.

Treatment of 1,3,5,7-cyclooctatetraene with one equivalent of bromine at -60° in the dark produced cis-7,8-dibromocycloocta-1,3,5-triene, which was warmed to room temperature and flash vacuum distilled to provide a 92% yield of the known trans-7,8-dibromobicyclo[4.2.0]octa-2,4-diene (188, 189) as a colorless solid. This material was subjected to exhaustive ozonolysis at -78° in 10% ethanolic dichloromethane, and the hydroperoxidic products were reduced with two equivalents of triethyl phosphite (190) at the same temperature. Three equivalents of triethyl orthoformate in absolute ethanol containing
p-toluenesulfonic acid were added to the cold solution, which was then allowed to warm to room temperature and stirred overnight under nitrogen. The reaction mixture was treated with solid sodium bicarbonate, and the solvent was removed under reduced pressure. The residue was thoroughly extracted with 5% sodium bicarbonate solution to remove triethyl phosphate, the bulk of the by-product 1,1,2,2-tetraethoxyethane was removed under vacuum, and final purification was carried out by column chromatography on basic alumina to give two epimeric products in 81% yield. The first isomer to elute from the column was a colorless solid, m.p. 112-113°, which was identified as trans-6,7-dibromo-cis,exo-2,4-diethoxy-3-oxabicyclo[3.2.0]heptane (Ic) on the basis of its spectra and elemental analysis. The stereochemistry of this product was clearly reflected in its n.m.r. spectrum (Figure 1, p. 104), in which the acetal methine hydrogens appear as two sharp singlets at δ5.50 and δ5.13. The lack of coupling
Figure 1. Nuclear Magnetic Resonance Spectra (CDCl₃, 60 MHz)

Top: trans-6,7-Dibromo-cis,exo-2,4-diethoxy-3-oxabicyclo[3.2.0]heptane (Ic)

Bottom: endo-6-exo-7-Dibromo-endo-2-exo-4-diethoxy-3-oxabicyclo[3.2.0]heptane (It)
to the bridgehead hydrogens established the cis,exo arrangement of the ethoxy groups, and the chemical non-equivalence of the same two hydrogens confirmed that the trans stereochemistry of the starting dibromide had been retained.

The second isomer to elute was isolated as a colorless oil, and was assigned the structure endo-6-exo-7-dibromo-endo-2-exo-4-diethoxy-3-oxabicyclo[3.2.0]heptane (It). The n.m.r. spectrum (Figure 1, p. 104) included a singlet at δ5.40 assigned to H-4 and a doublet with a coupling constant of 2.5 Hz at δ5.30, establishing the trans disposition of the ethoxy groups.
Reduction of the dibromo acetals by zinc dust proceeded smoothly in refluxing tetrahydrofuran to give, after distillation, a 91% yield of two olefinic products. These were separated by vapor phase chromatography and identified as cis,exo-2,4-diethoxy-3-oxabicyclo[3.2.0]-hept-6-ene (IIc) and trans-2,4-diethoxy-3-oxabicyclo[3.2.0]hept-6-ene (IIt). Both isomers were colorless, fragrant liquids at room temperature, and each displayed an infrared absorption band at 1560 cm⁻¹ attributable to the cyclobutene stretching mode. The n.m.r. spectrum of the cis isomer IIc (Figure 2, p. 108) included cyclobutene absorption as a singlet at δ6.07, and acetal methine absorption, also a singlet, at δ4.97. In the case of IIt (Figure 2, p. 108), cyclobutene absorption occurred as a singlet at δ6.14, and the non-equivalent acetal hydrogens appeared as a doublet at δ5.07, J = 5 Hz, and a singlet at δ4.90. The sharp absorption of the cyclobutene hydrogens of each isomer was followed by an amplitude-modulated ringing pattern, known as a "wiggle beat". This behavior is indicative of a very small coupling constant, and is a characteristic of the AA'XX' cyclobutene system in bicyclo[3.2.0]hept-6-enes (191).

Hinshaw (192) has reported a preparation of the related dimethyl acetals from maleic anhydride and 2,5-dimethoxy-2,5-dihydrofuran. Acid-catalyzed hydrolysis of the dimethyl acetals under a variety of conditions was found to lead to cis,trans-muconic dialdehyde as the only chloroform-soluble product. Fortunately, this report appeared after the present synthesis had been accomplished.
Figure 2. Nuclear Magnetic Resonance Spectra (CDCl$_3$, 60 MHz)

Top: cis,exo-2,4-Diethoxy-3-oxabicyclo[3.2.0]hept-6-ene (IIc)

Bottom: trans-2,4-Diethoxy-3-oxabicyclo[3.2.0]hept-6-ene (IIt)
The mixture of epimeric diethyl acetals II was stirred with dilute sulfuric acid at 35° until a homogeneous solution was obtained. This was added to a stirred solution of 3-oxoglutaric acid, methylamine hydrochloride and sodium dihydrogen phosphate at 10°, and the pH of the reaction mixture was adjusted to 5.5 using saturated aqueous sodium carbonate. After stirring for three days at room temperature, the solution was made basic with solid sodium carbonate, saturated with sodium chloride, and continuously extracted with diethyl ether for twenty-four hours. The solvent was removed from the extract in vacuo, and the residue was sublimed to give an oily solid. The sublimate was recrystallized from diethyl ether at low temperature, the mother liquor was chromatographed on a column of basic alumina, and the combined product was sublimed once again to give a 66% yield of 10-methyl-10-
azatricylo[4.3.1.0\(^2,5\)]dec-3-en-8-one (III) as a colorless solid, m.p. 122.5-123.5°.

While the success of this reaction does not invalidate Hinshaw's findings, it is clear that a species can be generated by hydrolysis of the acetal which serves as a dialdehyde equivalent, a hydrate or hemiacetal for example. No attempt was made to isolate a dialdehyde from the hydrolysis reaction.

The n.m.r. spectrum of III (Figure 3, p. 112) is characteristic of tropinone derivatives and clearly shows the presence of a fused cyclobutene, consisting of a singlet at δ6.00 (2H), a multiplet at δ3.4-3.2 (2H), a singlet at δ3.06 (2H), a singlet at δ2.70 (3H), and methylene absorption at δ3.0-1.8 (4H). The infrared spectrum (Figure 3, p. 112) includes absorption at 3122 and 3045 cm\(^{-1}\) (cyclobutene C-H stretches), 2790 cm\(^{-1}\) (N-methyl stretch), 1715 cm\(^{-1}\), 1565 cm\(^{-1}\) (cyclobutene olefinic stretch), and 1455 cm\(^{-1}\) (methyl asymmetric bend). The ultra-
Figure 3. 10-Methyl-10-azabicyclo[4.3.1.0^{2,5}]dec-3-en-8-one (III)

Top: Nuclear magnetic resonance spectrum (CDCl₃, 60 MHz)

Bottom: Infrared spectrum (KBr)
violet spectrum of the amino ketone in ethanol consists of one maximum at 2410 Å (log ε 2.9). The mass spectrum includes a parent ion at m/e 163, and combustion analysis is consistent with a C_{10}H_{13}N composition.

The use of cyclic cis vicinal dialdehydes in the Robinson-Schöpf procedures has invariably resulted in the formation of tropinone derivatives in which the fused ring is disposed syn to the nitrogen bridge (193). Base-catalyzed exchange of the methylene hydrogens of amino ketone III in deuterium oxide produced 10-methyl-7,7,9,9-tetradeutero-10-azatricyclo[4.3.1.0^{2,5}]dec-3-en-8-one (IIId), which displayed an n.m.r. spectrum consisting of four singlets in a ratio of 2:2:2:3. The lack of vicinal bridgehead-bridgehead coupling exhibited by the deuterated molecule is consistent only with the expected geometry, which results in a dihedral angle between the two carbon-hydrogen bonds of approximately ninety degrees.

\[ J_{1,2} = J_{6,7} \approx 0 \]
As a result of the steric crowding experienced by the nitrogen atom, such tropinone derivatives are resistant to N-alkylation (185). Amino ketone III was inert to refluxing iodomethane, but could be converted to 10,10-dimethyl-8-oxo-10-azoniatrireno[4.3.1.0²5]dec-3-ene tosylate (IV) by heating the amine at 75° for three hours in neat methyl p-toluenesulfonate. The crystalline mass which formed was stirred with dry tetrahydrofuran, filtered under nitrogen and washed with diethyl ether to give a 94% yield of the colorless, hygroscopic ammonium salt IV, m.p. 194-195°, which was suitable for elemental analysis. Alkylation of the deuterated amino ketone III(d) proceeded similarly to give IV(d).

Elimination of the nitrogen bridge of quaternary tropinone salts has been accomplished with several different bases, but steam distillation of an aqueous solution of the salt and sodium bicarbonate has become the method of choice. The degradation occurs via an initial Hofmann elimination to give a dimethylamino-enone, which then
must undergo a reverse Michael addition. Since this last step is reversible in the presence of free dimethylamine, the use of aqueous bicarbonate aids in driving the reaction to completion by buffering the solution near pH 8 and converting the eliminated amine predominately to its ammonium salt. The steam-volatility of the cycloheptadienones formed allows rapid removal of the product from the reaction mixture and simplifies subsequent purification.

\[ \text{H}_3\text{C}^+\text{CH}_3 \rightarrow \text{O} \quad \text{H}_3\text{C}^+\text{CH}_3 \]

Dissolution of the quaternary tosylate IV in aqueous sodium bicarbonate followed by distillation to near-dryness produced a slightly yellow two-phase distillate, which was saturated with sodium chloride and extracted with diethyl ether. The ether solution was washed with 10% hydrochloric acid, 5% sodium bicarbonate solution, and brine, and reduced in volume to give a colorless oil in 80% yield, based on a molecular weight of 132. The mass spectrum of the product exhibited prominent ions at m/e 132 and 104, indicating a facile loss of either carbon monoxide or ethylene. The n.m.r. spectrum consisted of two narrow multiplets centered at δ5.80 and 63.0 with an intensity ratio of 3:1. Carbonyl absorption occurred at 1760 cm\(^{-1}\) in the infrared.
spectrum, and the ultraviolet spectrum of an ethanol solution of the ketone displayed maxima at 2150 Å (log ε 3.50), 2700 Å (3.60), 2780 Å (3.57), and 3250 Å (2.75). The spectra and physical characteristics of the steam distilled product were identical to those of a sample of bicyclo[4.2.1]nona-2,4,7-trien-9-one (V), prepared by reaction of the cyclooctatetraene dianion with dimethylcarbamoyl chloride according to the procedure of Antkowiak et al. (194).

The production of a C₉H₈O isomer was gratifying, since the lack of a plausible mechanism for direct formation of the bridged ketone V from quaternary tosylate IV suggested the involvement of an intermediate in the reaction. Accordingly, milder conditions for effecting the elimination were sought. The quaternary salt IV was added to an ice-cold mixture of excess sodium bicarbonate and water under a layer of diethyl ether. The mixture was stirred and kept below 5°C for one hour, when an aliquot of the ether layer was removed and examined by n.m.r. The spectrum of this extract showed complex olefinic absorption, the presence of a large amount of aliphatic hydrogen, and a strong N-methyl resonance, indicating that elimination of dimethyl-
amine had not taken place and that longer reaction times or higher temperatures were necessary.

The quaternary salt IV was next added to an aqueous sodium bicarbonate solution under a layer of diethyl ether at room temperature, and the ultraviolet absorption spectrum of the ether layer was recorded at fifteen minute intervals. The intensity of absorption at 2250 and 3400 Å was constant between ninety and one hundred eighty minutes' reaction time, after which new absorption at 2650-2800 Å began to appear, indicating the presence of the undesired [4.2.1] trienone V. After separation of the layers and extraction of the aqueous layer with additional diethyl ether, the combined organic extracts were washed with 10% hydrochloric acid, saturated sodium bicarbonate solution, and brine. Thin layer chromatography of the pale yellow oil obtained after evaporation of the ether showed the presence of two compounds, one of which displayed an r.f. identical to that of the [4.2.1] trienone. N.m.r. analysis showed the presence of bicyclo[4.2.1]nona-2,4,7-trien-9-one and additional absorption, consisting of a multiplet at $\delta$6.25-6.05, a singlet at $\delta$6.12, a doublet with a coupling constant of 12 Hz at $\delta$5.8, and a narrow multiplet at $\delta$3.9, in a ratio of 1:1:1:1. Column chromatography on either silica gel or neutral alumina resulted in collection of a narrow band of the [4.2.1] trienone followed by a very broad band, which was initially composed of the second component of the mixture, but became increasingly rich in the bridged ketone as elution progressed. Complete separation of the two components was effected using
a grade III neutral alumina column developed with carbon tetrachloride and maintained at 3° in a refrigerated room. Considerable isomerization of the initial product occurred upon deposition of the sample onto the top of the column, but the \([4.2.1]\) ketone eluted as a narrow band and was followed by the desired product, which tailed to the extent of three column volumes. The solvent was removed from product fractions which appeared to be homogeneous by thin layer chromatography to give a pale yellow oil, which degraded rapidly in the presence of moist air even at 0°. The best yield of the pure trienone obtainable from quaternary tosylate IV was 30%, since long reaction times under these conditions favored the production of bicyclo[4.2.1]nona-2,4,7-trien-9-one.

The n.m.r. spectrum of bicyclo[5.2.0]nona-2,5,8-trien-4-one (VI) (Figure 4, p. 121) in carbon tetrachloride solution consists of an AB quartet centered at δ6.13 and δ5.80, a singlet at δ6.12, and a narrow multiplet at δ3.9, all of equal integrated intensity. The coupling constant exhibited by the enone AB system is 12 Hz, typical of cyclo-
heptadienones (185). H_2 and H_6 are strongly coupled to the bridgehead hydrogens, while allylic coupling in the system is less than 1 Hz in magnitude. Irradiation at the absorption frequency of the bridgehead hydrogens sharpens the AB quartet to four narrow lines, while irradiation at the H_2 and H_6 absorption position sharpens the bridgehead absorption to a narrow multiplet consistent with the small magnitude typical of cyclobutene allylic coupling constants. The lack of allylic coupling of the bridgehead hydrogens to the \( \alpha \) hydrogens of the enone system is consistent with the folded geometry of the system. The infrared spectrum of the ketone (Figure 4, p. 121) displays olefinic carbon-hydrogen stretches at 3060 and 3030 cm\(^{-1}\), tertiary carbon-hydrogen stretching at 2880 cm\(^{-1}\), carbonyl absorption at 1668 cm\(^{-1}\), and enone double bond stretching at 1615 cm\(^{-1}\). The ultraviolet spectrum of the trienone in anhydrous diethyl ether solution consists of maxima at 3850 Å (shoulder, log \( \varepsilon \) 1.03), 3580 (1.32), 3480 (1.33), 2620 (shoulder, 3.15), and 2210 (3.90). The mass spectrum of the ketone includes major peaks at \( m/e \) 132 (relative intensity 100), 131 (98), 130 (64), 104 (100), 103 (86), 102 (55), 78 (80), 77 (45), and 76 (78). The measured exact mass of the parent ion, 132.0575 ± 0.0007, corresponds exactly with that calculated for an ion of composition C_9H_8O, 132.0575. The mass spectrum can reasonably be analyzed in terms of facile loss of hydrogen radicals, carbon monoxide, and acetylene in various combinations.
Figure 4. Bicyclo[5.2.0]nona-2,5,8-trien-4-one (VI)

Top: Nuclear magnetic resonance spectrum (CCl₄, 100 MHz)

Bottom: Infrared spectrum (neat)
This yield and procedure were considered to be unacceptable, and an improved method for eliminating the nitrogen bridge from the tropinone skeleton was sought. The major problem appeared to be the low rate of elimination of dimethylamine from the intermediate amino-enone, which necessitated long reaction times in order to produce even poor yields of the trienone VI. Additionally, the bridged ketone V appeared to arise through the intermediacy of the desired product, so
that long reaction times favored the production of this unwanted [4.2.1] isomer at the expense of the [5.2.0] trienone. The solution to this problem was suggested by the high rate of Hofmann elimination displayed by quaternary tosylate IV. As has been noted, the first step of the degradation occurred readily even below 5°, as evidenced by the isolation of an amino-enone at that temperature after only an hour's reaction time. A second Hofmann elimination was thus substituted for the reverse Michael addition as a means of generating the third double bond of the target molecule.
The quaternary tosylate IV was added to anhydrous dimethylamine under nitrogen at 0°, and stirred until a homogeneous solution was obtained. The excess dimethylamine was removed under vacuum, and was replaced by anhydrous diethyl ether. The mixture was stirred vigorously, and a colorless, water-soluble solid crystallized from the residual oil. The solid was filtered off under nitrogen to give a clear, colorless solution, a portion of which was removed, reduced in volume, and analyzed by n.m.r. The ether solution contained a mixture of products, so that integration of the peak areas was equivocal. The spectrum observed, however, was consistent with formation of the expected product, trans-2,6-bis(dimethylamino)-cis-bicyclo[5.2.0]non-8-en-4-one, and included an AB quartet with a coupling constant of 3 Hz at 66.29 and 66.17, attributable to non-equivalent cyclobutene olefinic hydrogens, and two strong singlets at 2.24 and 2.20, assigned to the trans dimethylamino groups. A multiplet centered at 3.4 typical of cyclobutene methine absorption was present, and the remainder of the spectrum consisted of a complex pattern from 2.7 to 2.0. This product was not further characterized, since attempted purification by distillation or chromatography resulted in decomposition and polymer formation. Instead, the ethereal solution of the diamine was treated with an excess of iodomethane and refluxed overnight to give, after filtration and washing with ether, a hygroscopic, light- and heat-sensitive pink powder. Attempts at recrystallization of this material from methanol, ethanol, water, or aqueous acetone led to decomposition accompanied by the strong odor of a low molecular weight amine. The
mode of formation and the reactivity (vide infra) of this powder suggested that its major constituent was trans-2,6-bis(trimethylammonio)bicyclo[5.2.0]non-8-en-4-one diiodide (VII). The bis-quaternary diiodide was certainly not the sole product, however, since the pink powder was obtained in an embarrassingly high yield of 103%, based on a formula weight of 504, from quaternary tosylate IV. Reasons for the excessive yield might have included solvent retention by the salt, incomplete removal of dimethylammonium tosylate, or irreversible hydration during brief exposure to the atmosphere. This problem was not pursued further, since the pink powder did indeed serve as an improved precursor to the desired product.

Addition of the pink bis-quaternary diiodide VII over a period of thirty minutes to a stirred mixture of excess sodium bicarbonate, distilled water and pentane under nitrogen at 0-5°, followed by thirty minutes' additional reaction time, led to the formation of two C₉H₈O isomers. The two ketones were isolated by transfer of the pentane layer into an ice-cold flask containing anhydrous sodium sulfate and repeated extraction of the reaction mixture with cold pentane. The
dried organic extracts were filtered under nitrogen and reduced in volume to give a yellow oil, which was separated into its components by column chromatography at -20° to -25° on grade III neutral alumina using a 1:1 mixture of pentane and dichloromethane as the developing solvent. Care was taken to avoid warming the top layers of adsorbent during and after sample introduction in order to minimize isomerization of the product to the [4.2.1] system. The cold fractions were collected under a dry nitrogen atmosphere to exclude water from the purified products, and the composition of the eluate was monitored by thin layer chromatography. The first compound to elute was identified as bicyclo[4.2.1]nona-2,4,7-trien-9-one (V) by its n.m.r. spectrum. This bridged ketone was a very minor product, and was probably formed during loading of the column. The second band, which was well separated from the first, was composed of a new C₉H₈O isomer, as demonstrated by its conversion to bridged ketone V by hot water. This compound was a conjugated ketone with infrared carbonyl absorption at 1674 cm⁻¹, and a first order n.m.r. spectrum due to eight non-equivalent hydrogens. These absorptions were tentatively assigned with the aid of decoupling experiments to the hydrogen atoms of bicyclo[5.2.0]nona-1,5,8-trien-4-one (VIII), isolated in 10% yield. This product was not produced during degradation of the quaternary tosylate IV under similar conditions of pH and temperature, so that its formation from the desired trienone VI by an acid- or base-catalyzed double bond shift can be discounted. The isolation of this
$\beta,\gamma$-unsaturated ketone may be viewed as a result of a tendency toward syn elimination of the exo-trimethylammonium group of diiodide VII or of conformational influences operating during this reaction. The aqueous thermal conversion of VIII to the bridged trienone V can reasonably be ascribed to prior isomerization of the $\beta,\gamma$ isomer to the cross-conjugated ketone VI, followed by its reaction with water (vide infra). Interconversion of $\alpha,\beta$- and $\beta,\gamma$-enones in a similar system has been reported by Paquette and co-workers (195).
The last compound to elute from the -20°C column was bicyclo[5.2.0]-
nona-2,5,8-trien-4-one (VI), obtained in 77% yield from the bis-
quaternary diiodide VII. The aminolysis-quaternization procedure
resulted in more than a two-fold improvement in the yield of the target trienone over that obtained by elimination of dimethylamine from the bridged quaternary salt IV, and can be considered to be a reasonably general and mild method for the degradation of tropinone derivatives. The overall yield of the [5.2.0] trienone VI from cyclooctatetraene was 33%.

The Aqueous Thermal Rearrangement of Bicyclo[5.2.0]nona-2,5,8-trien-4-one

Evidence obtained during development of the synthesis of bicyclo-[5.2.0]nona-2,5,8-trien-4-one suggested that its isomer, bicyclo-[4.2.1]nona-2,4,7-trien-9-one, was formed by a thermal rearrangement of the [5.2.0] trienone VI under the conditions required for degradation of the quaternary tosylate IV, and upon contact of VI with chromatographic adsorbents at room temperature. The mechanism of this transformation was not immediately obvious, and the possible influence of the polarity of these media on the stabilization of a reactive intermediate which might participate in the rearrangement was first considered.
The folded geometry of the [5.2.0] system and the resulting proximity of the two π-electron systems suggested a series of internal cycloaddition reactions involving initial formation of a charge-separated intermediate. A precedent for the final reaction in this hypothetical sequence has been provided by Paquette and co-workers (196), who reported that treatment of 7-chlorobicyclo[4.3.0]nona-2,4-dien-8-one with base in aprotic solvents led to formation of the bridged trienone V. A mechanism involving generation of an oxyallyl ion, \(\pi^4_s + \pi^2_s\) closure to a bridged bishomotropone, and a \(\sigma^2_a + \sigma^2_a + \pi^2_s\) ring opening to the observed product was proposed.

Solutions of the trienone VI in n.m.r. grade \(d_6\)-dimethylsulfoxide, \(d_3\)-acetonitrile, \(d_6\)-acetone, deuterochloroform and carbon tetrachloride were prepared and heated to \(100^\circ\) in a steam bath for ten to thirty
minutes. The n.m.r. spectra of the resulting solutions showed complete conversion of the starting material to a mixture of the bridged ketone V and 1-indanone. The ratio of the two products superficially reflected the solvent polarities, in that trienone V was by far the major product in the dimethylsulfoxide solution, while 1-indanone predominated in the halomethane solvents. Examination of the spectra of the solutions obtained prior to the isomerization, however, showed the presence of adventitious water in each of the samples, and the oxygenated solvents were particularly wet. A solution of the [5.2.0] trienone VI in d₆-dimethylsulfoxide from a freshly opened container was prepared, and the absorption due to water in the n.m.r. spectrum was much less intense. Brief thermolysis of this sample at 100° produced 1-indanone as the major product. Further, addition of a stoichiometric excess of deuterium oxide to a similarly prepared sample followed by warming to 50° in the n.m.r. spectrometer resulted in the exclusive formation of the bridged ketone without detectable absorption due to an intermediate. It was clear that solvent polarity was not an important factor in determining the course of rearrangement of the [5.2.0] trienone, but that water functioned as a catalyst in its conversion to bicyclo[4.2.1]nona-2,4,7-trien-9-one.

3,5-Dideuterobicyclo[5.2.0]nona-2,5,8-trien-4-one (IIIId) was prepared by quaternization of the d₄ amino ketone IIIId and reaction of the resulting salt at 20° with aqueous sodium bicarbonate under a layer of pentane for thirty minutes. Under these conditions very little of the [4.2.1] ketone was formed from the initial product, and
although the yield of the labeled [5.2.0] trienone VId was low, application of the alternate procedure would have necessitated the use of deuterodimethylamine, and was not considered to be economical. The pentane layer was removed, and the aqueous solution was extracted twice more. Deuterium oxide was added to the pentane solution of the labeled trienone, and the pentane was removed under vacuum without heating the mixture. The remaining aqueous solution of the trienone was then rapidly distilled, and the rearranged product was extracted from the distillate and purified by microdistillation. Samples of this labeled [4.2.1] trienone and the unlabeled isomer obtained by steam distillation of a bicarbonate solution of quaternary tosylate IV were dissolved in deuterochloroform and analyzed by n.m.r. (Figure 5, p. 134).

The ratio of olefinic to aliphatic hydrogen in each sample was obtained by measuring the integrated intensity of the multiplets at $\delta5.85$ and $\delta3.1$ several times and averaging the results. The measured ratio of the unlabeled ketone was 3.00:1, while the value obtained from the spectrum of the labeled trienone Vd was 4.97:1 under exactly the same conditions. This result located one deuterium atom at a bridgehead position. Both samples were then treated with europium-(III)tris(1,1,1,2,2,3,3-heptaflouro-7,7-dimethyl-4,6-octanedione) in order to separate the resonance positions of each pair of equivalent olefinic hydrogen atoms. The shifted spectrum of the unlabeled trienone consisted of (beginning at low field) a doublet, $J = 8$ Hz, assigned to bridgehead absorption, a doublet of doublets of doublets,
Figure 5. Nuclear Magnetic Resonance Spectra (CDCl$_3$, 100 MHz)

Top: Bicyclo[4.2.1]nona-2,4,7-trien-9-one (V)
Bottom: 1,2-Dideuterobicyclo[4.2.1]nona-2,4,7-trien-9-one (Vd)
J = 3, 8, and 9 Hz, assigned to the α-dienyl hydrogens, a singlet, due to absorption of the isolated olefinic hydrogens, and a multiplet at the highest field, assigned to the β-dienyl hydrogens. All of the absorptions were of equal intensity. The appearance of H-7 and H-8 as a singlet allowed assignment of the 8 Hz coupling exhibited by the bridgehead hydrogens to an interaction with the α-dienyl hydrogens H-2 and H-5. The shifted spectrum of the labeled trienone Vd consisted of, in the same order, a doublet, J = 8 Hz, due to bridgehead absorption, a multiplet, corresponding in resonance position to the α-dienyl absorption, a singlet, and a multiplet, in an integrated intensity ratio of 1:1:2:2. The second deuterium was thus located at an α-dienyl position. Further, the appearance of the remaining bridgehead hydrogen absorption as an 8 Hz doublet demanded that the adjacent α-dienyl position be occupied by a hydrogen nucleus, so that the structure of the product of aqueous thermal rearrangement of 3,5-dideuterobicyclo[5.2.0]nona-2,5,8-trien-4-one VId could be identified as 1,2-dideuterobicyclo[4.2.1]nona-2,4,7-trien-9-one (Vd).

The loss of the original plane of symmetry during the course of this rearrangement ruled out the series of internal cycloadditions originally considered, since that mechanism would have resulted in formation of a bridged trienone labeled at both bridgehead positions. The catalytic effect of water on the course of reaction and the absence of an n.m.r.-observable concentration of any product of addition of water to the [5.2.0] trienone suggested that a reactive
intermediate of constitution $\text{C}_9\text{H}_{10}\text{O}_2$ was involved in the rearrangement. That species is suggested to be $9,9$-dihydroxybicyclo[6.1.0]nona-$2,4,6$-triene.

This ketone hydrate would be expected to undergo a particularly facile 1,5 sigmatropic shift by analogy with the behavior of the 9-flouro- and 9-dimethylaminobicyclo[6.1.0]nona-$2,4,6$-triens (101) to give the hydrate of the bridged ketone product, which could lose the elements of water rapidly to form the ketone itself. The deuterium labeling observed in the rearranged product reflects a structural
reorganization consistent with a stereospecific 1,5 sigmatropic shift of the hydrated carbonyl carbon of such a species. Silica gel and alumina promotion of the rearrangement is also consistent with the involvement of a hydrated ketone, since the amphoteric nature of the surface of these supports can be expected to accelerate the formation of such an intermediate. Several mechanistic alternatives exist for the conversion of trienone VI to the proposed intermediate, and discussion of these is best included with a treatment of the entire thermally accessible energy surface of this system.

The Non-Aqueous Thermal Rearrangement of Bicyclo[5.2.0]nona-2,5,8-trien-4-one

It has been mentioned that the product mixture obtained upon brief thermolysis at 100° of a solution of trienone VI in any of several dry, aprotic solvents is composed largely of 1-indanone. Two observable intermediates are involved in this process.

Heating of a carbon tetrachloride solution of bicyclo[5.2.0]-nona-2,5,8-trien-4-one, VI, or of its 3,5-dideutero derivative (Figure 6, p. 142), VI\text{Id}, at temperatures between 45° and 55° produced rapid ($t_{1/2}^{45°} - 30'$) rearrangement to a new compound, IX. The n.m.r. spectrum of unlabeled IX (Figure 7, p. 144) consisted of a multiplet at $\delta6.45-6.05$ (2H), a narrow multiplet at $\delta5.95$ (2H), a multiplet at $\delta5.9-5.6$ (2H), a doublet at $\delta4.05$ (1H), $J = 5$ Hz, and an apparent triplet at $\delta3.80$ (1H), $J = 5$ Hz. The n.m.r. spectrum of the labeled rearrangement product IX\text{Id} (Figure 7, p. 144) consisted of a multiplet
at 6.12 (2H), a narrow multiplet at 5.95 (2H), a doublet of doublets of doublets centered at 5.75 with coupling constants of 11, 6 and 1 Hz and due to only one hydrogen atom, no absorption at 4.05, and a doublet, J = 6 Hz, at 3.80 (1H).

Attempted purification of intermediate IX by column chromatography on alumina or silica gel at temperatures as low as 0° resulted in its quantitative conversion to bridged trienone V. Addition of dimethyl acetylenedicarboxylate to a solution containing IX at room temperature failed to produce any change in the n.m.r. spectrum indicative of the formation of an adduct after twenty-four hours, and subsequent slow heating of the mixture resulted only in the production of 1-indanone.

Thermolysis of the n.m.r. sample of IX at 60° produced further rearrangement (t_2 Δ 60°) to a second intermediate, X, contaminated with 1-indanone. In the case of IXd, however, the rearrangement to Xd proceeded without accompanying indanone production at temperatures as
high as 75°. The n.m.r. spectrum of X (Figure 8, p. 146) consisted of a doublet of multiplets with a major coupling constant of 5 Hz at δ7.45 (1H), a multiplet at δ6.6-6.3 (2H), a multiplet at δ6.2-5.9 (3H), a doublet of multiplets at δ3.24 with a major coupling constant of 14 Hz and due to one hydrogen, and a doublet of multiplets at δ2.85, again with a major coupling constant of 14 Hz and due to one hydrogen. The n.m.r. spectrum of the labeled intermediate Xd (Figure 8, p. 146) consisted of a narrow multiplet at δ7.48 (1H), a broad multiplet at δ6.6-6.3 (2H), a broad multiplet at δ6.2-5.9 (2H), and a broad singlet at δ3.32 (1H). Absorptions due to one hydrogen were thus lacking near δ6.1 and δ2.85. Intermediate X was converted to 1-indanone by attempted distillation under vacuum at 30°, and upon contact with chromatographic adsorbents.

The solution of X was heated to 80° for one hour, and the resulting n.m.r. spectrum (Figure 9, p. 148) revealed the contents of the tube to be mostly 1-indanone, with a small amount of the bridged trienone V absorbing at δ5.78. The production of this ketone was probably due to the small amount of moisture present in solution, appearing as a singlet at δ1.3. The labeled intermediate Xd was heated for thirty minutes at 85°, and then immersed in a steam bath for twenty minutes more. The sample was contaminated with water after the cap on the tube popped off during this operation, but the spectrum obtained immediately afterwards (Figure 9, p. 148) emphasized the reluctance of Xd to aromatize. Due to this accident, the deuterium distribution in the labeled indanone could not be accurately determined,
but the appearance of the α-keto resonance as a broad doublet and
the integral deficiency of the α-keto resonance at δ2.6 indicated
that at least one deuterium had been located in the α-keto position
prior to the accident.

In order to provide further evidence upon which to base structural
assignments of intermediates IX and X, an attempt was made to follow
the isomerization by infrared spectroscopy. A variable temperature
infrared cell was filled with a sample of the trienone VI in carbon
tetrachloride and heated, first to 45°, and then to 60°, and the
spectrum of the sample was recorded periodically. The sample had
undergone some rearrangement before the experiment was begun, but
comparison of the spectra that were obtained with the known spectra
of VI and 1-indanone allowed assignment of a carbonyl stretching
frequency of 1660 cm⁻¹ to IX, and of 1710 cm⁻¹ to X.

The structure of the first stable rearrangement product of
trienone VI during the non-aqueous thermolysis was concluded to be
bicyclo[5.2.0]nona-3,5,8-trien-2-one on the basis of the available
evidence. The simplicity of the n.m.r. spectrum excluded dimeric
structures, so that the constitution of both intermediates can be
assumed to be C₉H₈O. This formula, the retention of carbonyl func-
tionality as demonstrated by the infrared absorption, and the six
olefinic and two aliphatic hydrogens displayed in the n.m.r. spectrum
of IX demanded a bicyclic structure. The n.m.r. spectrum was differ-
ent from that reported for any other bicyclic C₉H₈O derivative, and
perfectly consistent with the proposed structure, as were the results
Figure 6. Nuclear Magnetic Resonance Spectra (CCl₄, 100 MHz)

Top: Bicyclo[5.2.0]nona-2,5,8-trien-4-one (VI), prior to thermolysis

Bottom: 3,5-Dideuterobicyclo[5.2.0]nona-2,5,8-trien-4-one (VId), prior to thermolysis
Figure 7. Nuclear Magnetic Resonance Spectra (CCl₄, 100 MHz)

Top: Bicyclo[5.2.0]nona-3,5,8-trien-2-one (IX), obtained by thermolysis of VI at 45° for 286 minutes

Bottom: 1,3-Dideuterobicyclo[5.2.0]nona-3,5,8-trien-2-one (IXd), obtained by thermolysis of VId at 54° for 100 minutes
Figure 8. Nuclear Magnetic Resonance Spectra (CCl₄, 100 MHz)

Top: trans-Bicyclo[4.3.0]nona-2,4,7-trien-9-one (X) and 1-indanone, obtained by thermolysis of IX at 60° for 257 minutes, then at 65° for 165 minutes

Bottom: 1,8-Dideutero-trans-bicyclo[4.3.0]nona-2,4,7-trien-9-one (Xd), obtained by thermolysis of IXd at 74° for 90 minutes
Figure 9. Nuclear Magnetic Resonance Spectra (CCl₄, 100 MHz)

Top: 1-Indanone and bicyclo[4.2.1]nona-2,4,7-trien-9-one (V), obtained by thermolysis of X at 80° for 60 minutes

Bottom: 1-Indanone (d₂) and 1,8-dideutero-trans-bicyclo[4.3.0]-nona-2,4,7-trien-9-one (Xd), obtained by thermolysis of Xd at 85° for 30 minutes, then at 100° for 20 minutes
of deuterium labeling.

The narrow multiplet centered at δ5.95 was assigned to the non-equivalent cyclobutene hydrogens. The multiplets at δ6.45-6.05 and δ5.90-5.6 were assigned to H-4 and H-6, and to H-3 and H-5, respectively. The labeled compound exhibited a resonance due to only one hydrogen in the δ5.8 region, consistent with replacement of H-3 with deuterium, which consisted of a doublet of doublets of doublets with coupling constants of 12, 7, and 1 Hz, and which was assigned to H-5. The n.m.r. spectrum of the four spin olefinic system of cyclohepta-2,4-dien-1-one has been analyzed in detail by Bertelli and co-workers using carbon tetrachloride containing 10% benzene as solvent (197). The agreement of the resonance positions exhibited by this model system, and in particular the essential identity of the coupling constants of the γ-hydrogen absorption, with those of the dienone segment of IX are highly supportive of the assignment. The geometry of the rearrangement product should resemble closely that of the starting trienone VI, so that the low magnitude of allylic coupling of the bridgehead hydrogens of IX into the dienone system is not
 surprising. The absorptions of the bridgehead hydrogens of IX appear adjacent to those of the starting trienone VI, responding to the asymmetry of the new dienone system. The triplet, assigned to H-7, at δ3.80 is shown to be a result of coincidental equivalence of two vicinal coupling constants by its collapse to a doublet in the dideutero derivative. The carbonyl stretching frequency is typical of α,β,γ,δ-unsaturated ketones in this ring system (184). The failure of bicyclo[5.2.0]nona-3,5,8-trien-2-one to undergo Diels-Alder addition to dimethyl acetylenedicarboxylate is not disturbing in light of the fact that the reaction of cyclohepta-2,4-dien-1-one itself with N-phenylmaleimide required eight days' reflux in benzene to reach 60% completion (184).

The presence of an absorption at δ7.5 in the n.m.r. spectrum of X, together with the disappearance of one hydrogen's absorption near δ6.2 in the spectrum of the deuterated intermediate, suggested the
presence of a simple enone functionality, and carbonyl absorption at 1710 cm$^{-1}$ established this as a cyclopentenone. The coupling constant relating the two aliphatic hydrogens, 14 Hz, was suggestive of a trans-coplanar or geminal relationship, and the remainder of the spectrum appeared to be consistent with the absorption expected of a locally symmetric conjugated diene. On the basis of these features, of the results of deuterium labeling, and of its ease of aromatization, X was assigned the structure trans-bicyclo[4.3.0]nona-2,4,7-trien-9-one.

These transformations can be discussed in terms of the known features of the bicyclo[6.1.0]nona-2,4,6-triene system. Conrotatory opening of the cyclobutene ring of trienone VI can lead to $Z,E,Z,Z$-cyclononatetraenone, which can undergo a conformational change, as suggested by Anastassiou in the case of the related N-acetylazonin (142), to produce a rotamer which can close conrotatorily to trienone IX. It is not known whether VI and IX exist in an equilibrium, since slow conversion to X even at $45^\circ$ precludes prolonged observation of this pair. Symmetry-allowed ring-opening of IX can give $E,Z,Z,Z$-
cyclononatetraenone, which in turn can close to the *trans*-dihydro-indenone X.

The apparent deuterium isotope effect exhibited during the aromatization of X implies that the rate-determining step in the process is enolization of that ketone, which is rapidly followed by a 1,5 hydrogen shift to generate an aromatic enone, ketonizing to give the observed 1-indanone.
The most intriguing aspect of this chemistry, however, is what is not observed. cis-Dihydroindenone (78), if it is produced at all, is at least not present in the products of rearrangement of VI in n.m.r. observable concentrations. This rigid adherence to orbital symmetry control is unique among all of the derivatives of the bicyclo[6.1.0]nonatriene system. An additional oddity, and perhaps a related one, is that no trace of the Cope rearrangement product of the [5.2.0] trienone VI has been detected during any of the non-aqueous thermolyses, either by n.m.r. or infrared spectroscopy. It is possible that bicyclo[6.1.0]nona-2,4,6-trien-9-one exists as a very minor component in equilibrium with the trienones VI and IX, and that its direct reaction with water is responsible for the formation of the proposed hydrate precursor to bicyclo[4.2.1]nona-2,4,7-trien-9-one. The hydration of cyclopropanones is known to be nearly instantaneous even at -78°C (198), and rearrangement of the hydrate would also be expected to be rapid (101).
A second alternative mechanism for the production of the cyclopropanone hydrate would involve direct hydration of the trienone VI, followed by Cope rearrangement to the [6.1.0] system. This scheme would explain the observed catalysis of the transformation of VI to V on silica gel or alumina, since the acidic sites and the water present in these adsorbents could reasonably be expected to accelerate hydration of VI, but should have little effect upon any equilibrium involving VI and its [6.1.0] isomer. The success of chromatographic
purification of trienone VI at low temperatures could be ascribed to a retardation of the rate of one of these processes.

The conversion of the [5.2.0] non-aqueous rearrangement product IX to bridged ketone V on the same adsorbents seems mysterious if Jones' (137) report that bicyclo[5.2.0]nona-2,4,8-triene is stable to gas chromatography at 110° is given credence. This report seems odd, since the molecule could be formed from Z,E,E,E-cyclononatetraene during the rearrangement of bicyclo[6.1.0]nona-2,4,6-triene, but has never been observed as a product of that rearrangement. No basis for the structural assignment was given. If this report is ignored, a mechanism involving hydration of [5.2.0] ketone IX, ring opening to a dihydroxy-Z,E,E,E-cyclononatetraene, closure to the symmetric [5.2.0] hydrate of VI and Cope rearrangement to the cyclopropanone hydrate can be considered.
A third possibility for production of V from either VI or IX would involve ring opening of these isomers to \( Z,E,Z,Z \)-cyclonona-2,4,6,8-tetraen-1-one and hydration of that ketone. The tetraenone is formally an 8\( \pi \)-electron system analogous to the 4\( \pi \)-electron cyclopentadienone, and a reaction which would eliminate the carbonyl group and interrupt cyclic conjugation might be quite favorable. The electrocyclic reactions leading from \( Z,E,Z,Z \)-cyclononatetraenes to the [6.1.0] framework are known to be rapid even at 0\( ^\circ \), so that this rearrangement might compete with dehydration of the geminal diol. Uncatalyzed hydration of this monocyclic ketone during the aqueous thermal rearrangement of VI, its catalyzed hydration on the chromatographic supports at 0\( ^\circ \), and suppression of its formation during lower temperature chromatography would account for the production of the bridged ketone under all of the circumstances under which this rearrangement is observed.

The operation of this last mechanism would demand that the rate of formation of V from VI in the presence of a large excess of water be equal to the initial rate of formation of IX from VI in the absence of water. This appears to be the case. Heating a solution of bicyclo-[5.2.0]nona-2,5,8-trien-4-one in hexadeuteroacetone containing a large molar excess of deuterium oxide at 45\( ^\circ \) produced rapid rearrangement to the bridged ketone V with a half-life of approximately thirty minutes, the same as the value observed in the non-aqueous rearrangement of [5.2.0] trienone VI to [5.2.0] trienone IX. This result implies that the rate-determining step in both rearrangements is
conrotatory opening of VI to $Z,E,Z,Z$-cyclononatetraenone, and further supports the operation of the third mechanism considered.

Bicyclo[6.1.0]nona-2,4,6-triene produced approximately 90% of a symmetry-forbidden thermolysis product, cis-bicyclo[4.3.0]nona-2,4,7-triene, through the intermediacy of $Z^4$-cyclononatetraene. The immediate precursor to this monocycle is unknown, but has been suggested to be formed directly from the [6.1.0] triene, from bicyclo[5.2.0]nona-2,5,8-triene, or from $Z,E,Z,Z$-cyclononatetraene (vide supra). The absence of any evidence for the formation of bicyclo[6.1.0]nona-2,4,6-trien-9-one and the strict adherence to the dictates of orbital symmetry during the rearrangement of VI, as well as the details of the reported behavior of the 9-azabicyclo[6.1.0]nona-2,4,6-trienes studied by Anastassiou (136, 146, 148), provide strong evidence supporting the view that the $Z^4$-cyclononatetraene derivatives formed during the rearrangement of the bicyclo[6.1.0]nonatriene system arise directly from the [6.1.0] skeleton.

The Nature of the 4-Hydroxybicyclo[5.2.0]nona-2,5,8-trien-4-ylium Cation

Cyclooctatrienone, bicyclo[5.1.0]octa-3,5-dien-2-one, and bicyclo-[5.1.0]octa-2,5-dien-4-one have been protonated in concentrated sulfuric acid to produce the corresponding hydroxyhomotropylium cations, but no bis-homotropylium ion has been observed under such nucleophilic conditions. Several attempts to dissolve bicyclo[5.2.0]nona-2,5,8-trien-4-one in sulfuric acid led only to carbonization of the sample.
The ketone could be protonated cleanly in "super acid" media, however. Rapid mixing of a solution of fluorousulfuric acid in fluorousulfonyl chloride with a solution of the trienone VI in a mixture of deuterochloroform and dideuterodichloromethane at -115° under a nitrogen atmosphere using an apparatus similar to that described by Winstein and co-workers (50) led to an orange solution. The sample tube was sealed and transferred to an n.m.r. spectrometer cooled to -110°, and the n.m.r. spectrum was recorded. The spectrum of the solution was unchanged from -100° to -40°, except for viscosity broadening at the temperature extremes. The sample decomposed and separated into two layers at -20°. Hydroxyl absorption was visible at δ12.2 as a shoulder on the fluorousulfuric acid absorption at temperatures below -90°, confirming the nature of the species under observation. The remainder of the spectrum (Figure 10, p. 165) of the 4-hydroxybicyclo[5.2.0]nona-2,5,8-trien-4-ylium cation (XI) consisted of a doublet of doublets at δ7.45, J = 12 and 4 Hz, a doublet at δ6.35, J = 12 Hz, a singlet at δ6.12, and a doublet at δ4.20, J = 4 Hz, all of equal integrated intensity.
Comparison of the spectra of the protonated and neutral ketones revealed that the absorption position of the cyclobutene olefinic hydrogens was unchanged in the cation, the bridgehead absorption had been shifted downfield slightly, and the hydrogens of the enone system had experienced a substantial downfield shift. The charge distribution in the pentadienyl system of the protonated ketone appeared to be considerably different from that exhibited by a model system, the cyclooctadienyl cation (50). Since the n.m.r. spectrum of a 3-hydroxycycloheptadienyl cation had not been reported, the preparation of such an ion with geometry and substitution similar to that of XI was undertaken.

Bicyclo[5.2.0]nona-2,5-dien-4-one had been prepared by Chapman and Fugiel (185) by the Robinson-Schöpf condensation and Hofmann elimination sequence. The required cis-cyclobutane-1,2-dicarboxaldehyde had been obtained by ozonolysis of bicyclo[6.2.0]deca-2,4,6-triene, which was prepared by reaction of the cyclooctatetraene dianion with 1,2-dibromoethane. The poor overall yield of the dienone was due primarily to inefficiency of the first and last steps of the synthesis. This procedure was modified to exploit some of the features of the preparation of bicyclo[5.2.0]nona-2,5,8-trien-4-one.
The mixture of epimeric 2,4-diethoxy-3-oxabicyclo[3.2.0]hept-6-ynes (II) was catalytically hydrogenated over 10% palladium on charcoal, absorbing one equivalent of hydrogen to give the epimeric 2,4-diethoxy-3-oxabicyclo[3.2.0]heptanes (XII) as a colorless oil in 99% yield after distillation. The n.m.r. spectrum of the mixture consisted of ethoxy absorption at δ1.0-1.4 and δ3.2-4.1 (10H), cyclobutane methylene absorption at δ1.5-2.4 (2H), cyclobutane methine absorption at δ2.6-3.1 (2H), and acetal methine absorption (2H) attributable to the cis isomer as a singlet at δ5.0, and to the trans isomer as a singlet at δ4.86 and a doublet, J = 5 Hz, at δ5.22. The infrared spectrum of the mixture lacked absorption above 3000 cm⁻¹ and near 1660 cm⁻¹, and the mass spectrum included a parent ion at m/e 186.
The mixture of epimeric cyclobutane acetals XII was stirred with dilute sulfuric acid at 35° until a homogeneous solution resulted. This was combined with methylamine hydrochloride and 3-oxoglutaric acid under the usual Robinson-Schöpf conditions. After three days' reaction time, the product was extracted and purified by recrystallization and sublimation to give 10-methyl-10-azatricyclo[4.3.1.0²,5]decan-8-one (XIII) as a colorless solid, m.p. 89-90°, identical to that prepared by Fugiel (186).

The amino ketone XIII was dissolved in methyl p-toluenesulfonic acid, heated to 75°, and maintained at that temperature for sixty hours. The reaction mixture was then cooled to room temperature and stirred with tetrahydrofuran. Filtration and washing with diethyl ether provided the known (186) quaternary tosylate (XIV), m.p. 187-188°, as white crystals in 88% yield. Since direct degradation of this salt was known to give a poor (33%) yield of the desired dienone, the sequence of reactions used to produce trienone VI was applied.
Dissolution of the quaternary tosylate XIV in anhydrous dimethylamine, removal of the excess amine under vacuum, and addition of dry diethyl ether to the residue resulted in precipitation of a solid. This mixture was filtered under nitrogen, and the filtrate was treated with an excess of iodomethane and refluxed overnight. Filtration of the resulting suspension and washing with anhydrous ether gave the desired precursor as a yellow, hygroscopic powder in 105% yield based on its formulation as 2,6-bis(trimethylammonium)-4-oxobicyclo[5.2.0]-nonane diiodide (XV). This material was added to a stirred mixture of sodium bicarbonate, water, and pentane under nitrogen at room temperature. After two hours' reaction time, the aqueous layer was saturated with sodium chloride, separated from the pentane layer, and extracted several times with fresh pentane. Removal of the solvent from the combined pentane extracts and distillation of the residue gave the known (186) bicyclo[5.2.0]nona-2,5-dien-4-one (XVI) as a clear, colorless liquid in 72% yield, or 32% overall from cyclo-octatetraene.

The n.m.r. spectrum of [5.2.0] dienone XVI in carbon tetrachloride solution consisted of an AB quartet centered at δ5.10 and δ5.83, J = 12 Hz, broad bridgehead hydrogen absorption at δ3.40, and cyclobutane methylene absorption at δ2.5-2.0, in an integrated intensity ratio of 1:1:1:2. The lower field (§) olefinic absorption was broadened due to coupling with the bridgehead hydrogens.
Figure 10. Nuclear Magnetic Resonance Spectra (100 MHz)

Top: The 4-hydroxybicyclo[5.2.0]nona-2,5,8-trien-4-ylium cation (XI)

Bottom: The 4-hydroxybicyclo[5.2.0]nona-2,5-dien-4-ylium cation (XVII)
The dienone was protonated at -115° in exactly the same way as the trienone VI had been, and the n.m.r. spectrum of the resulting cation was recorded. Again, the features of the spectrum were unchanged over the temperature range of -100° to -40°, and sample decomposition occurred above the latter temperature. The spectrum of the 4-hydroxybicyclo[5.2.0]nona-2,5-dien-4-ylum cation (XVII) (Figure 10, p. 165) consisted of a doublet of multiplets at δ7.30, with a major coupling constant of 11 Hz, a doublet at δ6.40, J = 11 Hz, a multiplet at δ3.75, and a multiplet at δ2.7, in an integrated intensity ratio of 1:1:1:2.

\[
\begin{array}{c|c|c|c|c}
\hline
& \delta & \Delta\delta & \delta & \Delta\delta \\
\hline
H_{1,7} & 4.20 & +0.25 & 3.75 & +0.35 \\
H_{2,6} & 7.49 & +1.34 & 7.30 & +1.20 \\
H_{3,5} & 6.38 & +0.58 & 6.40 & +0.57 \\
H_{8,9} & 6.14 & +0.02 & 2.2 & +0.35 \\
\hline
\end{array}
\]
It is clear from comparison of the spectra of the two ions that the 4-hydroxybicyclo[5.2.0]nona-2,5,8-trien-4-ylium cation does not benefit from homoconjugative stabilization. The similarity between absorption positions of the hydroxypentadienyl hydrogens in the two cations, and the insignificant (0.02 p.p.m.) downfield shift of the olefinic cyclobutenyl absorption of the protonated trienone relative to that of the neutral ketone, indicate the complete absence of any through-space interaction in this species. The downfield shift exhibited by the bridgehead hydrogen nuclei of the trienylium cation XI must be due to an inductive effect rather than a diamagnetic ring current, since the corresponding hydrogens of the reference dienylium cation XVII show an even greater shift in resonance position. In the absence of a ring current effect, the positive charge densities on the observable carbon-hydrogen units in these two cations can be estimated from the measured value $\Delta \delta$, the change in chemical shift of the hydrogen resonance positions of the ketones upon protonation, using a proportionality constant of ten (14, 15). The total charge accommodated by the $\alpha$ and $\beta$ carbon atoms of the protonated trienone is calculated to be +0.38, and the same positions in the protonated dienone bear 35% of the total charge on the ion. Clearly, the protonated carbonyl group plays a dominant role in the stabilization of these ions, and such species are best viewed not as hydroxycarbonium ions, but as trivalent oxonium species, as suggested by Olah and Colin (199). The best opportunity for observation of bishomoaromaticity in this system would lie in the formation of the unsubstituted ion, which
might be accessible via protonation and dehydration of the alcohol related to VI, bicyclo[5.2.0]nona-2,5,8-trien-4-ol. Reduction of the carbonyl group of VI was expected to lead to bicyclo[6.1.0]nona-2,4,6-trien-9-ol, however, and this route was not explored.

An Attempt to Prepare a Bishomoaromatic Radical Anion

Although protonation of bicyclo[5.2.0]nona-2,5,8-trien-4-one led to a cation which was highly stabilized by oxygen substitution and was correspondingly unlikely to display bishomoaromatic character, the presence of carbonyl functionality in the molecule provided the means for a separate opportunity to observe through-space interaction within this system. One-electron reduction of the trienone VI was expected to lead to a radical anion, or ketyl, which might be observable by the electron spin resonance technique. Any appreciable overlap of the \( \pi \)-electron systems of the radical might result in the transfer of spin density to the cyclobutenyl moiety, which in turn would give rise to an observable splitting of the unpaired electron's spin-energy states. The e.s.r. spectrum of the ketyl could then be used to arrive at an estimate of the magnitude of any such overlap and to evaluate the degree of aromatic character of this seven-\( \pi \)-electron system in the relative absence of polar effects exerted by the oxygen atom. Homo-conjugation leading to homoaromaticity has been observed in an odd-electron species studied by Riecke et al. (200) and by Katz and Talcott (201).
Russell and Blankespoor (202) have reported one-electron reduction of several \(\alpha,\beta\)-unsaturated ketones in basic dimethylsulfoxide solution to give the corresponding ketyl's. Their procedure was used in an attempt to prepare the ketyl of bicyclo[5.2.0]nona-2,5,8-trien-4-one.

Solutions of trienone VI and of potassium t-butoxide in anhydrous, deoxygenated dimethylsulfoxide were prepared and pumped separately by motor-driven syringes into a quartz flow-cell which was designed to mix the two solutions and pass the resulting basic solution of the trienone into the microwave cavity of the e.s.r. spectrometer. No radical signal could be detected at the high flow rates (5-15 ml./sec.) reported by Russell and Blankespoor to be necessary for observation of the short-lived ketyl's which they studied. When the flow was stopped, however, a signal was observed which slowly reached a maximum intensity and subsequently disappeared. The optimal flow rate of the two solutions for production of this radical was determined to be a very low 0.018 ml./min. The spectrum recorded under these conditions (Figure 11, p. 174) was interpretable as a triplet of pentets of triplets, and was accurately simulated by
computer using hyperfine splitting constants (hfsc's) of 8.57 gauss (2H), 5.66 gauss (4H), and 0.51 gauss (2H). Splitting of the unpaired electron by four equivalent hydrogen atoms was inconsistent with the spectrum expected from the ketyl of the starting trienone, unless an extreme of delocalization had taken place. Further, the long reaction times necessary for the generation of this radical, and its stability once formed, were incompatible with the known behavior of simple cyclic conjugated ketyl and were suggestive of slow formation of a relatively stable species. Comparison of the measured hfsc's of the unknown radical to those of the ketyl of cycloheptatrienone (202) in the same medium revealed a close correspondence. This fact, together
with the known (203) high efficiency of hyperconjugative splitting in 
π-centered radicals and consideration of the experimental conditions, 
suggested that the observed radical might be the ketyl of bicyclo-
[5.2.0]nona-1(7),2,5-trien-4-one (XVIII), a known derivative of 
tropone.

The feasibility of a conversion of VI to XVIII was tested by 
addition of the yellow precursor to VI (VII) to a solution of po-
tassium t-butoxide in t-butanol under nitrogen. After stirring the 
mixture for one-half hour, water was added and the t-butanol was 
removed under reduced pressure. The aqueous residue was extracted with 
diethyl ether, and the n.m.r. spectrum of the ether-soluble components 
was recorded. The spectrum was complex, but did contain singlets at 
δ6.77 and δ2.90 of equal intensity, characteristic of the tropone 
derivative XVIII (186).

Bicyclo[5.2.0]nona-1(7),2,5-trien-4-one (4,5-dimethylenetropone) 
had been prepared by Fugiel (186) in 2% yield through the reaction of 
palladium chloride with bicyclo[5.2.0]nona-2,5-dien-4-one. It was 
felt that a more straightforward approach to introduction of the 
third double bond might be successful. Equimolar quantities of N-
bromosuccinimide and the dienone XVI were added to anhydrous carbon 
tetrachloride, and the mixture was heated to reflux with a General 
Electric sunlamp. The lamp was replaced by a standard infrared bulb, 
and reflux was continued until the brominating agent had been 
consumed. An excess of dry triethylamine was then added, and the 
mixture was heated for three hours more and cooled to room temperature.
Filtration, evaporation of the solvent, and sublimation of the oily residue gave a yellow solid. This was taken up in diethyl ether and deposited on an alumina preparative thin layer plate. Development with diethyl ether produced three well-defined bands, which were extracted and identified as succinimide, the starting dienone XVI, and dimethylenetropone XVIII. The product was recrystallized from diethyl ether at -78° and sublimed to give the pure tropone, m.p. 120-121, in 57% yield.

\[
\begin{align*}
\text{O} & \quad \text{1) NBS} \\
\text{1} & \quad \text{O} \\
\text{2) N(Et)}_3 & \quad 57%
\end{align*}
\]

Dry, deoxygenated dimethylsulfoxide solutions of 4,5-dimethylene tropone and potassium t-butoxide were prepared and pumped separately into the e.s.r. mixing cell. A radical spectrum was observed which duplicated that obtained from bicyclo[5.2.0] nona-2,5,8-trien-4-one exactly (Figure 11, p. 174).
Figure 11. Electron Spin Resonance Spectra (±25 gauss)

Top: Spectrum obtained from bicyclo[5.2.0]nona-2,5,8-trien-4-one (VI)

Middle: Computer simulation: 8.57 gauss (2H), 5.66 gauss (4H), 0.51 gauss (2H), linewidth 0.25 gauss

Bottom: Spectrum obtained from bicyclo[5.2.0]nona-1(7),2,5-trien-4-one (XVIII)
In light of the production of tropone XVIII by base in t-butanol, a non-reducing medium, it would appear that the ketyl of this ketone is produced from trienone VI by a base-catalyzed isomerization followed by reduction of the tropone derivative to its radical anion, rather than arising from an initially formed ketyl of VI. Electrolytic reduction of trienone VI to its radical anion was not investigated.

4,5-Bis(methylene)cyclohepta-2,6-dien-1-one,

a p-Tropoquinone Dimethide

The ready availability of the 4,5-tropocyclobutene XVIII prompted a reinvestigation of its electrocyclic reactivity. This molecule is of interest as a potential precursor to 4,5-bis(methylene)cyclohepta-2,6-dien-1-one (XIX), an analog of o-xylene in the tropone system. This exocyclic diene might be of synthetic value in the construction of bicyclo[5.4.0] systems by Diels-Alder reactions, or of bicyclo[5.3.0] skeletons through nucleophilic conjugate addition to the two dienone moieties present in the molecule.
Fugiel (186) has reported that flash vacuum pyrolysis of tropone XVIII and condensation of the pyrolysate onto a sodium chloride window at 77K allowed infrared observation of a species proposed to be the ring-opened product XIX. This labile ketone was found to decompose above -100°C, and attempts to chemically intercept the intermediate with methanol or with N-phenylmaleimide failed.

Ito and co-workers have recently reported the preparation of both the ortho- and para-tropoquinones (204, 205) by DDQ oxidation of the corresponding hydroxytropolones. The para isomer was isolable as a

\[ \text{CHCl}_3 \]

I.R. 1672, 1650, 1613, 1395, 1385, 1174, 1071, 868, 668 cm\(^{-1}\)

m.p. 52-53°C
stable, crystalline solid, m.p. 52-53°, contrasting sharply with the reactivity of the intermediate observed by Fugiel.

The availability of the equipment necessary for matrix isolation of reactive intermediates and for observation of their infrared and ultraviolet spectra was exploited in an attempt to confirm the identity of the thermolysis product of 4,5-tropocyclobutene.

A sample of bicyclo[5.2.0]nona-1(7),2,5-trien-4-one XVIII was sublimed at room temperature and co-deposited with argon onto a cesium iodide window cooled to 20K. The infrared absorption spectrum of the matrix-isolated ketone consisted of bands at 3020, 2970, 2955, 2840, 1636, 1587, 1560, 1548, 1442, 1430, 1412, 1315, 1215, 1205, 1180, 1148, 868, 862, 807, 770, and 660 cm$^{-1}$ (Figure 12, p. 181). The spectrum also exhibited evidence of water contamination (3800-3400 and 1630-1600 cm$^{-1}$) and the presence of volatile silicones evaporated from the vacuum fittings of the apparatus (1262 cm$^{-1}$, sharp, 1075 cm$^{-1}$, broad).

The photochemical response of the tropone XVIII under these conditions was next examined. Fugiel (186) had reported that thirty minutes' irradiation through Pyrex of a thin film of the neat ketone at 77K followed by an hour's unfiltered mercury arc irradiation produced no observable changes in the infrared spectrum. Irradiation of an argon matrix containing the tropone at 8K through a Corning F-12 filter ($\lambda >3100$ Å) for three hours resulted in the production of four weak absorption bands at 2120, 1720, 1660, and 645 cm$^{-1}$. Nine hours' more irradiation at these wavelengths produced no further changes in
intensity or absorption position. The filter was removed, and irra-
diation (\( \lambda > 2000 \text{ Å} \)) was continued for three more hours, after which
the spectrum was unchanged except for diminution of the bands produced
by the longer wavelength light.

This behavior is consistent with either photochemical reaction
and subsequent destruction of an impurity in the starting material or
with the establishment of a wavelength-dependent steady-state distri-
bution of isomerization products of tropone XVIII. The latter process
would be the more interesting, of course, but in the absence of
further evidence no conclusion can be drawn. Nevertheless, a scheme
can be proposed which is consistent with the known details, and which
involves two unusual molecules which might be thermally stable at 8K.
The ring-closure of cycloheptatrienes to bicyclo[3.2.0] systems is a

\[
\begin{array}{ccc}
\text{K} & \xleftrightarrow{h\nu} & \text{K} \\
\text{Cycloheptatriene} & \text{Bicyclo[3.2.0]} & \text{Cyclopropyl ketene}
\end{array}
\]

\(1720, 1660 \text{ cm}^{-1}\) \(2160 \text{ cm}^{-1}\)

well-known reversible photochemical process, and the rearrangement of
bicyclo[3.2.0]hepta-3,6-dien-2-ones to cyclopropyl ketenes has prece-
dent (206). In any case, this phenomenon was not further investigated,
since the major conclusion drawn from this experiment was that unfil-
tered mercury arc radiation did not effect any substantial change in sample composition, and did not promote ring opening of the cyclobutene XVIII.

The flash pyrolyses were carried out by sublimation of a sample of tropone XVIII at room temperature through a quartz tube which was electrically heated by a coil of nichrome wire. The pyrolysis temperature was monitored by means of a thermocouple placed inside of the tube at the center of the area covered by the heating coil. The effluent from the oven was co-deposited with argon onto a cesium iodide window cooled to 20K. An oven temperature of 620°C was found to be optimal for production of the intermediate, conversion efficiencies of greater than 90% (i.r.) being obtainable.

The infrared spectrum (Figure 12, p. 181) of an argon matrix of the pyrolysate consisted of absorption bands at 3020, 2970, 2940, 2680, 1648, 1636, 1584, 1560, 1548, 1430, 1372, 1318, 1252, 1214, 1180, 1148, 1030, 919, 910, 870, 862, 810, 770, 721, 660, 630, 525, and 410 cm\(^{-1}\). This matrix was irradiated with an unfiltered mercury arc for a total of sixty-two hours, during which time the bands at 1648, 1584, 1430, 1372, 1252, 1146, 918, 910, 721, 630, 525 and 410 cm\(^{-1}\) slowly disappeared. The spectrum obtained after complete destruction of the intermediate (Figure 12, p. 181) was composed of the bands characteristic of the starting tropocyclobutene XVIII and additional absorption at 2342 and 660 cm\(^{-1}\), due to carbon dioxide from atmospheric leakage, and at 2140 cm\(^{-1}\), due to carbon monoxide, probably produced in a minor photochemical process during the lengthy irradiation.
Figure 12. Matrix-Isolated Infrared Spectra (Argon, 8K)

- Top: Bicyclo[5.2.0]nona-1(7),2,5-trien-4-one (XVIII)
- Middle: Product of pyrolysis of XVIII at 620°C (XIX)
- Bottom: Product of pyrolysis of XVIII at 620°C followed by 62 hours' unfiltered mercury arc irradiation at 8K
Substitution of sapphire for cesium iodide as the window material enabled the observation of the ultraviolet spectrum of tropocyclobutene XVIII and of its thermolysis product matrix-isolated in argon. The ultraviolet absorption spectrum of bicyclo[5.2.0]nona-1(7),2,5-trien-4-one in 95% ethanol has been reported (186) to consist of maxima at 2280 Å (log ε 4.28), 3100 Å (3.96), and 3210 Å (shoulder, 3.89). The spectrum of the tropone in an argon matrix (Figure 13, p. 184) consisted of maxima at 2200, 3085, and 3200 Å. Scattering of the analyzing beam by the matrix material produced a baseline which rose gradually as the wavelength decreased. The ultraviolet spectrum of the matrix-isolated thermolysis product (Figure 13, p. 184), produced in the manner described previously, consisted of a maximum at 2288 Å, a shoulder at 2650 Å, and featureless, smoothly decreasing absorption to 4000 Å. Irradiation of this matrix with an unfiltered mercury arc led to the disappearance of these features and the generation of a spectrum which was superimposable upon that of the starting tropocyclobutene XVIII (Figure 13, p. 184).

\[
\text{O} \quad \overset{620^\circ}{\text{h} \nu} \quad \overset{\text{I.R. 1648, 1584, 1430, 1372, 1318, 1252, 1146, 918, 910, 862, 721, 630, 525, 410 \text{ cm}^{-1}}}{\text{O}} \quad \overset{\text{Ar}}{\text{U.V. } \lambda_{\text{max}} 2285, 2650 \text{ Å (shoulder)}}
\]
Figure 13. Matrix-Isolated Ultraviolet Spectra (Argon, 8K)

Top: Bicyclo[5.2.0]nonya-1(7),2,5-trien-4-one (XVIII)

Middle: Product of pyrolysis of XVIII at 620°C (XIX)

Bottom: Spectra obtained during irradiation of the matrix containing XIX with an unfiltered mercury arc
The observed infrared spectrum of the intermediate is completely consistent with that expected of 4,5-bis(methylene)cyclohepta-2,6-dien-1-one (XIX). The more intense absorptions can be assigned to the carbonyl stretching mode (1584 cm⁻¹), the carbon-carbon double bond stretch (1648 cm⁻¹), terminal methylene wagging (918, 910 cm⁻¹), and the olefinic carbon-hydrogen stretching mode (862 cm⁻¹). The ultraviolet spectrum is consistent with that expected of a 4-methylene cyclohept-2-en-1-one, and displays no special characteristics. The failure to observe an n-π* transition during the experiment may have been due to masking of this absorption by unconverted starting material, since the transitions of the tropone derivative in the 3000-3300 Å region are particularly intense.

Interception of the intermediate by chemical reaction was attempted, relying upon the expected ease of nucleophilic addition to such a system and upon the anticipated reactivity of the exocyclic diene moiety toward Diels-Alder addition. Two preparative thermolyses were carried out in a manner exactly analogous to the procedure used for spectroscopic identification of the intermediate except that the argon was replaced by either methanol or ethyl vinyl ether and approximately ten milligrams of the tropocyclobutene XVIII was sublimed through the pyrolysis oven. After the sample had been completely consumed (50-60 hrs.), the oven was cooled and the solid mixture of thermolysate and trapping agent was allowed to warm to room temperature under an atmosphere of methanol or ethyl vinyl ether. The apparatus was disassembled and the products were removed from the cold
finger by washing with chloroform. In each experiment a substantial amount of yellow, insoluble polymer was formed.

The chloroform-soluble portion of each product mixture was examined by n.m.r., and alkoxy resonance was not detected in either spectrum, although the mixtures appeared to be similarly constituted. Thin-layer chromatographic analysis showed the presence of the same two major components in each sample. The product mixture from the methanol trapping experiment was separated on a column of grade III neutral alumina developed with chloroform to give bicyclo[5.2.0]nona-1(7),2,5-trien-4-one (3 mg.), identified by its n.m.r. spectrum, and a pale yellow oil (4 mg.) which displayed a complex n.m.r. spectrum and gave a parent ion in its mass spectrum at m/e 264. The product mixture from the ethyl vinyl ether trapping experiment appeared to consist of the same two compounds by n.m.r., so the combined product of both runs was chromatographed on a grade III alumina column developed with a mixture of 35% diethyl ether and 65% chloroform, which gave an improved separation. A total of seven milligrams of the pale yellow oil was obtained which appeared to be homogeneous by t.l.c., and which polymerized rapidly when neat. This material was identified by its spectra and its mode of formation as 4'-methylene-spiro[bicyclo[5.4.0]undec[1(7),2,5]triene-9,5'-cyclohepta[2',6']diene]-4,1'-dione (XX), a Diels-Alder dimer of 4,5-bis(methylene)cyclohepta-2,6-dien-1-one (XIX). Elemental analysis and the determination of an exact mass of its parent ion were precluded by its reactivity, low volatility, and sensitivity toward heat.
The infrared spectrum of the dimer in carbon tetrachloride solution (Figure 14, p. 189) included absorption bands at 3050, 2923, 1645, 1614, 1575, 1522, 1458, 1440, 1402, 1310, 1275, 1205, 1100, 917, 859, and 715 cm\(^{-1}\). Of these, the bands at 1614 and 1522 cm\(^{-1}\) can be assigned to the cycloheptatrienone moiety, the bands at 1645 and 1575 cm\(^{-1}\) can be assigned to the conjugated dienone, and absorption at 917 cm\(^{-1}\) is ascribed to wagging of the terminal methylene group.

The ultraviolet absorption spectrum of the dimer in diethyl ether solution consists of maxima at 2284 Å (log \(\varepsilon\) 4.39), 2650 Å (shoulder, 3.98), and 3045 Å (4.04), corresponding to a superposition of tropone and 4-methylene cyclohept-2-en-1-one absorptions.

The n.m.r. spectrum of the dimer in deuterochloroform (Figure 14, p. 189) was completely analyzed with the aid of shift reagent and
Figure 14: 4′-Methylenespiro[bicyclo[5.4.0]undec[1(7),2,5]triene-9,5′-cyclohepta[2′,6′]dienes]-4,1′-dione (XX)

Top: Nuclear magnetic resonance spectrum (CDCl₃, 100 MHz)

Bottom: Infrared spectrum (CCl₄)
decoupling experiments, and consists of a multiplet at $\delta 6.95-6.75$ ($H-2,3,5,6,6$), a doublet at $\delta 6.31$ ($H-3$), a broadened doublet at $\delta 6.15$ ($H-7$), a doublet of doublets at $\delta 6.06$ ($H-2$), singlets at $\delta 5.42$ and $\delta 5.38$ (terminal methylene), a broad singlet at $\delta 3.03$ ($CH_2-8$), a multiplet at $\delta 2.7$ ($CH_2-11$), and a multiplet at $\delta 2.05$ ($CH_2-10$). Coupling constants were determined to be as follows; $J_{5,6} = J_{2,3} = 13$ Hz, $J_{7-6} = J_{2-3} = 12$ Hz, and $J_{2-7} = 2$ Hz. The unusually low field absorption position of $H-6$ deserves comment, and undoubtedly occurs as an effect of the anisotropy of the nearby tropone system.

The mass spectrum of this compound contains peaks at $m/e$ 265 (relative intensity 21), 264 (parent, 100), 252 (14), 248 (11), 236 (17), 208 (13), 193 (23), 180 (14), 158 (26), 157 (96), 133 (16), 132 (53), 130 (19), 129 (25), 108 (32), 104 (32) and 87 (12), with a metastable ion appearing at $m/e$ 93.3. The magnitude of the $P + 1$ peak is in good agreement with that calculated for a parent ion of composition $C_{16}H_{16}O_2$, 19.79 (207). The major peaks in this spectrum can be accounted for by a fragmentation scheme involving quite reasonable processes.

The isolation of this dimer, which is structurally related to that formed at low temperatures from o-xylene (208), firmly establishes the identity of the species observed in the matrix isolation studies as 4,5-bis(methylene)cyclohepta-2,6-dien-1-one, and establishes a parallel in reactivity between the quinones and quinone methides of the benzenoid and troponoid systems.
EXPERIMENTAL

General

Melting points were determined by use of a Thomas-Hoover "Uni-Melt" capillary melting point apparatus calibrated between 80° and 240° against a set of standards provided by the Arthur H. Thomas Co., and are estimated to be accurate within 0.5°. Boiling points are uncorrected. Some purifications were performed by microdistillation in a Hickman still, and since liquid-vapor equilibrium is not always attained in this apparatus only distillation pressure and temperature are reported. Microanalyses were performed by Galbraith Laboratories or Chemalytics, Inc. Preparative vapor phase chromatography was carried out using a Varian-Aerograph Model 920 instrument. Infrared spectra were recorded on Beckman IR-12 or IR-4250 spectrometers. Absorption frequencies reported are estimated to be accurate to within 3 cm⁻¹. Nuclear magnetic resonance spectra were obtained using the Hitachi Perkin-Elmer model R20-B, and Varian models A-60, T-60 or HA-100 spectrometers. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane at δ0.0. Coupling constants are reported in Hertz. Estimated errors in the reported values are 0.05 ppm and 0.5 Hz respectively. Ultraviolet spectra were obtained using the Cary 14 or Beckman Acta CV spectrometers. Errors in reported absorption maxima and molecular absorptivity are estimated to be 5 Å and 1.5%, respectively. Mass spectra were determined using Atlas CH-4 or Associated Electrical Industries MS-9 spectrometers at an energy of
Preparation of trans-7,8-dibromobicyclo[4.2.0]octa-2,4-diene

The procedure followed was adapted from that of Cope and Burg (209). A 1 liter round-bottomed flask was fitted with a low temperature thermometer, a 125 mL pressure-equalizing dropping funnel, a distillation adapter carrying a nitrogen inlet, and a magnetic stirring bar. The apparatus was purged with nitrogen, and dichloromethane (350 mL) was distilled into the flask. Cyclooctatetraene (10.0 g, 0.096 mole) was added to the dichloromethane and the flask was immersed in a chloroform-Dry ice cooling bath. When the solution had cooled to -55°C, a solution of bromine (16.0 g, 0.10 mole) in dichloromethane (75 mL) was transferred to the dropping funnel against a flow of nitrogen. The room lighting was dimmed, and the bromine solution was added at a rate adjusted so as to maintain the reaction temperature at -50°C. The cooling bath was removed, and the pink solution was allowed to warm to room temperature. Solid sodium bicarbonate was added to the stirring solution, and the colorless reaction mixture was filtered into a 1 liter round-bottomed flask. The solvent was removed in vacuo at 25°C, and the residual oil was transferred to a 25 mL addition funnel mounted on a 50 mL round-bottomed flask which was fitted with a magnetic stirring bar, a glass stopper, and a short path distillation head carrying a thermometer and a 50 mL collection flask. The distillation flask was immersed in an oil bath maintained at 90°C, and oil pump vacuum was applied to the apparatus. The pressure in the addition
funnel was adjusted with a manostat to 20 Torr in order to facilitate control of the rate of addition. The addition funnel and the upper portion of the distillation head were wrapped loosely with aluminum foil, and the apparatus was heated from above by an infrared lamp. The receiver was immersed in an ice-water bath and dropwise addition of the crude dibromide was begun. The rate of addition was continuously adjusted to equal the rate of distillation. The product distilled between 70° and 85° at pressures ranging between 0.1 and 0.5 Torr and was collected as a colorless oil which solidified rapidly in the receiver (24.0 g, 92%). Infrared and n.m.r. spectra were as reported (188). The dibromide was stored under nitrogen at -30° to avoid decomposition.

Preparation of trans-6,7-dibromo-(cis,exo,-and trans-)2,4-diethoxy-3-oxabicyclo[3.2.0]heptane (I)

A 250 mL round-bottomed flask was fitted with a magnetic stirring bar, a 25 mL dropping funnel, a low temperature thermometer and a gas inlet-outlet tube. The inlet tube extended nearly to the bottom of the flask and was flame polished. All joints were carefully greased and a solution of trans-7,8-dibromobicyclo[4.2.0]octa-2,4-diene (10.0 g, 0.038 mole) in dry dichloromethane (75 mL) was introduced into the flask. Absolute ethanol (10 mL) was added to the solution, the flow of dry oxygen from a Welsbach Laboratory Ozonator, Model T-408, was adjusted to 0.045 s.c.f.m., and the oxygen line was connected to the gas inlet tube. The reaction vessel was lowered into an acetone-Dry ice
cooling bath, stirring was begun, and the electrical discharge of the ozonator was turned on. Addition of ozone was allowed to continue at -78° until the solution had taken on a deep blue color. The ozone generation was stopped, and the ozone inlet line was replaced by a dry nitrogen line. Nitrogen was bubbled through the solution for 15 minutes to displace the excess ozone. The addition funnel was charged with triethyl phosphite (13.3 mL, 0.076 mole), and the dropwise, exothermic addition was carried out below -40°. The solution was allowed to warm to 0° and tested with moist potassium iodide-starch paper to ensure removal of all peroxides. Triethyl orthoformate (16.9 g, 0.114 mole) was added to the solution through the dropping funnel and solid p-toluenesulfonic acid monohydrate was added to the reaction mixture until the solution indicated pH 2 to test paper. The solution was allowed to stir for 12 hours under nitrogen. The clear, colorless solution was transferred to a 1 liter round-bottomed flask containing solid sodium bicarbonate (10.0 g), and the solvent was removed in vacuo at 30°. The residue was stirred vigorously with saturated sodium bicarbonate solution for ten minutes. The aqueous layer was decanted through filter paper, and the process was repeated three times with distilled water. The filter paper was extracted with diethyl ether, and the extract was returned to the flask. The ether was removed in vacuo at aspirator pressure, and the rotary evaporator was connected to an oil pump. Distillation was continued at 45°, 1 Torr, until no more 1,1,2,2-tetraethoxy ethane could be seen collecting on the cooling coils. The residue remaining in the flask was dissolved in a minimum
amount of carbon tetrachloride and subjected to column chromatography
on grade III neutral alumina (350 g), developed with a 1:1 mixture of
carbon tetrachloride and hexane. The composition of the eluant was
monitored by the t.l.c., which showed two overlapping bands due to the
desired products well separated from some residual 1,1,2,2-tetraethoxy-
ethane. The product-bearing eluant was concentrated to give the white,
semi-crystalline mixture of isomers of I (10.5 g, 81%) in approximately
equal proportions. The leading and tailing edges of the product-
containing band could be collected and reduced in volume to give the
two isomers as a liquid and a solid. The liquid fraction was micro-
distilled (90°, 0.01 Torr) to give endo-6-exo-7-dibromo-endoe-2-exo-4-diethoxy-3-oxabicyclo[3.2.0]heptane (It) as a colorless oil: n.m.r.
(Figure 1, p. 104) (CDCl₃) δ1.1-1.4 (2t, 6H), 3.0-4.2 (m, 6H), 4.70-
4.85 (m, 2H), 5.3 (d, J = 4.5 Hz, 1H), 5.4 (s, 1H); ir (CCl₄) 2970,
2910, 2870, 1480, 1443, 1375, 1355, 1295, 1245, 1220, 1200, 1180, 1150,
1130, 1100, 1075, 1050, 990, 895, 840 cm⁻¹.

The solid isomer was recrystallized from 30% aqueous acetone to
give trans-6,7-dibromo-cis,exo-2,4-diethoxy-3-oxabicyclo[3.2.0]heptane
(Ic) as colorless needles, m.p. 112-113°: n.m.r. (Figure 1, p. 104)
(CDCl₃) δ1.22 (t, 6H), 3.2-4.25 (m, 7H), 4.6-4.9 (m, 1H), 5.13 (s, 1H),
5.50 (s, 1H), ir (CCl₄) 2990, 2940-2885, 1375, 1347, 1322, 1290, 1225,
1204, 1157, 1120, 1076, 1035, 965, 922, 887, 682 cm⁻¹; mass spectrum,
m/e (relative intensity) 342.1 (metastable), 342 (1), 341 (2), 340 (1),
300 (12), 299 (25), 298 (12), 271 (4), 270 (9), 269 (6), 192 (3), 191
(30), 190 (3), 189 (30), 163 (12), 161 (14), 135 (5), 133 (5), 110 (11),
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109 (7), 103 (10), 85 (4), 83 (10), 82 (40), 81 (100), 75 (5), 65 (10), 58 (10), 55 (7), 53 (28). Only the cis isomer was subjected to combustion analysis.

Anal. Calcd. for C_{10}H_{16}O_{3}Br_2: C, 34.88; H, 4.65; Br, 46.51.

Found: C, 35.21; H, 4.83; Br, 46.69.

Preparation of cis,exo- and trans-2,4-diethoxy-3-oxabicyclo[3.2.0]hept-6-enes (II)

The mixture of dibromoacetals (I) (18.0 g, 0.052 mole) was transferred to a 1 liter round-bottomed flask. Dry tetrahydrofuran (800 mL) was distilled into the flask under dry nitrogen. A magnetic stirring bar, zinc powder (6.0 g, 0.092 mole) and iodine (1.0 g, 0.004 mole) were added and the mixture was stirred at reflux under nitrogen for 16 hours. The reaction was monitored by thin-layer chromatography, which showed that the two isomers of starting material had been converted to two new compounds after this period. The reaction mixture was allowed to cool, and the solvent was removed in vacuo at 20°. Solid sodium bicarbonate (15.0 g, 0.18 mole), distilled water (100 mL) and diethyl ether (100 mL) were added to the residue, and the mixture was stirred vigorously for five minutes. The resulting suspension was filtered under vacuum through a medium porosity sintered glass funnel, and the filter cake was washed with three 50 mL portions of diethyl ether. The filtrate was saturated with sodium chloride, and the layers were separated. The organic layer was dried with anhydrous sodium sulfate, filtered, and the solvent was removed in vacuo with no external
heating. The greenish oil remaining was microdistilled (45°, 10-2 Torr) to give the mixture of unsaturated acetals (II) (8.7 g, 91%) as a colorless oil. The isomers were separated by preparative vapor phase chromatography (10% carbowax 20 M on Chromosorb W, 120°).

**Trans-2,4-dioxy-3-oxabicyclo[3.2.0]hept-6-ene (IIt)** was isolated as a colorless oil with a very faint odor: n.m.r. (Figure 2, p. 108) (CDCl₃) δ 1.20 (t, 3H), 1.23 (t, 3H), 3.16-4.13 (m, 6H), 4.90 (s, 1H), 5.07 (d, J = 5 Hz, 1H), 6.14 (s, wiggle beat, 2H); ir (CCl₄) 3070, 3035, 2980, 2910, 2880, 1560, 1380, 1360, 1335, 1320, 1298, 1280, 1250, 1172, 1120, 1105, 1090, 1050, 995, 982, 865, 840, 690 cm⁻¹. **Cis,exo-2,4-dioxy-3-oxabicyclo[3.2.0]hept-6-ene (IIc)** was isolated as a colorless oil with a pronounced sweet odor: n.m.r. (CDCl₃) δ 1.18 (t, 6H), 3.15-4.05 (m, 6H), 4.97 (s, 2H), 6.07 (s, wiggle beat, 2H); ir (CCl₄) 3140, 3060, 2990, 2905, 2800, 1560, 1495, 1380, 1350, 1290, 1160, 1122, 1080, 1055, 970, 930, 890, 860 cm⁻¹; mass spectrum, m/e (relative intensity) 184 (parent, 1), 140 (2), 139 (20), 138 (2), 131 (4), 111 (9), 110 (24), 109 (5), 108 (A), 107 (20), 105 (4), 103 (5), 91 (5), 83 (50), 82 (63), 81 (27), 79 (5), 77 (7), 75 (4), 70 (6), 65 (9), 60 (6), 59 (100), 55 (15), 54 (10), and 53 (22). Only the cis isomer was subjected to combustion analysis.

**Anal. Calcd. for C₁₀H₁₆O₃:** C, 65.22; H, 8.70.

**Found:** C, 65.12; H, 8.70.
Preparation of cis,exo- and trans-2,4-diethoxy-3-oxabicyclo[3.2.0]-heptanes (XII)

The mixture of 2,4-diethoxy-3-oxabicyclo[3.2.0]hept-6-enes (II) (7.5 g, 0.041 mole) was dissolved in absolute ethanol (100 mL) and hydrogenated over 10% palladium on carbon at atmospheric pressure in the presence of sodium bicarbonate (0.2 g). Uptake of hydrogen was rapid, and ceased after the consumption of 940 mL (0.042 mole, uncorrected for ethanol vapor pressure) of gas. Filtration and removal of solvent in vacuo followed by microdistillation (50°, 0.5 Torr) gave the epimeric cyclobutane acetals (XII) (7.5 g, 99%) as a colorless oil: n.m.r. (CDCl₃) 61.0-1.4 (3t, 6H), 1.5-2.4 (m, 4H), 2.6-3.1 (m, 2H), 3.2-4.1 (m, 4H), (5.0 (s, cis), 4.86 (s, trans), 5.22 (d, J = 5 Hz, trans) (2H)); ir (CCl₄) 2980, 2935, 2895, 1375, 1350, 1180, 1105, 1100, 1075, 1045, 975, 960, 885 cm⁻¹; mass spectrum, m/z (relative intensity) 186 (parent, 5), 143 (12), 142 (95), 141 (5), 114 (50), 113 (35), 112 (50), 103 (52), 98 (10), 97 (7), 96 (100), 85 (60), 84 (100), 83 (97), 82 (15), 81 (7), 75 (36), 71 (12), 69 (22), 68 (27), 67 (100), 66 (20), 65 (11), 59 (9), 58 (9), 57 (76), 56 (58), 55 (98), 54 (9), 53 (20), 47 (62).

Preparation of 10-methyl-10-azatricyclo[4.3.1.0²⁵]dec-3-en-8-one (III)

The mixture of cyclobutene acetals (II) (4.50 g, 0.025 mole) was stirred vigorously with 1 N sulfuric acid (50 mL) at 35° until a homogeneous solution resulted. This solution was added to a slowly stirred
solution of 3-oxoglutaric acid (7.3 g, 0.05 mole), methylamine hydrochloride (3.4 g, 0.06 mole) and potassium dihydrogen phosphate (7.1 g, 0.05 mole) in distilled water (950 mL). The pH of the solution was adjusted to 5.5 by careful addition of solid potassium carbonate, and the solution was allowed to stir for 72 hours. At the end of this period the pH of the solution was raised to 10 with solid potassium carbonate. The solution was saturated with sodium chloride and continuously extracted with diethyl ether for 48 hours. The organic extract was transferred to a sublimator and the solvent was evaporated by passage of a stream of dry nitrogen over the surface. The residue was sublimed (50°, 0.01 Torr) to give yellow, oily crystals. The sublimate was dissolved in anhydrous ether (50 mL) and cooled slowly to -78°. When crystallization was complete, the supernatant liquid was drawn off and the crystals were washed at -78° with another portion of dry ether. This was also drawn off, and the crystals were warmed to room temperature in vacuo. The mother liquor and washings were combined and concentrated to give a second crop of solid. The mother liquor and wash from the second crystallization were concentrated, and the residue was subjected to column chromatography on grade IV basic alumina, developed with hexane. The eluant was monitored by thin layer chromatography, and the product-containing fractions were combined with the recrystallized solid. The combined product was sublimed once more (50°, 0.01 Torr) to give 10-methyl-10-azatricyclo[4.3.1.0²5]dec-3-en-8-one (III) (2.5 g, 66%), m.p. 122.5-123.5°. N.m.r. (Figure 3, p. 112) (CDCl₃) δ1.8-3.0 (m,
4H), 2.70 (s, 3H), 3.06 (s, 2H), 3.2-3.4 (m, 2H), 6.00 (s, 2H), ir (Figure 3, p. 112) (CCl₄) 3122, 3045, 2930, 2840, 2790, 1715, 1565, 1455, 1411, 1349, 1341, 1318, 1305, 1285, 1240, 1215, 1178, 1160, 1138, 1098, 1002, 956, 860, 575 cm⁻¹; mass spectrum, m/e (relative intensity) 164 (9), 163 (parent, 16), 135 (5), 134 (4), 121 (7), 120 (25), 111 (8), 110 (100), 107 (5), 106 (8), 95 (7), 94 (58), 82 (10), 81 (7), 80 (9), 79 (19), 78 (11), 77 (15), 70 (7), 69 (5), 68 (6), 67 (5), 66 (5), 65 (7); uv (ethanol) 241 (log ε 2.9).

Anal. Calcd. for C₁₀H₁₃NO: C, 73.62; H, 7.98; N, 8.59;

Found: C, 73.37; H, 7.88; N, 8.79.

Preparation of 10-methyl-10-azatricyclo[4.3.1.0²⁵]decan-8-one (XIII)

The mixture of cyclobutane acetals (XII) (4.5 g, 0.024 mole) was treated exactly as described for the unsaturated analog to give the saturated amino ketone (XIII) (2.3 g, 56%), m.p. 89-90°, with n.m.r. and i.r. spectra identical to those reported by Fugiel (186).

Preparation of 10-methyl-7,7,9,9-tetradeutero-10-azatricyclo[4.3.1.0²⁵]-dec-3-en-8-one (IIIId)

The amino ketone (III) (2.0 g, 0.012 mole) was added to a 50 mL round-bottomed flask containing deuterium oxide (25 mL, 99.5% D), sodium carbonate (0.5 g, 0.005 mole) and a magnetic stirring bar. The flask was stoppered, and the solution was allowed to stir for 30 minutes. The liquid was removed in vacuo (5 Torr, 20°) and replaced with fresh deuterium oxide (25 mL). This cycle was repeated
once more. The third portion of deuterium oxide was removed, and the labeled aminoketone was collected by bulb-to-bulb sublimation from a heated air bath (80°, 0.1 Torr) (1.95 g, 97%). N.m.r. analysis indicated that the labeled aminoketone was greater than 95% d4: n.m.r. (CCl4) δ2.60 (s, 3H), 2.92 (s, 2H), 3.10 (s, 2H), 5.75 (s, 2H).

Preparation of 10,10-dimethyl-10-azoniatricyclo[4.3.1.0^2,5]dec-3-en-8-one p-toluenesulfonate (IV)

The unsaturated amino ketone (III) (2.0 g, 0.012 mole) was added to a magnetically stirred melt of methyl p-toluenesulfonate (15 mL, m.p. 28-29°) in a 100 mL round-bottomed flask. The flask was stoppered and stirred at 30° until the amino ketone had dissolved. The solution was then heated to 75° in an oil bath and maintained at that temperature for three hours. The reaction mixture was allowed to cool to room temperature and dry tetrahydrofuran (80 mL) was distilled into the flask under nitrogen. The reaction mixture was stirred vigorously until all lumps had been broken up. The resulting suspension was filtered under nitrogen, and the crystals were washed with three portions of dry diethyl ether. The solid was dried under a stream of dry nitrogen to give the quaternary tosylate as hygroscopic colorless crystals (IV) (4.1 g, 94%), m.p. 192-193 (dec.): n.m.r. (D2O) δ7.7 (d, J = 9 Hz, 2H), 7.4 (d, J = 9 Hz, 2H), 6.3 (s, 2H), 4.2 (m, 2H), 3.6 (s, 6H), 3.35 (s, 2H), 2.6-3.8 (m, 6H), 2.15 (s, 3H).

Anal. Calcd. for C_{18}H_{25}NO_{4}S: C, 61.89; H, 6.59; N, 4.01; S, 9.17.

Found: C, 61.76; H, 6.67; N, 3.99; S, 9.67.
Preparation of 10,10-dimethyl-7,7,9,9-tetradueto-10-azoniatricyclo-
[4.3.1.0^2,5]dec-3-en-8-one tosylate (IVd)

A procedure identical to that used for the preparation of IV gave
the labeled quaternary tosylate (IVd), m.p. 184-188°, in 88% yield.

Preparation of 10,10-dimethyl-10-azoniatricyclo[4.3.1.0^2,5]decan-8-one
tosylate (XIV)

The saturated amino ketone (XII) (2.0 g, 0.012 mole) was treated
exactly as described for the unsaturated analog, except that the
reaction time was extended to 60 hours, to give the quaternary tosylate
(XV) (3.75 g, 88%), m.p. 187-188° (dec.), with n.m.r. and i.r. spectra
identical to those of material prepared by Fugiel (186).

Preparation of 2,6-bis(trimethylammonio) bicyclo[5.2.0]non-8-en-4-one
diiodide (VII)

The unsaturated quaternary tosylate (IV) (4.0 g, 0.012 mole) was
added against a flow of dry nitrogen to anhydrous dimethylamine (40 mL)
at -10° in an 80 mL tubular flask equipped with a nitrogen inlet, a
sidearm terminated by a 14/35 standard taper inner joint and a magnetic
stirring bar. The mixture was stirred at 0° until a colorless
solution resulted. The excess dimethylamine was removed under vacuum
at 0°, and then anhydrous diethyl ether (75 mL) was distilled into
the flask. The viscous residue was stirred vigorously during the
addition of the ether and colorless crystals began to separate as the
liquid diamine dissolved. Stirring was continued until the solid
appeared to be free of the oily diamine and did not adhere to the walls of the flask. The mixture was filtered under nitrogen pressure into a 200 mL round-bottomed flask containing a magnetic stirring bar. The filter cake and the reaction flask were washed twice with dry diethyl ether (20 mL). Iodomethane (15 mL, 0.24 mole) was added to the combined filtrate and washings, and the solution was stirred for 12 hours in the dark under nitrogen. The suspension produced was filtered and washed with dry diethyl ether under nitrogen and dried in a stream of nitrogen to give the bis-quaternary diiodide (VII) (6.0 g, 103%) as a hygroscopic pink powder.

**Preparation of 2,6-bis(trimethylammonio)-4-oxabicyclo[5.2.0]nonane diiodide (XV)**

The saturated quaternary tosylate XIV (3.5 g, 0.010 mole) was treated exactly as described for the unsaturated analog to give the bis-quaternary diiodide XV as a hygroscopic yellow powder (5.25 g, 105%).

**Attempted preparation of bicyclo[5.2.0]nona-2,5,8-trien-4-one (VI) by steam distillation from base of 10,10-dimethyl-10-azoniatricycl[4.3.1.0^2,5]dec-3-en-8-one tosylate (IV); isolation of bicyclo[4.2.1]-nona-2,4,7-trien-9-one (V)**

The unsaturated quaternary tosylate (IV) (0.5 g, 0.0014 mole) was dissolved in distilled water (15 mL). Sodium hydrogen carbonate (1.5 g, 0.01 mole) was added, and the mixture was distilled nearly to dry-
ness. The distillate (12 mL), which had separated into two layers, was transferred to a separatory funnel. The aqueous layer was saturated with sodium chloride and extracted with diethyl ether (20 mL). The ether layer was washed with 10% hydrochloric acid solution (2 mL) and saturated sodium bicarbonate solution (3 mL), and dried over magnesium sulfate. The ether was removed in vacuo, and the residue was micro-distilled (50°, 0.010 Torr) to give a colorless oil (0.150 g, 79%), identified as bicyclo[4.2.1]nona-2,4,7-trien-9-one (V) by comparison of its physical and spectroscopic properties with an authentic sample (194): n.m.r. (Figure 5, p. 134) (CDCl₃) δ 4.8 (nm, 6H), 3.0 (m, 2H); ir (neat) 3030, 2945, 1780, 1720, 1665, 1595, 1390, 1325, 1298, 1270, 1245, 1220, 1155, 1115, 1045, 975, 920, 870, 820, 760, 715, 680, 645 cm⁻¹; uv max (ethanol) 325 (2.75), 278 (3.58), 270 (3.60), 215 (3.49); mass spectrum, m/e (relative intensity) 132 (80), 131 (85), 104 (100), 103 (90).

Preparation of bicyclo[5.2.0]nona-2,5,8-trien-4-one (VI)

A 100 mL 3-necked round-bottomed flask was connected in the vertical plane by one of the side necks to a pentane still. The center neck was fitted with a short straight adapter carrying a 25 mL round-bottomed flask. The larger flask was charged with sodium bicarbonate (1.0 g, 0.012 mole) and distilled water (10 mL). The apparatus was purged with nitrogen, and the remaining neck was fitted with a 14 mm. serum cap. An ice-water bath was positioned to cool the lower half of the reaction flask and stirring was begun. While pentane was dis-
tilling into the flask under a nitrogen flow the 25 mL round-bottomed flask was removed and the bis-quaternary diiodide VII (0.50 g, 0.001 mole) was packed into one side of it by tapping the flask on the bench top. The flask was carefully reinstalled on the apparatus. When distillation was halted, and the mixture of liquids had cooled to below 10°, the stirring rate was slowed to avoid emulsification. The bis-quaternary diiodide was added in portions over a period of 30 minutes by slowly rotating or tapping the addition flask. The mixture was stirred at 0° for 1 hour. Stirring was halted, and the organic layer was withdrawn by syringe and transferred to a 250 mL stoppered flask containing sodium sulfate (4 g) and cooled in ice. Pentane (30 mL) was distilled into the reaction flask, allowed to stir for 20 minutes and transferred to the drying flask. This extraction was repeated twice. The flask containing the pentane extracts was stored at 3° in a refrigerator for 12 hours and was swirled occasionally to speed drying. The pentane solution was filtered under nitrogen, and the solvent was removed in vacuo without heating to give a yellow oil. This was carefully deposited on a column of grade III neutral alumina at -25°, which was developed with a 1:1 mixture of pentane and dichloromethane. The eluant was collected in dim light under nitrogen, and its composition was monitored by t.l.c. The first compound to elute was identified as bicyclo[4.2.1]nona-2,4,7-trien-9-one (V) (0.006 g, 4%) by its n.m.r. spectrum. The second component of the mixture to elute was a colorless oil, tentatively identified as bicyclo[5.2.0]nona-1,5,8-trien-4-one (VIII) (0.013 g, 10%) by its spectra: n.m.r. (CCl4) δ2.95 (ddd, J =
14, 8, 2 Hz, 1H), 3.40 (dd, J = 14, 6 Hz, 1H), 4.05 (ddd, J = 4, 2, 2 Hz, 1H), 5.25 (ddd, J = 8, 6, 2 Hz, 1H), 5.90 (ddd, J = 12, 4, 2 Hz, 1H), 6.35 (dd, J = 2, 2 Hz, 1H), 6.50 (d, J = 12 Hz, 1H), 6.55 (d, J = 2 Hz, 1H); IR (CCl₄) 3100, 3050, 3020, 2875, 1700, 1674, 1390, 1242, 1205, 1167, 1025, 945, 915, 890 cm⁻¹. The last component of the mixture to elute was identified as bicyclo[5.2.0] nona-2,5,8-trien-4-one (VI) (0.100 g, 77%): n.m.r. (Figure 4, p. 121) (CCl₄) 63.95 (m, 2H), 5.8 (d, J = 12 Hz, 2H), 6.12 (s, 2H), 6.15 d (dofm, J = 12 Hz, 2H); IR (Figure 4, p. 121) (thin film) 3060, 3030, 2880, 1668, 1615, 1412, 1300, 1265, 1200, 1120, 1050, 875, 790, 738, 668 cm⁻¹; UV max (diethyl ether) 385 (shoulder, log ε 1.03), 358 (1.32), 348 (1.33), 262 (shoulder, 3.15), 221 (3.90); mass spectrum, m/e (relative intensity) 133 (10), 132 (parent, 100), 131 (98), 130 (64), 115 (10), 105 (12), 104 (100), 103 (86), 102 (55), 101 (8), 91 (11), 78 (80), 77 (45), 76 (28), 75 (15), 74 (15), 63 (20), 62 (10), 58 (21), 52 (25), 51 (75), 50 (40); exact mass of parent, calcd. for C₉H₈O: 132.0575; found, 132.0575 ± 0.0007.

**Preparation of bicyclo[5.2.0] nona-2,5-dien-4-one (XVI)**

The saturated bis-quaternary diiodide (5.25 g, 0.010 mole) was treated exactly as described for the unsaturated analog to give a yellow oil. Microdistillation (45°, 0.1 Torr) gave the desired dienone XVI (1.0 g, 72%) as a clear colorless oil, identical to material prepared by Fugiel (186): n.m.r. (CCl₄) 66.10 (d (dofm, J = 12 Hz, 2H), 5.83 (d, J = 12 Hz, 2H), 3.40 (m, 2H), 2.5-2.0 (m, 4H).
Determination of the effects of solvent polarity and water on the course of thermal rearrangement of bicyclo[5.2.0]nona-2,5,8-trien-4-one (VI)

N.m.r. samples of the trienone VI were prepared with anhydrous perdeuteroacetone, -acetonitrile, -chloroform, and -dimethylsulfoxide. The n.m.r. spectrum of each sample was recorded, and the sample tubes were placed in a steam bath for 15 minutes. In each case the major rearrangement product was 1-indanone, as shown by the n.m.r. spectra of the thermolyzed samples. A second set of samples were prepared in the same solvents with no precautions taken to exclude water. The spectra of all of the samples prior to heating showed some absorption due to water in the solution. These samples were heated in a steam bath for 15 minutes, and the n.m.r. spectra were recorded. A mixture of 1-indanone and bicyclo[4.2.1]nona-2,4,7-trien-9-one (V) was produced in each case (n.m.r.), the aromatic ketone predominating in those samples which had contained the least water (carbon tetrachloride and deuterochloroform), while the bridged ketone was the major product in the remaining wet solvents.

Preparation of 3,5-dideuterobicyclo[5.2.0]nona-2,5,8-trien-4-one (VI_d), and its rearrangement in aqueous media

The procedure and apparatus were identical to those used for the preparation of the trienone VI from the bis-quaternary diiodide with the following modifications: deuterium oxide and anhydrous sodium carbonate were substituted for distilled water and sodium bicarbonate in the same quantities, the d_4 quaternary tosylate (1.0 g, 0.0029 mole)
was substituted for the bis-quaternary diiodide VII, and the pentane was dried by reflux over and distillation from calcium hydride. The pentane extract from the degradation was dried over anhydrous sodium sulfate and concentrated in vacuo at \(-15^\circ\). The residue was dissolved in deuterium oxide, and the mixture was distilled nearly to dryness. The distillate was extracted with diethyl ether and the extract was distilled (50\(^\circ\), 0.01 Torr) to give the labeled trienone Vd. A sample of the unlabeled trienone V was prepared by steam distillation of the unlabeled quaternary tosylate IV, ether extraction of the distillate and microdistillation. The n.m.r. spectra (Figure 5, p. 134) of the labeled and unlabeled trienones, Vd and V, were recorded in deuterochloroform, and the integral areas were measured several times using both upfield and downfield sweeps. The measured ratio of olefinic to aliphatic hydrogen was 4.97 for the sample of Vd, and 3.00 for the sample of V. A paramagnetic shift reagent, Europium (III)tris(1,1,1,2,-2,3,3-heptafouro-7,7-dimethyl-4,6-octanedione), was added to both samples in a quantity sufficient to separate the resonance of each chemically non-equivalent hydrogen nucleus. The shifted spectrum of the unlabeled sample of V consisted of a doublet, \(J = 8\) Hz, at the lowest field (H-1, H-6), a multiplet (H-2, H-5), a singlet (H-7, H-8), and a multiplet at the highest field (H-3, H-4). The shifted spectrum of the labeled trienone Vd consisted of a doublet, \(J = 8\) Hz, at the lowest field (H-6), a multiplet (H-5), a singlet (H-7, H-8), and a multiplet at the highest field (H-3, H-4). This information served to establish the structure of Vd as 1,2-dideuterobicyclo[4.2.1]nona-2,4,7-
trien-9-one.

N.m.r. observation of the non-aqueous thermal rearrangement of bicyclo-
[5.2.0]nona-2,5,8-trien-4-one (VI)

A sample of trienone VI was dissolved in carbon tetrachloride
and placed in an n.m.r. sample tube, and its n.m.r. spectrum was
recorded (Figure 6, p. 142). Some dichloromethane was present, and
this was removed and the sample deoxygenated by passing dry nitrogen
through the solution for twenty minutes. This operation introduced
some water into the sample, as shown by its absorption at δ1.3. The
sample tube was then sealed and placed in a water bath at 45 ± 1°C.
The n.m.r. spectrum of the sample was recorded periodically, and
showed rapid (t₁/₂ ~ 30') rearrangement to be taking
place. After four hours' thermolysis at 45°C, the n.m.r. spectrum of
the sample showed it to consist almost entirely (<5% VI) of a new
compound IX, which had an n.m.r. spectrum (Figure 7, p. 144) consisting
of absorption at δ6.45-6.05 (m, 2H), 5.95 (nm, 2H), 5.9-5.6 (m, 2H),
4.05 (d, J = 5 Hz, 1H), and 3.80 (t, J = 5 Hz, 1H). The sample was
then heated to 60°C, when further, slow (t₂/ₐ ~ 60') rearrangement could
be detected by changes in the n.m.r. spectrum. After four hours at this
temperature, destruction of VI and IX appeared to be complete, and the
spectrum (Figure 8, p. 146) consisted of 1-indanone absorption at
δ7.5, 3.15, and 2.6, and peaks due to a new isomer, X, at δ7.45 (d of m,
J = 5 Hz, 1H), 6.6-6.3 (m, 2H), 6.2-5.9 (m, 3H), 3.24 (d of m, J = 14 Hz,
1 H) and 2.85 (d of m, J = 14 Hz, 1H). A small amount of insoluble
material was produced during this period. The tube was next heated to 80°, and after one hour the n.m.r. spectrum (Figure 8, p. 146) showed
the presence of 1-indanone, δ7.75–7.2 (m, 4H), 3.15 (m, 2H) and 2.6 (m, 2H), as the major component, together with small absorptions at δ5.8
and δ3.0, due to the presence of bicyclo[4.2.1]nona-2,4,7-trien-9-one (V). Vapor phase chromatography showed the presence of two components
in the final solution with retention times identical to those of authentic samples of 1-indanone and bicyclo[4.2.1]nona-2,4,7-trien-9-one.

N.m.r. observation of the non-aqueous thermal rearrangement of 3,5-
dideuterobicyclo[5.2.0]nona-2,5,8-trien-4-one (VId)

A pentane solution of the labeled trienone VId was prepared as
described on p. 208, and was purified by column chromatography on grade
III neutral alumina (deactivated with deuterium oxide) at -25° as
described on p. 205 for the unlabeled ketone VI. A carbon tetrachloride
solution of the d2-trienone was placed in an n.m.r. tube, and the
spectrum was recorded (Figure 6, p. 142), which consisted of a multi­
plet at δ6.12 (4H), and a multiplet at δ3.95 (2H). The sample was
then placed in a water bath at 54°. After sixty minutes at that
temperature, nearly complete conversion to a rearrangement product, IXd,
had taken place. The n.m.r. spectrum of IXd (Figure 7, p. 144) con­
sisted of absorption at δ6.12 (m, 2H), 5.95 (m, 2H), 5.75 (ddd, J = 11,
6, 1 Hz, 1H), and 3.80 (d, J = 6 Hz, 1H). The sample was then heated
to 65° for eighty minutes, and to 70° for one hour, when its n.m.r.
spectrum (Figure 8, p. 146) was almost totally due to absorption of a
second intermediate, Xd, at δ7.48 (n.m., 1H), 6.6-6.3 (m, 2H), 6.2-5.9 (m, 2H), and 3.35 (b.s., 1H). The tube was next heated to 85° for thirty minutes, after which the n.m.r. spectrum showed only slow conversion to 1-indanone, as indicated by absorption at δ7.7-7.2 and δ3.15. In order to accelerate this reaction, the sample was heated to 100° in a steam bath, and after twenty minutes the internal pressure blew the cap off. The spectrum of the remaining solution (Figure 9, p. 148) showed the presence of Xd and additional absorption at δ7.7-7.2, 3.15, and 2.6. The absorption at δ2.6 was much less intense than that at δ3.15.

Attempted isolation and trapping of intermediate IX

Carbon tetrachloride solutions of a mixture of VI and IX were prepared by thermolysis of solutions of trienone VI at 50°. Column chromatography of such a solution on grade III neutral alumina at 0°, developing with carbon tetrachloride, led to the isolation of a small amount of starting trienone VI and a narrow band of the [4.2.1] trienone V. Distillation of such a mixture at 30°, 0.010 Torr, led to the formation of a mixture of VI, IX, and 1-indanone (n.m.r.). Addition of an excess of dimethyl acetylenedicarboxylate to such a solution produced no changes in the n.m.r. spectrum of the mixture indicative of the formation of an adduct, and heating the solution slowly to 80° produced mainly 1-indanone in the normal course of rearrangement.

Attempted isolation of intermediate X

Carbon tetrachloride solutions of intermediate X and 1-indanone
were prepared by heating solutions of trienone VI to 65° and monitoring the rearrangement by n.m.r. Column chromatography of such a solution on grade III neutral alumina, developing with carbon tetrachloride, led to the isolation of 1-indanone. Similarly, distillation (30°, 0.010 Torr) of such a mixture resulted in the collection of 1-indanone as the major component in the distillate by n.m.r.

Procedure for the preparation of samples of protonated ketones at low temperatures for n.m.r. observation

The procedure and apparatus used were adapted from those described by Winstein, et al. (50). The low temperature cooling bath consisted of a 20 X 150 mm. Pyrex test tube filled with pentane and carrying a two-hole rubber stopper bored to fit an n.m.r. tube and a low temperature thermometer. This tube was inserted into the center hole of a 3-hole rubber stopper fitted onto a 500 mL unsilvered Dewar bottle. The two remaining holes were fitted with a short piece of glass tubing used as a nitrogen outlet and a double-walled, evacuated U-shaped gas transfer tube fabricated from Pyrex tubing. The other arm of the gas transfer tube was inserted into a rubber stopper fitted to a 1 liter Dewar bottle containing a resistive heater formed from several turns of nichrome wire. The second Dewar was filled with liquid nitrogen. When current was passed through the heater, cold nitrogen gas was evolved and passed through the Dewar containing the cold bath. The temperature of the bath could be maintained at any temperature between -20° and -120° by adjustment of the heating current with a variable transformer. An
n.m.r. tube was marked at levels corresponding to volumes of 75, 225 and 300 microliters and thoroughly dried in an oven. The tube was removed from the oven and inserted through one of the holes in the cold bath stopper until it was 5 mm. from the bottom of the bath. A dry nitrogen atmosphere was maintained within the tube for the duration of the preparation by directing a flow of the gas through a disposable pipette with a bent tip inserted into the mouth of the sample tube. A long, thin glass rod with a flattened end was inserted into the tube to serve as a mixing rod. The tube was filled to the 75 microliter mark with fluorosulfuric acid, taking care to avoid spreading the acid over the walls of the tube. A low temperature thermometer was inserted through the rubber stopper to within 10 mm. of the bottom of the test tube, and the bath temperature was lowered to -60°. Fluorosulfonyl chloride was passed through a drying tube packed with anhydrous sodium carbonate and condensed into the sample tube to the 225 microliter level, washing the walls of the tube in the process. The two layers were mixed, and the mixing bar was left in place. Fluorosulfonyl chloride was condensed into the tube to the 300 microliter mark, and the bath temperature was lowered to -115°. A solution of 20 mg. of the ketone to be protonated in a mixture of 110 microliters of dideuteromethylene chloride and 40 microliters of deuterochloroform was added carefully to form a third layer. The mixture was allowed to cool for five minutes, and the layers were rapidly mixed with the glass rod, which was then withdrawn. Tetramethysilane was added, and the tube was capped, frozen in liquid nitrogen and sealed with a flame.
The sample was transferred to the cold probe of the n.m.r. spectrometer, and spectra were recorded at gradually increased temperatures.

N.m.r. observation of protonated bicyclo[5.2.0]nona-2,5,8-trien-4-one (XI)

A solution of the 4-hydroxybicyclo[5.2.0]nona-2,5,8-trien-4-ylium cation XI was prepared, and the n.m.r. spectrum was recorded at temperatures between -103° and -40°. The only change in the spectrum over this temperature range was a variation in line width due to viscosity changes resulting from the cold solvent at the lower temperatures and sample degradation at the higher temperatures. The sample decomposed and separated into two layers above -25°. The best spectrum was obtained at -80°: n.m.r. (Figure 10, p. 165) δ7.48 (dd, J = 12, 5 Hz, 2H), 6.38 (d, J = 12 Hz, 2H), 6.14 (s, 2H), 4.20 (d, J = 5 Hz, 2H). Quenching of the mixture with an excess of cold saturated sodium bicarbonate solution did not produce any ether-soluble product.

N.m.r. observation of protonated bicyclo[5.2.0]nona-2,5-dien-4-one (XVII)

A solution of the 4-hydroxybicyclo[5.2.0]nona-2,5-dien-4-ylium cation XVII was prepared, and the n.m.r. spectrum was recorded at temperatures between -100° and -20°. The sample decomposed and separated into two layers above -25°. The best resolution was obtained at -60°: n.m.r. (Figure 10, p. 165) δ7.31 (d of m, J = 11 Hz, 2H), 6.40 (d, J = 11 Hz, 2H), 3.75 (m, 2H), 2.71 (m, 4H). Quenching of the mixture with an excess of cold, saturated sodium bicarbonate solution
did not produce any ether-soluble products.

**Generation of a radical anion from bicyclo[5.2.0]nona-2,5,8-trien-4-one (VI)**

Solutions of the trienone VI (0.019 M) and potassium t-butoxide (0.05 M) in anhydrous dimethyl sulfoxide were prepared and deoxygenated with a stream of dry nitrogen. These solutions were pumped into a mixing cell and then passed through the cavity of the e.s.r. spectrometer. A weak radical signal was observed at very low flow rates. Intensity of the signal was maximized at a flow of 0.015 mL/min. No other signal was present at higher flow rates. The spectrum (Figure 11, p. 174) was analyzed as a triplet of triplets of pentets, and the measured hyperfine splitting constants were 8.57 g (2H), 5.66 g (4H) and 0.51 g (2H).

**Preparation of bicyclo[5.2.0]nona-1(7),2,5-trien-4-one (XVIII)**

A 100 mL round-bottomed flask was fitted with a magnetic stirring bar, a distillation adapter and a reflux condenser. Carbon tetrachloride (50 mL) was distilled into the flask under dry nitrogen. N-Bromosuccinimide (0.140 g, 0.0079 mole) and bicyclo[5.2.0]nona-2,5-dien-4-one (XVI) (0.10 g, 0.0076 mole) were added, stirring was begun, and the flask was irradiated with a General Electric sunlamp. The sunlamp was replaced with an infrared lamp after the solution had developed a faint yellow color, and the solution was refluxed for 40 minutes. Triethylamine (3 mL, 0.022 mole) was added, and refluxing was con-
tinued for three hours more. The solution was cooled, filtered, and the solvent was removed in vacuo. The residue was sublimed (60°, 0.10 Torr) to give a yellow solid. The solid was subjected to preparative thin layer chromatography on alumina, using diethyl ether as developing solvent, and separated into three components identified as starting dienone (very small amount), succinimide, and the desired product. The tropone band was extracted, recrystallized from diethyl ether at -40° and sublimed (45°, 0.10 Torr) to give 4,5-dimethylene-tropone (bicyclo[5.2.0]nona-1(7),2,5-trien-4-one) (XVIII) (0.056 g, 57%), m.p. 120-121, identical to material prepared by Fugiel (186): n.m.r. (CDCl₃) δ 6.93 (s, 4H), 2.95 (s, 4H).

Generation and observation of a radical anion from bicyclo[5.2.0]nona-1(7),2,5-trien-4-one (XVIII)

Solutions of the trienone XVIII (0.0169 M) and potassium t-butoxide (0.066 M) in anhydrous dimethyl sulfoxide were prepared and deoxygenated with a stream of dry nitrogen. The solutions were pumped into a mixing cell and then passed through the cavity of the e.s.r. spectrometer. A radical signal was observed, which was maximized at a flow rate of 0.016 milliliters per minute. The spectrum (Figure 11, p. 174) was analyzed as a triplet of triplets of pentets, and the measured hyperfine splitting constants were 8.57 g (2H), 5.65 g (4H), and 0.51 g (2H), identical to those exhibited by the radical produced from trienone VI.
Preparation of 4,5-bis(methylene)cyclohepta-2,6-dien-1-one (XIX), and observation of its spectra and photochemistry at 8K in an argon matrix

The apparatus used for matrix isolation and the flash thermolysis oven have been described elsewhere (210). Oven temperature was determined by means of an iron-constantin thermocouple and a potentiometer, and remained within 5° of the specified temperature after thermal equilibrium had been reached. All depositions were performed without pre-mixing of the argon gas and the substrate. The infrared and ultraviolet absorption spectra of the starting material, bicyclo[5.2.0]-nona-1(7),2,5-trien-4-one (XVIII), isolated in an argon matrix at 8K, were recorded for reference purposes. The tropone was determined to be photostable under these conditions, as shown by the lack of substantive changes in the respective spectra after 3 hours' irradiation of the matrix with an unfiltered high pressure mercury arc lamp:

\[
\begin{align*}
\text{ir} (\text{Ar, 8°K}) & (\text{Figure 12. p. 181}) & 3023, 2985, 2970, 2940, 2925, 2840, 1636, 1587, 1560, 1548, 1442, 1420, 1412, 1315, 1267, 1215, 1205, 1180, 1148, 868, 862, 807, 770, 660; \\
\text{uv max} (\text{Ar, 8°K}) & (\text{Figure 13, p. 184}) & 3200, 3085, 2200.
\end{align*}
\]

The flash thermolysis oven was heated to 620°, and a sample of the dimethylenetropon XVIII was sublimed (250, 2 X 10^-6 Torr) through the oven. The thermolysate was co-deposited with argon gas on a cesium iodide window at 20K. The matrix thus formed was cooled slowly to 8°K, and the infrared spectrum was obtained: 

\[
\begin{align*}
\text{ir} (\text{Ar, 8°K}) & (\text{Figure 12, p. 181}) & 3020, 2970, 2940, 2680, 1648, 1636, 1584, 1560, 1548, 1430,
\end{align*}
\]
1372, 1318, 1262, 1252, 1214, 1180, 1148, 1030, 919, 910, 870, 862, 810, 770, 721, 660, 630, 525, 410. The matrix was irradiated with an unfiltered high pressure mercury arc lamp for 62 hours. During this period, the absorption bands at 1648, 1584, 1430, 1372, 1318, 1252, 1146, 918, 910, 862, 721, 630, 525 and 410 cm$^{-1}$ disappeared and the spectrum of the starting tropone was regenerated (Figure 12, p. 181). Additional weak absorption at 2342 (CO$_2$), 2140 (CO), 1040-1020, 800, 660 cm$^{-1}$ was present in the final spectrum.

Deposition of the dimethylenetropone thermolysate was repeated in exactly the same manner onto a sapphire window. Enough material was deposited to produce an optical density of 2.9 at the largest absorption maximum in the ultraviolet spectrum. The ultraviolet spectrum (Figure 13, p. 184) consisted of two maxima at 2285 and 2650 Å, and tailed smoothly into the visible region. Irradiation of the matrix with an unfiltered high pressure mercury arc lamp for 120 minutes produced a spectrum (Figure 13, p. 184) with maxima at 2200, 3100 and 3200 Å, which was very nearly superimposable on the spectrum of the starting dimethylenetropone deposited without thermolysis.

**Attempted trapping of the reactive intermediate produced by flash thermolysis of bicyclo[5.2.0]nona-1(7),2,5-trien-4-one (XVIII), and isolation of a dimer of 4,5-bis(methylene)cyclohepta-2,6-dien-1-one**

Bicyclo[5.2.0]nona-1(7),2,5-trien-4-one (10 mg.) was sublimed (25°, 2 X 10$^{-6}$ Torr) through a flash pyrolysis oven at 620° and co-condensed with methanol on a 20°K surface for 50 hours. The methanol
matrix was warmed to room temperature under a methanol atmosphere, and the thermolysate was washed from the apparatus with diethyl ether. A small amount of polymer was removed from the apparatus with chloroform. The washings were reduced in volume in vacuo, and the residue was examined by thin layer chromatography and n.m.r. The n.m.r. spectrum was complex, and showed the presence of starting material and the absence of any -OCH₃ absorption. Thin layer chromatography (CHCl₃, Al₂O₃) showed the presence of two mobile components. The mixture was subjected to column chromatography on grade III alumina, eluting with 35:65 diethyl ether-chloroform, to give 3 mg. starting dimethylene tropone XVIII and a yellow oil which displayed a complex n.m.r. spectrum and a mass spectrum with major peaks at m/e 264, 157 and 132.

The procedure was repeated, substituting ethyl vinyl ether for methanol. Again only insoluble polymer, starting material and the unknown product were present after warming the condensed mixture. The product from both runs was combined and chromatographed once more to give 7 mg. of a pale yellow oil which tended to polymerize when stored neat. This compound was identified as a Diels-Alder dimer of 4,5-bis(methylene)cyclohepta-2,6-dien-1-one, 4'-methylenespiro[bicyclo[5.4.0]undec[1(7),2,5]triene-9,5'-cyclohepta[2,6]diene]-4,1'-dione (XX): n.m.r. (Figure 14, p. 189) (CCl₄) 66.95-6.75 (m, H-2,3,5,6,6'), 6.45-5.99 (m, H-2',3',7'), 5.42 (s, term. CH₂), 5.38 (s, term. CH₂), 3.03 (bs, 2H-8), 2.70 (m, 2H-11), 2.05 (m, 2H-10); ir (Figure 14, p. 189) (CCl₄) 3050, 2923, 1645, 1614, 1575, 1522, 1458, 1440, 1428, 1402, 1310, 1275, 1248, 1205, 1100, 917, 859, 715; uv max (diethyl ether) 3045 (log
(relative intensity) 266 (7), 265 (21), 264 (parent, 100), 252 (14), 248 (11), 236 (17), 208 (13), 193 (23), 180 (14), 158 (26), 157 (96), 133 (16), 132 (53), 130 (19), 129 (25), 108 (32), 104 (32), 93.3 (metastable), 87 (12).

Infrared observation of the non-aqueous rearrangement of bicyclo[5.2.0]-nona-2,5,8-trien-4-one (VI)

A solution of trienone VI in carbon tetrachloride which had been stored at 30° for several days after purification was placed in a variable temperature infrared cell, manufactured by Research and Industrial Instruments Company. The cell was constructed of stainless steel, and sample temperature was measured using an iron-constantin thermocouple inserted into a small recess in the potassium bromide window. The poor thermal conduction characteristics of stainless steel resulted in a non-uniform temperature distribution in the cell, so that the indicated temperature could be regarded as the minimum sample temperature. The infrared spectrum of the sample was recorded using a Perkin-Elmer variable path length cell to cancel the absorption of solvent in the sample. The spectrum obtained was identical to that displayed by a neat sample of pure VI, except for absorptions at 1760 cm\(^{-1}\) and 1710 cm\(^{-1}\), indicating that some isomerization of the starting material had occurred during storage of the sample. The variable temperature cell was then heated to 45° for four hours. After this period the spectrum was recorded, and showed nearly complete disappearance of the absorp-
tion bands due to the starting trienone VI, increased absorption at 1710 cm\(^{-1}\), strong absorption at 1660 cm\(^{-1}\), and new bands at 1380, 1335, 1290, 1260, 1190, 1160, 1090, 940, 920, 900, 695, 680, 660 and 640 cm\(^{-1}\). Some small peaks characteristic of 1-indanone were also present, as was a peak at 1760 cm\(^{-1}\), characteristic of the bridged trienone V. The sample temperature was next raised to 60°, when the absorptions at 1660 cm\(^{-1}\), 1290, 1260, 1190, 940, 920, 860, 695, and 640 cm\(^{-1}\) decreased in intensity while the bands at 1710, 1335, 1290, 1160, 1090, 900, 680 and 660 cm\(^{-1}\) increased in intensity, as did those due to 1-indanone. The sample was removed after four hours at 60°, and was found to consist of bicyclo[4.2.1]nona-2,4,7-trien-9-one (V), intermediate X, and 1-indanone by n.m.r. analysis. The absorptions at 1660, 1290, 1260, 1190, 940, 920, 860, 695 and 660 cm\(^{-1}\) were assigned to intermediate IX, and those at 1710, 1335, 1290, 1160, 1090, 900, 680 and 660 cm\(^{-1}\) were assigned to intermediate X on the basis of the known order of appearance of these compounds during the rearrangement.


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