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Dissertation

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

By

Robert Henry Meisinger, A.A., B.S.

The Ohio State University
1973

Approved by

Leo A. Pagnotto
Adviser
Department of Chemistry
DEDICATION

To my wife, Marcia
ACKNOWLEDGMENTS

My sincere gratitude is extended to Professor Leo A. Paquette for his guidance and enthusiasm during the course of this work. Appreciation is also extended to my coworkers for many helpful suggestions and discussions.
VITA

September 5, 1945 ......................... Born - Chicago, Illinois
1965 ................................. A.A., Morton College, Cicero, Illinois
1968 ................................. B.S., The University of Illinois, Urbana, Illinois
1969-1970 ............................... Teaching Assistant, The Ohio State University, Columbus, Ohio
1970-1972 ............................... Research Assistant, The Ohio State University, Columbus, Ohio

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PART I

INTRODUCTION

The Favorshki reaction is a common process in the chemistry of α-halo ketones when they are treated with strong bases. Initially the mechanism was believed to involve abstraction of a proton from the α'-position of α-halo ketone \( \text{I} \) with reversible formation of enolate anion \( \text{II} \). This anion

\[
\begin{align*}
\text{I} & \quad \xrightarrow{\text{B}^-} \quad \text{II} \\
R_1 - C - C - C - R_3 & \quad \xrightarrow{\text{HB}} \quad R_1 - C - C - C - R_3 \quad (-B^-)
\end{align*}
\]

could then displace halide ion to afford the proposed cyclopropanone intermediate \( \text{III} \), which undergoes subsequent attack by a nucleophile present in the system to give the final product. This mechanism was given added cre-
dence by the early work of Stork, who showed that Favorovskii rearrangements can be stereospecific under certain experimental conditions. This result led to the misconception that zwitterionic species such as $\frac{1}{2}$ are not viable intermediates in the reaction.

However, more recent work has provided a large body of evidence for the existence of dipolar species in the Favorovskii rearrangement. Stereospecific rearrangements have been observed in non-polar media, whereas when the same reactions were performed in a polar solvent, non-stereospecific rearrangements, which have been attributed to the presence of a dipolar intermediate such as $\frac{1}{2}$ in polar solvents, resulted. The polar media are apparently favoring this form relative to closed form $\frac{3}{2}$.

Molecular orbital analysis has indicated that the conversion of anion $\frac{3}{2}$ into zwitterion $\frac{1}{2}$ is accompanied by an increase in delocalization and consequently results in a driving force for the reaction. Also, extended Hückel calculations have predicted that zwitterion $\frac{1}{2}$ is actually more stable than closed form $\frac{3}{2}$. When Turro subjected a cyclopropanone to the identical experimental conditions as the $\alpha$-bromo ketone from which it could arise via the Favorovskii rearrangement, different products were observed, therefore casting further doubts on the intermediacy of cyclopropanones.

Additional evidence for the zwitterionic nature of the Favorovskii intermediate is available. By investigating $\alpha$-halo ketones containing substituted phenyl rings in the $\alpha$- and $\alpha'$-positions, Bordwell showed that the rate-determining transition state displayed extensive ionic character at the O-Cl bond. The large negative $\rho$'s observed for the loss of halide ion from $5a$ (-2.37) and $5b$ (-4.97) are consistent with an
intermediate zwitterion (6) in which a positive charge is associated with the carbon atom originally bonded to the halogen. Large Br to Cl rate

\[
\begin{array}{ccc}
\text{Cl} & \text{\text{ArCHCCH}}_2 & \text{\text{ArCHCCH}}_2\text{Cl} \\
\text{\text{\text{ArCHCCH}}_2} & \text{\text{\text{ArCHCCH}}_2} & \\
\text{O} & \text{O} & \\
5a & 6 & 5b
\end{array}
\]

can be attributed to the carbocation associated with the carbon atom originally bonded to the halogen. Large Br to Cl rate ratios and appreciable salt and solvent effects are also consistent with a dipolar intermediate.

Also, the ejection of halide ion is not an intramolecular $S_N2$ process, since the negative $\rho$ value associated with $5$ shows that electron donation actually enhances the rate of rearrangement. This and other data support the concept that C-X bond heterolysis is incurred with the assistance of $\pi$ participation of the enolate anion.$^8,11$ The resultant delocalized zwitterion (6) may then collapse to a cyclopropanone in a symmetry allowed disrotatory fashion.

The zwitterionic species (7c) derived from $\alpha$-halo ketone $7a$ and $\alpha,\alpha'$-dihalo ketone $7b$ has recently been prepared in order to confirm its postulated intermediate existence in an excited state process.$^{32}$ This use of
α-halo ketone \textit{7a} to independently synthesize \textit{7c} clearly is an indication of the widespread acceptance of the existence of such dipolar species.

A class of compounds which is closely related to the α-halo ketones is that of the α-halo sulfones. Although α-halo sulfones are known to be quite inert towards intermolecular nucleophilic displacement reactions,\textsuperscript{13,14} presumably due to either steric or field effects, they do undergo ready base-induced 1,3-elimination, accompanied by loss of sulfur dioxide and formation of an olefin (the Ramberg-Bäcklund reaction).\textsuperscript{15-18} The mechanism of this reaction is depicted below.

\begin{align*}
\text{X} & \quad \text{H} \\
\text{R}_1 - \text{C} - \text{SO}_2 - \text{C} - \text{R}_3 & \quad \text{S} \quad \text{R}_1 \quad \text{C} \quad \text{R}_3 \\
\text{R}_2 & \quad \text{R}_4
\end{align*}

\begin{align*}
\text{s} & \quad \text{X} \\
\text{C} & \quad \text{C} \\
\text{R}_2 & \quad \text{R}_3
\end{align*}

\begin{align*}
\text{10} & \quad \text{(slow)} \quad \text{(-Br)} \\
\text{R}_2 & \quad \text{R}_4 \\
\text{Br} & \quad \text{R}_1
\end{align*}

Abstraction of an α'-proton from α-halo sulfone \textit{8} is believed to occur from a conformation in which the proton removed is flanked by the two oxygen atoms of the sulfone group (as shown). Rapid inversion of the
carbanion center in 2 results in 10, which undergoes a rate-determining intramolecular 1,3-displacement of halide ion to afford episulfone 11. This episulfone then undergoes rapid cheletropic loss of sulfur dioxide, a symmetry allowed process, producing alkene 12 in a stereospecific manner.

Although the double inversion mechanism operating in the 1,3-elimination of α-halo sulfones appears superficially to be quite akin to that of α-halo ketones, closer inspection reveals that it does differ from the latter in certain significant details. As with the Favorskii mechanism, the Ramberg-Bäcklund mechanism is initiated by rapid and reversible anion formation. However, the analogy ends here, for the α-sulfonyl carbanion does not promote assisted halide ion departure with formation of a dipolar intermediate like the Favorskii process. Rather, rate-determining displacement of halide ion by the α'-anion operates as substantiated by the positive ρ (+0.8) associated with the Ramberg-Bäcklund rearrangement.

Nevertheless, episulfones may actually undergo C-C bond cleavage rather than loss of sulfur dioxide as was realized independently by Mock and Paquette when they observed the valence isomerization of 14 to 15 under very mild conditions. Rearrangements via this new mode of reactivity of episulfones demonstrates that with suitably constructed molecules, C-C
bond cleavage can actually become kinetically dominant over the usual C-S bond cleavage.

Of even greater relevance is the experimentally determined C-C bond length in cis-dimethyl episulfone. This value (1.60 Å) far exceeds the theoretical value (1.47-1.49 Å), and consequently leads to the consideration that perhaps dipolar contributions are responsible for this long bond, as has been suggested for cyclopropanones and has recently been supported by Paquette and Houser when they isolated tert-butyl ether 18 as the sole product when 16 was subjected to Ramberg-Bäcklund conditions. This reaction

\[
\begin{align*}
\text{Cl} & \quad \text{KOTBu} \quad \text{THF, } 10^\circ C \\
\text{O}_2\text{S} & \quad \text{16} \quad \text{17} \quad \text{18} (40\%) \\
\end{align*}
\]

was not the result of an S_n2 process, since 18 displays retention at the α-carbon. Also, the reaction is not proceeding by initial epimerization, since the epimer of 16 gave a different product. The epimer of 18 would be the result of an elimination-readdition mechanism. Therefore, the zwitterionic intermediate 17 was deemed responsible for the production of this ether.

That excessive strain factors were not preventing the normal Ramberg-Bäcklund from occurring and thereby allowing another pathway (zwitterionic) to predominate was shown by the production of tert-butyl ethers from α-chloro sulfones whose normal alkene products are relatively strain free.
Treatment of 19 and 20 with strong base in tetrahydrofuran resulted in the production of tert-butyl ethers 23 and 24 along with the normal Ramberg-Bäcklund products 21 and 22.

Therefore, between the established involvement of dipolar intermediates in the base-induced rearrangement of \( \alpha \)-halo ketones and new evidence of their involvement in certain instances in the base-induced rearrangement of \( \alpha \)-halo sulfones, it appeared that, under proper experimental conditions, both \( \alpha \)-halo ketones and \( \alpha \)-halo sulfones would be capable of giving rise to zwitterionic dipoles. By constructing molecules with the proper geometry, it was deemed possible that such reactive intermediates could be intercepted on an intramolecular basis by means of a proximate functionality, thereby unveiling a new dimension to the chemistry of \( \alpha \)-halo ketones and sulfones.
The capability of zwitterionic species for cycloaddition has been amply recognized in the past. Examples of this process involving thermally allowed additions of dipolarophiles to three-membered heterocyclic molecules, the so-called class C ionic [4+2] cycloaddition, are numerous.  

\[
\begin{align*}
\text{Class C} & \\
& + \\
\text{Class A} & \\
& + \\
\end{align*}
\]

In this context, Favorov intermediates themselves have actually been intercepted with dienes. These are examples of Class A ionic cycloadditions. For example, when α-chloro ketone 25 is treated with base in the presence of furan, cycloadduct 26 results. Whether 26 is the result of the intermediacy of zwitterion 27 or the addition of the strained sigma bond in cyclopropanone 28 has not been established. It is not unlikely
that cyclopropanones are actually in equilibrium with zwitterionic species such as 27. This is implied by the long C2-C3 bond length in the parent compound (1.58 Å), although the microwave spectrum exhibits no such evidence. Dihalo ketones, when treated with sodium iodide in the presence of a diene, afford these same adducts.

An intramolecular ionic cycloaddition has been observed in the formation of pipitzols (30) from perezone (29).

The system chosen for this study was 31. It was felt that, under the proper experimental conditions, treatment of 31 with base would result in
the production of a dipolar species. The close proximity of the diene moiety could then trap this zwitterion in a class A intramolecular ionic cycloaddition. The resultant dicyclopentyldiethyl compound 32, formally a derivative of bishomobenzene, would be expected to undergo $[\sigma^2s + \sigma^2s + \pi^2s]$ bond reorganization, a thermally allowed process, 12 to produce 34. Because of the involvement of a bishomobenzene type intermediate, these transformations have been termed "bishomoconjugative rearrangements" for the sake of simplicity.
PART I
DISCUSSION

The first ketone chosen in order to study the bishomoconjugative rearrangement of α-halo ketones was the parent, 7-bromo-cis-bicyclo[4.3.0]non-2,4-dien-8-one (42). Its successful synthesis is depicted in Scheme I.

Two key features of this synthesis are the preparation of the imino nitrile intermediate 37 and the selective α-bromination of a ketone in the presence of double bonds as in 41.

Reduction of 1,2,3,6-tetrahydrophthalic anhydride with an excess of lithium aluminum hydride in refluxing tetrahydrofuran, followed by acidic and subsequent basic work-up, afforded the known diol 33 in good yield. Some loss of material is incurred due to the water solubility of the product. Continuous extraction was not utilized for fear of ether formation.

Tosylation was performed with the use of p-toluenesulfonyl chloride in pyridine at 0° in good yield to give 36. This bis-tosylate was then treated with sodium cyanide in dimethylsulfoxide at 100° followed by the addition of sodium hydride to effect a Thorpe-Ziegler cyclization of the intermediate bis-nitrile according to the method of Bloomfield. The resultant imino-
SCHEME I

1. $\text{LiAlH}_4$ in THF (74%)
2. TsCl in pyridine (81%)
3. NaCN/DMSO (90%)
4. NaH/DMSO (90%)

[Chemical structures and reactions]

1. $\text{CN}$
2. $\text{NaOH}$ in HO, CH$_2$OH, H$_2$O (86%)
3. BaO (55%)
4. HO, CH$_2$OH, TsOH (94%)

[Additional chemical reactions and structures]
nitrile $\mathcal{Z}_7$ was easily recovered from the reaction in high yield. A bis-tosylate was utilized in this reaction rather than a bis-mesylate because of the reported inability of the latter to undergo the double $S_N2$ displacement with cyanide ion. The use of hexamethylphosphorus triamide as a solvent gave a comparable yield.

Initially, it was felt that ketone $\mathcal{Z}_9$ could result from the imino nitrile $\mathcal{Z}_7$ directly when subjected to strong acid hydrolysis. Hydrolysis of $\mathcal{Z}_7$ in refluxing acetic acid-water-phosphoric acid did give a good yield (73%) of volatile material. Unfortunately, these acidic conditions were isomerizing the double bond in $\mathcal{Z}_7$ to presumably give the more thermodynamically stable isomers $\mathcal{Z}_{14}$ and $\mathcal{Z}_{15}$, determined by the large aliphatic to olefinic ratio of proton resonances displayed in the pmr spectrum of this mixture. When $\mathcal{Z}_7$ was hydrolyzed under milder conditions, isomeric $\alpha$-cyano ketones were produced.

It was apparent that a sequence had to be developed which would not involve prolonged exposure to acid. Since it is known that vigorous alkaline hydrolysis of iminonitriles yields dicarboxylic acids, $\mathcal{Z}_7$ iminonitrile was heated with potassium hydroxide in refluxing ethylene glycol-water and afforded the known diacid $\mathcal{Z}_8$ in good yield. Esterification of diacid $\mathcal{Z}_8$ with diazomethane gave a quantitative yield of diester $\mathcal{Z}_6$. Best results
are obtained by cautiously distilling an ethereal diazomethane solution into a 1,2-dimethoxyethane (glyme) solution of 38. The substitution of other solvents for glyme results in prolonged reaction times, as observed by R. E. Wingard, Jr., presumably due to the poor solubility of the diacid. Cyclization of diester 46 with sodium ethoxide in refluxing benzene resulted in a high yield of epimeric β-keto esters (47) via a Dieckmann condensation. When 47 was subjected to basic hydrolysis and subsequent decarbonylation conditions, unchanged 47 was recovered in good yield. The apparent inertness of 47 to this procedure may be the result of attack of base at the carbonyl position (48) rather than at the ester site, which would result in ring opening (49) and, under the reaction conditions could recyclize. Standard acid hydrolysis of 47 resulted in a high yield of a ketone which displayed no olefinic resonance in the pmr, presumably 44.
Ketone 32 was successfully prepared by heating an intimate mixture of barium oxide and 32 at a slightly reduced pressure (100 mm) and simply collecting the volatile product by distillation. The yield of this reaction is a function of the quantity of barium oxide utilized. As the molar ratio of 32 to barium oxide was increased from 7 to 10 to 15, the yield of distilled 32 increased from 38 to 49 to 55%, respectively. A similar result has been obtained by other workers on the cyclization of adipic acid. These results indicate that dimerization reactions may successfully compete with intramolecular reactions when larger amounts of barium oxide are employed. The spectral properties of 32 were consistent with reported data.

In order to convert the lone double bond in 32 to a conjugated diene moiety such as is present in 41, the ketone functionality was first blocked by preparing the ketal 40 under standard conditions in high yield. The double bond of this ketal was then brominated with one equivalent of molecular bromine in methylene chloride at -70°C under an atmosphere of dry nitrogen. The resultant crystalline dibromide (95%) contained very little residual olefinic protons by pmr analysis. Treatment of this crude dibromide with lithium chloride and lithium carbonate in hexamethylphosphorus triamide at 90-95°C followed by acid hydrolysis of the resulting ketal afforded crude 41, which was purified by preparative vpc on column A in 30% overall yield. The isolated yield of this reaction is somewhat misleading, in that large quantities of the thermally labile product are lost during the chromatographic purification. The major impurity in the crude product was 32. The presence of a conjugated diene unit in 41 follows from its
ultraviolet spectrum (isoctane), which displays maxima at 265 (ε 3240) and 276 nm (2930) and a shoulder at 257 nm (ε 2360). The infrared spectrum (neat) displays a strong carbonyl absorption at 1740 cm⁻¹, while the pmr spectrum (CDCl₃) consists of multiplets at 2.25-2.48 δ for the four α-carbonyl protons, 2.93-3.27 δ for the two bridgehead protons, and 5.53-6.10 δ for the four olefinic protons. Owing to the sensitivity of 44 to the atmosphere, combustion data were obtained on the semicarbazone derivative, mp 186-188° dec.

Introduction of a bromine into the α-carbonyl position of 44 was effected by the use of pyrrolidone hydrotribromide (PHT) in tetrahydrofuran. This stable red crystalline salt is reported to selectivity brominate ketones in the presence of double bonds according to the following equation. Tetrahydrofuran is the solvent of choice, since although PHT is

\[(\text{Pyr})_3\text{H} \rightleftharpoons \text{Br}_3\text{O} + \overset{\text{THF}}{\overset{\text{H}}{\overset{\text{N}}{\overset{\text{O}}{\text{N}}}}} \rightarrow 2(\text{Pyr})_2\text{HBr} + \overset{\text{O}}{\overset{\text{Br}}{\text{C}}}\]

soluble in it, the resultant pyrrolidone hydrobromide is not, and can consequently be removed by filtration.

Treatment of 44 with one equivalent of PHT and 2-pyrrolidone in tetrahydrofuran in the absence of light as prescribed by the reported procedure resulted in the gradual disappearance of the red color of the PHT and a simultaneous precipitation of the white pyrrolidone hydrobromide. Although the same molarities were employed as reported in the literature, it was
necessary to replace the tetrahydrofuran with a small quantity of ether in order to precipitate most of the pyrrolidone hydrobromide. The crude α-bromo ketone \( h_2 \) so obtained was quite unstable, and consequently was used immediately in the subsequent reaction without further purification.

There was some doubt whether the desired degree of reactivity was attained by the use of this reagent. The combined yield of this and the proceeding reaction was quite low, and varying amounts of \( h_1 \) were always isolated along with the final product. Numerous modifications were attempted to increase the yield, but to no avail. Prolonged addition times, varied dilutions, and meticulously purified reagents had little effect. Also, 2-pyrrolidone, added to the reaction to trap the hydrobromic acid produced, was always present in varying amounts in the crude product.

The selectivity of PHT is presumably due to its capability to maintain a low-concentration of bromine, which then selectively reacts with the enol form of a ketone rather than a double bond. Molecular bromine has been reported to display this same selectivity if added very slowly to dilute solutions of an unsaturated ketone in nonpolar solvents such as carbon tetrachloride, but was not realized with \( h_1 \). Perhaps the enol content of \( h_1 \) is lower than expected. 2-Indanone, which would be the result of allylic bromination of \( h_1 \) and loss of HBr, was never detected.

\[
\begin{align*}
\text{(or an isomer)} \\
\end{align*}
\]
When crude bromo ketone 42 was treated with 1 equivalent of potassium tert-butoxide in freshly distilled dimethylsulfoxide at 25°, an immediate dark red color developed. After 15 min the solution was treated with water, extracted with pentane, and purified by preparative vpc techniques on Column A. In this manner up to 30% of 43 was isolated, along with varying amounts (10-25%) of 42. The product was identified by direct comparison with an authentic sample prepared by the method of Shechter via its pmr spectrum, infrared spectrum (neat), which displays a strained bicyclic carbonyl absorption at 1760 cm⁻¹, and vpc retention time.

Although the transformation of 42 to 43 indicated the operation of a bishomoconjugative pathway when α-halo ketones are treated with base, it became apparent that additional examples would be necessary in order to determine whether this structural rearrangement was general in nature. Furthermore, by preparing a suitably labeled compound information concerning the precise mechanistic pathway followed by this rearrangement could be realized. For these reasons, the preparation of 7-bromo-cis-1,6-dimethyl-bicyclo[4.3.0]non-2,4-dien-8-one (52) was undertaken.

The multistep synthesis of 52 is shown in Scheme II. As in the preparation of 52, the key features of this synthetic scheme are the prepara-
tion of the imino nitrile intermediate \(47\) and the selective bromination of \(51\).

Dimethylmaleic anhydride, prepared by known methods \(^{44,45}\) involving monoaalkylation of acetoacetic ester, formation of the bisulfite addition product, cyanohydrin formation, hydrolysis, and finally thermolysis, was reacted with butadiene in a sealed glass tube at 160° for four days to afford the reported Diels-Alder adduct \(44\) in moderate yield. \(^{46}\) Although a free radical inhibitor (hydroquinone) was added to the reaction, polymerization predominated in some runs. This could be avoided by either using a new tube or by "pre-conditioning" the reaction vessel through thorough washing with ammonia. Most of the unreacted anhydride could be recovered from the crude product and recycled (see Experimental). Reduction of anhydride \(44\) with excess lithium aluminum hydride in refluxing tetrahydrofuran afforded an excellent yield of diol \(45\), which was subsequently tosylated in good yield with \(p\)-toluenesulfonyl chloride in pyridine at 7° to give \(46\). The latter reaction is quite sluggish due to the neopentyl reaction sites and requires seven days for completion. The tosylation could easily be monitored by quenching small aliquots with dilute acid. The reaction is completed when crystalline material results. Mechanical stirring is necessary so that the intermediate monotosylate will not crystallize
from solution and become encrusted with pyridine hydrochloride, thereby inhibiting bis-tosylate formation. The use of higher temperatures to increase the rate of reaction resulted in lower yields.

On treatment with sodium cyanide in hexamethylphosphorus triamide at 110-115°, bis-tosylate 46 produced a bis-nitrile, which was cyclized in situ with sodium hydride via a Thorpe-Ziegler reaction to afford imino nitrile 47 in good yield. As was the case with the preparation of 46, prolonged reaction times were necessary for steric reasons. Sodium cyanide was of sufficient basicity under the reaction conditions to effect the cyclization, since 47 was recovered from 46 without the use of sodium hydride, albeit at a slower rate. This was also observed by R. E. Wingard with a similar compound. Hexamethylphosphorus triamide was employed as solvent rather than dimethylsulfoxide, as in the preparation of 37, because of its greater ability to accommodate nucleophilic displacement reactions. The structure of 47 follows from its pmr spectrum (CDCl₃), which displays methyl singlets at 1.05 and 1.08 δ, a multiplet at 1.38-2.37 δ for the six methylene hydrogens, a broad singlet at 4.58 δ for the two amino hydrogens, and a multiplet at 5.67-5.83 δ for the two vinyl hydrogens, and from its infrared spectrum (Nujol), which most notably contains a strongly conjugated nitrile band at 2180 cm⁻¹.

As was the case in the previous series, acid hydrolysis of 47 under a variety of conditions always led to isomerization of the double bond, as indicated by pmr. The appearance of many spikes in the methyl region suggested that Wagner-Meerwein rearrangements were probably occurring.
In order to determine whether the unsuccessful decarboxylation sequence attempted for the preparation of the parent ketone 52 was also inoperative in this series, diacid 48, resulting from prolonged and stringent basic hydrolysis of imino nitrile 47, was subjected to the same sequence of reactions. Some of the desired ketone 49 was isolated by column chromatography, despite its apparent decomposition on the column (see Experimental). It is interesting to note that this sequence was quite successful for R. E. Wingard in the preparation of 52.

Ketone 49 was produced in good yield directly from diacid 48 by heating it with barium oxide. The yield (71%) was actually higher than experienced with the parent diacid 38 (55%). Unreacted 48 (ca. 10%) was recovered from the reaction vessel. Ketone 49 was characterized by its pmr spectrum (CDCl₃), which displays a methyl singlet at 1.05 δ, a multiplet at 2.00-2.58 δ for the four allylic protons, a singlet at 2.15 δ for the
four \( \alpha \)-carbonyl protons, and a triplet with a coupling constant of 1.5 Hz for the two vinyl protons, by its infrared spectrum (Nujol), which displays a carbonyl band at 1740 cm\(^{-1}\), and by its mass spectrum, which indicated a parent \( m/e \) of 164.1201 (calculated 164.1199).

Ketone \( \text{I} \) is a waxy, low-melting solid, which slowly decomposes at room temperature. For this reason, combustion data were obtained on the semicarbazone derivative, mp 214-216\(^{\circ}\)dec. Other ketones in this series show signs of decomposition after several hours, and consequently were also converted into derivatives for combustion analysis. This behavior has been noted by other workers on similar ketones.

Introduction of the diene moiety into the system was accomplished by blocking the carbonyl as the ketal, brominating \( \text{I} \) under anhydrous conditions with one equivalent of molecular bromine, and eliminating two moles of hydrogen bromide from the dibromide with lithium chloride and lithium carbonate in hexamethylphosphorus triamide at 90\(^{\circ}\) followed by acid hydrolysis of the resultant diene ketal. \( \text{cis-1,6-Dimethylbicyclo[4.3.0]non-2,4-dien-8-one} \) (\( \text{II} \)) was isolated from the crude reaction mixture by vpc chromatographic techniques on Column A in moderate yield, along with some monoene ketone \( \text{I} \) (14\%). The presence of the conjugated diene follows from its electronic spectrum (isooctane), which displays maxima characteristic of this chromophore at 255 (\( \varepsilon \) 2518), 263 (3450), and 272 nm (3110). Its infrared spectrum (neat) contains a carbonyl band at 1740 cm\(^{-1}\), while its pmr spectrum (CDCl\(_3\)) exhibits a methyl singlet at 1.07 \( \delta \), two AB doublets centered at 2.13 and 2.53 \( \delta \) with a coupling constant of 18 Hz for the four methylene hydrogens (\( \text{H}_B \) and \( \text{H}_A \) respectively), and a multiplet at 5.37-6.03 \( \delta \).
for the four vinyl hydrogens. Due to instability, obtention of combustion data on 51 was precluded, but correct data were obtained for the semicaprazone, mp 203-206° dec. A high resolution mass spectrum of 51 seemed to indicate the correct empirical formula: calculated m/e 162.1044, observed m/e 162.1043. Conversion of 51 to the bromo ketone 52 was effected with the use of pyrrolidone hydrotribromide as previously described for the preparation of 42.

Treatment of crude bromo ketone 52 with an excess of freshly sublimed potassium tert-butoxide in dry dimethylsulfoxide at 25° resulted in an instantaneous development of a deep red color. After 20 minutes, the reaction was quenched with water (dissipation of the deep red color), extracted with pentane, and separated into its two components by preparative vpc on column A. In this manner 16% of 7,8-dimethylbicyclo[4.2.1]nona-2,4,7-trien-9-one (56) was isolated along with 11% of unreacted 51. The structure of 56

![Reaction Scheme](https://example.com/chemical_scheme.png)

was established on the basis of both spectroscopic and chemical evidence. Its ultraviolet spectrum (isoctane) displays maxima at 322 (ε 580), 283 (1840), 273 (1910), and 218 nm (2040). This spectrum compares nicely to that obtained by Shechter for the parent ketone, bicyclo[4.2.1]nona-2,4,7-
9-one (43), which displays maxima at 325 (ε 567), 277 (3820), 269 (4010), and 216 nm (3080) in the ultraviolet region.

\[ \text{\includegraphics[width=0.2\textwidth]{43.png}} \]

The pmr spectrum (CDCl₃) of 56 shows a methyl singlet at 1.77 δ, a rounded multiplet at 2.80-3.17 δ for the two bridgehead hydrogens, and a multiplet at 5.68-5.97 δ for the four vinyl hydrogens. These chemical shifts correspond exactly to those reported for the parent ketone (43), whose pmr spectrum (CDCl₃) consists of a multiplet at ca. 2.8-3.1 δ for the bridgehead hydrogens and a multiplet at ca. 5.8-6.0 δ for the vinyl hydrogens.⁴³

Bicyclic ketone 56 showed signs of decomposition after just several hours at room temperature, but could be stored under nitrogen at 0° for several days without any apparent discoloration. This behavior was also noted by Shechter for the parent structure (43).⁴³ Consequently, combustion data were obtained on the semicarbazone, mp 212-213.5⁰dec, while a high resolution mass spectrum of 56 confirmed its empirical formula: calculated m/e 160.0888, observed 160.0885.

Chemical confirmation of the structure of 56 was obtained via its photochemistry. A report states that direct irradiation of the parent ketone (43) results in a high yield (80%) of cyclooctatetraene.⁴³ Photolysis of 56 under singlet conditions afforded 1,2-dimethylcyclooctatetraene.
as the sole product identified by comparison of its spectral properties with those of an authentic sample.

Additional chemical confirmation of the structural assignment to 56 was derived from its catalytic hydrogenation to 58. Under the reaction conditions employed, the uptake of only two equivalents of molecular hydrogen was observed. The structure of 58 follows from its pmr spectrum (CDCl₃), which displays a methyl singlet at 1.65 δ, a broad envelope at 1.25-1.63 δ for the eight methylene hydrogens, and a multiplet at 2.58-2.70 δ for the two allylic bridgehead hydrogens, its accurate mass determination (calculated m/e 164.1201, observed 164.1199), and its elemental analysis as the 2,4-dinitrophenylhydrazone; mp 114-116°. This structure determination is of particular significance, since it serves to exclude 58 and related positional isomers from further consideration as alternative structural possibilities for this molecule.
A recent report states that the sensitized irradiation of the parent ketone $\text{42}$ affords barbarolone (60) via a di-π-methane process. $^{43,51}$

When Michler's ketone (4,4'-bis(dimethylamino)benzophenone) was used as the sensitizer, and the reaction performed at 0$^\circ$, a high yield of 60 was isolated as the sole product. Photolysis of 56 under these same conditions would produce a disubstituted barbarolone derivative (61). Temperature

Temperature
data would then indicate the ground state substituent effect of a methyl group on this particular Cope rearrangement.

Irradiation of $\text{66}$ under these conditions led to the isolation of $\text{61}$. Ketone $\text{61}$ was characterized by its electronic spectrum (isoctane), which displayed only a shoulder on end absorption at 217 nm ($e \, 3580$), its infrared spectrum (neat), which contained a carbonyl band characteristic of a cyclopropyl ketone at 1700 cm$^{-1}$, and by its accurate mass determination; calculated m/e 160.0888, observed 160.0885.

These data compare well with those of barbaralone ($\text{61}$), which displays two shoulders on end absorption at 225 ($e \, 2710$) and 243 nm ($1840$) in the ultraviolet and a carbonyl band at 1700 cm$^{-1}$ in the infrared.

At ambient temperature in the nmr probe (34°), the nmr spectrum (CS$_2$) of $\text{61}$ consists of two methyl spikes at 1.75 and 1.78 $\delta$, multiplets at 1.92-2.20 and 2.48-2.95 $\delta$ for the four ring hydrogens, and a multiplet at 5.17-5.83 $\delta$ for the two vinyl hydrogens, which is in agreement with a preponderance of $\text{61a}$ at this temperature. There is no signal corresponding to a methyl group bonded to a cyclopropyl ring as in $\text{61b}$. The ratio of aliphatic to vinyl hydrogens is exactly five to one, as expected for $\text{61a}$. Isomer $\text{61b}$ would have a ratio of three to one. A small concentration of $\text{61b}$ in the equilibrium would not be detected in this spectrum, since time averaging would generate a spectrum whose chemical shifts would be very similar to that of pure $\text{61a}$.

As the temperature of the probe was lowered to -3.5° and then to -18.5°, the spectrum remained essentially unchanged, except for some broadening of all the resonances due to viscosity effects. However at -39.5°,
the two multiplets associated with the ring hydrogens did undergo a change in relative intensities and extensive broadening. Changes were even more pronounced at $-62^\circ$, when a third multiplet appeared between the two initial multiplets. This was also the case at $-69^\circ$. Since the lower temperatures are expected to "freeze out" the more stable isomer (61a), these changes are most likely associated with this phenomenon, although solvent effects cannot be excluded from consideration. In any case, these equilibrium data have unequivocally established that isomer 61a is substantially preferred over 61b to the extent of at least 85% over the entire temperature range of $-70^\circ$ to $+40^\circ$.

This result demonstrates substantial preference of a methyl substituent for bonding to an olefinic (sp$^2$-hybridized) rather than a cyclopropyl (sp$^{2.3}$-hybridized) carbon. This same preference has been demonstrated by Paquette in azabullvalene 62 where 62a predominates by a ratio of nine to one over 62b at ambient temperature. Of all the monosubstituted bullvalenes studied to date with the exception of fluorobullvalene, the substituent preferentially occupies an olefinic rather than a cyclopropyl position. Also, Schleyer has recently shown that 63a predominates (> 75%) over 63b in the equilibrium at ambient temperature.

\[ \text{62a} \quad \text{62b} \]
Additional evidence to substantiate the general nature of the bishomoconjugative pathway of \(\alpha\)-halo ketones was obtained by R. E. Wingard, Jr., who observed the conversion of \(\alpha\)-bromo ketone 64 under the predescribed conditions to 1,2,3,4,5,10-hexahydro-5,10-methanobenzocycloocten-11-one (65).

Now that the base induced bishomoconjugative rearrangement of \(\alpha\)-halo ketones had been shown to be a workable reaction, consideration was given to expanding the mechanistic potential of this new intramolecular process. This reaction type was not expected to be unique to \(\alpha\)-halo ketones, but rather a general phenomenon for molecules with the proper functionality and geometry. Other classes of compounds which are capable of generating a carbanion under rather mild conditions should also undergo this transformation. For this purpose, the preparation of \(\alpha\)-halo sulfone 72 was initiated. Its successful synthesis was modeled on the synthesis of related molecules developed earlier by Paquette, and is depicted in Scheme III.
Diol \( \text{I2} \), whose preparation has been described earlier, was converted into the corresponding bis-mesylate (66) with methanesulfonyl chloride in dry pyridine at \( 0^\circ \). Cyclization of 66 to sulfide 67 was effected in high yield by the use of dehydrated sodium sulfide nonahydrate. Both of the reaction sites involved in this double nucleophilic displacement reaction are neopentyl, so hexamethylphosphorus triamide was utilized as a reaction solvent because of its known facility in accommodating hindered nucleophilic reactions. Residual solvent was conveniently removed from the crude sulfide by column chromatography on alumina, from which 67 was isolated as a low-melting waxy solid in 93% yield.

In order to introduce the conjugated diene unit into the molecule, the sulfur atom in sulfide 67 was first blocked by oxidation to sulfone 68, mp 151-152\( ^\circ \), by treatment with two equivalents of an ethereal monoperphthalic acid solution. This was followed by free radical allylic bromination with N-bromosuccinimide and dehydrobromination of the resultant allylic bromide 69 with sodium methoxide in refluxing tetrahydrofuran to afford \( \text{cis-1,6-dimethyl-8-thiabicyclo[4.3.0]non-2,4-diene 8,8-dioxide (70)} \) in 84% overall yield. The position of the halide in 68 is probably as shown, the result of an allylic shift, by analogy with the behavior of a very similar system. The structure of 70, mp 93-94.5\( ^\circ \), is best characterized by its pmr spectrum (CDCl\(_3\)), which displays a singlet at 1.25 \( \delta \) for the
methyl groups, two AB doublets centered at 3.02 and 3.33 δ corresponding to the α-sulfonyl hydrogens which are syn (H3) and anti (H4) to the cyclo-hexadienyl ring, respectively, and a multiplet at 5.45-6.20 δ for the four vinyl hydrogens.

Halogen was introduced into the α-sulfonyl position of the structure by initially reducing the sulfone to sulfide 71 with lithium aluminum hydride in refluxing ether in 78% yield. Even when prolonged reaction times (63 hrs) and a ten-fold excess of reducing agent were employed, a sizeable amount (10-20%) of sulfone 70 was still recovered from the reaction. Ionic chlorination of sulfide 71 with N-chlorosuccinimide via the intermediacy of the chlorosulfonium ion and oxidation of the epimeric α-chlorosulfides (72) with two equivalents of an ethereal monoperphthalic acid solution resulted in the production of epimeric α-chloro sulfones 73a and 73b in a ratio of 63% to 37%, as determined by manual integration of suitably expanded 60 MHz pmr spectra of the crude mixture. Differentiation of these two structures was made on the basis of the chemical shifts of their respective α-sulfonyl hydrogens. Paquette has established, ultimately by an X-ray structure analysis, that the chemical shift of an α-hydrogen positioned above unsaturated carbon atoms in an α-chlorosulfone of the propellane type is shifted to higher field relative to its epimeric counterpart. Such a geometry is present in 73b, and the chemical shift of Hα is shifted upfield by 0.28 δ relative to that in 73a. The two epimeric α-chloro sulfones 73a, mp 90-91°, and 73b, mp 91.5-92°, were completely separated by modified gradient elution column chromatography on silica gel (see Experimental). Minor epimer 73b was eluted from the column
first and displayed sulfone bands at 1125 and 1325 cm\(^{-1}\) in the infrared (Nujol). The pmr spectrum (CDCl\(_3\)) showed singlets at 1.16 and 1.32 \(\delta\) for the 1-methyl and 6-methyl groups respectively, a doublet at 3.12 \(\delta\) with a coupling constant of 13.5 Hz for H\(_B\), a doublet at 3.43 \(\delta\) with the same coupling constant for H\(_A\), a singlet at 5.18 \(\delta\) for H\(_C\), and a multiplet at 5.42-6.25 \(\delta\) for the four vinyl hydrogens. Major epimer 73a followed immediately. Its infrared spectrum (Nujol) contained sulfone bands at 1120 and 1320 cm\(^{-1}\), while its pmr spectrum (CDCl\(_3\)) had singlets at 1.12 and 1.47 \(\delta\), corresponding to the 1-methyl and 7-methyl groups respectively, a doublet at 3.05 \(\delta\) with a coupling constant of 13.5 Hz for H\(_B\), a doublet at 3.33 \(\delta\) with the same coupling constant for H\(_A\), a singlet at 4.90 \(\delta\) for H\(_C\), and a multiplet at 5.25-6.25 \(\delta\) for the four vinyl hydrogens.

When the \(\alpha\)-chlorosulfone mixture was treated briefly with a slight excess of potassium tert-butoxide in dimethylsulfoxide at 25\(^\circ\)C, workup of the resultant dark solution followed by recrystallization from methylene chloride-ether afforded 7,8-dimethyl-9-thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-dioxide (74), mp 201.5\(^\circ\)dec, in 27\% yield. The structure rests firmly

![Chemical Structure](image)

on both spectroscopic and chemical evidence. Combustion data were correct for C\(_{10}\)H\(_{12}\)O\(_2\)S. The presence of extended conjugation was evident from the ultraviolet spectrum (ethanol), which displays a maximum at 282 nm (\(\varepsilon\) 2100)
and the existence of a sulfonyl group follows from the infrared spectrum (Nujol), which contains sulfone bands at 1110 and 1290 cm\(^{-1}\). The pmr spectrum (CDCl\(_3\)) consists of a singlet at 1.88 \(\delta\) for the methyl groups, a multiplet at 3.62-3.95 \(\delta\) for the two bridgehead hydrogens, and a multiplet at 5.83-6.08 \(\delta\) for the four vinyl hydrogens. These spectra compare favorably with those of the parent sulfone, 9-thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-dioxide (76), prepared by the oxidation of the known sulfoxide.

\[\text{S} \rightarrow \text{O}\]

\[\text{ClCH}_2\text{CO}_2\text{H} \xrightarrow{\text{ether}} \text{SO}_2\]

75

[Diagram]

76

\(\text{SO}_2\)

\(\text{CH}_3\)

75\(^{88a-c}\) Bicyclic sulfone 76 displays multiplets in the pmr (CDCl\(_3\)) at 3.78-4.15 \(\delta\) for the two bridgehead hydrogens and at 5.80-6.37 \(\delta\) for the six vinyl hydrogens, sulfone bands in the infrared (Nujol) at 1100, 1125, and 1290 cm\(^{-1}\), and maxima in the ultraviolet spectrum (ethanol) at 225 (\(\epsilon\ 2820\)) and 279 nm (2340).

Additional evidence for the structure of 74 results from its photochemistry. Symmetry rules predict that irradiation of 74 will result in a concerted, linear cheletropic bond reorganization with the extrusion of

\[\text{hv} \quad [\sigma^1_s + \sigma^1_s + \sigma^2_s] \quad \text{H}_3\text{C} \quad \text{SO}_2 \quad \text{H}_3\text{C} \]

74

[Diagram]

57
sulfur dioxide and formation of 1,2-dimethylcyclooctatetraene (S) via the disrotatory mode. When 74 was irradiated, S was actually isolated as the only volatile product and was identified by comparison of spectral properties with those of an authentic sample. Bicyclic sulfoxide 75 is reported to also undergo a cheletropic reaction to give cyclooctatetraene when exposed to ultraviolet light.

Compelling evidence for the generality of the bishomoconjugative pathway in the case of α-chloro sulfones was gained by R. E. Wingard Jr. Treatment of α-chloro sulfones 77a, 77b, and 78 under the predescribed conditions led to 79a, 79b, and 80, respectively.

\[
\begin{align*}
\text{Cl} & \quad \text{(CH}_2\text{)}_n \quad \text{KOTBu} \quad \text{DMSO} \quad (\text{CH}_2\text{)}_n \quad \text{SO}_2 \\
77a, \ n = 2 & \quad 79a, \ n = 2 \\
77b, \ n = 3 & \quad 79b, \ n = 3
\end{align*}
\]

\[
\begin{align*}
\text{Cl} & \quad \text{C}_2\text{S} \quad \text{KOTBu} \quad \text{DMSO} \\
78 & \quad 80
\end{align*}
\]
Although four examples of this intramolecular rearrangement of α-halo sulfones were already at hand, it was of considerable interest to study this rearrangement in the parent system, which would involve the synthesis of α-chloro sulfone 81. Treatment of this compound with base as described earlier should result in the production of 76, a molecule of considerable synthetic utility in conjunction with later studies. At the time this work was initiated, no other route to this compound was available.

Initially the synthetic sequence utilized to gain entry to 81 proceeded smoothly. Bis-mesylate 82, mp 86-87°, prepared by the action of methane sulfonyl chloride on diol 35 in pyridine at 0° in high yield, was cyclized with dehydrated sodium sulfide nonahydrate 58 in hexamethylphosphorus tri-

amide to afford sulfide 83 in 89% yield as a low melting, waxy solid. Subsequent oxidation with two equivalents of an ethereal monoperphthalic acid solution 57 resulted in the formation of cis-8-thiabicyclo[4.3.0]non-
3-ene 6,8-dioxide (84), mp 74-75°, in good yield. The structure of 84 was verified by its pmr spectrum (CDCl₃), which displayed a broad envelope of multiplets at 1.92-3.50 δ for the ten aliphatic hydrogens and a triplet at 5.72 δ with a coupling constant of 1.5 Hz for the two olefinic protons; its infrared (Nujol) which exhibited sulfone bands at 1110, 1280, and 1295 cm⁻¹, and its correct combustion analysis for C₉H₁₂O₂S.

Oxidation of the double bond in 84 to the conjugated diene unit in 86 was realized only with difficulty. Treatment of the allylic bromide of 84

![Structure](image)

under a variety of conditions, which included different bases, solvents, temperatures, and exposure times resulted in poor mass return (after extraction) and formation of complex mixtures (tlc). In an attempt to circumvent this difficulty, dibromide 85 was prepared and subjected to various dehydro-bromination conditions. A trend was observed from these data. Weak bases, such as 2,6-lutidine (even in refluxing xylene), left 85 untouched while stronger bases, such as potassium tert-butoxide, resulted in extensive decomposition. From the low mass balances, it appeared that water soluble
sulfur salts were perhaps arising from attack of the base at sulfur or abstraction of an α- or β-hydrogen followed by destructive bond reorganization. In fact, acidification of aqueous washes resulted in the isolation of large quantities of unidentified material. It is possible that the lack of substituents at the bridgehead positions permits reactions with base that were prohibited in molecules previously subjected to these conditions.

Whatever the case, conditions were found from which a high yield of 86 could be realized. Treatment of 85 with lithium chloride and lithium carbonate in hexamethylphosphorus triamide at 90° resulted in a 78% yield of 86, bp (0.06 mm) 134-135°. Extended conjugation is indicated by the electronic spectrum (ethanol), which displays maxima at 255 (ε 1800), 262 (2050), and 271 nm (1910), while bands in the infrared spectrum (neat) at 1115 and 1295 cm⁻¹ are characteristic for a sulfone. The pmr spectrum (CDCl₃) contains a broad singlet centered at 3.23 δ for the six aliphatic hydrogens and a multiplet at 5.57-6.40 δ for the four vinyl hydrogens. Although numerous attempts to induce the crystallization of 86 were unsuccessful, correct combustion data were obtained on a sample purified by vpc techniques on column C at 165°. A second product of this reaction, which plagued the purification and characterization of 86 until conditions
were developed to minimize its production, was isolated from a higher temperature reaction by preparative vpc techniques on column C. This compound, mp 112-114°, was found to contain a sulfone linkage from bands at 1095 and 1275 cm⁻¹ in the infrared spectrum (Nujol). A high resolution mass spectrum showed that this sulfone was isomeric with 86; calculated m/e 170.0401, observed m/e 170.0399. The presence of heteroannular conjugation was determined from the ultraviolet spectrum (ethanol), which displays a maximum at 245 nm (ε 18,700). The pmr spectrum (CDCl₃) contains multiplets at ca. 1.3-2.4 and 2.7-3.7 δ integrating for seven aliphatic hydrogens and a multiplet at 6.22-6.45 δ for three vinyl hydrogens. The only structure which could conceivably arise from this reaction and still satisfy all these data is 87. It is apparently the result of a [1,5] sigmatropic shift on 86.

\[
\text{\chem{\begin{array}{c}
\begin{array}{c}
\text{86}
\end{array}
\end{array}}\quad \text{[1,5] shift} \quad \begin{array}{c}
\begin{array}{c}
\text{86}
\end{array}
\end{array} \quad \text{base} \quad \begin{array}{c}
\begin{array}{c}
\text{87}
\end{array}
\end{array}}
\]

followed by a base induced rearrangement.

Attempted α-halogenations of 86 and its sulfide 88, prepared by the hydride reduction of 87, were eminently unsuccessful. The use of N-chloro-
sucinimide in refluxing carbon tetrachloride followed by oxidation to the sulfone led to a low mass balance of a dark oil which displayed no resonance for an $\alpha$-hydrogen of an $\alpha$-chlorosulfone in the pmr, but rather a large amount of absorption in the aromatic region. It will be recalled that this method was highly successful in compounds where the allylic positions in 88 were blocked by substitution. Halogenation of 86 by the method of Corey, which involved the use of tert-butyllithium to abstract an $\alpha$-hydrogen and trichloromethanesulfonyl chloride as a source of $\text{Cl}^+$, gave a similar result. The utilization of other sources of halide, including sulfuryl chloride, N-bromosuccinimide, and iodine (ethereal solution) were also unsuccessful. The difficulty was not with the production of the $\alpha$-sulfonyl anion, since it could be generated with tert-butyllithium and quenched with water to afford a good return of 86. Further work on this halogenation was abandoned when alternative preparations of the synthetically useful end product of this sequence appeared in the literature.

As mentioned in the Introduction, the preparation of $\alpha$-halo ketones and sulfones containing the bicyclo[4.2.1]nona-2,4,7-triene framework was initiated with the expectancy that carbonyl and sulfonyl 1,3-dipolar ions could be produced as transient intermediates under the proper experimental conditions. These dipolar species were then expected to be trapped by the proximate diene functionality in an intramolecular [4+2] cycloaddition to
give bishomobenzene derivatives and their rearrangement via the retro Diels-Alder pathway to give the observed products. Although the available experimental evidence presently does not provide confirmation of this mechanism, it remains the most plausible pathway.

The wealth of analogy available from extensive past studies of the Favorskii rearrangement suggests that α-bromo ketones 42, 52, and 64 proceed along the bishomoconjugative pathway by initial deprotonation to give 89, followed by π-assisted heterolysis of the C-Br bond to form 90. These

\[
\begin{align*}
\text{Base} & \quad \frac{\text{Br}}{\text{BR}} \\
\text{89} & \quad \frac{\text{O}}{\text{O}} \\
\text{20} & \quad \frac{\text{O}}{\text{O}} \\
\text{21} & \quad \frac{\text{O}}{\text{O}} \\
\text{22} & \quad \frac{\text{O}}{\text{O}}
\end{align*}
\]

zwitterions may now undergo a class A intramolecular ionic cycloaddition with the geometrically accessible diene unit to afford 21, which because of excessive strain would suffer rapid \([\pi^2 s + \sigma^2 s + \sigma^2 s]\) bond reorganization.
to produce the observed product. The use of the highly polar solvent dimethylsulfoxide should favor such a dipolar mechanism, since numerous reports in the literature attribute the nonstereospecificity of the Favorskii reaction in polar solvents to the intervention of zwitterionic species, as discussed in the Introduction. The zwitterionic forms (92) should be favored over the closed forms (92) not only through solvation by the dimethylsulfoxide, but also because of the severe ring strain inherent in the bicyclopentanone part structure in the latter species. Actually, no evidence for the intervention of cyclopropanones 92 has been obtained. If such intermediates should arise, they would be expected to be in mobile equilibrium with oxyallyl 96.

In the cases of α-chloro sulfones 73, 77, and 78, the base induced elimination of HCl most likely occurs through initial, reversible carbonation formation (92) followed by an intramolecular nucleophilic displacement of halide ion as is the case in the Ramberg-Bäcklund reaction (see Introduction) to produce episulfones 94. Because of ring strain, this episulfone could undergo C-C bond heterolysis with generation of 95, which then proceeds to product via its intramolecular cycloaddition adduct 96 as previously described for the ketone analogs. In this eventuality, the intramolecular capture of zwitterion 95 by the proximate diene moiety must be appreciably more facile than the extrusion of sulfur dioxide from episulfone 94. Again, the use of the highly polar aprotic solvent dimethylsulfoxide should facilitate the intervention of a dipolar species.

Some information concerning the effect of solvent polarity on bis-homoconjugative rearrangements is available from the work of R. E. Wingard,
During an effort to determine the optimum conditions for this reaction, it was found that although α-chlorosulfone \( \text{IIa} \) rearranges smoothly when treated with dry sodium methoxide in dimethysulfoxide, only unreacted \( \text{IIa} \) was recovered from similar treatment in tetrahydrofuran. Also, when α-chloro sulfone \( \text{Ib} \) was subjected to the action of potassium tert-butoxide in ether, the normal Ramberg-Bäcklund product, \([4,4,2]\)propella-2,4,6,8,11-pentaene, was isolated in preparatively useful quantities. Evidently, the loss of sulfur dioxide prevails over intramolecular reaction with the diene unit in these solvents. This may be construed to mean that tetrahydrofuran and diethyl ether, because of their poorer solvating power relative to dimethysulfoxide, are not conducive to zwitterion formation, and that under these conditions the cheletropic expulsion of sulfur dioxide
from \( \text{regains its customary position as the kinetically dominant pathway.} \)

A mechanistic alternative to the intramolecular ionic cycloaddition of zwitterions \( \text{22 and 25 would be the intervention of closed forms 22 and 24 in this capture process. Of the two stereoisomers possible for these} \)

\[
\begin{align*}
\text{22} & \quad \text{23} \\
\end{align*}
\]

structures, only \( \text{27 contains the proper geometry for good overlap of orbitals. In 28, the internal bond of the three-membered ring is actually pointed away from the diene orbitals. By observing the mode of addition of maleic anhydride to 22, it has been determined that inside approach to} \)

\[
\begin{align*}
\text{22} & \quad \xrightarrow{120^\circ} \text{100} \\
\end{align*}
\]

the bicyclo[2.1.0]pentane structure is necessary (cf. \( \text{100).} \)). If this reactivity preference is maintained with these structures, only \( \text{28 could undergo cycloaddition. Not only does 28 suffer from poor orbital overlap, but also its geometry is significantly inferior to that of 22 and 25 as determined from molecular models. Also, the electrophilic character of oxyallyl (a 2\( \pi \) component) has been calculated to be far superior to that of the neutral closed form (cyclopropanone).} \)
Another conceivable mechanistic pathway from which bishomobenzene intermediate 102 could arise involves displacement of halide ion from the initially formed carbanion (101) in a bishomoconjugative 1,8-displacement. A vinylogous S_{N}^{2} intramolecular reaction where so many bonds are formed and broken would not be expected to choose a concerted pathway, especially in the light of Bordwell's recent and well substantiated skepticism of the concerted nature of simple S_{N}^{2} reactions. The stepwise attack of a carbanion on a conjugated diene is an inherently unattractive alternative. For these reasons, along with the absence of an energetically favorable driving force and the large energy that must be associated with such a dramatic structural reorganization, the S_{N}^{2} process is not considered a viable possibility. In contrast, the conversion of zwitterions 20 and 25 into 102 is an allowed ionic cycloaddition and proceeds with charge annihilation.

The intramolecular ionic cycloaddition mechanism, a \([\pi^4s + \pi^2s]\) process, is quite similar to the internal Diels-Alder reaction utilized by certain unsaturated propellanes such as 106 when subjected to thermal activation. Appropriate deuterium labeling attested to the intermediacy of bishomobenzene 104 in the production of cyclooctatetraene derivative 105. This
same pathway may be operative in isomerization and degenerate rearrangement reactions of properly labeled cyclooctatetraenes.

Once access is gained to 102, its facile thermally allowed \([\sigma^2 a + \sigma^2 a + \pi^2 a]\) bond reorganization is expected to follow immediately. Many examples of this process have now been reported. 

Although trishomobenzene 107 does display moderate thermal stability \(t_{1/2} = 60 \text{ min at } 90^\circ\), most cases where bis- and trishomobenzene structures exhibit thermal stability are those where a heteroatom occupies a position in the molecule, as in 108a and 108b.

Even trishomobenzenes 109a and 109b are stable at 25\(^\circ\), although they do undergo bond reorganization at 70\(^\circ\). Very recently, the preparation of syn-
benzenetricoxide (109c) has appeared. This material, mp 242°, is amazingly thermally stable, but does undergo bond reorganization slowly at 200° in acetonitrile or more conveniently, in the gas phase at 400-500° to

![Chemical structure]

109c \[ \xrightarrow{\Delta} \] 109d

give 109d. The presence of heteroatoms is apparently displaying a pronounced effect on the stability of bis- and trishomobenzenes.

Additional evidence for the intervention of 21 (R = H) is found in a recent report by Vedejs, who observed 43 as the sole product when bromo ketone 108 was treated with potassium tert-butoxide in tetrahydrofuran.

![Chemical structures with reaction arrows]
Since the epimer of 108 did not give 13, the mechanism suggested involves intramolecular 1,3-displacement of bromide ion from enolate 109 to give bishomobenzene 21, which then leads easily to 13.

By invoking the principle of intercepting reactive intermediates with proximate olefinic linkages in an intramolecular manner, the bishomoconjugative reaction pathway has given rise to a previously unrecognized mechanistic possibility with significant synthetic potential. Further expansion of the scope of this reaction is anticipated to permit preparation of polyunsaturated carbocyclics and heterocyclics which may not be attainable by other methods.
PART I
EXPERIMENTAL

All melting points were taken in open capillaries and are corrected, while boiling points are uncorrected. Nmr spectra were determined with Varian A-60A Varian HA-100, or Jeol JNM-MH-100 spectrometers. Infrared spectra were determined with Perkin-Elmer Model 237 or Model 467 spectrometers, while ultraviolet and visible spectra were recorded on a Cary Model 14 spectrometer. Mass spectra were measured with an AEI MS-9 or Dupont 21-490 mass spectrometer. Microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Unless otherwise stipulated, organic solutions were dried with magnesium sulfate and the alumina and silica gel employed for column chromatography were neutral and of activity I. All dimethylsulfoxide and hexamethylphosphorus triamide utilized was dried before use of vacuum distillation from calcium hydride and stored over molecular sieves under an atmosphere of nitrogen. All vpc columns employed are tabulated on p 206.

cis-1,2-Bis(hydroxymethyl)cyclohex-4-ene (35). To a refluxing suspension containing 24.7 g (0.65 mole) of lithium aluminum hydride in 500 ml of dry tetrahydrofuran was added 76.0 g (0.5 mole) of 1,2,3,6-tetrahydrophthalic anhydride in 800 ml of
dry tetrahydrofuran over a period of 2 hrs (drying tube). The suspension was refluxed 3 days at which time ca. 1 L of tetrahydrofuran was removed by distillation (Newman still). The reaction was diluted with ether and a basic workup at 0° was employed (dropwise and cautious addition of 25 ml of water, followed by 25 g of a 20% sodium hydroxide solution and 75 ml of water). The cold suspension was filtered, whereupon the basic salts were acidified by cautious addition to 700 ml of an ice cold 10% hydrochloric acid solution. This acidic solution was extracted portionwise with ether, the extractions washed with a saturated sodium bicarbonate solution, water, a saturated sodium chloride solution, and the combined organic layers dried and concentrated in vacuo. Distillation at reduced pressure afforded 52.3 g (74%) of 35 as a viscous, clear liquid, bp (0.5 mm) 130° [lit 33 bp (12 mm) 165-170°]; $^1$ $^H$ 2.08 (br s, 6H, allylic and bridgehead), 3.33-3.92 (br m, 4H, >CH-OH), 4.33 (s, 2H, -CH), and 5.63 (br s, 2H, vinyl).

cis-1,2-Bis(p-toluenesulfonoyloxymethyl)cyclonex-4-ene (36). To a stirred solution containing 30.0 g (0.211 mole) of 35 in 50 ml of dry pyridine was added 100 g (0.525 mole) of re-crystallized p-toluenesulfonyl chloride (petroleum ether, 30-60°) in 125 ml of dry pyridine at such a rate as to maintain the temperature below 5° (ice-salt bath) under an atmosphere of dry nitrogen. After the addition was completed (2.5 hrs) the solution was stirred an additional 3 hrs at 5°, at which time it was poured into a large quantity of ice and
diluted with an ice cold 10% hydrochloric acid solution (350 ml) to a volume of 1 L. After several hrs at 0°C the precipitation was complete, and the product was collected on a Buchner funnel and recrystallized from anhydrous methanol (800 ml total volume) to afford 77.2 g (81%) of 36, mp 92-94°C (lit mp 96°C).

**cis-8-Amino-7-cyanobicyclo[4.3.0]nona-3,7-diene (37).** A stirred mixture containing 109.4 g (0.243 mole) of 36 and 35.8 g (0.729 mole) of sodium cyanide in 400 ml of freshly distilled dimethylsulfoxide was cautiously heated to 100°C under an atmosphere of dry nitrogen. After 1.5 hrs of treatment the homogeneous solution was cooled to 25°C, 10.73 g (0.255 mole) of a 57% dispersion (mineral oil) of sodium hydride, pre-washed with benzene, in dimethylsulfoxide was added over a period of 10 min, and the mixture was very cautiously heated to 100°C. After 45 min of heating, the mixture was poured into ice, diluted with ice water to a volume of 3 L, cooled, filtered, washed with small portions of ice water, and dried to a constant weight in a vacuum oven at 25°C to afford 35.2 g (90.5%) of 37 as an off-white solid, mp 96-97°C (lit mp 195.4-196°C); δ<sup>CDCl₃</sup> 1.67-3.25 (m, 8H, methylenes and bridgehead), 4.68 (br s, 2H, -NH₂), and 5.78-5.97 (m, 2H, vinyl); ν<sub>Nujol</sub> max 3380, 3310, 3220, 2180, 1660, and 1600 cm⁻¹.

A comparable yield was realized when hexamethylphosphorus triamide was utilized as a solvent.
cis-1,2-Bis(carboxymethyl)cyclohex-4-ene (38). A mixture containing 32.0 g (0.20 mole) of 37 and 110 g (2.75 moles) of sodium hydroxide in 200 ml of ethylene glycol and 275 ml of water was refluxed under an atmosphere of dry nitrogen for 12 hrs, at which time it was cooled to 25°, diluted to a volume of 1.25 l with water, washed with methylene chloride and slowly added to 500 ml of an ice cold 6M hydrochloric acid solution with external cooling when necessary. After several hours at 0° the product was collected on a Buchner funnel and dried to a constant weight in a vacuum oven at 25° to afford 27.7 g (70%) of 38, mp 156-157° (lit mp 157°); ν\text{max} 1685 and 2900 cm\(^{-1}\). Extraction of the filtrate with several portions of ether afforded, upon concentration in vacuo and drying as before, 6.1 g (15.5%) of additional material. The total yield was 33.8 g (85.5%).

cis-1,2-Bis(carboxymethyl)cyclohex-4-ene Dimethyl Ester (46). Diazomethane, prepared from N-methylnitrosourea, as was slowly introduced into a solution containing 9.9 g (58 mmole) of 38 in 250 ml of freshly distilled glyme, maintained at 0° by the use of a glass "U" tube extending below the surface of the glyme, as described by Anet. The solution was stirred at ambient temperature overnight, at which time it was gently warmed on a
steam bath, cooled to 25°, filtered, dried, and concentrated in vacuo to afford 11.18 g (99%) of \( \text{h6} \); \( \delta^{1} \text{CDCl}_3 \) \( 1.75-2.52 \) \( \text{m} \), \( 10\text{H} \), methylenes and bridgehead), \( 3.65 \) \( \text{s} \), \( 6\text{H} \), \(-\text{CH}_3 \), and \( 5.62 \) \( \text{t} \), \( J = 1.5 \text{ Hz} \), \( 2\text{H} \), vinyl); \( \nu_{\text{max}} \) 1750 cm\(^{-1}\). An analytical sample was prepared with the use of preparative vpc on column A at 180°, \( t_r = 8 \) min.

**Anal.** Calcd for \( C_{12}H_{18}O_4 \): C, 63.70; H, 8.02.

**Found:** C, 63.54; H, 8.16.

### syn- and anti-\( \gamma \)-Carbethoxy-cis-bicycle\([4.3.0]\)non-3-en-8-one (47)

A solution containing 10.95 g (48.5 mmole) of \( \text{h6} \), 5.75 g (0.25 g-atom) of sodium, and 13.8 g (0.30 mole) of absolute ethanol in 250 ml of benzene was refluxed for 13 hrs (drying tube), at which time it was cooled to 10°, acidified with 100 ml of a 6M hydrochloric acid solution and diluted with 400 ml of ether. The organic layer was washed with small portions of water until neutral. The combined aqueous layers were extracted several times with methylene chloride, whereupon these combined extracts were also washed with water as before. The combined organic portions were washed with a saturated sodium chloride solution, dried, and concentrated in vacuo to afford 9.08 g (91%) of \( 47 \); \( \delta^{1} \text{CDCl}_3 \) \( 2.1 \) \( \text{t} \), \( J = 7 \text{ Hz} \), \( 3\text{H} \), \(-\text{OCH}_2\text{CH}_3 \), \( 1.85-3.00 \) \( \text{m} \), \( 9\text{H} \), all hydrogens except ester and olefinic), \( 4.20 \) \( \text{q} \), \( J = 7 \text{ Hz} \), \( 2\text{H} \), \(-\text{OCH}_2\text{CH}_3 \), and \( 5.70 \) \( \text{br s} \), \( 2\text{H} \), vinyl); \( \nu_{\text{max}} \) 1750 and 1760 cm\(^{-1}\).
**cis-Bicyclo[4.3.0]non-3-en-8-one (39).** A stirred mixture of 4.95 g (0.025 mole) of \( ^8 \) and 256 mg (1.07 mmole) of barium oxide was distilled through a short pass condenser equipped with an ice cooled collector at 275° and 100 mm pressure for 5 hrs, at which time the distillate was diluted with 100 ml of hexane, filtered, washed with a saturated sodium chloride solution, dried, and concentrated in vacuo. Distillation at reduced pressure afforded 1.86 g (55%) of 39, bp (0.25 mm) 41.5-42.5°; \( \delta^{\text{CDCl}_3}_{\text{TMS}} \) 1.8-2.7 (m, 10H, methylenes and bridgehead) and 5.70 (t, J = 1.5 Hz, 2H, vinyl), [lit \( ^{40b} \) bp (11 mm) 101°]; \( \nu_{\text{max}} \) neat 1740 cm\(^{-1}\). An analytical sample was prepared with the use of preparative vpc on column A at 140°, \( t_r = 6 \) min.

Anal. Calcd for C\( _6 \)H\( _{12} \)O: C, 79.37; H, 8.88.


**cis-8,8-Dioxethylenebicyclo[4.3.0]non-3-ene (40).** A solution containing 2.75 g (0.0189 mole) of 39, 2.5 ml of ethylene glycol, and 100 mg of p-toluenesulfonic acid in 80 ml of dry benzene was refluxed under a Dean-Stark trap for 90 hrs (drying tube), at which time it was cooled to 25°, washed with a saturated sodium bicarbonate solution, water, a saturated sodium chloride solution, dried, and concentrated in vacuo. Distillation at
reduced pressure afforded 3.214 g (94%) of $^{14}O$, bp (0.25 mm) 57-60°; $^1$CDCl$_3$ 
1.6-2.5 (m, 10H, methylenes and bridgehead), 3.57 (s, 4H, -OC$_2$H$_5$CH$_2$O-), and 
5.67 (t, $J$ = 1.5 Hz, 2H, vinyl); $\nu$$_{max}$$^\text{neat}$ 1055, 1065, 1080, and 1120 cm$^{-1}$.
An analytical sample was prepared with the use of preparative vpc on column A at 140°.

Anal. Calcd for C$_{11}$H$_{16}$O$_2$: C, 73.30; H, 8.95.

Found: C, 73.11; H, 8.92.

cis-Bicyclo[4.3.0]non-2,4-diene-8-one (48). To a stirred solution containing 4.157 g (23.00 mmole) of 32 in 
100 ml of methylene chloride was added one equivalent of molecular bromine in methylene chloride over a 
period of 40 min at -70° (drying tube). The solution was diluted with 
200 ml of methylene chloride, at which time it was washed with a 0.5M sodium hydroxide solution, water, saturated sodium chloride solution, dried, and 
concentrated in vacuo to afford 7.217 g (92%) of the crystalline dibromide, which contained no vinyl resonance in the nmr.

A stirred mixture containing the crude dibromide, 4.83 g (115 mmole) of lithium chloride, and 8.52 g (115 mmole) of lithium carbonate in 125 ml of freshly distilled hexamethylphosphorus triamide was heated at 90-95°
for 40 hrs under an atmosphere of dry nitrogen, at which time it was cooled to 25°, diluted with 500 ml of ice water, and extracted numerous times with pentane. The combined organic extracts were washed several times with
water, saturated sodium chloride solution, dried, and concentrated \textit{in vacuo}.

This material was hydrolyzed by stirring in 320 ml of 3:1 ethanol-water containing 400 mg of \( p \)-toluenesulfonic acid at 25° for 17 hrs, whereupon it was poured into 1 l of saturated sodium bicarbonate solution and extracted portionwise with ether. The combined organic extracts were washed with water until neutral, saturated sodium chloride solution, dried, and concentrated \textit{in vacuo}. Flash distillation (50-100° and 0.3 mm) afforded 1.862 g of colorless, crude \( 4l \). Chromatographic analysis (vpc) showed one major and one minor volatile peak, along with four less volatile peaks. This mixture was separated with the use of preparative vpc on column A at 115° to afford 918 mg (30%) of \( 4l \), which was contaminated with a small amount of \( 32 \) (longer retention time). Very pure material could be prepared by repurification as before; \( ^{1}^\text{H} \) NMR, 3.23-2.48 (m, \( 4H \), methylenes), 2.93-3.27 (m, \( 2H \), bridgehead), and 5.53-6.10 (m, \( 4H \), vinyl); \( \nu \) \text{max} 1740 cm\(^{-1} \), \( \lambda \) \text{max} 276 \text{nm} (e 2930), 265 (3240), and 255 nm sh (2360); calculated m/e 154.0732, observed m/e 154.0729.

A semicarbazone was prepared by standard methods \textit{in situ} in 80% yield, mp 181-185° dec. An analytical sample was prepared by recrystallization from ethanol-water, mp 186-189° dec.

\textbf{Anal.} Calcd for \( C_{10}H_{13}N_{3}O \): C, 62.80; H, 6.85; N, 21.98.

\textbf{Found:} C, 62.80; H, 6.97; N, 22.52

\textbf{Bicyclo[4.2.1]nona-2,4,7-trien-9-one (43).} To a stirred solution containing 58 mg (0.433 mmole) of \( 4l \) and 37 mg (0.433 mmole) of 2-pyrrolidone in 2.5 ml of freshly distilled tetrahydrofuran was added dropwise 215 mg

\[ \text{Bicyclo[4.2.1]nona-2,4,7-trien-9-one (43).} \]
(0.433 mmole) of pyrrolidone hydrotribromide in 10 ml of freshly distilled tetrahydrofuran over a period of 30 min at 25° in the absence of light. As the reaction proceeded, the insoluble pyrrolidone hydrobromide precipitated from the solution as a white solid. After 1.5 hrs the mixture was filtered, concentrated in vacuo, and dissolved in ether, at which time it was refiltered, washed with water, saturated sodium chloride solution, dried, and concentrated in vacuo to afford the crude bromoketone 42. To a stirred solution containing bromoketone 42 in 5 ml of freshly distilled dimethylsulfoxide was added 58 mg (20% excess) of freshly sublimed potassium tert-butoxide in one portion at 25°. The reaction immediately turned dark red. After 15 min of stirring, the solution was quenched by the dropwise addition of 20 ml of ice cold water, at which time the solution was extracted numerous times with pentane. The combined organic extracts were washed several times with water, saturated sodium chloride solution, dried, and concentrated in vacuo. The product was isolated from this crude mixture by the use of vpc on column A at 95°. Its infrared and nmr spectra, along with its vpc retention time, were identical with those of authentic material. 43 The isolated yield was 10-30%, along with 10-25% of recovered 41.

cis-1,2-Dimethyl-1,2,3,6-tetrahydrophthalic Anhydride (44). A thick-walled glass bomb, containing 100 ml (1.3 mole) of butadiene, 38 g (0.3 mole) of dimethylmaleic anhydride 44 and 50 mg of hydroquinone dissolved in 30 ml of
benzene at -78°, was heated for 4 days in a Woods metal bath maintained at 160-180°. The bomb was cooled (-78°), cautiously opened, and its contents poured into a round-bottomed flask. The transfer was facilitated with several small portions of hot tetrahydrofuran. After the solvents were removed by distillation (atms.), the residue was subjected to a bulb-to-bulb distillation (90-220° and 0.2 mm). The distillate was dissolved in 500 ml of ether and 150 ml of methylene chloride, and was washed with 125 ml portions of a 10% solution of potassium carbonate for 45 min periods with vigorous mechanical stirring until the washes were distinctly basic. The organic layer was washed with water until neutral, saturated sodium chloride solution, dried, and concentrated in vacuo. Trituration of the crystalline residue with petroleum ether (65-120°), followed by sublimation (100° and 0.2 mm), afforded 24.0 g (44%) of \( \frac{4}{4} \), mp 98-98.5° (lit. mp 99.2-99.6°); \( \delta_{\text{CDCl}_3} \) 1.35 (s, 6H, -CH₃), 1.83-1.92, 2.06-2.25, 2.42-2.60, 2.72-2.90 (m, 4H, allylic), and 3.49-3.60 (m, 2H, vinyl). Cautious acidification of the combined basic washes at 0°, followed by extraction with methylene chloride and drying, afforded 14.2 g (37%) of recovered dimethylmaleic anhydride upon concentration in vacuo; \( \delta_{\text{CDCl}_3} \) 2.07 (s, CH₃).

cis-1,2-Bis(hydroxymethyl)-1,2-dimethylcyclohex-4-ene (45). To a refluxing suspension containing 6.0 g (0.158 mole) of lithium aluminum hydride in 400 ml of dry tetrahydrofuran was added 21.81 g (0.121 mole) of 45 in 200
ml of dry tetrahydrofuran over a period of 2.5 hrs. (drying tube). The mixture was refluxed for 3 days, at which time it was cooled to 0°. Ice water (90 ml) was added dropwise, followed by dilution with 600 ml of an ice cold 5% sulfuric acid solution. The product was extracted from this aqueous solution with small portions of methylene chloride. The combined dried organic extracts were concentrated in vacuo and sublimed (130° and 0.2 mm) to afford 19.3 g (94%) of white crystalline \( \text{H}_5 \), mp 195-200°; \( \delta_{\text{CDCl}_3} \) 0.90 (s, 6H, -CH\(_3\),) 1.52-2.43 (m, 4H, allylic), 3.45 (s, 4H, -CH\(_2\)OH), 5.02 (s, 2H, -OH), and 5.55 (t, \( J = 1.5 \) Hz, 2H, vinyl); \( \nu_{\text{max}}^{\text{Nujol}} \) 3090 cm\(^{-1}\). An analytical sample was prepared by recrystallization from hexane, mp 198-201°.

**Anal. Calcld for C\(_{10}\)H\(_{16}\)O\(_2\): C, 70.54; H, 10.66.**

**Found: C, 70.47; H, 10.57.**

cis-1,2-Bis(p-toluenesulfonyloxymethyl)-1,2-dimethylcyclohex-4-ene (\( \text{H}_6 \)).

To a stirred solution containing 13.3 g (0.0772 mole) of \( \text{H}_5 \) in 40 ml of dry pyridine was added 59.5 g (0.313 mole) of recrystallized p-toluenesulfonyl chloride (petroleum ether, 30-60°) in 80 ml of dry pyridine at 0° over a period of 1 hr (drying tube). The mixture was stirred at ca. 7° for 7 days, at which time it was poured into a large quantity
of ice and diluted with an ice cold 10% hydrochloric acid solution to a volume of 1 l. After several hrs at 0° the precipitation was completed, and the product collected on a Buchner funnel and recrystallized from anhydrous methanol to afford 31.1 g (83%) of 46, mp 80-82.5°; δ^CDCl3 0.88 (s, 6H, -CH3), 1.84 (br s, 4H, allylic), 2.47 (s, 6H, CH3Ar), 3.89 (s, 4H, -CH2O-), 5.47 (t, J = 1.2 Hz, 2H, vinyl), 7.36 (d, J = 8 Hz, 4H, aromatic), and 7.61 (d, J = 8 Hz, 4H, aromatic). An analytical sample was prepared by several recrystallizations from absolute methanol, mp 83.5-84°.


Found: C, 60.32; H, 6.36; S, 13.27.

cis-8-Amino-7-cyano-1,6-dimethylbicyclo[4.3.0]nona-3,7-diene (47). A stirred mixture containing 16.7 g (0.0349 mole) of 46 and 5.15 g (0.105 mole) of sodium cyanide in 175 ml of freshly distilled hexamethylphosphorus triamide was heated at 110-115° under an atmosphere of dry nitrogen for 70 hrs, at which time it was cooled to 60° and 1.50 g (0.0356 mole) of a 57% dispersion (mineral oil) of sodium hydride, pre-washed with benzene, was added in hexamethylphosphorus triamide over a period of several minutes. After heating the mixture an additional 4 hrs as before, it was poured into a large volume of ice and diluted with ice water to a volume of 1 l. After several hrs at 0°, the product was collected on a Büchner funnel, washed with several portions of cold water, and dried in a
vacuum oven at 25° to constant weight to give 5.24 g (80%) of \( \text{I7} \) as an off-white solid, mp 130.5-131°dec; \( \delta^\text{CDCl}_3 \) 1.05 (s, 3H, -CH3), 1.08 (s, 3H, -CH3), 1.88-2.37 (m, 6H, methylenes), 4.58 (br s, 2H, -NH2), and 5.67-5.83 (m, 2H, vinyl); \( \nu_{\text{max}}^\text{Nujol} \) 3400, 3325, 3215, 2180, 1650, and 1600 cm\(^{-1}\). An analytical sample was prepared by several recrystallizations from carbon tetrachloride, mp 130.5-131°.

**Anal.** Calcd for C\(_{12}\)H\(_{14}\)N\(_2\): C, 76.55; H, 8.75.

**Found:** C, 76.97; H, 8.53.

\( \text{cis-1,2-Bis(carboxymethyl)-1,2-dimethylcyclohex-4-ene (48)} \). A mixture containing 16.95 g (0.0901 mole) of \( \text{I7} \) and 75 g (1.87 mole) of sodium hydroxide in 150 ml of ethylene glycol and 180 ml of water was refluxed under an atmosphere of dry nitrogen for 93 hrs, at which time it was cooled to 10°, diluted to a volume of 800 ml with cold water, washed with methylene chloride, filtered, and slowly added to 375 ml of a 6M hydrochloric acid solution with external cooling when necessary. After several hrs at 0°, the suspension was filtered and the filtrate dried to constant weight in a vacuum oven at 40° to afford 17.44 g of \( \text{I8} \); \( \nu_{\text{max}}^\text{Nujol} \) 1695 cm\(^{-1}\). The aqueous mother liquor was extracted several times with ether to afford 0.70 g of additional material. The total yield was 18.14 g (89%).

\( \text{cis-1,2-Bis(carboxymethyl)-1,2-dimethylcyclohex-4-ene Dimethyl Ester (53)} \). Diazomethane, prepared from N-methylnitrosourea, was slowly introduced at 0° into a solution containing 9.96 g (44 mmole) of \( \text{I8} \) in 250 ml of
fresly distilled glyme by the use of a glass "U" tube extending below the surface of the glyme as described by Anet. The solution was stirred at ambient temperature overnight, at which time it was gently warmed on a steam bath, dried, and concentrated in vacuo to afford 11.19 g (100%) of \( \text{C}_{14}\text{H}_{22}\text{O}_{4} \). 

\[ \delta_{\text{TMS}}^{\text{CDCl}_3} 1.00 (s, 6H, -CH_3), 2.0-2.5 (m, 4H, allylic), 2.31 (s, 4H, -CH_2CO_2CH_3), 3.63 (s, 6H, -OCH_3), \text{ and } 5.61 \text{ (t, } J = 1.5 \text{ Hz, 2H, vinyl); } \]

\[ \nu_{\text{max}} \text{ neat } 1750 \text{ cm}^{-1}. \]

An analytical sample was prepared with the use of vpc on column A at 190°C.

**Anal.** Calcd for \( \text{C}_{14}\text{H}_{22}\text{O}_{4} \): C, 66.11; H, 8.72.

Found: C, 65.92; H, 8.67.

**syn- and anti-7-Carbethoxy-cis-1,6-dimethylbicyclo[4.3.0]non-3-en-8-one** (54). A solution containing 11 g (44 mmole) of \( \text{C}_{14}\text{H}_{22}\text{O}_{4} \), 5.75 g (250 mg-atoms) of sodium, and 13.8 g (300 mmole) of absolute ethanol in 250 ml of benzene was refluxed for 7 hrs (drying tube), at which time it was cooled to 10°C, acidified with 100 ml of a 6M hydrochloric acid solution, and diluted with 400 ml of ether. The organic layer was washed with small portions of water until neutral. The combined aqueous layers were extracted several times with methylene chloride, whereupon these combined extracts were washed
as before with water. The combined organic extracts were washed with a saturated sodium chloride solution, dried, and concentrated in vacuo to afford 9.645 g (94.5%) of crude $\frac{54}{5}$, $\nu_{\text{max}}$ $1720$ and 1760 cm$^{-1}$.

**cis-1,6-Dimethylbicycle[4.3.0]non-3-en-8-one (59).** A solution containing 9.64 g (40.8 mmole) of $\frac{54}{5}$ and 40 g of potassium hydroxide in 360 ml of absolute ethanol and 40 ml of water was refluxed 15 hrs (drying tube), at which time it was cooled to 25°, acidified with 270 ml of a 6M hydrochloric acid solution, and refluxed an additional 1.5 hrs. The solution was then cooled to 0°, diluted to 2.5 l with cold water, and extracted portionwise with methylene chloride. The combined organic extracts were washed with water, saturated sodium chloride solution, dried, and concentrated in vacuo to afford 7.744 g of a crude mixture of 59 and 54 in a ratio of ca. 2:1 (pmr analysis).

When a portion of this mixture was recycled, the effect on the product ratio was negligible. This crude mixture was chromatographed on a column prepared by wet-packing 150 g of neutral alumina with ether followed by elution with ether. The ketone eluted from the column immediately, whereupon it was distilled at reduced pressure, bp (0.2 mm) 60°, and sublimed (75° and 0.2 mm) to afford 1.85 g (27%) of 59; $\delta^{\text{CDCl}_3}_{\text{TMS}}$ 1.05 (s, 6H, -CH$_3$), 2.00-2.58 (m, 4H, allylic), 2.15 (s, 4H, -CH$_2$C=0), and 5.65 (t, $J = 1.5$ Hz, vinyl); $\nu_{\text{Nujo}}$ 1740 cm$^{-1}$; calculated m/e 164.1201, observed 164.1199.
A semicarbazone was prepared by standard methods in 76% yield, mp 214-216 °C dec. An analytical sample was prepared by recrystallization from ethanol-water, mp 215-216 °C dec.

**Anal. Calcd for C₁₂H₁₅N₃O: C, 65.12; H, 8.65; N, 18.99.**

**Found: C, 64.73; H, 8.62; N, 18.88.**

Continued elution with ether afforded 1.37 g of cis-1,6-Dimethylbicyclo[4.3.0]non-3-en-8-one (49).

Sublimation (90-95 °C and 0.2 mm) of the distillate afforded 5.071 g (70%) of 49 as a white, low melting solid, which was identified by comparison of its pmr spectrum with that of previously prepared material. From the residue remaining in the reaction vessel 760 mg (9%) of 48, identified by its infrared spectrum, was also isolated.

**cis-1,6-Dimethyl-8,8-dioxyethylenebicyclo[4.3.0]non-3-ene (50).** A solution containing 7.421 g (45.1 mmole) of 49, 7 ml of ethylene glycol, and 500 mg of p-toluenesulfonic acid in 400 ml of dry benzene was refluxed under Dean-Stark conditions for 90 hrs (drying
tube), at which time it was cooled to 25°, washed with saturated sodium bicarbonate solution, water, saturated sodium chloride solution, dried, and concentrated in vacuo. Distillation at reduced pressure afforded 6.669 g (71%) of 50, bp (0.3 mm) 69°; δCDCl₃ 0.97 (s, 6H, -CH₃), 1.40-2.48 (m, 8H, methylenes), 3.82 (s, 4H, -CH₂O-), and 5.55 (t, J = 1.3 Hz, 2H, vinyl); νmax 1015, 1060, 1110, and 1145 cm⁻¹. An analytical sample was prepared with the use of preparative vpc on column A at 140°, tᵣ = 23 min.

Anal. Calcd for C₁₅H₂₀O₂: C, 74.96; H, 9.68.

Found: C, 74.84; H, 9.68.

cis-1,6-Dimethylbicyclo[4.3.0]non-2,4-dien-8-one (51). To a stirred solution containing 5.20 g (25 mmole) of 50 in 125 ml of methylene chloride was added 1 equivalent of molecular bromine in 70 ml of methylene chloride over a period of 2.5 hrs at -70° (drying tube). The dibromide precipitated at this temperature, but redissolved as the solution was allowed to reach 0°. This solution was washed with a 0.5 M sodium hydroxide solution, water, a saturated sodium chloride solution, dried, and concentrated in vacuo.

A stirred solution containing the crude dibromide, 5.25 g (0.125 mole) of lithium chloride, and 9.25 g (0.125 mole) of lithium carbonate in 250 ml of freshly distilled hexamethylphosphorus triamide was heated at 90° for 18 hrs under an atmosphere of dry nitrogen, at which time it was cooled to 25°, diluted to a volume of 1 l with ice water, and extracted
numerous times with pentane. The combined organic extracts were washed numerous times with water, saturated sodium chloride solution, and concentrated in vacuo. This material was hydrolyzed by stirring in 500 ml of ethanol-water (3:1) containing 1 g of p-toluenesulfonic acid at 25° for 23 hrs, whereupon it was poured into 1.3 l of a saturated sodium bicarbonate solution and extracted numerous times with ether. The combined organic extracts were washed numerous times with water, saturated sodium chloride solution, dried, and concentrated in vacuo. This crude material was subjected to flash distillation (90-120° and 0.3 mm) to afford 3.040 g of a colorless liquid. Chromatographic analysis (vpc) showed a major and minor volatile peak along with two less volatile peaks. This mixture was separated with the use of preparative vpc on column A at 140° to afford 1.074 g (26.5%) of 51 as a low melting solid; δ\text{CDCl}_3 1.07 (s, 6H, -CH₃), 2.53 and 2.13 (center of AB doublets, and J = 18 Hz, 4H, H₃ and H₄), 5.37-6.03 (m, 4H, vinyl); ν\text{max} 1740 cm⁻¹; λ\text{max} 272 (ε 3110), 263 (3450), and 255 nm sh (2510); calculated m/e 162.1044, observed 162.1043; and 584 mg (14%) of 4g (longer retention time), characterized by its pmr spectrum.

A semicarbazone was prepared by standard methods in 73% yield; mp 203-206° dec. An analytical sample was prepared by recrystallization from ethanol-water, mp 205-206° dec.

\textbf{Anal. Calcd for C}_{12}H_{17}N_{3}O: ~ C, 65.72; H, 7.81; N, 19.16.}

\textbf{Found: ~ C, 65.69; H, 7.74; N, 19.13.}

7,8-Dimethylbicyclo[4.2.1]nona-2,4,7-trien-9-one (56). To a stirred solution containing 602 mg (3.72 mmole) of 51 and 368 mg (3.72 mmole) of 2-pyrrolidone in 100 ml of dry tetrahydrofuran was added dropwise 1.84 g
(3.72 mmole) of pyrrolidone hydrotribromide in 100 ml of dry tetrahydrofuran over a period of 4 hrs at 25° in the absence of light. The mixture was stirred 20 hrs at 25° at which time it was filtered, concentrated in vacuo, dissolved in ether (125 ml), filtered, and concentrated in vacuo to afford crude 52 as a yellow liquid.

To a stirred solution containing crude α-bromo ketone 52 in 100 ml of freshly distilled dimethylsulfoxide was added 1.70 g (15.2 mmole) of potassium tert-butoxide in one portion at 25° with slight external cooling. The reaction immediately developed a deep brick red color. After 30 min of exposure, the reaction was quenched by the dropwise addition of 400 ml of ice water (initially, moderate external cooling), at which time the solution was extracted numerous times with pentane. The combined extracts were washed several times with water, saturated sodium chloride solution, dried, and concentrated in vacuo to afford 284 mg of a crude mixture of 56 and 52 in a ratio of ca. 3:2 (vpc). This mixture was separated with the use of preparative vpc on column A at 140° to afford 97 mg (16%) of 56 as a low melting solid; $^{1}H\text{CDCl}_3$ 1.77 (s, 6H, -CH$_3$), 2.80-3.17 (m, 2H, bridgehead), and 5.68-5.97 (m, 4H, vinyl); $\lambda_{\text{isoctane}}$ 322 (e 1580), 283 (1840), 273 (1910), and 218 nm (2040); calculated m/e 160.0888, observed 160.0885; and 67 mg (11%) of 52, identified by its nmr spectrum.

A semicarbazone of 56 was prepared by standard methods in 84% yield, mp 212-214°dec. An analytical sample was prepared by recrystallization
from ethanol-water, mp 212-213.5°dec.

Anal. Calcd for C$_{12}$H$_{15}$N$_3$O: C, 66.34; H, 6.96; N, 19.34.

Found: C, 66.12; H, 7.13; N, 19.17.

**1,2-Dimethylcyclooctatetraene (57).** A 10 mg (0.0625 mmole) sample of 56 in 9 ml of dry ether, previously deoxygenated with dry nitrogen, was irradiated in a quartz vessel with 2537 Å germicidal lamps in a Rayonet Reactor for 15 min. A vpc tracing exhibited the absence of 56 and the presence of a single volatile product. The solution was concentrated with a stream of dry nitrogen at 25° (water jacket) and isolated with the use of preparative vpc on column A at 70° to afford 7 mg (85%) of 57, whose infrared spectrum was identical with that of an authentic sample.$^{48,49}$

**7,8-Dimethylbicyclo[4.2.1]non-7-en-9-one (59).** Hydrogenation of 56 (26 mg) was effected by the use of 10% palladium on carbon in ethyl acetate at atmospheric pressure. The solution was filtered through a pad of Celite, concentrated in vacuo, and purified with the use of preparative vpc on column A at 130° to afford 7 mg of 59; $^6$CDCl$_3$ 1.25-1.83 (m, 8H, methylenes), 1.65 (s, 6H, -CH$_3$), and 2.58-2.70 (m, 2H, bridgehead); calculated m/e 164.1201, observed 164.1199.
A 2,4-DNP was prepared by standard methods, and an analytical sample prepared by recrystallization from ethanol, mp 114-116\(^\circ\)\textsuperscript{50}.

**Anal.** Calcd for C\textsubscript{17}H\textsubscript{20}N\textsubscript{4}O\textsubscript{4}: C, 59.29; H, 5.85.

**Found:** C, 59.29; H, 5.99.

3,4-Dimethyltricyclo[3.3.1.0\textsuperscript{2,8}]nona-3,6-dien-9-one (61). A solution, deoxygenated with dry nitrogen, containing 65 mg (0.406 mmole) of 56 and 65 mg of 4,4'-bis(dimethylamino)-benzophenone (Michler's ketone) in 30 ml of dry benzene was irradiated with a 450-W, medium pressure Hanovia lamp through quartz optics at 0\(^\circ\) for 2 hrs. The resultant yellow solution, which contained a fair amount of insoluble polymeric material, was filtered and concentrated in vacuo. Most of the sensitizer was removed by repetitious dilution with ether followed by filtration and concentration in vacuo to afford 67 mg of a crude mixture of sensitizer and five compounds (vpc), the last compound, \(t_r = 16\) min on column A at 140\(^\circ\), being ca. 75\% of the volatile products. Separation was effected by the use of preparative vpc on the above column to afford 17 mg (26\%) of 61 as a colorless liquid; \(\nu_{\text{max}}^{\text{neat}} = 1700\ \text{cm}^{-1}\); \(\lambda_{\text{isoctane}} = 217\ \text{nm} \) sh on end absorption (\(\epsilon = 3580\)); calculated m/e 160.0888, observed 160.0885. The nmr spectrum at ambient temperature (34\(^\circ\)) appeared to indicate > 85\% 61a; \(\delta_{\text{CH}_3}^{\text{Me}} = 1.75\ (s, 3\text{H}, -\text{CH}_3), 1.78\ (s, 3\text{H}, -\text{CH}_3), 1.92-2.20, 2.48-2.98 (m, 4\text{H}, ring hydrogens), and 5.17-5.83 (m, 2\text{H}, vinyl).
cis-1,2-Bis(methanesulfonyloxyethyl)-1,2-dimethylcyclohex-4-ene (66). To a stirred solution containing 19.3 g (0.1135 mole) of \( \frac{1}{2} \) in 300 ml of dry pyridine was added 71.5 g (0.625 mole) of methanesulfonyl chloride at such a rate as to maintain the temperature below 5\(^\circ\) under an atmosphere of dry nitrogen. After the addition was completed (2 hrs), the mixture was stirred an additional 2 hrs at 0-5\(^\circ\), at which time it was poured into a large quantity of ice and diluted with a 10% solution of hydrochloric acid (300 ml) to a volume of 1 l. After several hours at 0\(^\circ\) the precipitation was completed, and the product was collected on a Buchner funnel and recrystallized from 95% ethanol to afford 31.9 g (86%) of white, crystalline 66, mp 84-86\(^\circ\). \( \delta^{DCl}_{TMS} \) 1.07 (s, 6H, \(-CH_3\)), 2.03 (t, \( J = 1.5 \) Hz, 4H, allylic), 3.05 (s, 6H, \( CH_3SO_2^- \)), 4.17 (s, 4H, \(-CH_2O^-\)), and 5.63 (t, \( J = 1.5 \) Hz, 2H, vinyl); \( \nu_{max}^{Nujol} \) 1170 and 1350 cm\(^{-1}\). An analytical sample was prepared by recrystallization from ethanol, mp 85-86\(^\circ\).

Anal. Calcd for \( C_{12}H_{22}O_7S_2 \): C, 44.15; H, 6.79; S, 19.65.

Found: C, 44.17; H, 6.72; S, 19.35.

cis-1,6-Dimethyl-8-thiabicyclo[4,3.0]non-3-ene (67). With vigorous mechanical stirring, a slurry containing 72 g (0.3 mole) of sodium sulfide nonahydrate and 200 ml of freshly distilled hexamethyl phosphorus triamide was heated to 130\(^\circ\) and cautiously
evacuated to ca. 15 mm until no more water distilled as determined by the change in refractive index of the distillate and a drop in temperature of the condensing vapor. The slurry was cooled to 25° and 31.9 g of 66 was added in one portion. The stirred solution was heated in an oil bath maintained at 120° under an atmosphere of dry nitrogen for 17 hrs, at which time it was cooled to 0°, diluted with 1 l of ice cold water, and extracted portionwise with a total of 1 l of ether. The combined ether layers were washed with ice water, concentrated in vacuo, pre-coated on neutral alumina, and chromatographed on a column prepared by wet-packing 50 g of neutral alumina in petroleum ether (65-110°) and eluting with 5% ether in petroleum ether (65-110°). The sulfide was eluted from the column in the first fraction to afford 15.2 g (93%) of 67 as a white, low melting, crystalline solid; \( ^{1}H \) NMR \( \delta \) CDCl\(_3\) 1.03 (s, 6H, -CH\(_3\)), 1.57-2.48 (m, 4H, allylic), 2.77 (d, \( J_{AB} = 10 \) Hz, 2H, H\(_B\)), 2.83 (d, \( J_{AB} = 10 \) Hz, second half of AB pattern, 2H, H\(_A\)), and 5.53 (t, \( J = 1.5 \) Hz, 2H, vinyl); \( \nu_{\text{max}} \) neat 1465, 1665, and 2940 cm\(^{-1}\).

**cis-1,6-Dimethyl-8-thiabicyclo[4.3.0]non-3-ene 8,8-Dioxide (68).** To a stirred solution containing 15.2 g (0.0905 mole) of 67 in 175 ml of dry ethyl ether was added 268 ml of a 0.69 M (0.185 mole) monoperphthalic acid solution under an atmosphere of dry nitrogen. After the addition was completed (2 hrs), the ice bath was removed and the mixture stirred at ambient tempera-
ture for 24 hrs, at which time the reaction was filtered, diluted with ethyl ether, washed with a 0.5 M sodium hydroxide solution until distinctly basic, water until neutral, saturated sodium chloride solution, dried, and concentrated in vacuo to a white solid. Recrystallization from 550 ml of petroleum ether (65-110°) afforded 15.2 g (84%) of 68 as spectacular white leaflets, mp 151-152°; $^{1}^{1}$H NMR $^{13}$CDCl$_{3}$ 1.22 (s, 6H, -CH$_{3}$), 1.78-2.72 (m, 4H, allylic), 3.08 (s, 4H, -CH$_{2}$SO$_{2}$-), and 5.63 (t, $J = 1.5$ Hz, 2H, vinyl); $\nu_{\text{max}}$ 1115, 1135, and 1325 cm$^{-1}$. An analytical sample was prepared by an additional recrystallization from petroleum ether (65-110°), mp 151-152°.

Anal. Calcd for C$_{10}$H$_{16}$O$_{2}$S: C, 59.96; H, 8.05; S, 16.01.

Found: C, 59.93; H, 7.92; S, 15.83.

cis-1,6-Dimethyl-8-thiabicycle[4.3.0]nona-2,4-diene 8,8-Dioxide (70). A stirred mixture containing 2.335 g (0.01168 mole) of 68, 2.18 g (0.01224 mole) of recrystallized N-bromosuccinimide, and a catalytic amount of benzoyl peroxide in 100 ml of carbon tetrachloride was refluxed for 15 min under an atmosphere of dry nitrogen at which time the reaction was complete, as indicated by the presence of succinimide floating on the solvent surface and the absence of N-bromosuccinimide, which settles to the bottom. The mixture was cooled to 10°, the succinimide removed by filtration, and the solvent removed in vacuo to afford a quantitative yield of 69 as a yellow, viscous oil.
This oil was dissolved in 100 ml of dry tetrahydrofuran containing 10 g of sodium methoxide (not alcohol free) and refluxed for 24 hrs under an atmosphere of dry nitrogen, at which time the mixture was cooled to 0° and 25 ml of ice cold water was added dropwise. The layers were separated, whereupon the aqueous layer was washed 3 times with a 3:1 mixture of ether and methylene chloride. All of the organic layers were combined, washed with saturated sodium chloride solution, dried (sodium sulfate), and concentrated in vacuo to a yellow oil, which was sublimed (110° and 0.2 mm) to afford 1.937 g (84%) of 70 as white crystals; δCDCl3 1.25 (s, 6H, -CH3), 3.02 (d, JAB = 13 Hz, 2H, Hb), 3.33 (d, JA,B = 13 Hz, second half of AB pattern, 2H, Ha), and 5.45-6.20 (m, 4H, vinyl); υmax Nujol 1110 and 1290 cm⁻¹. The analytical sample was prepared by several recrystallizations from ethyl ether, mp 93-94.5°.

Anal. Calcd for C10H14O2S: C, 60.59; H, 7.12; S, 16.15.

Found: C, 60.31; H, 7.04; S, 15.98.

cis-1,6-Dimethyl-8-thiabicyclo[4.3.0]nona-2,4-diene (71). To a refluxing suspension containing 4.30 g (0.113 mole) of lithium aluminum hydride in 50 ml of dry ethyl ether was added 3.75 g (0.0188 mole) of 70 in 200 ml of dry ethyl ether over a period of 1.5 hrs (drying tube). The mixture
was refluxed 43 hrs, at which time it was cooled to 0° and a basic workup
employed (dropwise and cautious addition of 4.3 g of ice cold water, fol-
lowed by 4.3 ml of a 20% sodium hydroxide solution and 12.9 ml of water).
Filtration, followed by concentration in vacuo afforded a yellow oil,
which was pre-coated on neutral alumina and chromatographed on a column
prepared by wet-packing 50 g of neutral alumina in petroleum ether (65-110°)
and eluting with 5% ether in petroleum ether (65-110°). The sulfide was
eluted from the column in the first fraction to afford 2.39 g (78%) of \( \text{11} \)
as a white, low melting, crystalline solid; \( \text{CDCl}_3 \) 1.03 (s, 6H, -CH₃),
2.75 (d, \( J_{AB} = 10 \text{ Hz} \), 2H, \( H_B \)), 3.03 (d, \( J_{AB} = 10 \text{ Hz} \), second half of \( AB \)
pattern, 2H, \( H_A \)), and 5.28-6.03 (m, 4H, vinyl). By continued elution with
ether, ca. 10% of crude sulfone 70 was also recovered.

\[ \text{syn- and anti-7-Chloro-cis-1,6-dimethyl-8-thiabicyclo[4.3.0]nona-2,4-diene} \]
8,8-Dioxides (73a) and (73b). A stirred mixture containing 889 mg (5.35
mmole) of 71 and 786 mg (5.89 mmole)
of N-chlorosuccinimide in 20 ml of
carbon tetrachloride was refluxed for
2 hrs under an atmosphere of dry ni-
trogen, at which time the reaction
was cooled to 10°, filtered, and con-
centrated in vacuo to afford a quanti-
tative yield of 72.
This residue was dissolved in 20 ml of dry ether and 19 ml of a 0.620 M (11.8 mmole) monoperphthalic acid solution was added at such a rate as to maintain the temperature below 5° under an atmosphere of dry nitrogen. After the addition was completed (45 min), the ice bath was removed and the reaction mixture was stirred at ambient temperature for 24 hrs, at which time it was filtered, diluted with ether, washed with a 0.5 M sodium hydroxide solution until distinctly basic, water until neutral, saturated sodium chloride solution, dried, and concentrated in vacuo to afford 1.078 g (87%) of the crude epimeric α-chloro sulfones. The ratio of 73a to 73b was determined by pmr to be 63:37.

A complete separation of the two epimers was realized by pre-coating the above mixture on silica gel and chromatographing the mixture on a column prepared by wet-packing 40 g of silica gel with petroleum ether (65-110°) and eluting with 200-ml portions of 1-20% ether in petroleum ether (65-110°) by 1% increments (200 ml fractions).

The minor epimer 73b eluted first (ca. 9% ether); δCDCl_3 1.12 (s, 3H, -CH_3), 1.47 (s, 3H, 6-CH_3), 3.05 (d, J_A,B = 13.5 Hz, 1H, H_B), 3.33 (d, J_A,B = 13.5 Hz, second half of AB doublet pattern, 1H, H_A), 4.90 (s, 1H, H_C), and 5.25-6.25 (m, 4H, vinyl); ν_{max}^Nujol 1120 and 1320 cm⁻¹. An analytical sample was prepared by recrystallization from ether-petroleum ether (65-110°), mp 91.5-92°.

Anal. Calcd for C_{10}H_{13}ClO_2S: C, 51.62; H, 5.63; Cl, 15.24.

Found: C, 51.58; H, 5.65; Cl, 15.38.
The major epimer \( \text{T}_3a \) eluted somewhat later (ca. 19\% ether); \( \delta_{\text{CDCl}_3}^{\text{TMS}} \)

1.16 (s, 3H, 1-CH\(_3\)), 1.32 (s, 3H, 6-CH\(_3\)), 3.12 (d, \( J_{A,B} = 13.5 \text{ Hz}, 1H, H_B \)),

3.43 (d, \( J_{A,B} = 13.5 \text{ Hz}, \) second half of AB pattern, 1H, \( H_A \)), 5.18 (s, 1H, \( H_C \)), and 5.42-6.25 (m, 4H, vinyl); \( \nu_{\text{max}}^{\text{Nujol}} \) 1125 and 1325 cm\(^{-1}\). An analytical sample was prepared by recrystallization from ether-petroleum ether (65-110\(^\circ\)), mp 90-91\(^\circ\).


Found: C, 51.33; H, 5.61; Cl, 15.48.

7,8-Dimethyl-9-thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-Dioxide (\( \text{T}_4 \)). To a stirred solution containing 3.32 g (0.0144 mole) of crude epimeric chlorosulfones \( \text{T}_3a \) and \( \text{T}_3b \) in 100 ml of dry dimethylsulfoxide was added 1.613 g (0.014 mole) of potassium tert-butoxide in one portion at room temperature. The temperature slowly rose to 30-35\(^\circ\). After 10 min of exposure the resultant dark solution was cooled to 20\(^\circ\) and 300 ml of cold water was cautiously added, at which time the solution was extracted five times with ether. The combined organic layers were washed with water, saturated sodium chloride solution, dried, and concentrated in vacuo. Tri-

turation with petroleum ether (65-110\(^\circ\)) afforded 273 mg of \( \text{T}_4 \) as a white solid, mp 198-200\(^\circ\)dec; \( \delta_{\text{CDCl}_3}^{\text{TMS}} \) 1.88 (s, 6H, -CH\(_3\)), 3.62-3.95 (m, 2H, bridgehead), and 5.83-6.08 (m, 4H, vinyl); \( \nu_{\text{max}}^{\text{Nujol}} \) 1110, 1290, and 1600 cm\(^{-1}\);

\( \lambda_{\text{EtOH}}^{\text{max}} \) 282 nm (e 2100). Additional material, obtained by acidifying the
aqueous layers and extraction with ether, brought the total yield to 509 mg (27%). An analytical sample was prepared by recrystallization from methylene chloride-ether, mp 201.5°dec.

**Anal.** Caled for C_{10}H_{12}O_2S: C, 61.19; H, 6.16; S, 16.34.

**Found:** C, 61.21; H, 6.41; S, 16.08.

1,2-Dimethylcyclooctatetraene (57) from (74). A solution containing 68 mg (0.347 mmole) of 74 in 6 ml of acetone was irradiated with a 450-W medium pressure Hanovia lamp through quartz optics and a Vycor filter for 2 hrs. Tlc analysis (CH_2Cl_2/alumina) showed that most of the contents of the solution still was at the origin. An additional hour of irradiation did not alter this situation. The solution was concentrated to ca. 2 ml of volume by distillation at atmospheric pressure through a Vigreux column and purified by preparative vpc on column B to afford 5 mg (11%) of 57; δ CDCl_3 1.69, 1.83 (two s, 6H, -CH_3), 5.58 and 5.78 (2 br s, 6H, vinyl).

**cis-1,2-Bis(methanesulfonyl)cyclohex-4-ene (82).** To a stirred solution containing 46.3 g (0.526 mole) of 35 in 600 ml of dry pyridine was added 206 g (1.80 mole) of methanesulfonyl chloride at such a rate as to maintain the temperature below 5° under an atmosphere of dry nitrogen. After
the addition was complete (5 hrs), the mixture was stirred an additional
2 hrs at 5°, at which time it was poured into a large quantity of ice and
diluted with 1.8 l of cold 10% hydrochloric acid solution. After several
hours at 0° the precipitation was completed, and the product was collected
on a Buchner funnel and recrystallized from 95% ethanol to afford 86.5 g
(89%) of white, crystalline \( \text{82} \), mp 85.5-86.5°; \( \delta_{\text{CDCl}_3} \) 1.92-2.75 (m, 6H,
allylic and bridgehead), 3.06 (s, 6H, -OSO\(_2\)CH\(_3\)), 4.18-4.35 (m, 4H, -CH\(_2\)O-),
and 5.71 (t, \( J = 1.5 \) Hz, 2H, vinyl); \( \nu_{\text{max}} \) Nujol 1165, 1175, and 1340 cm\(^{-1}\).
An analytical sample was prepared by several recrystallizations from 95%
ethanol, mp 86-87°.

Anal. Calcd for C\(_{10}\)H\(_{16}\)O\(_2\)S\(_2\): C, 40.25; H, 6.08; S, 21.49.
Found: C, 40.33; H, 6.20; S, 21.27.

cis-8-Thiabicyclo[4.3.0]non-3-ene (83). With vigorous mechanical stirring,
a slurry containing 290 g (1.21
mmole) of sodium sulfide nonahydrate
and 500 ml of freshly distilled hexa-
methylphosphorus triamide was heated
to 135° and cautiously evacuated to
ca. 15 mm until water no longer dis-
tilled as determined by the change in refractive index of the distillate
and a drop in temperature of the condensing vapor. The slurry was cooled
to room temperature and 119.5 g (0.40 mole) of \( \text{82} \) was added in one portion.
The stirred mixture was heated at 120° under an atmosphere of dry nitrogen
for 22 hrs, at which time it was cooled to 0°, diluted with 3 l of ice
water, and extracted portionwise with ether. The combined organic extracts were washed with ice cold water, saturated sodium chloride solution, concentrated in vacuo, pre-coated on neutral alumina, and chromatographed on a column prepared by wet-packing 300 g of neutral alumina in petroleum ether (65-110°) and eluting with 5% ether in petroleum ether (65-110°). The sulfide was eluted from the column in the first few fractions to afford 49.82 g (89%) of 83 as a low melting, white solid; $^1$H NMR (CDCl$_3$, 1.92-3.17 (m, 10H, methylene and bridgehead) and 5.63 (t, $J$ = 1.3 Hz, 2H, vinyl); νwmax 1425, 1450, and 1635 cm$^{-1}$.

**cis-8-Thiabicyclo[4.3.0]non-3-ene 8,8-Dioxide (84).** To a stirred solution containing 49 g (0.35 mole) of 83 in 300 ml of dry ether was added 990 ml of a 0.724 M (0.717 mole) monoperphthalic acid solution at such a rate as to maintain the temperature below 5° under an atmosphere of dry nitrogen. After the addition was complete (3 hrs), the ice bath was removed and the mixture stirred at ambient temperature for 24 hrs, at which time the mixture was filtered, diluted with ether, washed with a 0.5 M sodium hydroxide solution until distinctly basic, water until neutral, saturated sodium chloride solution, dried, and concentrated in vacuo to a white, crystalline solid. Recrystallization from petroleum ether afforded 45.5 g (76%) of 84; $^1$H NMR (CDCl$_3$, 1.92-3.50 (m, 10H, methylene and bridgehead) and 5.72 (t, $J$ = 1.5 Hz, 2H, vinyl); νmax Nujol 1110, 1280, and 1295 cm$^{-1}$. An analytical sample was
prepared by several recrystallizations from petroleum ether (65-110°), mp 74-75°.

Anal. Calcd for C₈H₁₂O₂S: C, 55.78; H, 7.02; S, 18.61.
Found: C, 55.87; H, 7.05; S, 18.42.

**trans-3,4-Dibromo-cis-8-thiabicyclo[4.3.0]nonane 8,8-Dioxide (85).**

To a stirred solution containing 16.9 g (0.098 mole) of 84 in 450 ml of carbon tetrachloride was added an excess of bromine at 0° over a period of 1 hr. After stirring the mixture an additional 3 hrs, the crude dibromide was collected on a Buchner funnel and washed with several portions of ice cold carbon tetrachloride to afford 30.35 g (92.5%) of 85, mp 191.5-192.5°. An analytical sample was prepared by numerous recrystallizations from methylene chloride-ether, mp 197-197.5°.

Found: C, 28.73; H, 3.79; Br, 47.62.

**cis-8-Thiabicyclo[4.3.0]nona-2,4-diene 8,8-Dioxide (86).**

A stirred mixture containing 16.8 g (0.40 mole) of lithium chloride, 28.4 g (0.40 mole) of lithium carbonate, 26.9 g (0.081 mole) of 85, and 400 ml of freshly distilled hexamethylphosphorus triamide was heated at 85-90° for 21 hrs
under an atmosphere of dry nitrogen, at which time it was cooled to 25°,
diluted with 1200 ml of ice water and 800 ml of saturated sodium chloride
solution, and extracted numerous times with ether. The combined organic
extracts were washed repeatedly with water and saturated sodium chloride
solution, dried, concentrated in vacuo and distilled under reduced pressure
to afford 10.63 g (78%) of 86 as a clear liquid; bp (0.06 mm) 134-135°;
\[ \delta_{\text{CDCl}_3}^{\text{TMS}} \] 3.23 (br s, 6H, aliphatic) and 5.57-6.40 (m, 4H, vinyl); \( \nu_{\text{max}} \) 1115 and 1295 cm\(^{-1} \); \( \lambda_{\text{EtOH}}^{\text{max}} \) 255 (\( \epsilon \) 1800), 262 (2050), and 271 nm (1910).

An analytical sample was prepared with the use of preparative vpc on
column C at 165°.

**Anal.** Calcd for \( \text{C}_8\text{H}_{10}\text{O}_2\text{S} \): C, 56.44; H, 5.97; S, 18.84.

Found: C, 56.08; H, 6.02; S, 18.43.

8-Thiabicyclo[4.3.0]nona-4,6-diene (87). A portion of dibromide 85 was
subjected to identical conditions
and work-up as in the preparation
of diene 86, except that the reaction
was performed at a higher tem-
perature (140°). Vpc and nmr data
indicated ca. 25% of 87 present. A
portion of this material was separated by vpc on column C to afford pure
87, mp 112-114°; \[ \delta_{\text{CDCl}_3}^{\text{TMS}} \] 1.3-2.4, 2.7-3.7 (m, 7H, aliphatic), and 6.22-6.45
(m, 3H, vinyl); \( \nu_{\text{max}}^{\text{Nujol}} \) 1095 and 1275 cm\(^{-1} \); \( \lambda_{\text{EtOH}}^{\text{max}} \) 245 nm (\( \epsilon \) 18,700); calculated \( m/e \) 170.0400, observed 170.0401.
cis-8-Thiabicyclo[4.3.0]nona-2,4-diene (88). To a refluxing suspension containing 5.60 g (0.147 mole) of lithium aluminum hydride in 60 ml of dry ether was added 5.0 g (0.029 mole) of 86 in 250 ml of dry ether during 1 hr (drying tube). The mixture was refluxed for 68 hrs, at which time it was cooled to 0° and a basic work-up employed (cautious drop-wise addition of 5.6 g of water) followed by 5.6 g of 20% sodium hydroxide solution and 16.8 g of water. Filtration followed by concentration in vacuo afforded a yellow oil, which was pre-coated on alumina and chromatographed on a column prepared by wet-packing 100 g of alumina in petroleum ether (30-60°) and eluting with 5% ether in petroleum ether (30-60°). The sulfide was eluted from the column in the first few fractions to afford 3.14 g (77.5%) of 88; $^6\text{CDCl}_3$ 2.7-3.0 (m, 6H, methylenes and bridgehead) and 5.55-6.10 (m, 4H, vinyl).
PART I
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45. Professor R. B. Woodward has graciously provided us with an unpublished high yield, one step preparation of this compound through personal communication. Although this preparation was not at hand when this work was carried out, acknowledgment is extended with gratitude.


49. See Part II of this thesis for a detailed discussion of an improved preparation of this compound.

50. Gratitude is extended to Dr. R. E. Wingard, Jr., for preparing this derivative during my absence from the laboratory for personal reasons.

51. See Part III of this thesis for a detailed discussion of di-π-methane photorearrangements.


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The ability of certain molecules to undergo degenerate rearrangement has captured the interest of chemists in recent years. The sequential Cope rearrangements in bullvalene (1) render all of the carbon atoms equivalent, while dihydrobullvalene (2) displays two-fold degeneracy, as does the azabullvalene (3). Hypostrophe (4) homotropilidine (5), and barbaralone (6), among others, also exhibit degenerate behavior via facile [3,3] sigmatropic rearrangements.

The Cope rearrangement is by no means the only way in which a molecule may undergo degenerate isomerization. For instance, properly labeled cyclo-
pentadienes such as \( \mathcal{I} \) undergo self-interconversion via sequential \([1,5]\) sigmatropic shifts.\(^5\text{-}\text{7}\) In the case of \( \mathcal{I} \), this reaction is quite rapid

\[
\begin{array}{c}
\text{D} & \text{H} & \text{D} \\
\text{D} & \text{D} & \text{D}
\end{array}
\xleftrightarrow{[1,5]} 
\begin{array}{c}
\text{D} & \text{D} & \text{H} \\
\text{D} & \text{D} & \text{D}
\end{array}
\xleftrightarrow{[1,5]} 
\begin{array}{c}
\text{D} & \text{D} & \text{D} \\
\text{D} & \text{D} & \text{H}
\end{array}
\]

\( \mathcal{I} \)

\( \mathcal{S} \)

\( \mathcal{Z} \)

even at \( 50^\circ \text{C} \).\(^7\) When deuterated 1,3-cyclooctadiene \( \mathcal{J} \) was heated for 24 hrs. at \( 150^\circ \text{C} \), the isotopic label was found to be statistically scrambled over

\[
\begin{array}{c}
\text{D} & \text{D} \\
\text{D} & \text{D}
\end{array}
\xleftrightarrow{[1,5]} 
\begin{array}{c}
\text{D} & \text{D} \\
\text{D} & \text{D}
\end{array}
\xleftrightarrow{[1,5]} 
\begin{array}{c}
\text{D} & \text{D} \\
\text{D} & \text{D}
\end{array}
\xleftrightarrow{[1,5]} 
\begin{array}{c}
\text{D} & \text{D} \\
\text{D} & \text{D}
\end{array}
\]

\( \mathcal{J} \)

\( \mathcal{K} \)

\( \mathcal{L} \)

\( \mathcal{M} \)

all the possible positions (10-13) by this same mechanism.\(^8\) Sigmatropic shifts are responsible for the partial degeneracy of 1,3,5-cyclooctatriene \( \mathcal{N} \), as demonstrated by proper deuterium labeling.

\[
\begin{array}{c}
\text{D} & \text{D} \\
\text{D} & \text{D}
\end{array}
\xleftrightarrow{[1,5]} 
\begin{array}{c}
\text{D} & \text{D} \\
\text{D} & \text{D}
\end{array}
\]

\( \mathcal{N} \)

Circumambulatory degenerate rearrangements have been observed in polyenyl cations. All of the methyl groups on the periphery in \( \mathcal{O} \) become
equivalent at elevated temperatures, as determined by pmr spectroscopy. This is the result of symmetry allowed \([\pi^2s + \omega^0s + \sigma^2a]\) bond reorganizations (\([1,4] \) sigmatropic shifts). \(^{11}\)

In some instances, an internal Diels-Alder mechanism is responsible for degenerate behavior. The pyrolysis of \(16a\) results in the production of \(16b\) with the \([4+2]\) cycloaddition product \(16c\) serving as the common intermediate. The degenerate thermal valence isomerization of snoutene (\(17a\)) may possibly involve a thermally allowed \([\sigma^2s + \sigma^2a + \pi^2a]\) bond reorganization. \(^{13}\)
Several other mechanisms have been found responsible for degenerate behavior. In the case of lumibullvalene (18), a diradical process involving 19 is operative. This mechanism effects total scrambling in the molecule. The degenerate thermal rearrangement of cis-9,10-dihydronaphthalene (20) has been attributed to an electrocyclic, disrotatory ring opening to cyclodecapentaene (21), which then undergoes reclosure with consequential scrambling of the labels.

Although many examples of (CH)_{10} hydrocarbons are recognized to exhibit this remarkable capability for degenerate bond reorganization at elevated temperatures, very little is known about the capability of hydrocarbons on the (CH)_{9} energy surface to undergo such fascinating rearrangements. A notable exception is the facile [3,3] Cope rearrangement in semibullvalene (22), which is so rapid that it displays a temperature independent pmr spectrum down to -110^o. But the most extensively studied (CH)_{9} hydrocarbon, cyclooctatetraene (23), was notably absent from
the ranks of molecules capable of degenerate bond reorganization.

The thermal chemistry of cyclooctatetraene had its origins nearly 20 years ago when its fragmentation to acetylene, benzene, ethylene, and styrene, along with the formation of polymers and other unidentified volatile hydrocarbons, was reported. When this work was recently repeated, it was found that under certain conditions, dihydropentalene (25) was the major product. At 530° in the gas phase, the yield of 25 was maximized at 40%. The authors stated that 25 could arise via diradical 24, from 23 directly, or from semibullvalene (22). Diradicals such as 24 have also been postulated as intermediate species in the thermal isomerization of 1,3,5,7-tetramethyl-21a and octamethylcyclooctatetraenes 21c to the corresponding semibullvalenes. In contrast to these slow reactions, octachlorocyclooctatetraene undergoes this transformation quite rapidly.21b An intermediate of type 24 is apparently also involved in the thermal isomerization of 5,6- to 5,11-disubstituted dibenzocyclooctatetraenes (26 to 27).22
Cyclooctatetraene (23), the parent hydrocarbon, is quite thermally labile, and undergoes slow dimerization even at 25°. By pyrolyzing 23 at various temperatures, four dimers have been isolated and characterized. The most noteworthy of these dimers is 28, which is the result of a reversible intermolecular [4+2] cycloaddition of two molecules of 23. This dimer has also been proposed as the source of dimer 31, which also results from the pyrolysis of cyclooctatetraene; initial cyclooctatriene-bicyclo[4.2.0]-octadiene valence bond isomerization (22), followed by internal Diels-Alder cycloaddition (30) and subsequent bond reorganization has been advanced to account for this transformation.

The thermochemistry of certain halocyclooctatetraenes has also been reported. The conversion of bromocyclooctatetraene (32) to trans-β-bromostyrene (35) is rapid as low as 70°. Huisgen has proposed that this reaction proceeds by initial valence tautomerization to 33, which
then undergoes C-Br bond heterolysis to produce the homocyclopropenium salt \( \text{34} \). Halide capture at the other terminus of the delocalized cation
followed by thermally allowed conrotatory ring opening affords the observed product. This mechanism is supported by kinetic and chemical data, which includes the isolation of β-iodostyrene upon addition of sodium iodide, rate acceleration of the acetate derivative by acetic acid, and the dependency of rate on the nature of the leaving group (Br > Cl >> OAc). In a similar manner, pyrolysis of 1,4-dibromocyclooctatetraene (36) at 180° on a vpc column results in up to 95% isolation of p-bromo-trans-β-bromo styrene

(37). Another example of the thermochemistry of halogenated cyclooctatetraenes involves pyrolysis of the closed form 38 of octachlorocyclooctatetraene. Aromatization is apparently the driving force for the production of 39.

Although the available data concerning the thermal chemistry of cyclooctatetraene does not indicate either extensive isomerization reactions or degenerate behavior, it was considered at the onset of this work that this was mainly the result of the lack of a comprehensive study. By designing
molecules with appropriate levels of substitution, it was anticipated that processes which had heretofore gone unnoticed due to the absence of adequate labeling would be unveiled.
PART II

DISCUSSION

Our studies of possible isomerization reactions of the cyclooctatetraene ring system began with the preparation of 1,2-dimethylcyclooctatetraene (43), an improved synthesis of which was recently developed by Dr. R. E. Beckley in these laboratories. The preparation of 43 is depicted below.

Photochemical [2+2] cycloaddition of dimethyl acetylenedicarboxylate to benzene was facilitated by intermittent cleaning of the reaction vessel with an alcoholic potassium hydroxide solution to remove the opaque polymer formed during the reaction, a phenomenon first recognized by Bock.\(^{28}\) Diester 40 was reduced to diol 41 with aluminum hydride at 25\(^\circ\). The action of triphenylphosphine dibromide on 41 gave dibromide 42, subsequent reduction of which with lithium aluminum hydride afforded 1,2-dimethylcyclooctatetraene.
(43) as a yellow liquid, bp (45 mm) 78-80°. Its infrared spectrum was identical to that of an authentic sample. The pmr spectrum of 43 at ambient temperature in the nmr probe (ca. 40°) displays two sharp singlets at δ 1.68 and 1.82 for the methyl groups, with the low field signal being the more intense. As the temperature was raised to 94.5° (tetrachloroethylene), appreciable broadening of these two peaks was observed. The phenomenon was more pronounced at 108°. At 122°, the two signals coalesced into a sharp peak at δ 1.75. This temperature dependency is attributed to the bond shift isomers 43a and 43b. At ambient temperature, this equilibrium is slow on the pmr time scale and consequently the magnetically unequivalent methyl groups have different chemical shifts. As the temperature was increased so was the rate of equilibration, and the resonances broadened. At 122° this equilibrium was so rapid that the pmr could not distinguish between the different methyl groups and a singlet resulted. Extensive studies on various derivatives of cyclooctatetraene and on the parent by other workers has firmly established this interpretation. This isomerization very probably passes through a planar cyclooctatetraene (i.e. 44) in the transition state. The coalescence temperature for the equilibration 43a ⇌ 43b is compatible with values reported earlier for similar derivatives.
Samples of 43 were pyrolyzed in the gas phase at various temperatures as described in some detail in the Experimental Section. At 405°, only unchanged 43 was recovered (pmr analysis). At 450°, however, an absorption of chemical shift intermediate between the two methyl peaks of 43 began to appear; no visible change was noted in the olefinic region where the characteristic pattern remained essentially unchanged. Analysis by vpc on column D at 60° showed only two components, tr = 47 and 48.2 min.

The new nmr peak increased in size at 500° and 545° and represented nearly 90% of the methyl absorption after pyrolysis at 590° (see Figure 1), as determined by expanded scale 100 MHz nmr methods recorded with internal lock to improve peak shape. This new peak in the methyl region appeared to correspond to a positional isomer of 43, and since the only other dimethylcyclooctatetraene reported in the literature was 1,4-dimethylcyclooctatetraene (47), its preparation was undertaken.

Initially, the syntheses of 47 was realized by employing the sequence developed by Huisgen,24a,30 as shown below. The pmr spectrum of 47 displayed a singlet in the methyl region with the same chemical shift (δ 1.75) as the new peak noted in the pyrolysates of 43. The retention time (47 min)

```
\begin{align*}
\text{44} & \xrightarrow{\text{Br}_2, \text{CH}_2\text{Cl}_2, -70^\circ} \text{45} \\
\text{46} & \xrightarrow{\text{Li(CH}_3)_2\text{Cu}} \text{47}
\end{align*}
```
Figure 1. Expanded scale 100 MHz pmr spectra of $\text{H}_3$, pyrolysates of $\text{H}_3^+$, and $\text{H}_1$. 
of $^4\Gamma$ on column D at 60° prepared by this method was identical with that of
the unknown peak from the pyrolysis of $^2\Gamma$. However, the synthetic material
was contaminated with another compound (ca. 10%) with a slightly longer
retention time than $^4\Gamma$. This material was subsequently shown to be 1,5-
dimethylcyclooctatetraene ($^4\Omega$), which was determined by vpc retention time
when an authentic sample of $^4\Omega$ later became available, the result of
base induced loss of hydrogen bromide to produce $^4\Omega$ competitively with $^4\Gamma$.

\[ \text{Br} \quad \text{Br} \]

$^4\Omega$

\[ \text{CH}_3 \]

$^4\Omega$

In order to prepare $^4\Gamma$ in a manner which would guarantee the absence
of isomeric impurities, advantage was taken of the recently reported work
of Anastassiou. The addition of cyclooctatetraene ($^2\Sigma$) to sulfur mon-
oxide generated by in situ thermolysis of ethylene episulfoxide ($^5\Omega$) afforded
9-thiabicyclo[4.2.1]nona-2,4,7-triene 9-oxide ($^5\Omega$). The stereo-
chemistry of the sulfinyl oxygen was determined by the use of Eu(fo)\textsubscript{3}.
The $\Delta$Eu values for $\text{H}_B$ and $\text{H}_C$ were ca. twice that for $\text{H}_D$ in agreement with
that stereochemistry in which the sulfoxide oxygen is syn to the diene unit.
This sulfoxide was then oxidized to the sulfone ($^5\Omega$) which was dialkylated
by conversion to its dianion with two equivalents of n-butyllithium and
subsequent treatment with methyl iodide. Dimethyl sulfone 52 was obtained in quantitative yield. No monoalkylated product (54) was observed. The structure of 52 follows from its spectral properties and correct combustion data. Photochemically induced extrusion of sulfur dioxide from 52 afforded the desired hydrocarbon in moderate yield after purification by preparative vpc techniques on column A. This material was homogeneous by vpc analysis on column D at 60°.

Further verification of 57 as the pyrolysis product of 47 was possible once a pure sample of the former was available. The high resolution infrared spectra (CCl₄) of 47 and 57 differed significantly in the fingerprint region. By examination of the spectra of the pyrolysates of 47, it was realized that all of the peaks in these spectra could be accounted for by the presence of either 47 or 57. Furthermore when a known mixture of 47 and 57 was prepared and its infrared spectrum compared with that of the pyrolysate of 47 which contained the same composition, these two spectra
were superimposable. These data, along with the pmr and vpc results discussed previously, constitute compelling evidence for the thermally induced isomerization of \( \text{h3} \) to \( \text{h7} \). Results of these pyrolyses are summarized in Table I. The percentage compositions were determined by manual integration of the methyl absorptions from expanded scale 100 MHz pmr spectra, and the recovery values relate to dimethylcyclooctatetraenes isolated upon vpc purification and do not include aromatic fragmentation products to be discussed later.

**TABLE I**

**PRODUCT COMPOSITION DATA FROM THE PYROLYSIS OF 1,2-DIMETHYLCYCLOOCTATETRAENE (\( \text{h3} \)).**

<table>
<thead>
<tr>
<th>Temp, °C</th>
<th>Recovery, %</th>
<th>( \text{h3}, % )</th>
<th>( \text{h7}, % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>405</td>
<td>67</td>
<td>&gt; 99.9</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>450</td>
<td>46</td>
<td>94</td>
<td>6</td>
</tr>
<tr>
<td>500</td>
<td>25</td>
<td>71</td>
<td>29</td>
</tr>
<tr>
<td>545</td>
<td>20</td>
<td>44</td>
<td>56</td>
</tr>
<tr>
<td>590</td>
<td>7</td>
<td>12</td>
<td>88</td>
</tr>
</tbody>
</table>

Since the conversion of \( \text{h3} \) to \( \text{h7} \) appears to be an equilibrium reaction, one would expect that thermolysis of \( \text{h7} \) would reconvert it to \( \text{h3} \). From inspection of the data from the pyrolyses of \( \text{h7} \) in Table II, it can be seen that this is the case. Since \( \text{h7} \) dominates the equilibrium, the
quantitative aspects of this isomerization are less dramatic than those of the pyrolysis of \( \text{43} \). That these were the only two dimethylcyclooctatetraenes produced during the pyrolyses was determined as previously described. From comparison of the values for the pyrolyses at 560° and 585° in Table II and the values at 590° in Table I, it appears that an equilibrium mixture of \( \text{43} \) and \( \text{47} \) has been attained under these conditions.

### TABLE II

PRODUCT COMPOSITION DATA FROM THE PYROLYSIS OF
1,4-DIMETHYLCYCLOOCTATETRAENE (47).

<table>
<thead>
<tr>
<th>Temp, °C</th>
<th>Recovery, %</th>
<th>( \text{47}, % )</th>
<th>( \text{43}, % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>38</td>
<td>98.5</td>
<td>1.5</td>
</tr>
<tr>
<td>560</td>
<td>19</td>
<td>84.5</td>
<td>15.5</td>
</tr>
<tr>
<td>585</td>
<td>10</td>
<td>84</td>
<td>16</td>
</tr>
</tbody>
</table>

By inspection of the percent recoveries in Table I and II, it can be seen that these values are inversely proportional to the input of heat to the system. These data are the result of several factors. The parent hydro-
carbon 2J has been reported to undergo polymerization reactions, as was apparent in the present work since a white, pentane insoluble material was also produced. The quantity of this polymer increased significantly as the pyrolysis temperature was raised (visual assay), and was certainly a major source of the low recoveries at the higher temperatures. Another competing reaction is the symmetry forbidden retro [2+2] cleavage of the valence tautomeric closed form 55 of cyclooctatetraene, which is reported to yield benzene and acetylene. In the systems studied here, substituted benzenes would also result. The presence of such volatile components in the crude pyrolysates of 43 and 47 was indicated by the vpc data which revealed peaks with very short retention times. The quantity of these materials was directly proportional to the particular temperature at which the pyrolysis was performed.

In order to characterize these volatile components, 43 and 47 were both pyrolyzed at 600° and the highly volatile material cautiously separated from the other components by preparative vpc on column A and then injected into column D at 35°. The volatile components were identified by comparison of their respective retention times with those of authentic samples, and their relative abundances, determined by electronic integration, were corrected for detection coefficients. These data are tabulated in Table III.
### TABLE III

VOLATILE PRODUCT COMPOSITION DATA FROM THE PYROLYSIS OF 1,2- (43)
AND 1,4-DIMETHYLCYCLOOCTATETRAENES (47) AT 600°.

<table>
<thead>
<tr>
<th>Component</th>
<th>Retention time, min.</th>
<th>Pyrolysis of 43, %</th>
<th>Pyrolysis of 47, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8.82</td>
<td>1.3</td>
<td>2.6</td>
</tr>
<tr>
<td>+CH₃</td>
<td>18.63</td>
<td>96.2</td>
<td>70.5</td>
</tr>
<tr>
<td>+CH₃</td>
<td>52.57</td>
<td>1.3</td>
<td>21.6</td>
</tr>
<tr>
<td>+CH₃</td>
<td>44.37</td>
<td>1.1</td>
<td>5.4</td>
</tr>
</tbody>
</table>

The differences in the abundances of these components presumably reflect the relative concentrations of the various bicyclic forms (i.e. 56-58) of 43 and 47 and the expected nonequivalent rates attending their retro [2+2] cleavages. The absence of m-xylene, which could have easily been detected by its retention time and whose concentration could have been determined at a very low value (< 0.1%), is of particular significance.
This isomeric xylene cannot result from any of the valence tautomers of $\text{H}_3$ or $\text{H}_7$, but would result from closed forms of 1,5- and 1,3-dimethylcyclooctatetraene ($\text{H}_2$ and $\text{H}_3$), such as $\text{H}_0$ and $\text{H}_1$. This result constitutes additional evidence for the lack of $\text{H}_2$ and $\text{H}_3$ in the pyrolysis mixtures of $\text{H}_3$ and $\text{H}_7$. 

\[ \text{H}_3 \quad \text{H}_0 \quad \text{H}_1 \]
As previously mentioned, the key intermediate in the preparation of pure 47 involved quenching of dianion 56 with methyl iodide. This dianion, which resulted from the treatment of sulfone 52 with two equivalents of n-butyllithium in tetrahydrofuran at -70°C, or potassium tert-butoxide in dimethylsulfoxide at 20°C, displays a deep purple solution which was stable at 25°C for at least one hour under an inert atmosphere. What was even more intriguing was that when only one equivalent of base was employed, the dialkylated sulfone 53 was the only product (albeit in lower yield), as deduced from a pmr spectrum of the crude product. No
monoalkylation product was observed. In order to better understand these phenomena, a series of related sulfones 57-60 was prepared so that they could be subjected to identical reaction conditions.

The preparation of 9-thiabicyclo[4.2.1]nona-7-ene 9,9-dioxide (57) was realized by following the procedures described in the literature, as illustrated below. By purifying the sulfur dichloride used in the preparation of 61 (distillation from phosphorus pentachloride), the yield was increased to twice that reported in the literature. The hydrogenation of 57 to 58 has also been reported, although the yield was only moderate (52%) and the conditions stringent (Raney Ni, a dash of 1 M potassium hydroxide solution, 60 psi, 24 hrs). By utilizing 10% Pd on carbon at 50 psi for 9 hrs, a nearly quantitative yield of 58 resulted.
Sulfone 52 was prepared by the method of Mock. Bromination of 52 with molecular bromine proceeded with amazing selectivity, and afforded only dibromide 63. Hydrogenation of 63 with Adams catalysts in ethyl acetate at 50 psi resulted in a quantitative yield of 64. No hydrolysis was observed under these conditions, as indicated by pmr analysis. The loss of two moles of hydrogen bromide from 64 was effected with lithium chloride and lithium carbonate in hexamethylphosphorus triamide at 115° for 24 hrs to afford 60, mp 99-101° (lit mp 101.5-102°). The yield of this reaction was not optimized and is quite probably much higher. This is the first example of the use of this reagent to facilitate a bis-dehydrohalogenation from an unsymmetrical dibromide. Sulfone 60 has been previously prepared by a more tedious method in a lower yield (12% from 52) by Mock.
When the dianions of sulfones 57-60, generated by the action of n-butyllithium in tetrahydrofuran at -70°, were treated with methyl iodide, the dimethyl sulfones 65-68 were produced in purified yields of 88, 91, 80, and 50%, respectively. A longer time of exposure (1.5 hrs) was necessary to effect total reaction with sulfone 58, presumably due to its less acidic bridgehead protons. Sulfone 66 is a very low melting solid, which is somewhat of an anomaly for such a rigid bicyclic sulfone. Due to concern over this low melting point, the structure of 66 was verified by spectral data and synthesized alternatively by the hydrogenation of 65.
over 10% Pd on carbon. The structures of sulfones 65-68 follow from both spectroscopic and combustion data.

None of the dianions derived from 57-60 displayed a highly intense color, but rather were colorless to yellow. The only exception was dianion 68a, which slowly developed a brownish hue. This was interpreted to mean that 68a was unstable, and that the color was due to decomposition. Verification of this may be found in the only moderate yield of 68 (50%). Interestingly, all of these sulfones likewise undergo dialkylation rather than monoalkylation, as determined from experiments employing only one equivalent of base.

When sulfoxide 51 was treated with two equivalents of base, a yellow solution resulted. Upon warming to 25°, a very dark blue color resulted.

Treatment with methyl iodide afforded material which did not have the NMR features expected for the dialkylated product (very little vinyl absorption). Exposure of ketone 69 to potassium tert-butoxide in dimethylsulfoxide at
$20^\circ$ produced a deep red solution, which when treated with methyl iodide resulted in a mixture of at least 13 compounds, as determined by vpc and pmr techniques.

In order to better evaluate the relative rates of dianion production in sulfones 52 and 65-68 and to obtain a greater feeling for their relative stabilities, these compounds were subjected to carefully controlled conditions of generation, deuteration, and purification, as described in detail in the Experimental Section. Acetic acid-0-$\hat{d}$ (95% $\hat{d}$) was utilized to quench the dianions. This reagent not only simplifies the reaction to a simple proton transfer but also facilitates ready analysis of deuterium content by electronic integration of the pmr spectra. Chromatographic techniques were employed in the purification procedure in order to minimize losses and maximize reproducibility. Duplicate experiments confirmed the consistent nature of the experiments. A control experiment run without the addition of base resulted in a quantitative recovery of reactant. The results of these experiments are collected in Table IV, where $X$ denotes the addition time of the base and $Y$ the time of exposure. As can be seen from these data, generation of the dianion of 58 is rather sluggish. However, the significant result concerns the instability of dianion 68a, as suggested earlier by the methylation experiments. The yields of product stipulated in Table IV as arising from 68a are even lower than shown, since in this single instance the standard purification procedure did not remove all of the contaminants. In a control experiment, 60 was found to be completely stable to the chromatographic techniques utilized in its purification.
### TABLE IV

RESULTS OF THE DEUTERATION EXPERIMENTS PERFORMED ON THE DIANIONS OF SULFONES 52 AND 57-60.

<table>
<thead>
<tr>
<th>Compound</th>
<th>X, min</th>
<th>Y, min</th>
<th>Color of solution</th>
<th>Yield, %</th>
<th>d_2, %</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="compound" /></td>
<td>2</td>
<td>6</td>
<td>deep purple</td>
<td>68</td>
<td>90-95</td>
</tr>
<tr>
<td><img src="image" alt="compound" /></td>
<td>2</td>
<td>60</td>
<td>deep purple</td>
<td>68</td>
<td>90-95</td>
</tr>
<tr>
<td><img src="image" alt="compound" /></td>
<td>2</td>
<td>6</td>
<td>yellow</td>
<td>99</td>
<td>91</td>
</tr>
<tr>
<td><img src="image" alt="compound" /></td>
<td>2</td>
<td>60</td>
<td>yellow</td>
<td>90</td>
<td>94</td>
</tr>
<tr>
<td><img src="image" alt="compound" /></td>
<td>2</td>
<td>60</td>
<td>colorless</td>
<td>98</td>
<td>79</td>
</tr>
<tr>
<td><img src="image" alt="compound" /></td>
<td>2</td>
<td>6</td>
<td>yellow</td>
<td>96</td>
<td>86</td>
</tr>
<tr>
<td><img src="image" alt="compound" /></td>
<td>2</td>
<td>60</td>
<td>yellow</td>
<td>96</td>
<td>93</td>
</tr>
<tr>
<td><img src="image" alt="compound" /></td>
<td>1</td>
<td>1</td>
<td>yellow-greenish</td>
<td>34</td>
<td>90-95</td>
</tr>
<tr>
<td><img src="image" alt="compound" /></td>
<td>2</td>
<td>1</td>
<td>yellow-greenish</td>
<td>27</td>
<td>--</td>
</tr>
<tr>
<td><img src="image" alt="compound" /></td>
<td>2</td>
<td>9</td>
<td>yellow-greenish-green-brown</td>
<td>0</td>
<td>--</td>
</tr>
</tbody>
</table>
From the available data, it is apparent that the double bonds present in dianion 56 are capable of interacting with the negative charges in such a manner as to effect a transition of sufficiently low energy as to be observed in the visible portion of the electromagnetic spectrum. In an effort to more fully grasp the precise nature of this phenomena, Dr. R. Gleiter has performed extended Hückel calculations on sulfones 53 and 60 and on their respective dianions 56 and 68a. The results of these calculations are shown by their respective correlation diagrams (Figures 2 and 3). The geometries of 53 and 60 were constructed from Dreiding models, and it was assumed that the dianions had the same geometry.

Removal of the two bridgehead protons in 53 results in the formation of two high lying lone pair combinations n and n (Figure 2). These two combinations give rise to two allowed n → n* transitions of low energy. This qualitative picture clearly points out that the deep purple color of 56 is therefore not due to any transitions involving the sulfur atom of the sulfonyl group. The sulfone linkage only serves to make the bridgehead protons sufficiently acidic for facile abstraction by base. This is in agreement with the generation of highly colored species when sulfoxide 51 and ketone 62 were treated with base.

In the case of 60 and 68a (Figure 3), the MO-diagram is quite similar to that of 53 and 56 with the exception that the π and π* orbitals of the ethylene moiety are missing. The small separation between n and the lowest lying π* orbital suggests that 68a is not very stable. This, of course, has been confirmed by chemical data (see Table IV).
Figure 2. Partial correlation diagrams of the highest occupied and lowest unoccupied orbitals of 9-thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-dioxide (53) and its dianion (56).
Figure 3. Partial correlation diagrams of the highest occupied and lowest unoccupied orbitals of 9-thiabicyclo[4.2.1]nona-2,4-diene 9,9-dioxide (60) and its dianion 68a.
From these calculations, it appears that the lowest lying π* orbital in 56 and 68a is essentially located in the butadiene moiety, and suggests that the ultraviolet spectrum of 56 and 68a should be similar, concerning the first two bands. Dr. Gleiter is presently measuring the electronic spectrum of these two dianions at -70° in order to procure additional experimental confirmation of these calculations.

Observation of a thermally induced equilibrium between 1,2- and 1,4-dimethylcyclooctatetraenes (43 and 47) only partially satisfied the postulated thermal reactions available to such molecules. Of utmost importance is the existence of degenerate behavior. Such rearrangements could actually be transpiring during the equilibration of 43 and 47 only to go unnoticed due to the lack of adequate labeling. Construction of additional molecules would therefore be necessary if any capabilities for observing such phenomena were to be realized.

Additional labels were introduced into 1,2-dimethylcyclooctatetraene (43) by taking advantage of the highly acidic character of bridgehead α-sulfonyl hydrogens. Treatment of 7,8-dimethyl-9-thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-dioxide (70) with alkaline deuterium oxide in dioxane resulted in incorporation of deuterium into the bridgehead positions.
Photolysis of 70-\( d_2 \) effected extrusion of sulfur dioxide and the desired hydrocarbon 43-\( d_2 \) was isolated by preparative vpc techniques.

In order to observe the scrambling of deuterium in 43-\( d_2 \) which would be manifested by a degenerate rearrangement, a method had to be developed which would allow accurate and hopefully ready analysis of the positional concentrations of deuterium along the periphery of the ring. With this end in mind, recourse was made to adduct formation. Tetracyanoethylene (TCNE) appeared to be a reasonable choice for a dieneophile. Because of its high reactivity, only moderate temperatures (refluxing ethyl acetate) would be necessary to induce Diels-Alder reaction with the bicyclic form of the cyclooctatetraene derivative. This would preclude possible complications of thermal reactions during adduct formation. When the reaction of 43 and TCNE was carried out, it was found that only one adduct, 3,4-dimethyl-9,9,10,10-tetracyanotricyclo[4.2.0.3^2,5]deca-3,7-diene (71), was produced.

![Diagram](image)

This was the result of [4+2] cycloaddition with 43A, where the methyl groups are on the cyclobutene carbons. Selective reaction of the valence tautomeric form of a cyclooctatetraene derivative where the substituent is located on the cyclobutene carbon has widespread precedent. The pmr spectrum (acetone-\( d_6 \)) of 71 (Figure 4) is well suited for analysis of deuterium scrambling, for all the protons (in pairs) have quite different
Figure 4. The pmr spectra (acetone-$d_6$) of $3,4$-dimethyl-$9,9,10,10$-tetracyanotricyclo-$[4.2.2.0^{2,5}]$deca-$3,7$-diene (71) and its dideuterio counterpart (71-$d_2$).
chemical shifts. The methyl groups display a sharp singlet at δ 1.55, while the cyclobutane, bridgehead, and olefinic protons appear as multiplets centered at δ 3.08, 3.95, and 6.47, respectively. Analysis of adduct $\text{71-d}_2$ resulting from TCNE addition to $\text{24-d}_2$ with pmr techniques and manual integration indicated that $\text{d}_2$-incorporation had taken place to the extent of 95.5% (Figure 4).

Hydrocarbon $\text{43-d}_2$ was first pyrolyzed at 395°C. This low temperature was used in order to determine whether the anticipated degenerate behavior was more energetically accessible than the isomerization reaction. Also, use of this temperature would eliminate purification problems of the adduct, since no $\text{47}$ would be produced at this temperature (see Table I). Analysis of the TCNE adduct derived from this pyrolysate indicated that no scrambling had occurred (Table V). Subsequently, $\text{43-d}_2$ was pyrolyzed at a temperature where some (ca. 30%) isomerization to $\text{47}$ had occurred. Fortunately, the adduct of $\text{43}$ could be separated from those of $\text{47-d}_2$ by fractional recrystallization.

### Table V

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Cyclobutyl</th>
<th>Bridgehead</th>
<th>Vinyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.09</td>
<td>1.90</td>
<td>2.00</td>
</tr>
<tr>
<td>395</td>
<td>unchanged</td>
<td>1.65</td>
<td>2.06</td>
</tr>
<tr>
<td>510</td>
<td>0.38</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
stallization from methylene chloride-ether. Analysis by pmr techniques of
the adduct gave firm evidence of the operation of a degenerate rearrange-
ment, since some of the deuterium had in fact scrambled to the cyclobutane
position in the adduct (Table V). This data corresponds to the migration
of ca. 13% of the available deuterium for its original C3,8 position in
43-42 (cyclobutyl in adduct) to C4,7 (bridgehead in adduct). No measur-
able change in protium content at C5,6 was detected.

In order to verify that the deuterium content was not altered by pyroly-
sis, mass spectral analysis of the peaks in the vicinity of the parent was
performed on the TCNE adduct of 43 before and after pyrolysis at 510°.
These values, as determined from several scans in order to insure repro-
ducibility, are shown in Table VI, where they are normalized by giving the
parent peak the relative value of 1.00. Since both of these patterns
were identical, it was concluded that no measurable loss of deuterium had
occurred during the pyrolysis.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>P+2</th>
<th>P+1</th>
<th>P (262)</th>
<th>P-1</th>
<th>P-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.03</td>
<td>0.18</td>
<td>1.00</td>
<td>0.36</td>
<td>0.08</td>
</tr>
<tr>
<td>510</td>
<td>0.02</td>
<td>0.18</td>
<td>1.00</td>
<td>0.36</td>
<td>0.08</td>
</tr>
</tbody>
</table>

**TABLE VI**

MASS SPECTRAL ANALYSIS OF THE TCNE ADDUCTS OF 3,8-DIDEUTERIO-1,2-DIMETHYL-
CYCLOOCTATETRAENE (43-42) BEFORE AND AFTER PYROLYSIS.
Although the pyrolysis of \( \text{d}_{2} \text{e} \) at 510° does indicate a nondestructive skeletal isomerization, a gathering of additional data at higher temperatures, which should effect more extensive scrambling, was prohibited by the efficient competing reaction involving isomerization to \( \text{d}_{7} \). In order to circumvent this problem, the preparation and pyrolysis of 3,8-dideuteriobicyclo[6.4.0]dodeca-1,3,5,7-tetraene (\( \text{d}_{8} \text{e} \)) was undertaken. This compound is not capable of the positional isomerization reaction exhibited by \( \text{d}_{3} \), and therefore serves as a more convenient substrate with which to examine degenerate rearrangements.

The synthesis of \( \text{d}_{5} \text{e} \) is shown below. Sulfone \( \text{d}_{5} \) was prepared by the bishomoconjugative dehydrochlorination of \( \alpha \)-chloro sulfone \( \text{d}_{5} \).  

![Diagram](image)

Exchange of the bridgehead hydrogens in \( \text{d}_{5} \) for deuterium was accomplished with alkaline deuterium oxide and was followed by photolytic extrusion of
sulfur dioxide. Hydrocarbon \( \text{J5-d}_2 \) was isolated by preparative vpc techniques on column A as a pale yellow liquid. Fortunately, the known TCNE adduct \( \text{J6} \) of the undeuterated hydrocarbon also displays distinctly different chemical shifts for the various pairs of protons. The pmr spectrum

\[
\text{J6}
\]

(acetone-\( d_8 \)) of \( \text{J6} \) consists of multiplets at ca. \( \delta 1.5-1.8 \) for the eight methylene protons, a multiplet at \( \delta 3.16 \) for the two cyclobutane hydrogens, a multiplet at \( \delta 4.01 \) for the two bridgehead hydrogens, and a multiplet at \( \delta 6.51 \) corresponding to the two vinyl hydrogens. By pmr analysis \( \text{J5-d}_2 \) contained 89% \( d_2 \)-incorporation at \( C_3,8 \).

The data resulting from pmr analysis of the TCNE adducts prepared from the pyrolysates of \( \text{J5-d}_2 \) at various temperatures are collected in Table VII. Except for cleavage products, all of these pyrolysates were homogeneous by vpc analysis. \(^{48}\) As can be seen from the protio content at the various positions in these adducts, the stepwise shift of deuterium first to \( C_4,7 \) and then to \( C_5,8 \) is clearly evident. At the highest temperature studied (610°), almost 40% of the deuterium originally at \( C_3,8 \) in \( \text{J5-d}_2 \) (cyclobutyl in adduct) has migrated to \( C_4,7 \) (bridgehead in adduct) and to \( C_5,8 \) (vinyl in adduct).
TABLE VII

THERMALLY INDUCED DEUTERIUM SCRAMBLING IN 3,8-DIDEUTERIOBICYCLO[6.4.0]DODECA-1,3,5,7-TETRAENE (75-d2) AS DETERMINED BY MANUAL INTEGRATION OF THE PROTON RESONANCES OF THE PMR SPECTRA OF THEIR TCNE ADDUCTS

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Cyclobutyl</th>
<th>Bridgehead</th>
<th>Vinyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.21</td>
<td>1.99</td>
<td>2.00</td>
</tr>
<tr>
<td>545</td>
<td>0.31</td>
<td>1.85</td>
<td>2.03</td>
</tr>
<tr>
<td>575</td>
<td>0.70</td>
<td>1.70</td>
<td>1.80</td>
</tr>
<tr>
<td>610</td>
<td>0.94</td>
<td>1.66</td>
<td>1.60</td>
</tr>
</tbody>
</table>

In order to preclude the possibility of disproportionation of deuterium, 75-d2 was subjected to a mass spectral analysis as previously described for TCNE adduct 71-d2. Since it had already been shown that adduct formation does not cause deuterium loss (see Table VI), it was not necessary to perform such an analysis on 76-d2. The results of this work (Table VIII) confirm the absence of this phenomena.

TABLE VIII

MASS SPECTRAL ANALYSIS OF 3,8-DIDEUTERIOBICYCLO[6.4.0]DODECA-1,3,5,7-TETRAENE (75-d2) BEFORE AND AFTER PYROLYSIS

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>P+2</th>
<th>P+1</th>
<th>P (160)</th>
<th>P-1</th>
<th>P-2</th>
<th>P-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.02</td>
<td>0.14</td>
<td>1.00</td>
<td>0.21</td>
<td>0.11</td>
<td>0.03</td>
</tr>
<tr>
<td>575</td>
<td>0.02</td>
<td>0.14</td>
<td>1.00</td>
<td>0.23</td>
<td>0.13</td>
<td>0.04</td>
</tr>
</tbody>
</table>
Concerning the mechanistic details of these rearrangements, two possibilities suggest themselves. One involves an intramolecular \([\pi^4s + \pi^2s]\) cycloaddition of isomeric bicyclo[4.2.0]octatrienes (i.e. \(\text{III}\)) and results in the formation of a tetracyclo[4.2.0.0^2,8,0^5,7]octene intermediate (i.e. \(\text{IV}\)). Subsequent \([\pi^2s + \sigma^2s + \sigma^2s]\) bond reorganization results in a different valence tautomer (i.e. \(\text{V}\)). This mechanism is outlined for the reversible isomerization of \(\text{I}\) and \(\text{II}\). The other possibility involves a [1,5] sigmatropic rearrangement from these same bicyclics of a trigonal cyclobutene carbon atom (\(\text{B0 to B1}\)), again followed by disrotatory ring opening of the newly formed triene (i.e. \(\text{B1}\)). This mechanism is shown for the scrambling of deuterium in \(\text{I}\)-d. By simply utilizing the various closed forms, all of the available data may be rationalized by either of these mechanisms.
In the case of the degenerate rearrangement of $^{75-\text{d}_2}$, one would expect the internal Diels-Alder mechanism to be more energetically accessible to the molecule than the [1,5] sigmatropic shift route, due to the production of the highly strained intermediate $^S_2$ during the course of the latter sequence. This assumption has been verified recently by R. E. Wingard, Jr. when he found that a $[\pi^2s + \pi^4s]$ mechanism was exercised during the pyrolyses of certain "preformed" bicyclo[4.2.0]oct triene derivatives such as $^S_3$.

The [1,5] sigmatropic mechanism, although inoperative in the above example due to the necessary intervention of a very strained intermediate, could still be a viable alternative with other molecules which did not contain such geometric constraints. In order to test the feasibility of this option, the pyrolytic behavior of 3,8-dideuteriobenzocyclooctatetraene ($^{85-\text{d}_2}$) was studied. Rearrangement of $^{85-\text{d}_2}$ by way of a $[\pi^2s + \pi^4s]$ cyclo-
addition from the closed form 86a would result in destruction of the aromaticity of the benzene ring in 86b. No such energy barrier exists for a
[1,5] shift which would give $\delta_7$. Therefore, scrambling of the deuterium in this molecule would be indicative of the accessibility of the latter mechanism.

By taking advantage of known procedures, quantities of $\delta_5-d_2$ became readily available. Photobromination of biphenylene (88) gave 3,8-dibromobenzocyclooctatetraene (89), which upon metalation and quenching with methanol-0-d afforded $\delta_5-d_2$. The partial pmr spectra of $\delta_5$ and $\delta_5-d_2$ are shown in Figure 5. The pairs of hydrogens on the periphery of $\delta_5$ resonate at different chemical shifts. Their assignments had been previously determined by other workers by preparation of suitably deuterated derivatives. Owing to this well resolved spectrum, direct quantitative manual integration of pmr spectra of the pyrolyses of $\delta_5-d_2$ was possible without recourse to the preparation of adducts. This was fortunate, since $\delta_5$ is extremely sluggish in its reaction with TCNE. Integration of the pmr spectrum of $\delta_5-d_2$ showed a high level (94%) of $d_2$-incorporation at C3,a.

When $\delta_5-d_2$ was pyrolyzed at 565°, it was recovered with no detectable scrambling of the label. However, at temperatures in excess of this value, the influx of deuterium first into the C4,7 positions and subsequently the C5,a positions was observed. Degenerate rearrangement is again accompanied
Figure 5. The partial pmr spectra of benzocyclooctatetraene (85) and its dideuterio counterpart (85-d2).
by competing degradation, which in the current instance affords 1,4-di-deuterionaphthalene (20). The position of the deuterium, determined by integration of the pmr spectrum, was expected, and was the result of the loss of acetylene from 21. These results are collected in Table IX.

**TABLE IX**

RESULTS OF THE PYROLYSES OF 3,8-DIDEUTERIOBENZOCYCLOOCTATETRAENE

(85-d2) AS DETERMINED FROM PMR SPECTRA

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>H3,8</th>
<th>H4,7</th>
<th>H5,6</th>
<th>Recovery, %</th>
<th>20, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.13</td>
<td>2.00</td>
<td>2.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>565</td>
<td>0.13</td>
<td>2.00</td>
<td>2.00</td>
<td>46</td>
<td>-</td>
</tr>
<tr>
<td>625</td>
<td>0.29</td>
<td>1.85</td>
<td>2.00</td>
<td>22</td>
<td>4</td>
</tr>
<tr>
<td>675</td>
<td>0.67</td>
<td>1.57</td>
<td>1.88</td>
<td>5</td>
<td>10</td>
</tr>
</tbody>
</table>

The lack of any appreciable loss of deuterium from 85-d2 was confirmed by mass spectral analysis as previously stipulated; the data are compiled in Table X.
TABLE X

MASS SPECTRAL ANALYSIS OF 3,8-DIDEUTERIOBENZOCYCLOOCTATETRAENE

(85-d<sub>2</sub>) BEFORE AND AFTER PYROLYSIS

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>P+1</th>
<th>P (156)</th>
<th>P-1</th>
<th>P-2</th>
<th>P-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.16</td>
<td>1.00</td>
<td>0.67</td>
<td>0.21</td>
<td>0.05</td>
</tr>
<tr>
<td>675</td>
<td>0.15</td>
<td>1.00</td>
<td>0.66</td>
<td>0.20</td>
<td>0.05</td>
</tr>
</tbody>
</table>

In an effort to bypass transient destruction of aromatic character in 86b, [1,5] sigmatropic migration is advanced as the likely mechanism. Since the [4+2] mechanism was postulated for the degenerate behavior of 75-d<sub>2</sub> due to geometric constraints in 82, it appears that both of these mechanisms are accessible to the cyclooctatetraene system. The relevance of investigating a system which displays no energetic bias to either of these mechanisms and yet also leads to different products in accordance to its precise pathway is obvious.

The pyrolysis of 1,5-dimethylocyclooctatetraene (42) would lend itself quite nicely to such a study, as demonstrated in Scheme I. Because of its symmetry, there are only two valence isomers 22 and 23. By adhering to [1,5] sigmatropic shifts, 1,3-dimethylocyclooctatetraene (52) will be produced, along with return of 42. If an intramolecular [π<sup>2</sup>s + π<sup>2</sup>s] mechanism is followed, only the 1,4-isomer 47 will result by way of intermediates 24 and 25. Preliminary data from the pyrolysis of a small portion of 42, which
SCHEME I

\[ \text{92} \rightarrow \text{49} \rightarrow \text{93} \]

\[ [1,5] \]

\[ \text{[\(\pi^4_s + \pi^2_s\)]} \]

\[ \text{92} \rightarrow \text{49} \rightarrow \text{93} \]

\[ [1,5] \]

\[ \text{[\(\pi^4_s + \pi^2_s\)]} \]
was graciously donated by R. K. Russel, at 550° indicate that \( \text{by} \) is the major product, along with \( \text{b2} \) and a small amount of the 1,2-isomer \( \text{b3} \). The latter is a secondary product resulting from the thermal isomerization of \( \text{by} \) (see Table I). An additional product, presumably \( \text{b2} \), is also present. Detection of these compounds rests on spectroscopic (pmr and infrared) and chromatographic (column D at 30°) evidence. From these results it appears that both mechanisms are operative, although a more definitive statement must await the preparation of additional \( \text{b2} \), the independent synthesis of \( \text{b2} \), and the refinement of the chromatographic techniques utilized in the experiment.

With the behavior of \( \text{b3-d_e} \), \( \text{b5-d_e} \), and \( \text{b5-d_e} \) firmly pointing to the degenerate rearrangements of disubstituted cyclooctatetraenes, attention was directed to monosubstituted derivatives. It is conceivable that the disubstituted nature of the C8 ring is somehow facilitating these rearrangements. For this reason, along with the desire to further substantiate the generality of degenerate reactions in this molecule, the preparation of \( \text{b6-d_e} \) and \( \text{b7-d_e} \) was initiated. Also by studying the pyrolyses of derivatives

![Structural diagrams of b6-d_e and b7-d_e](image)

with both electron withdrawing (ester) and electron donating (methyl) substituents, the nature of any electronic effects could be determined.

Ester \( \text{b6-d_e} \) was prepared in one step by the photoaddition of benzene-\( \text{d_e} \) and methyl propiolate (28), as described by Bock. Formation of the
TCNE adduct $\text{22-d}_6$ once again enabled distinction of the various protons around the C$_8$ ring. The pmr spectrum (acetone-$d_3$) of 22 consists of a triplet at δ 3.38 with a coupling constant of 4 Hz for H$_5$, a triplet at δ 3.55 with the same coupling constant for H$_3$, a singlet at δ 3.68 for the ester methyl group, a multiplet at δ 4.05-4.22 for H$_1$, a multiplet between δ 6.37 and 6.51 for H$_7$, and a singlet at δ 6.63 corresponding to H$_4$. The pmr spectrum of $\text{22-d}_6$ lacked signals for H$_1$ and H$_5$-$8$. The proton on the ring was distributed between positions 2 and 4 in the adduct, as would result from reaction of TCNE with the two possible bicyclic forms $\text{100}$ and $\text{101}$ which contain the substituent on the cyclobutene ring.
Pyrolysis data for 26-<sup>de</sup> are given in Table XI. Again, analysis was performed by hand integration of suitably expanded pmr spectra of the TCNE adducts. These values were normalized to the value of H<sub>4</sub>, which was given a relative intensity of 1.00. Values for H<sub>5</sub> were not obtainable because of the close proximity of its chemical shift to that of the methoxyl absorption. Inspection of these data reveals once again the propensity of cyclooctatetraene for structural self-interconversion, as demonstrated by the migration of protium around the ring.

**TABLE XI**

**THERMALLY INDUCED PROTUM SCRAMBLING IN CARBOMETHOXYCYCLOOCTATETRAENE-<sup>de</sup> (26-<sup>de</sup>) AS DETERMINED BY MANUAL INTEGRATION OF THE PMR SPECTRA OF THE TCNE ADDUCTS**

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>H&lt;sub&gt;1,e&lt;/sub&gt;</th>
<th>H&lt;sub&gt;2&lt;/sub&gt;</th>
<th>H&lt;sub&gt;4&lt;/sub&gt;</th>
<th>H&lt;sub&gt;7,8&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.00</td>
<td>0.56</td>
<td>1.00</td>
<td>0.00</td>
</tr>
<tr>
<td>455</td>
<td>0.00</td>
<td>0.55</td>
<td>1.00</td>
<td>0.00</td>
</tr>
<tr>
<td>495</td>
<td>0.18</td>
<td>0.55</td>
<td>1.00</td>
<td>0.09</td>
</tr>
<tr>
<td>530</td>
<td>0.48</td>
<td>0.63</td>
<td>1.00</td>
<td>0.40</td>
</tr>
<tr>
<td>550</td>
<td>1.04</td>
<td>0.64</td>
<td>1.00</td>
<td>0.93</td>
</tr>
</tbody>
</table>

The integrity of the deuterium content was again substantiated on the basis of a mass spectral analysis (Table XII).
TABLE XII

MASS SPECTRAL ANALYSIS OF CARBOMETHOXYCYCLOOCTATETRAENED_{6}

(96-d_{6}) BEFORE AND AFTER PYROLYSIS

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>P+2</th>
<th>P+1</th>
<th>P (168)</th>
<th>P-1</th>
<th>P-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.02</td>
<td>0.12</td>
<td>1.00</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>545</td>
<td>0.02</td>
<td>0.12</td>
<td>1.00</td>
<td>0.04</td>
<td>0.01</td>
</tr>
</tbody>
</table>

The preparation of 101-d_{6} was patterned after that of Bock. Reduction of 96-d_{6} with lithium aluminum hydride afforded the alcohol 102, bp (0.05 mm) 64-73°, which displayed hydroxyl and C-D, but no carbonyl stretching frequencies in the infrared. Bromination with triphenylenphosphine di-
bromide in dimethylformamide gave bromide 10\textsubscript{3}. This transformation was previously realized by Bock with the aid of phosphorus tribromide in lower yield. Reduction of 10\textsubscript{3} with lithium aluminum hydride gave the desired hydrocarbon 27\textsubscript{d0}, bp (30 mm) 71-72°, which was identified by comparison of its retention time with that of the protio compound 27 on an analytical vpc column. The TCNE adduct 10\textsubscript{4} of 27 was well resolved, consisting of a singlet at δ 1.63 for the methyl group, a multiplet at δ 3.04-3.32 for the two cyclobutane hydrogens (H\textsubscript{2,5}), a multiplet at δ 3.80-4.12 for the two bridgeheads (H\textsubscript{1,6}), a singlet at δ 5.63 corresponding to the cyclobutene hydrogen (H\textsubscript{4}), and a multiplet at δ 6.32-6.54 for the two vinyl hydrogens (H\textsubscript{7,8}). The pmr spectrum (acetone-d\textsubscript{6}) of 10\textsubscript{4}-d\textsubscript{6} consisted of the methyl absorption and signals for H\textsubscript{2} and H\textsubscript{4}.

Pyrolysis data for 27-d\textsubscript{6} as deduced from spectral analysis of the TCNE adducts have been summarized in Table XIII. The migration of protium from its initial position one carbon removed from the methyl group in 27-d\textsubscript{6} to all the other positions of the ring is most dramatically demonstrated by the data obtained from pyrolysis at 610°. The last entry in Table XIII provides the theoretical results of complete scrambling of the hydrogen in this molecule. By comparison with the values at 610°, it can be seen that these statistical values have been nearly duplicated. The lower value
TABLE XIII

THERMALLY INDUCED PROTIIUM SCRAMBLING IN METHYLCYLOOCTATETRAENE-d_{6} (27-d_{6})

AS DETERMINED BY MANUAL INTEGRATION OF THE PMR SPECTRA OF THE TONE ADDUCTS

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>( \text{H}_{1,e} )</th>
<th>( \text{H}_{2,5} )</th>
<th>( \text{H}_{4} )</th>
<th>( \text{H}_{7,8} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.00</td>
<td>0.50</td>
<td>0.50</td>
<td>0.00</td>
</tr>
<tr>
<td>465</td>
<td>0.00</td>
<td>0.49</td>
<td>0.51</td>
<td>0.00</td>
</tr>
<tr>
<td>495</td>
<td>0.00</td>
<td>0.50</td>
<td>0.50</td>
<td>0.00</td>
</tr>
<tr>
<td>535</td>
<td>0.11</td>
<td>0.40</td>
<td>0.43</td>
<td>0.07</td>
</tr>
<tr>
<td>580</td>
<td>0.21</td>
<td>0.32</td>
<td>0.31</td>
<td>0.16</td>
</tr>
<tr>
<td>610</td>
<td>0.31</td>
<td>0.18</td>
<td>0.19</td>
<td>0.32</td>
</tr>
<tr>
<td>statistical</td>
<td>0.28</td>
<td>0.28</td>
<td>0.14</td>
<td>0.28</td>
</tr>
</tbody>
</table>

for the protium content at \( \text{C}_{2,5} \) is certainly the manifestation of the well documented preference of a hydrogen to occupy an \( \text{sp}^{2} \) rather than an \( \text{sp}^{3} \) center, and is complicated by the various valence tautomers responsible for positioning protium at the different sites in the TONE adducts. The pyrolytic behavior in \( 26-d_{6} \) and \( 27-d_{6} \) not only disproves the necessity of dissubstitution in cyclooctatetraenes for degenerate rearrangement, but also demonstrates the lack of electronic effects, at least in a qualitative sense, in these reactions.

A check of protium content was made by mass spectral analysis (Table XIV). These results again indicate the integrity of this value.

During the course of this work a new dimension in the chemistry of cyclooctatetraene has been uncovered. The capability of this nonaromatic polyolefin for circumambulatory degenerate rearrangement, a property which
had gone unnoticed in earlier studies, has now been elucidated by the use of proper substituent labeling. Conceptually, this fascinating propensity for self-interconversion should certainly add to the understanding of the chemistry of this well studied hydrocarbon.
PART II
EXPERIMENTAL

1,2-Dicarbomethoxycyclooctatetraene (40). A solution containing 22 ml of distilled dimethyl acetylenedicarboxylate in 500 ml of benzene was irradiated in a Rayonet reactor through quartz optics for six 15-hr periods, with intermittent cleaning of the apparatus with alcoholic potassium hydroxide to remove the opaque polymers formed during the reaction. The solution was then concentrated in vacuo and distilled at reduced pressure (120° and 0.5 mm) to remove the unreacted diester, which was recycled. The residue was dissolved in 30 ml of hot methanol and cooled to 0° to afford 5.23 g of 40 as yellow crystals. The mother liquor was combined with a later batch and chromatographed on alumina (activity 3) to afford additional material.

1,2-Bis(hydroxymethyl)cyclooctatetraene (41). To a mechanically stirred suspension containing 4.55 g (0.12 mole) of lithium aluminum hydride and 300 ml of ether was added 5.97 g (0.045 mole) of aluminum chloride portionwise under an atmosphere of
dry nitrogen at 20° (cold water bath). The white suspension was stirred 1 hr at ambient temperature, at which time a solution containing 12.93 g (0.059 mole) of \( \text{Br} \) in 350 ml of ether was added over a period of 45 min with moderate cooling (20-23°). The mixture was stirred at ambient temperature for 3.5 hrs, whereupon it was quenched by the cautious addition of a saturated ammonium chloride solution (ca. 40 ml). Filtration, followed by exhaustive extraction of the salts with boiling ether, afforded, after the usual workup and very thorough drying, 7.9 g (82%) of \( \text{I} \) as a viscous oil, whose infrared spectrum was identical with that of an authentic sample.

1,2-Bis(bromomethyl)cyclooctatetraene (42). To a stirred solution containing triphenylphosphine dibromide in dimethylformamide, prepared by the slow addition of 31.2 g (0.193 mole) of molecular bromine to a solution containing 51 g (0.195 mole) of triphenylphosphine in 400 ml of dimethylformamide at 25° with occasional cooling (ice bath) under an atmosphere of dry nitrogen (pptn forms), was added a solution containing 7.9 g (0.048 mole) of \( \text{I} \) in 80 ml of dimethylformamide over a period of 75 min at 25°. The mixture was stirred at ambient temperature for 2 hrs, at which time it was poured into 1500 ml of ice water and extracted several times with ether. Filtration of the first extract was necessary to remove precipitated triphenylphosphine oxide. The combined extracts were washed with ice water, saturated sodium bisulfite solution and ice water, dried,
and concentrated in vacuo. Digestion of the residue with hot pentane (400 ml) and vacuum filtration through 20 g of silicic acid afforded, after concentration in vacuo, 9.6 g (69%) of \( \text{42} \) as light yellow crystals. Caution should be exercised with this material, since it is a very potent lacrymator.

\[ \text{1,2-Dimethylcyclooctatetraene (43).} \]

\[ \text{CH}_3 \]

\[ \text{CH}_3 \]

\[ \text{43} \]

To a stirred suspension containing 6.3 g (0.165 mole) of lithium aluminum hydride and 150 ml of ether was added 9.6 g (0.033 mole) of \( \text{42} \) in 100 ml of ether over a period of 25 min at ambient temperature (drying tube). The mixture was refluxed for 12 hrs, cautiously hydrolyzed with 125 ml of saturated ammonium chloride solution, and diluted to 800 ml with dilute hydrochloric acid. After separation of the layers and several extractions with ether, the combined extracts were washed with saturated sodium chloride solution, dried, and cautiously concentrated in vacuo to a small volume at reduced pressure. The last traces of solvent were removed by distillation at atmospheric pressure, whereupon 3.81 g (87%) of \( \text{43} \) was collected by distillation, bp (45 mm) 78-80\(^\circ\). An infrared spectrum was identical to that of an authentic sample.

General Pyrolysis Procedure. Pyrolyses were conducted in the gas phase in a flow system by passing the vapor through a quartz tube packed with quartz chips at the stipulated temperatures under an atmosphere of nitrogen.
at reduced pressure (house vacuum). Under these conditions, the contact
time was ca. 1-3 sec. The resultant crude pyrolysates, which were col-
lected at -70° and usually recovered in 90-100% mass balance, were purified
by vpc techniques on column A. The reaction times (t_r) given refer to the
time required to pass all the material through the tube.

Pyrolysis of 1,2-Dimethylcyclooctatetraene (43). Pyrolysis of 35 mg of 43
at 405° and 20 mm, t_r = 14 min, afforded 28 mg of purified product.

Pyrolysis of 35 mg of 43 at 450° and 20 mm, t_r = 8 min, afforded 16
mg of purified product.

Pyrolysis of 40 mg of 43 at 500° and 30 mm, t_r = 17 min, afforded 10
mg of purified product.

Pyrolysis of 56 mg of 43 at 545° and 40 mm, t_r = 20 min, afforded 11
mg of purified product.

Pyrolysis of 77 mg of 43 at 590° and 30 mm, t_r = 20 min, afforded 5
mg of purified product.

A portion of 43 was pyrolyzed at 600° and 25 mm, whereupon the crude
pyrolysate was subjected to vpc separation on column A as usual. Care was
taken so that no material was lost during manipulation. The mixture of
volatile hydrocarbons so isolated was analyzed on column D at 35°. By com-
parison with retention times of authentic samples, benzene (1.3%), toluene
(96.2%), p-xylene (1.1%), and o-xylene (1.3%) were identified. Their rela-
tive abundances were determined by electronic integration.

9-Thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-Dioxide (52). To a stirred solu-
tion containing 1.485 g (9.64 mmoles) of 52, prepared by the addition of
sulfur monoxide to cyclooctatetraene, in 100 ml of methylene chloride was
added dropwise 1.86 g (9.65 mmoles) of \textit{m}-chloroperbenzoic acid (89.5\%) in 50 ml of methylene chloride over a period of 1 hr at 0\(^\circ\) under an atmosphere of dry nitrogen. The solution was stirred overnight at ambient temperature, at which time it was washed with 25 ml portions of a 0.5 M sodium hydroxide solution until basic, 15 ml portions of water until neutral, saturated sodium chloride solution, dried, and concentrated \textit{in vacuo} to afford beautiful white crystals. Recrystallization with methylene chloride-ether afforded 1.227 g (75\%) of \textit{52}, mp 190-190.5\(^\circ\) dec. (lit. mp 192.5-193\(^\circ\)); \(\delta_{\text{TMS}}^{\text{CDCl}_3}\) 3.78-4.15 (m, 2H, bridgehead) and 5.80-6.37 (m, 6H, vinyl); \(\nu_{\text{max}}^{\text{Nujol}}\) 1100, 1125, and 1290 cm\(^{-1}\); \(\lambda_{\text{max}}^{\text{Ethanol}}\) 225 (e 2820) and 279 nm (2840); calculated m/e 168.0244, observed 168.0242. An analytical sample was prepared by an additional recrystallization as before, mp 193\(^\circ\) dec.

**Anal. Calcd for C\(_{8}\)H\(_{14}\)O\(_{2}\)S:**
C, 57.12; H, 4.79.

**Found:** C, 56.90; H, 4.79.

\textbf{1,6-Dimethyl-9-thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-Dioxide (53).} To a stirred suspension (52 crystallized from solution when cooled) containing 170 mg (1.00 mmole) of \textit{52} in 10 ml of dry tetrahydrofuran was cautiously added 2.0 ml (2.64 mmoles) of \textit{n}-butyl-lithium solution in pentane through a
septum at -70° under an atmosphere of dry nitrogen. The deep purple solution was stirred for 5 min at -70° and then quenched by the addition of a large excess of methyl iodide, which left a light yellow solution. After the solution was allowed to warm to 25° the solvent was removed in vacuo, whereupon the residue was taken up in methylene chloride, washed with water, saturated sodium chloride solution, dried, and concentrated in vacuo to afford a quantitative yield of white crystals; δ_{CDCl₃} 1.55 (s, 6H, CH₃), 5.60 (s, 2H, one proton), and 5.50-6.27 (m, 4H, diene protons); ν_{max}^{Nujol} 1120, 1125, 1280, and 1290 cm⁻¹; λ_{max}^{Ethanol} 224 (ε 2200) and 278 nm (1530). An analytical sample was prepared by sublimation (95° and 0.2 mm) followed by recrystallization from methylene chloride-ether, mp 149-150°.


1,4-Dimethyloclooctatetraene (47). A solution containing 1.00 g (5.10 mmoles) of 52 in 100 ml of acetone and 300 ml of ether was irradiated with a 200 W Hanovia lamp fitted with a Corex filter in a quartz immersion well equipped with a condenser after dry nitrogen aeration for 30 min. The solution was then cautiously concentrated to a small volume at reduced pressure, whereupon the remaining solvent was removed by distillation at atmospheric pressure. The product was isolated by preparative vpc techniques on column A at 125°, tᵣ = 5 min, to afford 275 mg (41%) of 47 as a clear yellow liquid. Its spectral pro-
properties were in agreement with those of an authentic sample prepared by another route.

Pyrolysis of 1,4-Dimethylcyclooctatetraene (47). Pyrolysis of 47 mg of 47 at 500° and 30 mm, t\(_r\) = 13 min, afforded 18 mg of purified product.

Pyrolysis of 47 mg of 47 at 560° and 28 mm, t\(_r\) = 22 min, afforded 9 mg of purified product.

Pyrolysis of 60 mg of 47 at 585° and 35 mm, t\(_r\) = 16 min, afforded 6 mg of purified product.

Pyrolysis of 50 mg of 47 at 600° and 33 mm, t\(_r\) = 16 min, afforded 2 mg of crude, prepped product.

Pyrolysis of a portion of 47 at 600° and 33 mm, followed by vpc separation and analysis of the volatile hydrocarbons as previously described resulted in the detection of benzene (2.6%), toluene (70.5%), \(\pi\)-xylene (21.6%), and \(o\)-xylene (5.4%).

9-Thiabicyclo[4.2.1]nonane 9,9-Dioxide (58). Hydrogenation of 6.88 g (0.040 mole) of 58 in 100 ml of ethyl acetate was effected with the use of 10% Pd on carbon at 50 psi during 9 hrs on a Paar hydrogenation apparatus. The suspension was vacuum filtered through a pad of Celite, concentrated in vacuo, and recrystallized from ether-pentane to afford 4.0 g of fluffy crystals, mp 232-238° (lit 38 mp 235-237°). Manipulation of the mother liquor gave 0.9 g of 58, mp 232-237° and an additional 1.57 g, mp 215-235°, bringing the total yield to 6.47 g (93%).
2,3-Dibromo-9-thiabicyclo[4.2.1]nonane 9,9-Dioxide (64). Hydrogenation of 1.59 g (4.82 mmoles) of 64 in 120 ml of ethyl acetate was effected with the use of Adams catalyst at 50 psi in a Parr hydrogenation apparatus for 2 hrs. Vacuum filtration through a pad of Celite and removal of the solvent in vacuo was followed by thorough drying (25° and 0.05 mm) to afford 1.53 g (96%) of crystalline 64, which was identified by comparison to its reported pmr data.

9-Thiabicyclo[4.2.1]nona-2,4-diene 9,9-Dioxide (60). A mixture containing 5.11 g (15.4 mmoles) of 64, 3.24 g (77.0 mmoles) of lithium chloride, and 5.70 g (77.0 mmoles) of lithium carbonate in 100 ml of freshly distilled hexamethylphosphorus triamide was heated in a bath maintained at 115° under an atmosphere of dry nitrogen for 24 hrs. The suspension was then cooled to 25°, diluted with 500 ml of ice water, and extracted with 200 ml portions of ethyl acetate. The combined organic extracts were washed several times with 3 N hydrochloric acid, numerous times with water, saturated sodium chloride solution, dried, and concentrated in vacuo. The resultant residue (2.45 g) contained some hexamethylphosphorus triamide, and was purified with extensive loss of product by recrystallization from ethyl acetate-hexane to give 1.00 g (38%) of 60, mp 99-101° (lit. 101.5-102°).
1,6-Dimethyl-9-thin bicyclo[4.2.1]non-7-ene 9,9-Dioxide (65). To a stirred solution containing 172 mg (1.00 mmole) of 57 in 10 ml of tetrahydrofuran (57 crystallized from solution when cooled) was slowly added 1.1 ml (2.47 mmole) of n-butyllithium solution in pentane at -70° under an atmosphere of dry nitrogen. The resultant yellow solution was stirred at -70° for 5 min and then treated with an excess of methyl iodide. After the solution was allowed to warm to 25°, the solvent was removed in vacuo, whereupon the residue was taken up in methylene chloride, washed several times with water, saturated sodium chloride solution, dried, and concentrated in vacuo. Sublimation (90° and 0.1 mm) followed by recrystallization from ether-hexane afforded 175 mg (80%) of 65, mp 86-87.5°; δCDCl₃ 1.45 (s, 6H, CH₃), 1.85 (br s, 8H, methylene), and 5.92 (s, 2H, vinyl); νmax 1110 and 1285 cm⁻¹. An analytical sample was prepared by an additional recrystallization as before, mp 88-89°.

Anal. Calcd for C₁₀H₁₈O₂S: C, 59.96; H, 8.05; S, 16.01.
Found: C, 59.71; H, 7.98; S, 15.70.

1,6-Dimethylbicyclo[4.2.1]nonane 9,9-Dioxide (66). To a stirred solution containing 348 mg (2.00 mmoles) of 58 in 15 ml of tetrahydrofuran was slowly added 2.2 ml (4.94 mmole) of n-butyl-lithium solution in pentane at -70° under an atmosphere of dry nitrogen.
The resultant colorless solution was stirred at -70° for 1.5 hrs, at which time it was treated with an excess of methyl iodide and processed as previously described to give a pale yellow oil. Purification was accomplished by chromatographing this oil on a column prepared by wet-packing 10 g of silica gel with Skellysolve B. Elution with the same solvent removed hydrocarbon impurities while 66 eluted from the column with ether elution to afford 366 mg (91%) of material as a colorless oil; \( \delta_{\text{CDCl}_3} 1.41 \) (s, 6H, CH₃) and ca. 1.5-2.5 (m, 12H, methylene); \( \gamma_{\text{Nujol}} \) 1125 and 1280 cm⁻¹.

This material was also prepared by hydrogenation of 0.50 g (2.50 mmoles) of 65 in 50 ml of ethyl acetate with 10% Pd on carbon at 50 psi for 10 hrs in a Paar hydrogenation apparatus. Molecular distillation (80-100° and 0.05 mm) afforded 411 mg (82%) of 66 as a semisolid whose pmr spectrum was identical with that prepared above, mp 44-47°. An analytical sample was prepared by successive low temperature recrystallizations from hexane, mp 36.5-37°.

Anal. Calcd for C₁₀H₁₈O₂S: C, 59.36; H, 8.97; S, 15.85.

Found: C, 59.44; H, 8.94; S, 15.81.

1,6-Dimethyl-9-thiabicyclo[4.2.1]nona-2,7-diene 9,9-Dioxide (67). To a stirred solution containing 170 mg (1.00 mmole) of 59 in 10 ml of tetrahydrofuran (59 crystallized from tetrahydrofuran (59 crystallized from solution when cooled) was slowly added 1.1 ml (2.47 mmole) of n-butyllithium solution in pentane at -70° under an
atmosphere of dry nitrogen. The resultant yellow solution was stirred at
-70° for 5 min, whereupon it was quenched with an excess of methyl iodide.
Workup as usual and recrystallization from ether-hexane afforded 159 mg
(80%) of 6L, mp 115-116°; δ_{CDCl₃}^{TMS} 1.42 (s, 3H, 6-CH₃), 1.52 (s, 3H, 1-CH₃),
5.32 (dd, J₁,a = 11.5 Hz, J₂,₄ = 3.0 Hz, 1H, H₂), 5.80 (d, J₇,a = 8.0 Hz,
1H, H₇), 5.76-6.20 (m, 1H, H₃), and 6.06 (d, J₇,a = 8.0 Hz, 1H, H₈);
νₖₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑelijkewithstanding


\[ \text{Nujol \ 1115 \ and \ 1280 \ cm}^{-1} \] An analytical sample was prepared by an addi-
tional recrystallization as before, mp 117.5-118°.

**Anal. Calcd for C_{10}H_{14}O_{2}S: C, 60.57; H, 7.12; S, 16.17.**

**Found: C, 60.56; H, 7.13; S, 15.96.**

1,6-Dimethyl-9-thiabicyclo[4.2.1]nona-2,4-diene 9,9-Dioxide (68). To a
stirred solution containing 85 mg
(0.50 mmole) of 60 in 5 ml of tetra-
hydrofuran was added 0.55 ml (1.24
mmoles) of n-butyllithium solution in
pentane over a period of 1 min at -70°
under an atmosphere of dry nitrogen.

The resultant yellow solution was stirred at -70°, during which time the
solution gradually developed a light green and finally a light brown hue.
After 5 min an excess of methyl iodide was added and the slightly yellow
solution allowed to warm to 25°. The residue from this reaction was pre-
coated on silica gel and chromatographed on a column prepared by wet-packing
5 g of silica gel with Skellysolve B. Elution with the same solvent removed
hydrocarbon impurities, while ether eluted 50 mg (50%) of 68 as colorless
crystals; δ_{CDCl₃}^{TMS} 1.52 (s, 6H, CH₃), 1.98-2.24, 2.56-2.84 (m, 4H, methylene),
5.40-5.60, and 5.76-6.00 (m, 4H, vinyl); \( \lambda_{\text{max}}^{\text{Ethanol}} \) 270 nm (\( \varepsilon \) 3010). An analytical sample was prepared by sublimation (100° and 0.1 mm) followed by recrystallization from ether-hexane, mp 82-82.5°.

**Anal.** Calcd for C\(_{10}\)H\(_{14}\)O\(_2\)S: C, 60.57; H, 7.12; S, 16.17.

Found: C, 60.38; H, 7.03; S, 16.15.

Treatment of Bicyclo[4.2.1]nona-2,4,7-trien-9-one (69) with Strong Base.

To a stirred solution containing 132 mg (1.00 mmole) of 69 in 10 ml of freshly distilled dimethysulfoxide was added 336 mg (3.00 mmoles) of potassium tert-butoxide in one portion at 25°. The solution immediately developed a dark red color. After several minutes the solution was treated with ca. 0.5 ml of methyl iodide, which promptly dissipated the deep red color and produced a golden yellow color. This solution was diluted with water and extracted with ether, whereupon the combined ether extracts were washed with water, saturated sodium chloride solution, dried (MgSO\(_4\)), and concentrated in vacuo to give 138 mg of a golden yellow liquid which did not display a strained carbonyl band in the infrared. The pmr spectrum displayed a multitude of high field methyl spikes, and vpc analysis on column A at 80° showed at least 13 components, none of them present in relatively major amounts.

**General Procedure for Deuterium Incorporation.** To a stirred solution of the analytically pure sulfone in dry tetrahydrofuran (0.1 molar) was added an excess (25%) of n-butyllithium solution in pentane at -70° under an atmosphere of dry nitrogen in flame dried glassware over a period of 2 min. After stirring the solution at -70° for the prescribed time a large excess
of acetic acid-0-d, which contained 95% deuterium incorporation by pmr analysis, was added in one portion and the cooling bath removed. After several minutes the solution was pre-coated on silica gel (1 g) in situ and concentrated in vacuo. This material was then chromatographed on a column prepared by wet-packing 5 g of silica gel in Skellysolve B. Elution with this solvent removed hydrocarbon impurities, while elution with ether gave the desired product, which was thoroughly dried prior to mass determination and pmr analysis.

Treatment of 9-Thiabicyclo[4.2.1]non-7-ene 9,9-Dioxide (57). Exposure of 172 mg (1.00 mmole) of 57 as above for 6 min, deuteration, and subsequent purification afforded 173 mg (99%) of 57-d2, which contained 91% d2-incorporation as determined from electronic integration of its pmr spectrum.

Exposure as above for 1 hr gave 156 mg (90%) of 57-d2, which contained 94% d2-incorporation.

Treatment of 9-Thiabicyclo[4.2.1]nona-2,7-diene 9,9-Dioxide (59). Exposure of 170 mg (1.00 mmole) of 59 to base for 6 min, deuteration, and purification yielded 164 mg (96%) of 59-d2, which had 86% d2-incorporation.

Similar treatment with 1 hr of exposure resulted in the isolation of 165 mg (96%) of 59-d2 with 93% d2-incorporation.

Treatment of 9-Thiabicyclo[4.2.1]nonane 9,9-Dioxide (58). Reaction of 174 mg (1.00 mmole) of 58 for 1 hr, deuteration, and subsequent purification afforded 172 mg (98%) of 58-d2 with 79% d2-incorporation.
Treatment of 9-Thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-Dioxide (52). Treatment of 168 mg (1.00 mmole) of 52 for 6 min, deuteration, and purification gave 117 mg (68%) of 52-d₂, which contained 92% d₂-incorporation.

Treatment of 9-Thiabicyclo[4.2.1]nona-2,4-diene 9,9-Dioxide (60). Treatment of 85 mg (0.50 mmole) of 60 for 2 min followed by the usual deuteration and purification gave 23 mg (27%) of crude 60-d₂.

Reaction was repeated as above, except for the time required for addition of base, which was decreased from the normal 2 min to 1 min. Under these conditions, 29 mg (34%) of crude 60-d₂ containing 95% d₂-incorporation was isolated.

Treatment as usual with 9 min of exposure afforded no detectable product when chromatographed as previously described.

A solution containing 85 mg (0.50 mmole) of 60 in 5 ml of tetrahydrofuran was treated with acetic acid-d₄ at -70° and worked up as usual to afford 85 mg (100%) of 60, mp 99-101° (lit. mp 101.5-102°).

1,6-Dideutério-7,8-dimethyl-9-thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-Dioxide (70-d₂). To a stirred solution containing 545 mg (2.78 mmoles) of 70 in 25 ml of deuterium oxide and 100 ml of distilled dioxane was added 1.12 g (10 mmoles) of potassium tert-butoxide portionwise at 0° under an atmosphere of dry nitrogen. The resultant yellow solution was stirred at ambient temperature in the absence of oxygen for 10 days, at which time
analysis (pmr) of an aliquot indicated almost complete exchange. After a total of 11 days the reaction was poured into 250 ml of ether, washed three times with 50 ml portions of water, a saturated sodium chloride solution, dried, and concentrated in vacuo. The resultant white solid was thoroughly dried on a vacuum pump to afford 136 mg (80%) of 70-\(_2\), which was characterized by its pmr spectrum.

3,8-Dideutero-1,2-dimethylcyclooctatetraene (43-\(_2\)). A solution containing 426 mg (2.14 mmoles) of 70-\(_2\) in 100 ml of acetone and 300 ml of ether was irradiated with a 200 W Hanovia lamp fitted with a Corex filter in a quartz immersion well equipped with a condenser after dry nitrogen aeration for 30 min. The solution was cautiously concentrated to a small volume at reduced pressure (20°), whereupon the remaining solvent was removed by distillation at atmospheric pressure. The resultant residue was purified by preparative vpc techniques on column A at 110°, \(t_r = 9\) min, to afford 76 mg (26%) of 43-\(_2\), which was identified by its pmr spectrum.

3,4-Dimethyl-9,9,10,10-tetracyanoctacyclo[4.2.2.0^2,5]deca-3,7-diene (71). A solution containing 158 mg (1.20 mmoles) of 43 and 1.28 g (10.0 mmoles) of tetracyanoethylene in 10 ml of ethyl acetate was refluxed for several hours. The initial deep red color was rapidly
discharged. The solution was diluted with ethyl acetate, washed numerous times with 10% sodium bisulfite solution, several times with water, saturated sodium chloride solution, dried, and concentrated in vacuo. The crude product (305 mg) was recrystallized from methylene chloride-ether to afford 152 mg (52%) of \( \text{71} \), mp 253.5-256\(^{\circ}\) dec; \( \delta_{\text{TMS}}^{\text{acetone-d_6}} \) 1.55 (s, 6H, CH\(_3\)), 3.08 (m, 2H, cyclobutane), 3.95 (m, 2H, bridgehead), and 6.47 (m, 2H, vinyl).

An analytical sample was prepared by an additional recrystallization as before, mp 256-257\(^{\circ}\) dec.

**Anal.** Calcd for C\(_{16}H_{12}N_4\): C, 73.83; H, 4.65.

Found: C, 73.51; H, 4.73.

2,5-Dideutero-3,4-dimethyl-9,9,10,10-tetracyano
cyclo[4.2.2.0\(^2\)\(^5\)]deca-
3,7-diene (\( \text{71-d_2} \)). A solution containing 20 mg (0.149 mmole) of \( \text{4-d_2} \) and 256 mg (2.00 mmoles) of tetracyano-
ethylene in 5 ml of ethyl acetate was refluxed for 5 hrs, at which time it was worked up in the manner previously described. This material was pre-
coated on Florisil (0.5 g) and chroma-
tographed on a column prepared by wet-packing 5 g of Florisil in ether.

Elution with ether afforded 25 mg of crystalline \( \text{71-d_2} \), which was further purified by trituration with ether to give 12 mg (32%) of colorless cry-
stals. Pmr analysis indicated that \( \text{71-d_2} \) contained 95.5% d_2- incorporation.
Pyrolysis of 3,8-Dideuterio-1,2-dimethylcyclooctatetraene (43-d2). Pyrolysis of 27 mg (0.201 mmole) of 43-d2 at 395° and 30 mm, tR = 13 min, followed by treatment with tetracyanoethylene, subsequent workup, and chromatography as previously described resulted in the isolation of 20 mg (38%) of adduct after trituration with ether (47 mg crude).

When the pyrolysate resulting from thermolysis of 22 mg (0.164 mmole) of 43-d2 at 510° and 40 mm, tR = 9 min, was subjected to a similar treatment, 6 mg (14%) of adduct was isolated after recrystallization from methylene chloride-hexane (11 mg crude).

5,10-Dideuterio-1,2,3,4-tetrahydro-5,10-epithiobenzocycloocten-11,11-dioxide (74). To a stirred solution containing 1.027 g (4.63 mmoles) of 72 in 40 ml of deuterium oxide and 150 ml of distilled dioxane was added 1.68 g (15 mmoles) of potassium tert-butoxide portionwise at 0° under an atmosphere of dry nitrogen. The resultant reddish-brown solution was stirred at ambient temperature in the absence of oxygen for 10 days, at which time analysis (pmr) of an aliquot indicated ca. 90% d2-incorporation. After a total of 11 days the alkaline solution was poured into 500 ml of ether, washed three times with 100 ml portions of water, saturated sodium chloride solution, dried, and concentrated in vacuo. The resultant yellow solid was thoroughly dried on a vacuum pump to afford 565 mg (55%) of 74, which was identified by its pmr spectrum.
2,7-Dideuteriobicyclo[6.4.0]dodeca-1,3,5,7-tetraene (75-d2). A solution containing 565 mg (2.52 mmoles) of \( \text{74} \) in 100 ml of acetone and 300 ml of ether was irradiated with a 200 W Hanovia lamp fitted with a Vycor filter in a quartz immersion well equipped with a condenser after dry nitrogen aeration for 50 min. The solution was cautiously concentrated to a small volume at reduced pressure (20°C), whereupon the remaining solvent was removed by distillation at atmospheric pressure. The resultant residue was chromatographed on a column prepared by wet-packing 10 g of neutral silica gel in ether and eluting with the same solvent. After the solvent was removed, the product was isolated by preparative vpc techniques on column A at 135°C, \( t_r = 9 \) min, to afford 1.49 mg (37%) of \( \text{75-d2} \) as a clear, yellow liquid, which was characterized by its pmr spectrum.

Treatment of 2,7-Dideuteriobicyclo[6.4.0]dodeca-1,3,5,7-tetraene (75-d2) with Tetracyanoethylene. A solution containing 12.5 mg (0.078 mmoles) of \( \text{75-d2} \) and 128 mg (1.00 mmoles) of tetracyanoethylene in 5 ml of ethyl acetate was refluxed for 5 hrs (drying tube), during which time the initial pink color was discharged. Workup in the usual manner was followed by several triturations with ether to give 5 mg (23%) of \( \text{76-d2} \) (20 mg crude), which contained 89% \( d_2 \)-incorporation, as determined by pmr analysis.
Pyrolysis of 2,7-Dideuteriobicyclo[6.4.0]dodeca-1,3,5,7-tetraene (75-d2).

Pyrolysis of 33 mg (0.206 mmole) of 75-d2 at 545° and 2.0 mm and subsequent adduct formation and purification as usual afforded 6 mg (10%) of crystalline product after trituration with ether (19 mg crude).

Treatment of the pyrolysate resulting from thermolysis of 33 mg (0.206 mmole) of 75-d2 at 575° and 2.2 mm in the usual manner resulted in 8 mg (13%) of trituted (ether) adduct (28 mg crude).

In the same way, pyrolysis of 35 mg (0.218 mmole) of 75-d2 at 610° and 2.8 mm resulted in the isolation of 6 mg (10%) of adduct (28 mg crude).

Pyrolysis of 3,8-Dideuteriobenzocyclooctene (85-d2). Pyrolysis of 33 mg of 85-d2, prepared by the photochemical bromination of biphenylene and subsequent deuterium incorporation (93% d2-incorporation via pmr techniques) of the dilithio salt, was pyrolyzed at 565° and 2.0 mm. Purification of the crude pyrolysate by preparative vpc techniques on column A at 135° afforded 15 mg (46%) of C-12 product as a yellowish solid.

Pyrolysis of 53 mg of 85-d2 at 620° and 2.0 mm afforded, after vpc purification, 18 mg (34%) of product.

Pyrolysis of 168 mg of 85-d2 at 675° and 2.5 mm resulted in the collection of 150 mg of material, which was quite polymeric in appearance.

By utilizing the chromatographic techniques just described 8 mg (5%) of
C-12 product, along with 15 mg (10%) of 1,4-dideuterionaphthalene (92), identified by its pmr spectrum and vpc retention time, and 30 mg (ca. 20%) of an unidentified mixture with a longer retention time than the C-12 product were isolated.

Pyrolysis of 1,5-Dimethylcyclooctatetraene (49). Pyrolysis of ca. 25 mg of 49 at 550° and 25 mm, \( t_r = 11 \) min, resulted in the isolation of 23 mg of crude material, which was purified by preparative vpc techniques on column A at 120°, \( t_r = 5 \) min, to afford 11 mg of a mixture of the positional isomers of dimethylcyclooctatetraene. Identification of 1,2-, 1,4-, and 1,5-dimethylcyclooctatetraene in this mixture was made on the basis of analytical vpc data on column D, high resolution solution infrared spectra, and pmr spectra. An additional component, probably the 1,3-isomer, was also present.

2,3,4,5,6,7-Hexadeuteriocarbomethoxy cyclooctatetraene (26-d6). A solution containing 6 ml of methyl propiolate (98) in 120 ml of benzene-d6 was irradiated in a Rayonet reactor through quartz optics for six 20-hr periods. Additional portions (2 ml) of methyl propiolate were added each time the apparatus was cleaned with chlorosulfonic acid to remove the opaque polymer
formed during the reaction. The benzene-$d_6$ was recovered by distillation at atmospheric pressure, whereupon the residue was concentrated in vacuo and subjected to molecular distillation (90-130° and 0.02 mm). In this way 1.746 g of 26-$d_6$ was isolated as a clear yellow liquid. Its pmr spectrum was in agreement with that reported in the literature; $\delta_{\text{TMS}}$ 3.71 (s, 3H; CH$_3$), ca. 6.0 and 6.95 (br s, 1H, olefinic).

3-Carbomethoxy-9,9,10,10-tetracyanotricyclo[4.2.2.5]deca-3,7-diene (99).

A solution containing 138 mg (0.852 mmole) of carbomethoxycyclooctatetraene ($96^\text{80}$) and 1.28 g (10.0 mmoles) of tetracyanoethylene in 5 ml of dioxane was maintained at reflux for 5 hrs (drying tube). The dark color of this reaction still persisted after this treatment. Workup as usual was followed by recrystallization from methylene chloride-ether to afford 154 mg (62%) of $103$, mp 186-187° dec; $\delta_{\text{acetone}}$-$d_6$ 3.38 (t, $J_{2,5} = J_{5,6} = 4.0$ Hz, 1H, H$_5$), 3.55 (t, $J_{2,5} = J_{1,2} = 4.0$ Hz, 1H, H$_2$), 3.68 (s, 3H, CO$_2$CH$_3$), 4.05-4.22 (m, 2H, H$_1$, H$_2$), 6.37-6.51 (m, 2H, H$_7$, H$_8$), and 6.63 (s, 1H, H$_4$). An analytical sample was prepared by an additional recrystallization as before, mp 187-188° dec, followed by drying (110° and 0.1 mm) for 15 hrs.

**Anal.** Calcd for C$_{18}$H$_{10}$N$_4$O$_2$: C, 66.20; H, 3.47.

**Found:** C, 65.82; H, 3.53.
Treatment of 2,3,4,5,6,7-Hexadeuteriocarbomethoxycyclooctatetraene (26-de) with Tetracyanoethylene. A solution containing 44 mg (0.262 mmole) of 26-de and 0.64 g (5.0 mmoles) of tetracyanoethylene in 5 ml of ethyl acetate was refluxed for 14 hrs (drying tube). The usual workup was followed by recrystallization from methylene chloride-ether to give 23 mg (32%) of 26-de. Analysis by pmr indicated that hydrogen was present on the ring only at C-2 and C-4.

Pyrolysis of 2,3,4,5,6,7-Hexadeuteriocarbomethoxycyclooctatetraene (26). Pyrolysis of 67 mg (0.40 mmole) of 26-de at 550° and 2.7 mm, followed by treatment with tetracyanoethylene in refluxing ethyl acetate (16 hrs), normal workup, chromatography on Florisil (ether), and recrystallization from methylene chloride-ether resulted in the isolation of 12 mg (10%) of adduct.

Manipulation as above of the pyrolysate resulting from thermolysis of 70 mg (0.417 mmole) of 26-de at 530° and 2.3 mm yielded 16 mg (13%) of purified adduct (95 mg crude from column).

Pyrolysis of 72 mg (0.428 mmole) of 26-de at 495° and 2.3 mm followed by the usual treatment afforded 32 mg (25%) of recrystallized adduct.

In a similar manner, pyrolysis of 70 mg (0.417 mmole) of 26-de at 455° and 2.2 mm gave 34 mg (28%) of adduct.
2,3,4,5,6,7-Hexadeuteriohydroxymethylcyclooctatetraene (102). To a stirred suspension containing 8.28 g (0.218 mole) of lithium aluminum hydride in 200 ml of ether was added dropwise a solution containing 3.66 g (21.8 mmole) of 26-de in 100 ml of ether at 0° over a period of 45 min (drying tube). The mixture was stirred at 25° for several hours, at which time it was cooled to 0° and quenched by the cautious addition of 40 ml of water, whereupon it was diluted with 10% sulfuric acid solution (350 ml) to dissolve the salts, the layers separated, and the aqueous portion extracted several times with ether. The combined organic layers were washed with saturated sodium chloride solution, dried, and concentrated in vacuo. Distillation at reduced pressure afforded 1.933 g (64%) of 102 as a clear yellow liquid, bp (0.05 mm) 64-73° [lit bp (0.5 mm) 90-100°]. An infrared spectrum was identical with that described in the literature.

2,3,4,5,6,7-Hexadeuteriobromomethylcyclooctatetraene (103). To a stirred solution containing triphenylphosphine dibromide, prepared as previously described from 14.62 g (55.8 mmole) of triphenylphosphine and 8.85 g (55.3 mmole) of molecular bromine in 100 ml of freshly distilled dimethylformamide, was added a solution containing 1.933 g (13.8 mmole) of 102 in 25 ml of dimethylformamide over a period of 1 hr at 25° under an
atmosphere of dry nitrogen. The mixture was stirred for 3 hrs at ambient temperature, at which time it was poured into 500 ml of ice water and extracted with 200 ml of Skellysolve B. Solids were removed from the organic layer by vacuum filtration, and the filtrate was washed several times with Skellysolve B. The combined organic layers were washed with ice water, saturated sodium bicarbonate solution, ice water, dried, and concentrated in vacuo. The resultant residue was triturated with ca. 100 ml of Skellysolve B, the solvent evaporated, and the residue filtered through a small pad of Celite with the aid of ca. 3 ml of Skellysolve B. Thorough concentration in vacuo afforded 2.325 g (84%) of 107 as a clear yellow liquid which contained only a trace of solids.

2,3,4,5,6,7-Hexadeuteriomethylcyclclooctatetraene (27-d₈). To a stirred suspension containing 2.19 g (60.0 mmoles) of lithium aluminum hydride in 75 ml of ether was added dropwise a solution containing 2.325 g (11.55 mmoles) of 107 in 50 ml of ether over a period of 30 min at 25° (drying tube). The reaction was refluxed for 12 hrs, at which time it was cooled to 0° and quenched by the cautious addition of 10 ml of water. Enough 10% sulfuric acid solution was added to dissolve all of the salts (75 ml), the layers were separated, and the aqueous layer was extracted with ether. The combined organic layers were washed with water, saturated sodium chloride solution, dried, and the solvent was removed by distillation at atmospheric pressure. Distillation of the residue at reduced pressure afforded 952 mg
(67%) of 27-d₈ as a clear yellow liquid, bp (30 mm) 71-72°C. Identification was made on the basis of comparison of the bp with that of the previously prepared protio compound 10₁, bp (45 mm) 78-80°C, and by comparison of their retention times on an analytical vpc column.

3-Methyl-9,9,10,10-tetracyanotricyclo[4.2.2.0²⁶]deca-3,7-diene (10₄). A solution containing 198 mg (1.68 mmoles) of 27 and 1.28 g (10.0 mmoles) of tetracyanoethylene in 10 ml of ethyl acetate was refluxed for 4.5 hrs (drying tube). The initial deep red color was gradually dissipated during this time. Standard workup and chromatography on 10 g of Florisil gave 278 mg of adduct, which was recrystallized from methylene chloride-ether to afford 252 mg (61%) of 10₄, mp 201-204°C; δacetone-d₈ 1.63 (s, 3H, CH₃), 3.04-3.32 (m, 2H, cyclobutane), 3.80-4.12 (m, 2H, bridgehead), 5.63 (s, 1H, cyclobutene), and 6.32-6.54 (m, 2H, vinyl). An analytical sample was prepared by an additional recrystallization as before, mp 203-204.5°C, followed by sublimation (135°C and 0.02 mm), mp 203-204.5°C.

Found: C, 73.01; H, 4.12.

Treatment of 2,3,4,5,6,7-Hexadeuteriomethylcyclooctatetraene (27-d₈) with Tetracyanoethylene. Treatment of 62 mg (0.50 mmole) of 27-d₈ with 0.64 g (5.0 mmoles) of tetracyanoethylene in 5 ml of refluxing ethyl acetate for
9 hrs (drying tube) followed by the usual workup, chromatography, and recrystallization from methylene chloride-ether afforded 56 mg (45%) of $^{10\text{II}}\text{d}_8$. As expected, the only hydrogens present on the ring are at C-2 and C-4.

Pyrolysis of 2,3,4,5,6,7-Hexadeuteriomethylcyclooctatetraene ($^{27}\text{d}_8$).

Pyrolysis of 69 mg (0.556 mmole) of $^{27}\text{d}_8$ at 465° and 21 mm, $t_r = 7$ min, resulted in the isolation of 47 mg of crude pyrolysate. Treatment of this material with tetracyanoethylene in refluxing ethyl acetate followed by the established chromatographic purification and recrystallization with methylene chloride-ether, afforded 31 mg (22%) of adduct (78 mg from column).

Treatment of the crude pyrolysate (50 mg) resulting from the thermolysis of 73 mg (0.588 mmole) of $^{27}\text{d}_8$ at 495° and 17 mm as described above resulted in the isolation of 35 mg (24%) of adduct (77 mg from column).

Pyrolysis of 84 mg (0.677 mmole) of $^{27}\text{d}_8$ at 535° and 17 mm, $t_r = 10$ min, gave 56 mg of crude material, which was treated as usual to yield 34 mg (20%) of adduct (78 mg from column).

Pyrolysis of 87 mg (0.702 mmole) of $^{27}\text{d}_8$ at 580° and 19 mm, $t_r = 11$ min, afforded 62 mg of crude pyrolysate, which was converted into 33 mg (19%) of purified adduct as before (79 mg from column).

The pyrolysis of 104 mg (0.839 mmole) of $^{27}\text{d}_8$ at 610° and 20 mm, $t_r = 17$ min, resulted in the isolation of 47 mg of crude material. A vpc trace on column A at 95° showed that the pyrolysate consisted of essentially one
component, $t_r = 7.5$ min. Two small peaks, $t_r = 1.5$ and $2.0$ min, had the same retention times as benzene and toluene, respectively. Treatment of this material in the usual fashion resulted in the isolation of $14$ mg (7%) of adduct ($57$ mg from column).
PART II

REFERENCES


16. This field has been exhaustively reviewed by L. T. Scott and M. Jones, Jr., *Chem. Rev.*, 72, 181 (1972).


27. Gratitude is extended to Dr. R. E. Beckley for making available an authentic sample of this material.


29. A Jeol JNM-MH-100 was employed to gather these data, and it was found that external lock produced unacceptable spectra.

30. Gratitude is extended to Dr. R. E. Wingard, Jr., for donating a sample of 1/2 which had been prepared by this route.
31. A sample of $^{40}$ was kindly donated by Mr. R. K. Russel. The details of this preparation will be described in a forthcoming publication.


35. A simple, one step preparation of $^{52}$ has very recently appeared. J. Gasteiger and R. Huisgen, ibid., 92, 6541 (1972).


38. W. L. Mock, J. Amer. Chem. Soc., 92, 3807 (1970). Gratitude is extended to Professor Mock for making the experimental details of his preparation available to us prior to publication.


40. See Part I of this work for information concerning $^{62}$.


42. Consult Part I of this work for the multistep preparation of $^{70}$.

43. Acetone-$d_8$ was used as the solvent for pmr spectra of all the TCNE adducts because of good solubility properties.

44. Treatment of $^{57}$ with TCNE resulted in the formation of at least three adducts, as deduced from inspection of the methyl region of various pmr spectra.

45. See Part I of this work for a thorough discussion of this behavior.
46. L. A. Paquette, R. E. Wingard, Jr., and R. H. Meisinger, *ibid.*, 93, 1047 (1971). Gratitude is extended to Dr. R. E. Wingard, Jr., for supplying adequate quantities of 72 for use in this work.


48. This was also the case with the pyrolysis of other cyclooctatetraene derivatives which will be discussed shortly.

49. *A priori* a third possibility, the apparent antara-antara Cope rearrangement $[\pi^2\alpha + \sigma^2\alpha + \pi^2\alpha]$ involving the cyclobutene $\pi$ bond of the bicyclo-[4.2.0]trien e valence tautomer of cyclooctatetraene, does not satisfactorily account for the distinctive degenerate isomerizations. It should be noted however, that an example of a possible trans-cyclooctatetraene, a requisite of this mechanism, has been reported. E. H. White, E. W. Friend, R. L. Stern, and H. Maskill, *ibid.*, 91, 523 (1969).


56. This material was prepared in accordance to the procedure developed by Dr. R. E. Beckley, who kindly made this unpublished information available to us.

57. This material was first prepared by Cope, reference (2c).


60. Dr. K. A. Henzel kindly supplied the carbomethoxycyclooctatetraene (100) used in this experiment.
PART III
INTRODUCTION

The "di-π-methane process" has possibly done more to stimulate photochemical research in the past few years than any other excited state phenomenon. Its recent and exciting history began when Zimmerman described work on the photoisomerization of barrelene (1) to semibullvalene (2) and
cyclooctatetraene. A detailed mechanistic study of this reaction, involving deuterium labeling of the vinyl positions in 1, disclosed a unique
mechanism in which a divinylmethane moiety is converted into a vinylcyclo-propane group, a process which will hereafter be termed the di-\( \pi \)-methane transformation. In this mechanism, initial vinyl-vinyl bridging to form diradical \( 2 \) is followed by bond fission to produce \( k \), which undergoes intersystem crossing and rebonding to afford semibullvalenes \( 5a \) and \( 5b \). The hydrogen distribution in the product clearly supports this mechanism.

The di-\( \pi \)-methane rearrangement may also be explained in other mechanistic terms. It has been proposed, for instance, that the reaction is concerted rather than diradical in nature.

A concerted pathway is in agreement with the observed regiospecificity of the reaction. Thus, of the three centers of stereochemistry in molecules capable of undergoing the di-\( \pi \)-methane reaction, retention is observed at C-1 and C-5 and inversion is seen at C-3. Since the stereochemistry at these sites is not destroyed during reaction any diradical species must be short lived, otherwise rotation about carbon-carbon bonds could lead to stereomutation. Consequently, many reports in the literature favor a concerted mechanism.\(^5\) However, it should be noted that when diradicals are proposed, they don't necessarily have to be real intermediates, which would imply non-concertedness, but just be points along a concerted energy surface.\(^6\)
Very recently, Mariano has disclosed details of an elegant study of the stereochemistry of the di-\( \pi \)-methane rearrangement. He found that direct irradiation of \( \text{6} \) afforded \( \text{8} \) via an anti-disrotatory ring closure, along with \( \text{11} \), the result of intersystem crossing to the triplet, which underwent bond rotation (\( \text{2} \to \text{10} \)) faster than bond formation (\( \text{2} \to \text{8} \)). Therefore, both a concerted and a stepwise (diradical) mechanism were apparently operative.

The transformation of \( \text{6} \) to \( \text{8} \) is formally a \([\sigma^a + \pi^a]\) cycloaddition, which is photochemically allowed by the Woodward-Hoffmann symmetry rules. The bonding involved in such a mechanism is demonstrated below for the barrellene → semibullvalene photoisomerization.
Although a substantial number of $[\sigma^2a + \pi^2a]$ photorearrangements are known, its operation in the di-\(\pi\)-methane rearrangement has been disproved in a number of instances. For example, the inability of \(^{12}\) to afford di-\(\pi\)-methane product \(^{13}\) (instead of the observed product \(^{16}\)) and the capability of the diene analog (\(^{14}\)) to photoisomerize rapidly to \(^{15}\) are findings not in agreement with a $[\sigma^2a + \pi^2a]$ pathway. If such a pathway were operative, the rearrangement of \(^{12}\) to \(^{13}\) should be even more facile than that of \(^{14}\) to \(^{15}\), since the migrating bond in \(^{12}\) would be a weaker.
σ bond \( \text{sp}^3-\text{sp}^3 \) than that in \( \text{sp}^2-\text{sp}^3 \) σ bond.

An intriguing possibility with molecules which are capable of undergoing the di-π-methane reaction is to modify the structure so that more than one type of bridging is possible and to determine migratory preference if any. An example of such a molecule is benzobarrelene (17), which is capable not only of vinyl-vinyl bridging (18) as in the case of barrelene (1), but also of aryl-vinyl bridging (19). Both of these processes would lead to the same product (20).

However, when the deuterium labeled compound (21) was irradiated under sensitized conditions, the benzosemibullvalene (22) was found to be the result of exclusive vinyl-vinyl bridging. 11a No aryl-vinyl bridging was observed, as determined from the position of deuterium in the product. The same result was observed by Paquette in a related molecule. 11b It appears
that an appreciable activation energy is associated with the vinyl-aryl bridging process, and presumably, vinyl-vinyl bonding is less energetically demanding.\textsuperscript{12}

In the case of the naphthobarrelenes, α-naphthyl-vinyl bridging is preferred over vinyl-vinyl bridging, which in turn is preferred over β-naphthyl-vinyl bridging.\textsuperscript{13} In molecules where only aryl-vinyl or aryl-aryl bridging is possible, di-π-methane reactions do proceed through aryl-bridging intermediates.\textsuperscript{14}

When deuterated benzobarrelene (21) was photolyzed, 22 was not the only product. There was also isolated a trace of benzocyclooctatetraene (23). Upon direct irradiation of 21, 23 was the sole product. From deuterium positioning in the product, it was suggested that 23 result from aryl-vinyl bridging through a quadricyclene type intermediate (24). Through additional experiments, Zimmerman determined that 23 was derived from a singlet reaction
and \( 22 \) from a triplet process. This is a clear example of an intramolecular photochemical reaction in which different pathways are taken by the triplet and singlet excited states.

The propensity of the triplet state to undergo di-\( \pi \)-methane rearrangements while the singlet state is either very sluggish towards this route or actually takes a different pathway appears to be quite general for cyclic systems. \(^{15}\) Although there are a few notable exceptions to this rule, they are usually due to the lack of a competing singlet reaction as a result of geometric restraints. In these cases the singlet excited state either undergoes the di-\( \pi \)-methane directly or suffers intersystem crossing to the excited triplet state which then rearranges.

An interesting and well documented extension of this multiplicity relationship in di-\( \pi \)-methane rearrangements is the observation that acyclic compounds which, unlike their cyclic counterparts, prefer the singlet excited state for bond reorganization. For example, \( 25 \) and \( 26 \) undergo the \( \text{di-} \pi \text{-methane transformation via} \) their respective triplet states, while \( 27 \), \( 28 \), and \( 29 \) rearrange via their singlets.
An explanation of this apparent dichotomy suggests that molecules capable of possessing rotational freedom in the excited state, such as acyclic diene and exocyclic methylene compounds, rearrange most efficiently under singlet conditions while molecules which possess geometric constraints to rotational freedom, such as cyclic compounds and , prefer to rearrange under triplet conditions. This “free rotor” effect is proposed to efficiently dissipate triplet but not singlet excitation energy. In fact, photosensitized irradiation of effects instead an alternative isomerization without di-π-methane rearrangement.

A dependency on multiplicity has also been observed in conjunction with the oxa-di-π-methane rearrangement. The oxa-di-π-methane reaction is no more than a di-π-methane rearrangement where one of the vinyl groups has been replaced by a carbonyl group. Unsaturated ketones undergo this reaction in the triplet excited state, whereas their singlet excited states experience [1,3] acyl shifts, along with decarbonylation. The reason for this divergent behavior has been discussed in terms of MO theory and the “free rotor” effect.

Oxa-di-π-methane rearrangements may actually compete with di-π-methane rearrangements. For example, is certainly capable of undergoing a di-π-
methane rearrangement to afford 31 via aryl-vinyl bridging (32). An oxa-di-π-methane reaction is also accessible to the molecule via 32. When the dideutero-compound was irradiated under sensitized conditions, the positions of the deuterium (31-D₁) clearly describe an oxa-di-π-methane process.

Homologs of the di-π-methane process have also been observed. Irradiation of 34 affords a mixture of products which can be easily rationalized by postulating the di-π-ethane intermediate 35. The π-interaction processes...
proceed through intermediate \( \text{III} \). This di-\( \pi \)-propane process has recently been suggested for a similar system. Higher homologation was unsuccessful, presumably due to separation between reactive centers now sufficient to prevent \( \pi \)-interaction. A di-\( \pi \)-methane like intermediate has been suggested for the photocyclization of aryl substituted acetylenes to aryl-cyclopropenes.

By irradiating di-\( \pi \)-methane reactants which have substituents in appropriate positions along their frameworks, it has been possible to observe preferential production of one di-\( \pi \)-methane product over another. Direct photolysis of \( \text{III} \) resulted in the production of \( \text{IV} \) as the sole product. No \( \text{IV} \) was observed.

The directionality of this reaction is controlled by demand of the excited state to maximize electron delocalization during rearrangement. Cleavage of bond (a) in \( \text{IV} \) clearly produces a more stable diradical (\( \text{V} \))
(tertiary-benzhydryl) than cleavage of bond (b) to give \(^4\) (tertiary-tertiary). Another way to envision this selectivity would be to consider that there is more electron density at C\(_5\) available for bonding (scission of bond (a)) than at C\(_1\) (scission of bond (b)), where the electron density is relatively diffuse. That is to say, the reaction takes the pathway which least localizes odd electron density.

It has also been shown that a \(p\)-cyanophenyl substituent participates in the di-\(\pi\)-methane rearrangement with a \(1.4\) to \(1\) preference over a phenyl ring, and that a \(p\)-anisyl group shows an even greater preference,\(^{24a-c}\) the result of the stabilizing effects of the cyano and methoxy groups on the odd electron density of the di-\(\pi\)-methane intermediate.

In a very recent study, Hixson has shown that by decreasing the electron density at the migration terminus (\(\text{a}_4\)), the rate of rearrangement is enhanced. By increasing the electron density at the migrating center (\(\text{b}_4\) vs \(\text{c}_4\)), where one would expect odd electron density to be important, the rate of rearrangement is also increased.\(^{25}\)

\[
\begin{align*}
\text{a}_4, \quad X = \text{CN} &; \quad Y = \text{H} & \quad k_{rel} \rightarrow 41 \\
\text{b}_4, \quad X = \text{H} &; \quad Y = \text{OCH}_3 & \quad 13 \\
\text{c}_4, \quad X = \text{H} &; \quad Y = \text{CN} & \quad 3.8 \\
\text{d}_4, \quad X = \text{H} &; \quad Y = \text{H} & \quad 1.0 \\
\text{e}_4, \quad X = \text{OCH}_3 &; \quad Y = \text{H} & \quad < 0.04
\end{align*}
\]
A particularly intriguing example of a functionality effect is Paquette's work on the sensitized photoisomerization of \( \text{45a} \) and \( \text{45b} \). The imino ether afforded principally \( \text{46a} \), while lactam \( \text{45b} \) yielded mainly \( \text{47b} \). Since both products result from initial vinyl-vinyl bridging, the structural make-up of the heteroatomic bridge apparently determines the preferential scission of bond (c) and bond (d), respectively, in intermediate diradical \( \text{48} \).

The preponderance of \( \text{46a} \) over \( \text{47a} \) can be understood by invoking the established principle of maximum delocalization of odd electron density during rearrangement. One then wonders why lactam \( \text{45b} \) does not display this same preference. A possible explanation is that the lactam carbonyl is exerting a larger stabilizing effect on the non-benzylic odd electron center, possibly due to a homoconjugative charge-transfer interaction, than that resulting from maintaining the odd electron delocalization of the benzylic center.
In order to better evaluate the influence of the amide functionality on excited state free valence in the di-π-methane rearrangement, it was decided to investigate this photorearrangement in other molecules which contain this group. It was considered advantageous that this model be structurally designed in a manner which would preclude complications by extraneous substitution. In addition, if interaction could be exerted in the bridging step of the di-π-process rather than in a subsequent bond scission as in 45b, more definite information concerning the nature of its influence could perhaps be realized. Furthermore, it was desired to incorporate structural features whose effect on the di-π-methane rearrangement was already known. This "internal standard" could then perhaps permit some measure of comparative evaluation of the effect of interaction of the amide functionality.
PART III
RESULTS AND DISCUSSION

The 5,6-benzo-2-azabicyclo[2.2.2]octa-5,7-dien-3-one framework (49) was envisioned as an excellent model for studies concerning directionality effects of the amide function in the di-\(\pi\)-methane photorearrangement. This basic structure was selected because of its synthetic accessibility and because the influence of the amide function on bridging in the di-\(\pi\)-methane process could be easily recognized by the product structures. Also, methyl substitution \(28\) on the periphery could provide substituent effects against which the influence of the amide function could be compared. These methyl labeled compounds would in addition permit distinction between di-\(\pi\)-methane, oxa-di-\(\pi\)-methane, \(19\) and \([\sigma^2a + \pi^2a]\) processes. \(8\) Since a di-\(\pi\)-methane rearrangement in 49 would involve benzyl-vinyl bridging, its energy requirements should be quite different from those in 45a, the only other lactam studied to date.

The synthetic approach to the desired bicyclic lactams is depicted in Scheme I. Diazotization of 2-aminopyridines 50b-e by the method of
SCHEME I

\[
\text{Scheme diagram with reactions and product yields.}
\]
Adams afforded the 2-pyridones 51b-e, which were methylated by known procedures to produce 52b-e. Caution must be exercised with 52b-e, as they are quite deliquescent. Pmr data on 52b-e have not previously been reported in the literature, and consequently are collected in Table I.

Pyridones 52a-e were then reacted in Diels-Alder fashion with benzyne, prepared by aprotic diazotization of anthranilic acid with isomyl nitrite, to afford the known lactams 53a-e. The yields in these cycloadditions are quite low due to the quasi-aromatic character of the pyridones, but the products are easily isolated by column chromatography on neutral alumina. The unreacted pyridones may be recovered and recycled. Dimethoxyethane is commonly used as a solvent for benzyne additions, but its use in this instance had little or no effect on the yield, as did the employment of prolonged addition times.

With the lactams in hand, it appeared that the amines could become readily available by reduction of the carbonyl group. These amines have not been previously prepared, and their photolyses could reveal effects of basic nitrogen on the odd electron density in the di-α-methylene rearrangement. Unfortunately, lithium aluminum hydride reduction of 53b in refluxing tetrahydrofuran resulted only in the quantitative formation of α-methylnaphthalene rather than amine 67. This material may arise from an "unzipping"
<table>
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<td>6.22</td>
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<tr>
<td></td>
<td>H₆</td>
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</table>
process of the [2.2.2] bicyclic framework as depicted in 53c. Aromatization presumably provides the needed driving force. No multistep sequences to prepare these amines were attempted.

Lactams 55a-e were photolyzed in dilute acetone solutions with a Hanovia 450W mercury emission lamp through Pyrex optics, in accord with the established triplet multiplicity of cyclic di-\(\pi\)-methane rearrangements. The photoisomerizations were monitored with the use of vpc techniques on column A, and all product ratios cited have been corrected for detection coefficients. In all cases, only two photoproducts were observed in nearly quantitative yield, although prolonged photolyses did produce minor secondary products in some cases. Attempted separations of isomeric photoproducts by column chromatography (alumina) were unsuccessful, as the compounds underwent extensive decomposition. Consequently, the mixtures were separated by preparative vpc on column A.

Photolysis of the parent lactam 55a resulted in the formation of a mixture of the dihydrobenzazasemibullvalones 56a (25%) and 57a (75%). The structure of 56a [\(\delta^{CDCl_3}_{TMS}\) 2.70 (s, 3H, -CH\(_3\)), 2.81 (m, 1H, H\(_6\)), 3.12 (m, 1H, H\(_1\)), 3.53 (dd, J\(_{1,2}\) = 5.0 Hz, J\(_{2,3}\) = 7.5 Hz, 1H, H\(_2\)), 3.93 (d, J\(_{1,5}\) = 6 Hz, 1H, H\(_5\)), 7.08-7.58 (m, 4H, aromatic), \(\nu_{Nujol}^{max}\) 1680 cm\(^{-1}\) (C=O)] and 57a.
The assignments of the chemical shifts and coupling constants to $H_1$, $H_2$, $H_5$, and $H_6$ in 57a were accomplished with the aid of spin-decoupling studies at 100 MHz. Upon irradiation of the doublet at 4.63 $\delta$, the quartet at 3.38 $\delta$ collapsed to a triplet. This allowed assignment of $H_1$ and $H_5$, $J_{1,5} = 6.0$ Hz. Irradiation of the doublet of doublets at 3.38 $\delta$ collapsed the doublet at 4.63 $\delta$ to a singlet, the triplet at 2.93 $\delta$ to a doublet, $J_{1,8} = J_{1,2} = 6.5$ Hz, and the doublet of doublets at 2.60 $\delta$ to a doublet,
J₂,₆ = 8 Hz. This data, along with known chemical shifts of these protons in 57b-e (see Table II for a tabulation of pmr data for all the photoproducts), allowed the assignment of H₂ and H₆.

Assignment of the di-π-methane mechanism to this photorearrangement was accomplished by examination of the photoproducts of the methylated derivatives 53b-e. A priori, this photoisomerization could proceed to 56a and 57a via either the di-π-methane route or by [2σ + 2π] intramolecular cycloaddition. The oxa-di-π-methane route may be ruled out on the basis of the results of the parent 53a, since this mechanism would predict 57a as the sole product.

![Chemical structure](image)

53a

Inspection of the methyl labeling patterns of the photoproducts from 53b-e uniquely identifies the process prevailing as the di-π-methane rearrangement. Although this is not exceptional, since benzobicyclooctadiene has been shown to photorearrange by this route, other carbonyl compounds containing this ring system have been shown to utilize the oxa-di-π-methane pathway.

The data for all of the photoproducts is coupled in Table II. In order to elucidate the chemical shifts and coupling constants in 57e, expanded scale 100 MHz spectra were necessary. As can be seen from these data, all
TABLE II
CHEMICAL SHIFT AND COUPLING CONSTANTS DATA OF PHOTOPRODUCTS

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<td></td>
<td>H₆</td>
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<td></td>
<td>Aromatic</td>
<td>7.01-7.35</td>
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### TABLE II (Continued)

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<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift (δ)</th>
<th>Coupling Constant (Hz)</th>
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<td><img src="image" alt="Compound 56e" /></td>
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of the proton assignments and coupling constants readily follow when such
a large number of structures are available for comparison. For example, H₂
is always shifted downfield in 56a-e relative to its α-carbonyl counterparts
in 57a-e, the result of the expected greater deshielding effect
of an α-nitrogen relative to an α-carbonyl as previously mentioned. This
same effect is observed in H₅. The resonance for methyl on nitrogen is
always at a lower field (ca. 0.2 δ) when in 56a-e than in 57a-e,
presumably due to an interaction with the cyclopropane ring. Also, the
carbonyl absorptions in the infrared spectra of 57a-e are shifted to lower
energy (ca. 10 cm⁻¹) as compared to 56a-e due to a resonance effect of the
cyclopropyl ring.

The product distribution resulting from the photolysis of the parent
53a reveals a preferential formation of 57a over 56a by a factor of 3.
Therefore, of the two initial bridging species, $55a$ predominates over $54a$. A similar result is observed in the photoisomerization of $53b$ and $53e$. Again, the "front" diradicals (as drawn) $55b$ and $55e$ are preferred over $54b$ and $54e$, respectively.
This preference in the bridging step of the di-π-methane process can be understood on the following basis. As odd electron density begins to develop at C7 in 55a,b,e, it is stabilized by a resonance interaction with the carbonyl group via the intermediacy of the cyclopropane ring. Such a stabilizing effect is not available to 52a,b,e, where free radical character is developing on C8 and the geometry is not proper for such an interaction.

It is interesting that intermediate diradicals 52a,b,e are capable of competing with this stabilizing interaction. This may be interpreted in terms of a homoconjugative charge-transfer interaction of the free radical center at C8 with the proximate carbonyl group, as proposed earlier by Paquette for an analogous system. This homoconjugative interaction must certainly be less effective at stabilizing a free radical site than the resonance interaction, since products 57a,b,e predominate in the photoisomeric mixtures.

Irradiation of 53d displayed the greatest regioselectivity observed in the photoproduction distributions. Photoprodut 57d is preferred over 56d.
by a power of 10. In 55a, the free radical center at C7 is not only stabilized by resonance interaction of the carbonyl group through the intermediacy of the cyclopropane group, but also has the added stabilizing effect of a methyl group (tertiary center). In 54d, no such resonance interaction is possible, and the odd electron density at C8 is now on a secondary carbon. The large isomeric ratio is therefore the possible composite result of resonance interaction of the proximate carbonyl group and enhanced stability of tertiary over secondary free radical sites.

In the irradiation of 53c, these two effects are opposing. Diradical 54c displays a tertiary free radical site at C8 but is unable to interact with the carbonyl group. Diradical 55c is capable of interaction with the carbonyl group, but the free radical site at C7 is secondary. As can be seen from the product distribution, 57c predominates over 56c by almost 20%. This
is interpreted to mean that the resonance interaction of the carbonyl group via the cyclopropane ring in 55c is more stabilizing to a free radical center than the effect of the methyl group in 54c.

The effects of alkyl substitution on the directionality of the di-α-methane photo rearrangement have been observed by other workers. Photoisomerization of 58 affords 60a as the sole product, although a priori, two products are possible. The observed isomer results from diradical 59a, where the isopropyl group is positioned on the odd electron site (tertiary). No product is obtained which would result from the secondary diradical 59b.

Until now no mention has been made concerning possible steric effects on the photoisomeric ratios in these reactions. Steric effects are not considered to be of importance in these lactams, since the methyl groups in any given set of photoisomers, i.e. the methyl groups at C1 and C8 in 56c
and 57c, respectively, appear to have entirely comparable peri CH₃-H interactions as determined from examination of molecular models.

Examples of stabilization of a specific free radical site in the di-π-methane intermediate diradical by a proximate functionality are available. Some of these reports involve the same ring system studied here. For example, irradiation of ester 61 under triplet conditions afforded 63a as the sole product.¹⁵b,³³ The lack of production of any 63b in this photoisomerization was considered evidence for the stability of
diradical \(62a\) relative to that of \(62b\). In diradical \(62a\), the carbomethoxy group is bonded directly to a carbon bearing odd electron density. Its preferential formation is then a consequence of the ability of the carbomethoxy group to stabilize this free radical center, an effect which is analogous to that observed in the lactam compounds studied here.

Effects with other functionalities have also been observed. Thus, irradiation of alcohol \(64\) affords photoisomers \(66a\) and \(66b\) in a ratio of 3:2. From these data, it appears that diradical \(65a\) is energetically more accessible than diradical \(65b\). This is not the result of hydrogen bonding, since the acetates behave in an exactly analogous manner. The authors proposed a charge transfer interaction with oxygen to explain the greater stability of diradical \(65a\). Similar results were realized by interaction of an alcohol and an exocyclic methylene group with a radical center.
in the di-\(\pi\)-methane rearrangement of a similar structure.

From the results of effects of these various substituents on the photoproduct ratio in the di-\(\pi\)-methane rearrangement, it should be apparent that the construct of product determining intermediate diradicals in these transformations stands on firm grounds. All of these data may be interpreted in terms of stabilization of odd electron density at a particular free radical site in molecules which are capable of generating this free valence at various positions in their structures. The resultant directionality effects are then completely compatible with the relative stabilities of these intermediates.

It should be remembered, however, that by proposing diradicals in order to explain experimental observations, one is not disregarding other evidence which is best interpreted by a concerted mechanism (see Introduction). The isolation of only one epimeric alcohol (66a) from the photolysis of 64 is suggestive of such a mechanistic possibility, although a viable alternative would be a diradical route where bond formation is more rapid than bond rotation. As Zimmerman has previously suggested, diradical species in the di-\(\pi\)-methane rearrangement may be nothing more than points along a concerted potential energy surface.

Since lactams 53a-e and Paquette's work on the somewhat related system described earlier are the only examples where the influence of the amide functionality on the di-\(\pi\)-methane rearrangement has been studied, the interpretations presented here must, of course, be considered somewhat tentative. This is particularly the case with the proposed charge-transfer effects of the lactam carbonyl group. Nonetheless, the preparation of
heretofore unknown dihydrobenzazasemibullvalones has been realized, along with the recognition of the presence of directive effects of the amide functionality in an intramolecular photochemical transformation.
<table>
<thead>
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<th>Column</th>
<th>Liquid phase, %</th>
<th>Stationary phase</th>
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<td>Chromosorb G</td>
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<td>B</td>
<td>Carbowax, 20M, 5</td>
<td>Chromosorb G</td>
<td>6</td>
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<td>Chromosorb G</td>
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<td>24</td>
<td>1/8</td>
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n-Methyl-2-pyridones (51b-e). These materials were prepared by the method of Adams.

In a typical experiment, 67.5 g (0.978 mole) of sodium nitrite in 130 ml of water was added to a cold, stirred solution containing 100 g (0.925 mole) of 2-amino-3-methylpyridine (50b) and 103 ml of concentrated sulfuric acid in 770 ml of water via a dropping funnel at such a rate as to maintain the temperature below 5° under an atmosphere of nitrogen. After the addition was completed, the solution was stirred 1 hr at 5°, at which time it was heated on a steam bath to 90°, cooled to room temperature, and made slightly alkaline with 210 g of potassium carbonate. The resultant solution was then concentrated in vacuo; the resultant solid was powdered with a mortar and exhaustively extracted with boiling benzene. Concentration of the combined extracts in vacuo followed by recrystallization from benzene afforded 79.3 g (79.3%) of 3-methyl-2-pyridone (51b) as white crystals, mp 139.5-140.5° (lit mp 140°); $^{27}$H NMR 2.18 (s, 3H, methyl), 6.11-6.35 (3 lines, 1H, H$_5$), 7.36 (m, 2H, H$_4$ and H$_5$).

In a similar manner, diazotization of 90 g (0.83 mole) of 2-amino-4-methylpyridine (50c) afforded 77.1 g (86%) of crude 4-methyl-2-pyridone (51c).
Diazotization of 50 g (0.46 mole) of 2-amino-5-methylpyridine (50d) as before afforded 50 g (100%) of crude 5-methyl-2-pyridone (51d).

Diazotization of 100 g (0.92 mole) of 2-amino-6-methylpyridine (50e) as usual followed by subsequent recrystallization from benzene afforded three crops of crystals: 78.2 g of 6-methyl-2-pyridone (51e), mp 157.5-158.5° (lit mp 158-159°), 10.6 g, mp 157-158°; and 2.6 g, mp 156-157° (91%).

1,n-Dimethyl-2-pyridones (52b-e). These materials were prepared by the methods of Adams and Bradlow.

In a typical experiment, 54 g (0.50 mole) of 3-methyl-2-pyridone (51b) was dissolved in a warm, freshly prepared solution of 12.1 g (0.525 mole) of sodium in 200 ml of methanol with the aid of mechanical stirring. The reaction was cooled to 25° and 70.6 g (0.560 mole) of dimethyl sulfate was added over a period of 30 min at 30°. The solution was refluxed for 2 hrs at which time it was made strongly alkaline with a 25% sodium hydroxide solution and steam distilled until the odor of the by-product (O-alkylation) was absent from the distillate. Upon cooling, the residue was extracted with several portions of chloroform, dried (potassium carbonate), and concentrated in vacuo. Distillation at reduced pressure afforded 45.1 g (73%) of 1,3-dimethyl-2-pyridone as a colorless liquid, bp (0.4 mm) 72-76° (lit bp [1.5 mm] 83-84°); \( \delta_{\text{CDCl}_3}^{\text{TMS}} 2.15 (s, 3H, C-CH_3), 3.55 (s, 3H, N-CH_3), 6.10 \) (t, \( J_{4,5} = J_{5,6} = 7 \) Hz, 1H, \( H_5 \)), 7.11-7.43 (m, 2H, \( H_4 \) and \( H_6 \)).

In a similar manner, methylation of 26.4 g (0.245 mole) of 4-methyl-2-pyridone (51e) afforded 17.4 g (58%) of 1,4-dimethyl-2-pyridone (52e) as a whitish, deliquescent solid, bp (1.1 mm) 112° (lit bp (1 mm) 110°);
\begin{align*}
\delta_{\text{CDCl}_3} &\text{TMS}^2 2.17 \ (s, 3H, C-\text{CH}_3), 3.50 \ (s, 3H, N-\text{CH}_3), 6.00 \ (dd, J_{5,8} = 7.0 \text{ Hz}), \\
J_{3,8} &= 2.0 \text{ Hz}, 1H, H_5), 6.33 \ (br s, 1H, H_3), 7.25 \ (d, J_{5,8} = 7 \text{ Hz}, 1H, H_8), \\
\nu_{\text{KBr}} \max &\text{1665 cm}^{-1} \ (C=O).
\end{align*}

Methylation of 21.6 g (0.20 mole) of 5-methyl-2-pyridone (5ld) as before afforded 23.4 g (95\%) of 1,5-dimethyl-2-pyridone (52d) as deliquescent crystals; \delta_{\text{CDCl}_3}^\text{TMS} 2.22 \ (s, 3H, C-\text{CH}_3), 3.47 \ (s, 3H, N-\text{CH}_3), 6.47 \ (dd, J_{3,4} = 8.5 \text{ Hz}, J_{3,8} = 2.0 \text{ Hz}, 1H, H_3), 7.12-7.35 \ (m, 2H, H_4 \text{ and H}_6).

Methylation of 35.0 g (0.324 mole) of 6-methyl-2-pyridone (5le) afforded 31.7 g (79.5\%) of 1,6-dimethyl-2-pyridone (52e) as deliquescent crystals; \delta_{\text{CDCl}_3} 2.43 \ (s, 3H, C-\text{CH}_3), 3.63 \ (s, 3H, N-\text{CH}_3), 6.22 \ (br d, J_{4,5} = 7.0 \text{ Hz}, 1H, H_5), 6.58 \ (br d, J_{3,4} = 9.0 \text{ Hz}, 1H, H_3), 7.43 \ (dd, J_{4,5} = 7.0 \text{ Hz}, J_{3,4} = 9.0 \text{ Hz}, 1H, H_4).

5,6-Benz-o-n,2-dimethyl-2-azabicyclo[2.2.2]oct-7-en-3-one (53a-e). These materials were prepared by the method of Sheinin.

In a typical experiment, a solution containing 51.3 g (0.375 mole) of anthranilic acid in 300 ml of acetone was added dropwise to a stirred, refluxing solution containing 32.4 g (0.298 mole) of 1-methyl-2-pyridone and 44 g (0.375 mole) of iso-amyl nitrite, prepared by the method of Noyes, in 900 ml of methylene chloride via a dropping funnel over a period of 4 hrs under an atmosphere of nitrogen. After the addition was completed, the mixture was refluxed for 2 hrs, cooled, washed with small volumes of dilute base, water, and concentrated in vacuo. The residue was chromatographed on a column prepared by wet-packing 200 g of neutral alumina (Merck, activity 1) with Skellysolve B and eluting with the same solvent. Trituration of the first band eluted from the column with cold ether afforded 1.815 g (3.30\%).
of 5,6-benzo-2-methyl-2-azabicyclo[2.2.2]oct-7-en-3-one (53a) as white leaflets, mp 99-101° (lit mp 98-100°). Continued elution of the column with ether afforded recovered (52a).

In a similar manner, treatment of 44.0 g (0.358 mole) of 1,3-dimethyl-2-pyridone (52b) with benzyne afforded 5.46 g (7.66%) of 5,6-benzo-2,4-dimethyl-2-azabicyclo[2.2.2]oct-7-en-2-one (53b) as white crystals, mp 95.5-96.5° (lit mp 92.5-95°).

Treatment of 2.12 g (17.1 mmoles) of 1,4-dimethyl-2-pyridone (52c) with benzyne as before afforded 263 mg (3.82%) of 5,6-benzo-2,8-dimethyl-2-azabicyclo[2.2.2]oct-7-en-3-one (53c), mp 100-103° (lit mp 99-102°).

Treatment of 3.59 g (29.4 mmoles) of 1,5-dimethyl-2-pyridone (52d) with benzyne afforded 658 mg (11.3%) of 5,6-benzo-2,7-dimethyl-2-azabicyclo[2.2.2]oct-7-en-3-one (53d) as white crystals, mp 129-131° (lit mp 126-129°).

Treatment of 31.7 g (0.258 mole) of 1,6-dimethyl-2-pyridone (52e) with benzyne as usual afforded 2.068 g (3.92%) of 5,6-benzo-1,2-dimethyl-2-azabicyclo[2.2.2]oct-7-en-3-one (53e), mp 84-85° (lit mp 79-83°).

General Photolysis Procedure. Unless otherwise stipulated, all photochemical reactions were performed with a Hanovia 450 Watt mercury emission lamp, supported by a quartz immersion well through Pyrex optics with water cooling. When small volumes were irradiated, the solutions were contained in small test tubes which were fastened to the outer surface of the immersion well and oriented in such a way as to maximize exposure to the lamp's energy. Additional cooling was provided by a large beaker of water surrounding the
tubes. The conversions were monitored with a Varian Hi-Fi chromatograph employing a SE-30 column. Product ratios so obtained were corrected for detection coefficients of their individual components.

Photolysis of 5,6-Benzol-2-methyl-2-azabicyclo[2.2.2]oct-5,7-dien-3-one (53a). A solution containing 200 mg of 53a in 30 ml of acetone was irradiated for 3 hrs, at which time the reaction had proceeded to 95% completion to a mixture of two products, whose relative abundances were 75% and 25%. Further irradiation caused the formation of by-products. The solution was concentrated in vacuo, diluted with a small volume of methylene chloride, and separated into its components by the use of preparative vpc on column A at 155°C. In this manner 105 mg (52.5%) of the major photoisomer, 6,7-benzo-4-methyl-4-azatricyclo[3.3.0.02,8]oct-6-en-3-one (57a), was isolated;

![Chemical Structure](image)

\[ \text{57a} \]

\[ \delta_{\text{CDCl}_3} 2.53 (s, 3H, CH₃), 2.60 (dd, J₁,₈ = 6.0 Hz, J₂,₈ = 8.0 Hz, 1H, H₈), 2.93 (dd, J₁,₂ = 6.5 Hz, J₂,₈ = 8 Hz, 1H, H₂), 3.38 (dq, J₁,₂ = 6.5 Hz, J₁,₈ = 6 Hz, 1H, H₁), 4.63 (d, J₁,₅ = 6 Hz, 1H, H₅), 7.08-7.64 (m, aromatic); ν_{max}^\text{Nujol} 1670 \text{ cm}^{-1} (C=O). \]

An analytical sample was prepared by sublimation (82°C and 0.2 mm), mp 114-117°C.

Anal. Calcd for C₁₄H₁₁NO: C, 77.81; H, 5.99; N, 7.56.

Found: C, 77.54; H, 6.00; N, 7.37.

In the same manner, 79 mg (39.5%) of the minor photoisomer, 6,7-benzo-3-methyl-3-azabicyclo[3.3.0.0₂,₈]oct-6-en-4-one (56a), was isolated. This
material was contaminated with 57a (ca.
10%), and consequently was re-prepped at
a lower temperature (140°) to afford
pure 56a; \( \delta_{\text{CDCl}_3} \) 2.70 (s, 3H, CH₃),
2.81 (m, 1H, H₆), 3.12 (m, 1H, H₁),
3.53 (dd, \( J_{1,2} = 5.0 \) Hz, \( J_{2,8} = 7.5 \)
Hz, 1H, H₂), 3.93 (d, \( J_{1,5} = 6 \) Hz, 1H, H₅), 7.08-7.58 (m, 4H, aromatic);
\( \nu_{\text{Nujol}} \) 1680 cm\(^{-1}\) (C=O). An analytical sample was prepared by sublimation
(110° and 0.2 mm).

**Anal. Calcd for C₁₂H₁₁NO:** N, 7.56.

**Found:** N, 7.54.

Photolysis of 5,6-Benzо-2,4-dimethyl-2-azabicyclo[2.2.2]oct-5,7-dien-3-one
(53b). A solution containing 400 mg of 53b in 60 ml of acetone was irra-
diated for 3.75 hrs, at which time the reactant was entirely converted into
a mixture of two products, whose relative abundances were 82% and 18%.
Separation of this mixture was realized with the use of preparative vpc on
column A at 165°. In this manner 204 mg (51%) of the major photoisomer,
6,7-benzo-2,4-dimethyl-4-azatricyclo[3.3.0.0²⁸]oct-6-en-3-one (57b), was
isolated; \( \delta_{\text{CDCl}_3} \) TMS 1.50 (s, 3H, C-CH₃),
2.52 (s, 3H, N-CH₃), 2.70 (d, \( J_{1,8} =
6 \) Hz, 1H, H₈), 3.20 (t, \( J_{1,5} = J_{1,8} =
6 \) Hz, 1H, H₁), 4.58 (d, \( J_{1,5} = 6 \) Hz,
1H, H₅), 7.03-7.62 (m, 4H, aromatic);
\( \nu_{\text{Nujol}} \) 1670 cm\(^{-1}\). An analytical
sample was prepared by recrystallization from ether, mp 77-78°.

**Anal.** Calcd for C_{18}H_{13}NO: C, 78.36; H, 6.58; N, 7.03.

**Found:** C, 78.53; H, 6.63; N, 6.96.

In this manner, 32 mg of the minor photoisomer, 6,7-benzo-3,5-dimethyl-
3-azatricyclo[3.3.0.0²,8]oct-6-en-4-one (56b), was also isolated; δ_{CDCl₃}

\begin{align*}
1.63 & (s, 3H, C-CH₃), \\
2.72 & (s, 3H, N-CH₃), \\
2.70-2.94 & (m, 2H, H₁ and H₂), \\
3.50 & (dd, J₁,₂ = 5.5 Hz, J₂,₈ = 6.5 Hz, 1H, H₂), \\
7.05-7.63 & (m, 4H, aromatic); \nu_{Nujol} \text{max} 1680 \text{ cm}⁻¹ (C=O). 
\end{align*}

An analytical sample was prepared by sublimation (120° and 0.2 mm) followed by recrystallization from ether, mp 85-90°.

**Anal.** Calcd for C_{18}H_{13}NO: N, 7.03.

**Found:** N, 7.02.

Photolysis of 5,6-benzo-2,8-dimethyl-2-azabicyclo[2.2.2]oct-5,7-dien-3-one (53c). A solution containing 206 mg of 53c in 30 ml of acetone was irradiated for 2 hrs, at which time the reactant was entirely converted into a mixture of two products, whose relative abundances were 59% and 41%. Separation of this mixture was realized with the use of preparative vpc on column A at 172°. In this manner 59 mg (29.5%) of the major photoisomer, 6,7-benzo-
4,8-dimethylazatricyclo[3.3.0.0²,8]oct-
6-en-3-one (57c), was isolated; δ_{CDCl₃}

\begin{align*}
1.58 & (s, 3H, C-CH₃), \\
2.44 & (d, J₁,₂ = 6 Hz, 1H, H₂), \\
2.52 & (s, 3H, N-CH₃), \\
3.14 & (d, J₁,₂ = J₂,₈ = 6 Hz, 1H, H₁), 4.58
\end{align*}
(d, J_1, 5 = 6 Hz, 1H, H_5), 7.00-7.48 (m, 4H, aromatic); ^{\text{Nujol}} \nu_{\text{max}} 1670 \text{ cm}^{-1} (\text{C}=\text{O}). An analytical sample was prepared by recrystallization from ether, mp 135-136\textdegree.

 Anal. Calcd for C_{13}H_{13}NO: C, 78.36; H, 6.58; N, 7.03.

 Found: C, 78.19; H, 6.54; N, 6.98.

In addition, 30 mg (15%) of the minor photoisomer, 6,7-benzo-1,3-dimethyl-3-azatricyclo[3.3.0.0^{2,8}]oct-6-en-4-one (56a), was also isolated;

\begin{align*}
\delta_{\text{CDCl}_3}^\text{max} &= 1.43 (s, 3H, C-\text{CH}_3), 2.58 (d, J_2, a = 5 \text{ Hz}, 1H, H_2), 2.70 (s, 3H, N-\text{CH}_3), 3.32 (d, J_2, a = 5 \text{ Hz}, 1H, H_2), 3.68 (s, 1H, H_5), 7.01-7.51 (m, 4H, aromatic); ^{\text{Nujol}} \nu_{\text{max}} 1680 \text{ cm}^{-1} (\text{C}=\text{O}). An analytical sample was prepared by recrystallization from ether, mp 146-146.5\textdegree.

 Anal. Calcd for C_{13}H_{13}NO: N, 7.03.

 Found: N, 6.94.

Photolysis of 5,6-benzo-2,7-dimethyl-2-azabicyclo[2.2.2]oct-5,7-dien-3-one (53d). A solution containing 400 mg of 53d in 60 ml of acetone was irradiated for 1 hr, at which time the reactant was entirely converted into a mixture of two products, whose relative abundances were 91% and 9%. Separation of this mixture was realized with the use of preparative vpc on column A at 170\textdegree. In this manner 183 mg (46%) of the major photoisomer, 6,7-benzo-1,4-dimethyl-4-azatricyclo[3.3.0.0^{2,8}]oct-6-en-3-one (57a), was isolated.
recrystallization from ether, mp 111-113°.

An. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03.

Found: C, 78.21; H, 6.65; N, 6.90.

In addition, 21 mg (5%) of the minor photoisomer, 6,7-benzo-3,8-dimethyl-3-azatricyclo[3.3.0.0$^2$6]oct-6-en-4-one (56a), was also isolated;

$$\delta^{CDCl_3}_{TMS} 1.51 (s, 3H, C-CH_3), 2.40 (d, J_2,8 = 8 Hz, 1H, H_8), 2.55 (s, 3H, N-CH_3), 2.74 (d, J_2,8 = 8 Hz, 1H, H_2),$$
$$4.32 (s, 1H, H_5), 7.01-7.35 (m, 4H, aromatic); v_{max}^{Nujol} 1675 cm^{-1} (C=O).$$

An analytical sample was prepared by sublimation (120° and 0.1 mm).

An. Calcd for $C_{13}H_{13}NO$: N, 7.03.

Found: N, 6.79.

Photolysis of 5,6-benzo-1,2-dimethyl-2-azabicyclo[2.2.2]oct-5,7-dien-3-one (53e). A solution containing 400 mg of 53e in 60 ml of acetone was irradiated for 1 hr, at which time the reaction had proceeded to 90% completion with formation of a mixture of two products, whose relative abundances were 82% and 18%. Further irradiation caused the formation of by-products. Sep-
paration of this mixture was realized by preparative vpc on column A at 160°. In this manner 153 mg (38%) of the major photoisomer, 6,7-benzo-4,5-dimethyl-4-azatricyclo[3.3.0.0²,8]-oct-6-en-3-one (57e) was isolated; \( \delta_{\text{TMS}} \) CDCl₃ 1.70 (s, 3H, C-CH₃), 2.44 (s, 3H, N-CH₃), 2.61 (dd, J₂,₈ = 6 Hz, J₁,₈ = 7.6 Hz, 1H, H₈), 2.88 (dd, J₁,₂ = 6 Hz, J₁,₈ = 7.6 Hz, 1H, H₁), 3.08 (t, J₁,₂ = J₂,₈ = 6 Hz, 1H, H₂), 6.89-7.48 (m, 4H, aromatic); \( \nu_{\text{max}} \) Nujol 1670 cm⁻¹ (C=O). An analytical sample was prepared by recrystallization from ether, mp 103-104°.

**Anal. Calcd for C₁₃H₁₃NO:** C, 78.36; H, 6.58; N, 7.03.

**Found:** C, 78.16; H, 6.59; N, 7.02.

In addition, 11 mg of the minor photoisomer, 6,7-benzo-2,3-dimethyl-3-azatricyclo[3.3.0.0²,8]oct-6-en-4-one (56e), was also isolated; \( \delta_{\text{TMS}} \) CDCl₃ 1.62 (s, 3H, C-CH₃), 2.63 (s, 3H, N-CH₃), 2.63-2.98 (m, 2H, H₁ and H₃), 3.96 (d, J₁,₅ = 6 Hz, 1H, H₅), 7.00-7.58 (m, 4H, aromatic); \( \nu_{\text{max}} \) Nujol 1680 cm⁻¹ (C=O). An analytical sample was prepared by sublimation (85° and 0.1 mm).

**Anal. Calcd for C₁₃H₁₃NO:** N, 7.03.

**Found:** N, 6.81.
Reduction of 5,6-Benzо-2,4-dimethyl-2-aza[2.2.2]oct-5,7-dien-3-one (53b). A solution containing 1.0 g (5.03 mmoles) of 53b in 20 ml of tetrahydrofuran was added dropwise to a refluxing suspension containing 0.38 g (10 mmoles) of lithium aluminum hydride in 20 ml of tetrahydrofuran over a period of 15 min. The mixture was refluxed for 21 hrs, whereupon it was cooled and quenched by the cautious addition of 0.38 ml of water, followed by 0.38 ml of a 20% sodium hydroxide solution and finally 1.14 ml of water. The resultant slurry was dried (sodium sulfate), filtered, and concentrated in vacuo to afford 647 mg (91%) of 1-methylnaphthalene; \(^{1}H\) NMR (CDCl\(_3\)) 2.62 (s, 3H, CH\(_3\)), 7.22-8.13 (m, 7H, aromatic). When this reaction was repeated with only 4 hrs of reflux, 1-methylnaphthalene was again the sole product.
PART III

REFERENCES


2. For earlier observation, but not characterization of the di-\(\pi\)-methane process see: (a) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Patso, and G. Klose, ibid., 87, 1410 (1965); (b) G. W. Griffin, A. F. Marcantoni, and H. Kristinson, Tetrahedron Lett., 2951 (1965).


10. For examples of this see: (a) ref 5(b); (b) H. E. Zimmerman and A. A. Baum, ibid., 93, 3646 (1971); (c) L. A. Paquette, J. R. Malpass, and G. R. Krow, ibid., 92, 1980 (1970); (d) ref 5(a); (e) ref 9; (f) ref 5(f); (g) H. E. Zimmerman and R. D. Lettle, ibid., 94, 8257 (1972).
11. (a) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, 20, 4191, 6096 (1968); (b) ref 10(c).

12. The triplet energy for cisoid butadiene is 53.5 kcal/mole [D. F. Evans, *J. Chem. Soc.*, 1735 (1960)], while that for styrene is 61.8 kcal/mole [D. F. Evans, *ibid.*, 1351 (1957)].


17. (a) W. G. Dauben and W. A. Spitzer, *ibid.*, 92, 5817 (1970); (b) J. S. Swenton, A. R. Crumrine, and T. J. Walker, *ibid.*, 92, 1406 (1970); (c) H. E. Zimmerman and G. A. Eppling, *ibid.*, 92, 1411 (1970); (a) ref 5(b); (e) ref 5(e); (f) H. E. Zimmerman and G. E. Samuelson, *ibid.*, 82, 5971 (1967); (g) H. E. Zimmerman and P. S. Mariano, *ibid.*, 92, 1409 (1970); (h) ref 5(c).

18. It should be noted that cis-trans isomerization is characteristically a triplet state reaction.

19. The term “oxa-dimethane” was first used by Dauben see: W. G. Dauben, M. S. Kellogg, J. I. Seeman, and W. A. Spitzer, *ibid.*, 22, 1786 (1970).

20. A great deal of photochemistry has been done with β,γ-unsaturated ketones, and even a partial listing is not warranted here. Many references may be found in: (a) K. N. Houk, D. J. Northington, and R. E. Duke, Jr., *ibid.*, 94, 6233 (1972); (b) ref 8; (c) K. G. Hancock and R. O. Gridner, *Tetrahedron Lett.*, 4281 (1971).


23. (a) ref 6(j); (b) H. E. Zimmerman and A. C. Pratt, ibid., 92, 1407 (1970). For additional examples see: (c) ref 10(b); (d) ref 5(c); (e) ref 5(a); (f) ref 17(g).


26. The effects of alkyl substitution on the bridging step of the di-π-methane process have been reported: (a) W. Eberbach, P. Würsch, and H. Prinzbach, Helv. Chim. Acta, 53, 1235 (1970); (b) ref 14(b); (c) ref 14(a).


30. The double resonance experiments were generously performed by Dr. J. C. Stowell.


32. The C-H bond dissociation energy to form the tert-butyl free radical is 4 kcal/mole lower than that for the formation of the isopropyl free radical (94 kcal/mole) C. Walling, "Free Radicals in Solution," p. 50, John Wiley and Sons, Inc., New York, 1957.


35. This information was obtained during personal communication with Professor H. Hart.


38. For an example where this has been observed see: F. D. Lewis, J. Amer. Chem. Soc., 92, 5602 (1970).

39. The assistance of Dr. J. C. Stowell in obtaining these spectra is acknowledged with gratitude.