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The Ohio State University, Ph.D., 1975
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EQUILIBRIUM IMBALANCES OF SELECTED 2,8-ANNULATED SEMIBULLVALENES
AND REARRANGEMENTS OF 2,8-TETRAMETHYLENESEMIBULLVALENES

DISSERTATION

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

By
Ronald Keith Russell, B.S.

The Ohio State University
1975

Reading Committee:
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Dr. Melvin S. Newman
Dr. John A. Secrist, III

Approved by

Dr. Leo A. Paquette
Adviser
Department of Chemistry
DEDICATION

To my wife Nancy
ACKNOWLEDGMENTS

A scientific research group is a society of men and women, each having a particular expertise. The group of people that I have been associated with for the past four years have influenced my research and life in some manner; to these people I extend my thanks. In particular, I am deeply indebted to Professor Leo A. Paquette for his guidance as a research advisor and as a friend.

I would also like to thank Professor R. J. Ouellette for his help in the computer simulation work and Mr. M. Geckle for his generous donation of time and energy in discussing my research and obtaining cmr spectra.

I gratefully acknowledge financial support from The Ohio State University in the form of University and Dissertation Fellowships, from the Chemistry Department in the form of Teaching Associate positions, and from Professor Paquette in the form of Research Associate positions.
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PUBLICATIONS

''Structural Consequences of 2,8 Bridging of the Semibullvalene
Nucleus,' ' L. A. Paquette, R. E. Wingard, Jr., and R. K. Russell,

''Carbon-13 Nuclear Magnetic Resonance Spectral Analysis of Semi­
bullvalene and Related Substances,' ' E. Wenkert, E. W. Hagaman,

''The Thermochemical Behavior of Semibullvalenes. Annulation Effects
on the Course of Rearrangement,' ' L. A. Paquette, R. K. Russell,


FIELDS OF STUDY

Major Field: Organic Chemistry
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INTRODUCTION

The organic chemist has always taken pride in his ability to prepare complex new molecules. The scientific method is such that elegant synthetic schemes are conceived in a priori fashion. Frequently, however, the best laid plans go astray because of one or more unforeseen rearrangement processes. The study of molecular rearrangements is a fascinating topic which has been discussed in numerous manuscripts, books, and symposia. Ionic or radical reactions are most often implicated in such structural changes.

A third type of bond reorganization, possibly the most interesting and least understood, has eluded chemists for a long time. This general rearrangement is thermally induced but cannot be shown to involve either heterolytic or homolytic processes by the usual diagnostic tests. The isomerizations are relatively insensitive to external catalytic influences such as solvent, acid-base catalysis, and free radical initiators or inhibitors, and are often unresponsive to internal structural variation, the very effects which are the most definitive criteria for radical and ionic processes. The electronic reorganization involved in the bond-making and -breaking steps must then occur in a synchronized or 'concerted' fashion. At the mechanistic level, this type of rearrangement is thus both unimolecular and intramolecular and exhibits well-defined stereochemical characteristics. The Cope rearrangement is an example.
In the late 1950's, A. C. Cope devised a general method for the preparation of various (dialkylvinyl)-alkylcyanoacetic esters (1).\(^{1a}\)

\[
\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)=\text{C} (\text{CN})\text{COOEt} \xrightarrow{\text{NaOEt}} [\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{C}(\text{CN})\text{COOEt}]^{\ominus}\text{Na}^{\oplus}
\]

\[
\xrightarrow{\text{RX}} \quad \text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{C}(\text{CN})\text{COOEt}
\]

In his enthusiasm to vary R in 1, he prepared the allyl derivative (\(R = -\text{CH}_2\text{CH}=\text{CH}_2\)) and found it to be thermally unstable. In fact when the allyl ester was heated at 150-160° for 4 hours, it rearranged exclusively to 2. Cope concluded that 2 was formed from a 'thermally induced \(\alpha,\gamma\) shift in the three carbon system' and compared this 'new' bond reorganization to the Claisen rearrangement. Further study of such systems established that the minimum structural requirement for the isomerization
is the simple diallylic system, 2. Although the rearrangement is facilitated by the presence of cyano, carboalkoxy, and phenyl groups on one or both of the central methylene carbons,\textsuperscript{1c-d} even the simple molecule 3-methyl-1,5-hexadiene (4) rearranges at 300°.\textsuperscript{1e} The number of examples of this [3,3] sigmatropic rearrangement\textsuperscript{2} in synthetic and theoretical chemistry is numerous.
Further theoretical refinements have led to the concept of the degenerate Cope rearrangement, i.e., those valence isomerizations where the product is structurally equivalent to the starting material. The simplest system that displays this degeneracy is hexa-1,5-diene (5a ≠ 5'a); a process most conveniently analyzed via the 1,1-dideuterio compound (5b). Doering and Toscano heated 5b in vacuo and by means of ir spectroscopic analysis determined $\Delta H^\ddagger$ to be $33.5 \pm 0.5$ kcal/mol and $\Delta S^\ddagger$ to be $-13.8 \pm 1$ e.u. (deuterium isotope effects were neglected). The large negative entropy value suggests a highly ordered transition state. The geometry of this transition state was elegantly revealed by Doering and Roth during their study of the thermal behavior of meso and racemic 3,4-dimethyl-1,5-hexadienes (6). If meso-6 were to rearrange via the four-center quasi-chair conformation, then cis,trans-2,6-octadiene (7) would result. However, if the sigmatropic shift proceeds via the six-center quasi-boat transition state, then a mixture of trans,trans- and cis,cis-2,6-octadienes would be expected (Scheme 1). When meso-3,4-dimethyl-1,5-hexadiene was thermolyzed at 180°C, cis,trans-2,6-octadiene (7, 99.7%) and trans,trans-2,6-octadiene (8, 0.3%) were isolated. Thus,
Scheme I

**six-center overlapping**

![Diagram of six-center overlapping](image1)

**four-center overlapping**

![Diagram of four-center overlapping](image2)

**meso-6**

**trans,trans**

**cis,cis**

**rac-6**

**rac-6**

**cis,trans**

**meso-6**
bond reorganization proceeds through the quasi-chair conformation, the difference in free energy between the two conformations is at least 5.7 kcal/mol, and the rearrangement is highly stereospecific.

The nature of the Cope intermediate has for a long time been depicted as $\ce{\text{I}}$. This representation indicates that bond-breaking and -making are happening in concert. Recently, this intermediate has been

$\ce{\[\text{I]} \rightleftharpoons \text{I}}$

challenged by Doering and Dewar. They have shown by theoretical and chemical means that the intermediate may have 1,4-cyclohexanediyl character ($\ce{\text{II}}$). Before this species can be considered as an intermediate of the Cope rearrangement, further diradical trapping studies should be attempted.

The 1,5-hexadiene system necessarily serves as the basic structure for all Cope rearrangements. Just how this moiety may be contained in a molecule is unlimited. An exquisite example of a 1,5-hexadiene in a macrocyclic molecule is $\text{trans}$-bicyclo[8.4.0]tetradeca-$\text{trans}$-2, $\text{trans}$-8-
This substance was prepared and studied by Wharton \(^7\) who showed that partially resolved \(12\) racemizes by first-order kinetics with a \(\Delta H^\circ \sim 25\) kcal/mol. In fact any bicyclo[\(n^4\).\(n\).0]di-2,\((n^4)\)-enes, e.g. \(n = 1\) (13), \(n = 2\) (14), \(n = 3\) (15), \(n = 4\) (16), can in theory undergo degenerate Cope rearrangement.

Although the cis-divinylcyclopropane (17) and cis-divinylcyclobutane (19)\(^{3a}\) rearrangements do not represent degenerate isomerizations,
they are important in so far as they are the 'backbone' to most degenerate Cope processes (see 13 and 14). These rearrangements necessarily proceed through quasi-boat conformations with the cis-divinyl-cyclopropane rearrangement being more facile than the cyclobutane example.

The preparation and study of 14 has been reported by Grimme.\textsuperscript{7c} He prepared the hexadeuterio compound 21 by the elegant use of the rhodium complex of 9,9,10,10-tetradeuterio-cis-bicyclo[6.2.0]deca-2,4,6-triene and obtained a mixture of 21 and 22 after heating 21 for 3 hours at 185° in the gas phase. On the basis of his deuterium labeling,

Grimme concluded that the rearrangement must proceed through the coiled conformer 23. If this is true, then bonding between 4,10 and 5,9, as
In 2₄, should produce a molecule whose Cope rearrangement is greatly facilitated. Indeed, Pettit and coworkers demonstrated that hypostrophene (2₄) is capable of sequential degenerate Cope rearrangement at temperatures of 35° and below.⁷ᵈ,ᵉ Due to its symmetry, 2₄ is capable of endless interchange of all constituent atoms with regeneration of the starting material.
Bicyclo[5.1.0]octa-1,5-diene (13), homotropilidene, represents the first of a long series of compounds that incorporate the cis-divinylcyclopropane moiety. The preparation of 13 was first reported by Doering and Roth. To their astonishment, the pmr spectrum of 13 was temperature dependent, i.e., at room temperature the spectrum consisted of two broad absorptions but at -50°C and 180°C sharp, unique spectra were obtained. They concluded that the difference in the spectra corresponded to a change in the Cope rearrangement rate. At the lower temperature the rate is slow enough so that the spectrum is one form of the molecule, 13 or 13', while at higher temperatures the rate is sufficiently rapid as to 'average' the protons, e.g., H₈ and H₈'. Thus pmr spectroscopy was shown to be an invaluable tool for analyzing Cope rearrangements. A study of this rearrangement in the hexadeuterio case,
afforded the activation parameters \( \Delta H^\ddagger = 11.8 \pm 0.2 \) kcal/mol and \( \Delta S^\ddagger = -8.0 \pm 0.3 \) e.u. As in the molecule 23, the rearrangement must proceed through the 'coiled' conformer 13B.

Again it would seem logical that if one was to 'hold' homotropolidene in conformer 13B by a carbon chain, 26, that the Cope rearrangement would be facilitated. This has been demonstrated by the preparation of bullvalene (\( X = \text{CH}=\text{CH} \)), dihydrobullvalene (\( X = \text{CH}_2\text{CH}_2 \)), barbaralane (\( X = \text{CH} \)), barbaralone (\( X = \text{C}=\text{O} \)), and methylene-barbaralane (\( X = \text{C}=\text{CH}_2 \)) (Table I). As in the case of hypostrophene (24), bullvallene (27) represents a unique compound that is capable of interchange of all constituent atoms such that there are \( 10!/3 \) (ca 1.2 million) equivalent valence isomers. Table I shows that as the carbon
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<td>-8.0 ± 0.3</td>
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<td>+11.0 ± 0.4</td>
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<td>+11.5 ± 0.3</td>
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chain is decreased in length the barrier to the Cope rearrangement is lowered. This reduction is most spectacular for semibullvalene ($X = \text{null}$).

Semibullvalene (29) was first prepared by Zimmerman and coworkers by the photolysis of barrelene (28). Since this report, Zimmerman and other researchers have developed more accessible routes to this (CH)₈ hydrocarbon. The interest in semibullvalene was stimulated by Zimmerman's observation that this molecule displays a room temperature pmr spectrum of three distinct multiplets at δ 5.08, 4.17, and 2.97 in a 2:4:2 ratio and a temperature-independent pmr from +117 to -110°. After eliminating the possibility of bishomoaromatic species 30 by
and pmr arguments, Zimmerman concluded that semibullvalene was the first homotropilidene system whose Cope rearrangement rate could not be lowered below the pmr time scale. Theoretical calculations by Hoffmann and Dewar (EH and MINDO/2, respectively) suggested that $\Delta G^\ddagger$ resided in the region 2.3-3.6 kcal/mol; however, this was recently shown to be incorrect by Anet and coworkers. They were able to slow the Cope rearrangement of $\mathcal{2}$ between -100 and -170° and from their pmr data obtained $\Delta H^\ddagger = 4.8 \pm 0.2$ kcal/mol, $\Delta S^\ddagger = 5.4 \pm 3$ e.u., and $\Delta G^\ddagger = 5.5 \pm 0.1$ kcal/mol at -140°. This extraordinarily low activation energy for the Cope rearrangement arises as a consequence of the unique structural and geometric features of the ring system.

The replacement of hydrogen by a substituent in these homotropolilidene systems has been found to alter the position of equilibrium. Schröder has prepared several substituted bullvalenyl compounds and observed by pmr techniques that all but fluorine prefer attachment to olefinic sites. In a less complicated twofold-degenerate system, barbaralone, Schleyer demonstrated the effects of deuterium and methyl. For deuteriobarbaralone $\mathcal{3}$, it was ascertained that a deuterium isotope effect did exist, favoring attachment of deuterium to the cyclopropanoid
Although equilibrium deuterium isotope effects have been observed, it has long been recognized that deuterium prefers attachment to $C_{sp^3}$ over $C_{sp^2}$ carbons. This investigation extends such equilibrium studies to cyclopropyl carbon, the ordering $C_{sp^2}$ (cyclopropyl) > $C_{sp^2}$ (vinyl) being observed.

Preference of methyl for a vinylic rather than cyclopropyl position was demonstrated for $32$, where $32b$ was found to be preferred ($> 75\%$). This effect can be rationalized in terms of thermodynamic stabilization effects of the methyl group on the double bond.
Monosubstituted semibullvalenes have been prepared only recently. In a daring fashion, Hoffmann used Extended Hückel calculations to determine substituent effects on the Cope equilibrium in $33_a$. He concluded that if R was a $\pi$ acceptor it would strengthen the 2-8 bond in $33_a$ but have little effect on $33_b$, thus $33_a$ would be the predominant isomer. Similarly if R was a $\pi$ donor it would weaken the 2-8 bond of $33_a$ and shift the equilibrium to $33_b$. This theory has been partially tested with the preparation of monosubstituted semibullvalenes $3_{\frac{1}{2}}$ and

- $a$, $R = CH_3$
- $b$, $R = C_6H_5$
- $c$, $R = CH_2OCH_3$
- $d$, $R = CH_2OH$
- $e$, $R = CN$
Because of the low activation energy to the Cope rearrangement

\[
\begin{align*}
&35 \quad \longleftrightarrow \quad 35' \\
&\text{a, } R = \text{CH}_3 \\
&\text{b, } R = \text{CH}_2\text{OCH}_3 \\
&\text{c, } R = \text{F}
\end{align*}
\]

in these semibullvalenes, recourse to an approximation method of analysis of the low-temperature pmr spectra was required. Notwithstanding, the results clearly indicated a preferential attachment to olefinic > cyclopropyl > aliphatic, irrespective of the nature and location of the R group.
RESULTS AND DISCUSSION

Part I. Annulated Semibullvalenes

The studies by Schleyer of 2-substituted barbaralones and by James and Birnberg of monosubstituted semibullvalenes has demonstrated the sensitivity of the homotropilidene nucleus to substituent influences. From these results, annulation of the semibullvalene nucleus at positions 2 and 8 with saturated polymethylene chains of varying size would be expected to generate significant imbalances in the position of equilibrium.

Annulation effects have had a history of providing useful data for the interpretative analysis of valence isomeric phenomena. Table II records selected examples of case studies. Vogel initially demonstrated that annulation of a cycloheptatriene ring at its 1 and 6 positions with a trimethylene chain imposes sufficient strain to restrict the molecule to its valence tautomeric norcaradiene form. Lengthening of
<table>
<thead>
<tr>
<th>Ring System</th>
<th>Bridge Size</th>
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<tbody>
<tr>
<td><img src="#" alt="Diagram A" /></td>
<td><img src="#" alt="Diagram B" /></td>
</tr>
</tbody>
</table>

- **Table II.** Ground State Equilibrium Effects in Annulated Polyunsaturated Molecules.

<table>
<thead>
<tr>
<th>Ring System</th>
<th>Bridge Size</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="#" alt="Diagram A" /></td>
<td><img src="#" alt="Diagram B" /></td>
</tr>
</tbody>
</table>

- **a** See ref. 27 and 28.  
- **c** See ref. 29.  
- **d** See ref. 30.
the chain to four methylene units results in strain release adequate
to allow for complete reversal in favor of the bicyclic structure.\textsuperscript{28}
However, such equilibria are quite sensitive to the 'pinching effect'
exerted by the central bridge. For example, the related
cyclooctatetraene-bicyclo[4.2.0]octatriene system with its unsaturated
diatomic unit does not attain bicyclic characteristics until five \textit{sp}^3-hybridized
carbon atoms comprise the bracket.\textsuperscript{29} In the nitrogen analog, the azapropellane form is favored until \textit{n} = 6.\textsuperscript{30}

The present research relates to semibullvalenes of general struc-
ture \textit{36} and was prompted in the main by three considerations. Firstly,
the recognized sensitivity of the semibullvalene nucleus to substituent
influences is expected to reflect itself in rather delicate responses
to bracketing effects. A saturated polymethylene chain at positions 2
and 8 is expected to affect the position of equilibrium only by induc-
tive stabilization and to favor \textit{36a}, provided that the 'belt' is
sufficiently 'loose.' On the other hand, if the length of the bridge
is sufficiently short, isomer \textit{36b} should be overwhelmingly favored in
order to bypass the destabilization in \textit{36a} arising from Bredt's rule
violations. Also, because of the doubly degenerate nature of the
semibullvalene Cope rearrangement, a cis-divinylcyclopropane moiety is
retained in both \textit{36a} and \textit{36b}. Consequently, there exists no heavily
weighted ground-state preference for one of the constituent isomers as
is the case with the isomer pairs in Table II, and wide variations in
strain are no longer the necessarily dominant issue. Lastly, because
bracketing as in \textit{36} results in symmetrical substitution of the semibull-
valene ring system, evaluation of the substituent parameters can be made without concern for contributions arising from potentially complicating unsymmetrical perturbational effects.

The key to the preparation of semibullvalenes of general formula \( 36 \) was the observation that propellatriene \( 37 \) undergoes Diels-Alder reaction with N-phenyltriazolinedione exclusively from the endo face to give adduct \( 38 \) in high yield. In a fashion similar to that published by Paquette, \( 33 \) adducts of the type \( 39 \) could be transformed to 9,10-diazasnoutanes \( 41,34 \), their subsequent hydrolysis and oxidation affording the desired semibullvalenes (Scheme II).

In order to evaluate the effect of 'belt' strain on the semibullvalene nucleus, 2,8-trimethylenesemibullvalene (\( 57 \)) was prepared from the isomeric hydrocarbon \([4.3.2]\)propella-2,4,10-triene (\( 52 \)), the synthesis of which began with ethyl cyclopentanone-2-carboxylate (\( 42 \)) (Scheme III). This cyclopentanone derivative was treated with potassium cyanide under acidic conditions to form the cyanohydrin, which was immediately dehydrated to \( 43 \) with thionyl chloride in cold pyridine in 91% overall yield. Subsequent hydrolysis of \( 43 \) in refluxing concentrated
hydrochloric acid gave cyclopentene-1,2-dicarboxylic acid in 86% yield.
The corresponding anhydride \( \text{IV} \) was obtained by refluxing the diacid in acetic anhydride according to the procedure of Sen-Gupta. The cycloaddition of anhydride \( \text{IV} \) to 1,3-butadiene (in excess) was carried out in a sealed glass vessel at 120° for 12 hr according to the procedure
Scheme III

\[ \begin{array}{ccc}
0 & CO_2Et & 1) HCN \\
\text{2) SOCl}_2/ \text{pyridine} & (91\%) & 42 \\
& & \\
\text{CN} & CO_2Et & 1) H_3O^+ \\
& & \text{2) Ac}_2O \quad (80\%) & 43 \\
& & \text{1,3-butadiene} \quad (92\%) & 44 \\
\end{array} \]

\[ \begin{array}{ccc}
\text{45} & \text{LiAlH}_4 & \text{CH}_2OH \\
& (94\%) & 46 \\
& \text{CH}_3SO_2Cl/ \text{pyridine} & \text{CH}_2OSO_2CH_3 \\
& (100\%) & 47 \\
\text{48} & \text{1) NCS} & \text{Cl} \\
& \text{2) [0]} \quad (98\%) & \text{49} \\
& & \text{tBuOK} \quad \text{THF} \quad (41\%) \\
& & \text{50} \\
\end{array} \]

\[ \begin{array}{ccc}
\text{51} & \text{[0]} & \\
& & \\
& & \text{52} \\
& & \\
& & \text{1) C}_5\text{H}_5\text{N-HBr}_3 \\
& & \text{CCl}_4/\text{HOAc} \\
& & \\
& & \text{2) LiCl, Li}_2\text{CO}_3 \\
& & \text{HMPA} \quad (73\%) \\
& & \text{52} \\
\end{array} \]
of Ginsburg. When propellane anhydride $^{45}$ was reduced with lithium aluminum hydride in anhydrous tetrahydrofuran followed by basic workup, diol $^{46}$ was obtained in 94% yield. The diol was converted to the derived dimesylate $^{47}$ in quantitative yield by means of methanesulfonyl chloride in cold (0°) pyridine.

Ring closure of dimesylate $^{47}$ to thiapropellane $^{48}$ was effected in 95% yield by the agency of a dehydrated solution of sodium sulfide nonahydrate $^{39}$ in hexamethylphosphoramide (HMPA). This waxy sulfide was converted to the more crystalline sulfone $^{31}$ with two equivalents of $m$-chloroperbenzoic acid for purposes of characterization. Treatment of sulfide $^{48}$ with one equivalent of $N$-chlorosuccinimide (NCS) resulted in the introduction of chlorine at a carbon adjacent to sulfur. The crude α-chlorosulfide was immediately oxidized with two equivalents of monoperphthalic acid in ether to yield a mixture of the two possible epimeric α-chloro sulfones $^{49}$ (98% yield). The pmr spectrum (CDCl$_3$) of the mixture displays inter alia two >CHCl singlets at δ 4.83 and 4.73 in a 39 to 61 ratio, respectively. Major isomer $^{49a}$, assigned the
configuration with chlorine syn to the cyclopentane ring by analogy, was obtained in pure form by elution chromatography on silica gel (ether-petroleum ether).

Exposure of a mixture of the isomeric 7-chloro-8-thia[4.3.3]-propell-3-ene 8,8-dioxides (49) to a 4-fold excess of powdered potassium tert-butoxide in refluxing tetrahydrofuran afforded diene 50 in 41% yield and α-tert-butoxy sulfone 53 in 37% yield. The diene 50 displays the expected pmr spectrum [δ 5.72 (4, olefinic) and 0.9-2.47 (10, methylenes)], while 53 shows an olefinic multiplet centered at 5.61, a singlet at 4.52 (>CHO-), an AB quartet at 3.04 (JAB = 13 Hz, ΔνAB = 7.5 Hz; >CH2SO2-), methylenes at 1.84 to 2.3, and a sharp singlet at 1.31 (t-butyl). The infrared spectrum (CHCl3) of 53 shows the sulfone bands at 1300, 1155, and 1090 cm⁻¹. The formation of tert-butoxy sulfones in Ramberg-Bäcklund reactions of this type has been reported elsewhere.32,38 Treatment of diene 50 with one equivalent of pyridinium hydrobromide perbromide in carbon tetrachloride-acetic acid (1:1) afforded a viscous dibromide. Without further purification this dibromide was treated with lithium chloride and lithium carbonate in dry HMFA 39 to give propella-
triene 52 in 73% yield. The ultraviolet spectrum (cyclohexane) of this olefin shows maxima at 266 (ε 3380), 231 (1710), and 225 nm (2000), while the pmr spectrum in CDCl₃ consists of two sets of multiplets at δ 5.71-5.78 and 0.99-1.79 of equal area.

The [4,3,2]propella-2,4,10-triene (52) was then converted to 2,8-trimethylenesemibullvalene (57) according to Scheme IV. Based upon the

Scheme IV

![Scheme IV Diagram]
work of Paquette and Thompson, N-phenyltriazolinedione was added to 52 in cold (-70°) acetone to afford adduct 55 in 86% yield after chromatography. Characterization of this white crystalline solid is based on (a) its pmr spectrum in CDCl₃ which consists of absorptions at 6 7.41 (s, 5, aromatic), 6.24 (t, J = 3.8 Hz, 2, olefinic), 5.86 (s, 2, cyclobutenyl), 4.87 (br t, J = 3.8 Hz, 2, >C=CH<), and 1.50-2.08 (br m, 6, methylenes); (b) its infrared spectrum (CHCl₃) which consists, inter alia, of two strong carbonyl bands at 1775 and 1700 cm⁻¹; and (c) its ready sensitized (acetone) photocyclization to cubyl isomer 55 (92% yield).

The silver(I)-promoted isomerization of 9,10-diazabishomocubane 55 to 56 was accomplished by refluxing in the dark a solution of 55 in 0.2 N silver perchlorate-anhydrous benzene for 108 hr (86% yield). The gross structure of 56 was established on the basis of its elemental analysis and pmr spectrum in CDCl₃ [6 7.24-7.68 (br m, 5), 4.96-5.11 (m, 2), 1.88-2.04 (m, 6), and 1.38-1.82 (br m, 4)]. These spectral data are in agreement with that published for the nonannulated parent structure.

Hydrolysis of 56 and subsequent oxidation (with concomitant loss of nitrogen) were successfully realized by initial heating with potassium hydroxide in isopropyl alcohol at reflux under anaerobic conditions, acidification to pH 2 with 3 N hydrochloric acid, readjustment of the pH after 5 min at 0° to the mildly alkaline side with 3 N aqueous ammonia, and exposure to activated manganese dioxide. The workup afforded 57 and aniline as the volatile products. The fluxional olefin was isolated in 19% yield by preparative vapor phase chromatography.
The course of the hydrolysis-oxidation reaction is depicted in Scheme V. The urazole compound \(56\) is converted to the semicarbazide \(58\) which is subject to ready manganese dioxide oxidation. \(^{42,43}\) The exact mechanism of this oxidation is not known. Such facile departure of nitrogen has previously been observed for azo compounds \(60\) \(^{47}\) and \(61\), \(^{48}\) which decompose at \(-78^\circ\) to 1,3-cyclohexadiene and 1,4-cyclohepta-
diene, respectively, at relative rates of 1 and $10^{17}$. In intermediate 59 as in 61 the nitrogen molecule must be expelled in a direction syn to the fragmenting $\sigma$ bond of one of the cyclopropane rings, a stereochemical condition which is particularly favorable for the operation of the concerted retrograde homo Diels-Alder mechanism. 49

The 2,8-trimethylenesemibullvalene (57) was characterized by its accurate mass (calcd $m/e$ 144.0939, obs 144.0941) and spectral properties. The ultraviolet spectrum of this material exhibits only a shoulder on strong end absorption at 240 nm ($\epsilon$ 4600) in agreement with the spectra of those semibullvalenes which have been published (see Table III). The pmr spectrum in CDCl$_3$ (Figure 2, page 85) consists of four sets of multiplets at $\delta$ 4.99 (2), 4.12-4.26 (2), 2.73-2.93 (2), and 1.54-2.28 (6), the relevant chemical shifts of which correspond closely to those of semibullvalene (vide supra). Further discussion of the pmr spectrum appears in the following section. Confirmation of the gross structural features was achieved by catalytic hydrogenation. Under conditions where an anhydrous tetrahydrofuran solution of the trimethylene derivative was treated with 5% rhodium on carbon and hydrogen at atmospheric pressure, two hydrocarbons were isolated in a 4:1 ratio. The
Table III. Ultraviolet Data for Some Semibullvalenes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Compound 1" /></td>
<td>225-235 sh ($\varepsilon$ 2400)</td>
<td>17</td>
</tr>
<tr>
<td><img src="image2.png" alt="Compound 2" /></td>
<td>240 sh ($\varepsilon$ 3980)</td>
<td>50</td>
</tr>
<tr>
<td><img src="image3.png" alt="Compound 3" /></td>
<td>258 sh ($\varepsilon$ 3200)</td>
<td>51</td>
</tr>
<tr>
<td>Compound</td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>Reference</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------</td>
<td>-----------</td>
</tr>
<tr>
<td><img src="image1.png" alt="Image 1" /> $\Leftrightarrow$ <img src="image2.png" alt="Image 2" /></td>
<td>240 sh ($\varepsilon$ 4600)</td>
<td>This work</td>
</tr>
<tr>
<td><img src="image3.png" alt="Image 3" /> $\Leftrightarrow$ <img src="image4.png" alt="Image 4" /></td>
<td>235-250 sh ($\varepsilon$ 3200)</td>
<td>45,52</td>
</tr>
<tr>
<td><img src="image5.png" alt="Image 5" /> $\Leftrightarrow$ <img src="image6.png" alt="Image 6" /></td>
<td>230-250 sh ($\varepsilon$ 2000)</td>
<td>45,52</td>
</tr>
<tr>
<td>Compound</td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>Reference</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------</td>
<td>-----------</td>
</tr>
<tr>
<td><img src="image1" alt="Chemical Structure" /> $\Leftrightarrow$ <img src="image2" alt="Chemical Structure" /></td>
<td>238 sh ($\epsilon$ 3500)</td>
<td>This work</td>
</tr>
</tbody>
</table>
| ![Chemical Structure](image3) $\Leftrightarrow$ ![Chemical Structure](image4) | 242 ($\epsilon$ 2800)  
233 sh ($\epsilon$ 2400) | This work |
| ![Chemical Structure](image5) $\Leftrightarrow$ ![Chemical Structure](image6) | 240 sh ($\epsilon$ 1900) | This work |
major product, a C_{11}H_{18} compound on the basis of elemental and mass spectral data, was identical in melting point, infrared absorptions, and vpc retention times to an authentic sample of perhydrocyclopent-[cd]indene (62). The less predominant substance proved to be C_{11}H_{18}

\begin{align*}
\text{62} & \\
\text{63A} & \\
\text{63B} &
\end{align*}

in nature and was tentatively assigned structure 63A and/or 63B on the basis of its pmr spectrum (see Experimental).

Molecular models of 57 suggest that the trimethylene 'belt' provides enough strain on the semibullvalene nucleus to favor isomer 57b. However, as stated before, the relevant pmr chemical shifts of 57 correspond closely to those of semibullvalene, suggesting a 57b to 57a ratio of 1. Thus, either the earlier stated premise concerning strain on the semibullvalene nucleus is incorrect or other factors not considered are effecting the Cope equilibrium.

In order to further evaluate the effect of strain on the semibullvalene nucleus, 2,8-tetramethylenesemibullvalene (66) was prepared and examined spectroscopically. Adduct 38 of [4.4.2]propella-2,4,11-triene (37) was converted to semibullvalene 66 as before (Scheme VI). The mild hydrolysis and oxidation of 9,10-diazasnoutane 65 afforded desired semibullvalene 66 in 60% yield. Infrared and pmr spectra of these
compounds were identical to those previously reported. A discussion of the pmr (Figure 3) and cmr spectra of 66 is deferred to the next section.

Figure 3 reveals the pmr spectrum of 2,8-tetramethylenesemibullvalene (66) to be different than that of trimethylene derivative 57.
The most striking feature is the chemical shift of protons H₄ and H₆. In 57 these protons are found at δ 4.12-4.26 as in semibullvalene; however in 66 protons H₄ and H₆ are shifted upfield to 2.65. This upfield displacement can be accounted for in terms of an equilibrium imbalance which is weighted in favor of isomer 66a.

In this instance, molecular models of 2,8-tetramethylenesemibullvalene (66) suggest that there is little strain on the semibullvalene nucleus. This being the case, inductive effects should predominate and shift the equilibrium in the direction of 66a. Here theory and experiment agree.

In order to further study the effects of annulation on the semibullvalene nucleus, 2,8-pentamethylenesemibullvalene (71) was prepared (Scheme VII).

The synthesis of 2,8-pentamethylenesemibullvalene (71) began with the available olefin 67. Diels-Alder addition of N-phenyltriazolinedione to 67 afforded the white crystalline adduct 68 in 94% yield. Due to the low concentration of tricyclic form 67b, the reaction was performed in refluxing ethyl acetate for 18 hr. Compound 68 has the usual carbonyl stretching bands at 1770 and 1700 cm⁻¹ in the infrared spectrum (CHCl₃), while the pmr spectrum (CDCl₃) displays a cyclobutenyl singlet at δ 5.96 and a >CH=N< triplet at 4.60 (J = 4 Hz). Photocyclization to isomer 69 was accomplished in 67% yield upon irradiation with a 200-W Hanovia lamp (acetone solution, Vycor filter) for 2 hr. When the skeletal bond reorganization of 69 was attempted
Scheme VII

\[ \text{Scheme VII} \]

1) $\text{OH}^- / \text{i-PrOH}$
2) $\text{MnO}_2$

(64%)
in silver perchlorate-anhydrous benzene solution, a significant amount of decomposition was seen. However, the isomerization was successfully accomplished in a refluxing solution of isopropyl alcohol-water (4:1) containing silver nitrate. The isolated (66% yield) 9,10-diazasnoutane \( \text{70} \) was characterized by its elemental analysis, infrared spectrum \([\text{CHCl}_3, 1750 \text{ and } 1700 \text{ cm}^{-1}]\), and pmr features \([\text{CDCl}_3, \delta 7.23-7.68 \text{ (5, aromatic)}, 4.70-4.91 \text{ (2, } >\text{CHN}<\text{), and } 1.10-2.17 \text{ (14, cyclopropyl and methylenes)}]\).

Bridged snoutane \( \text{70} \) was hydrolyzed and oxidized under the mild conditions previously described to afford pure semibullvalene \( \text{71} \) after preparative vapor phase chromatography. Whereas the semicarbazide intermediates in the first two cases were very susceptible to manganese dioxide oxidation, the reaction of \( \text{72} \) with \( \text{MnO}_2 \) proved sluggish. Thus,

![Chemical structure](image)

after 4.5 hr semicarbazide \( \text{72} \) could be recovered in 32% yield. The gross structure of \( \text{72} \) was established by its accurate mass \([\text{calcd m/e } 321.1841, \text{ obs } 321.1844]\), infrared spectrum \([\text{CHCl}_3, 3180, 2980, 2880, 1770, 1600, 1540, 1450, 1320, 1110, \text{ and } 911 \text{ cm}^{-1}]\), and pmr signals
[CDCl₃, δ 8.6 (1, >NNHC<), 6.8-7.6 (5, aromatic), 4.78 (1, >CHNHC<), 3.78 (1, >NH), 3.58 (1, >CHNH<), and 0.6-2.2 (13, cyclopropyl and methylenes)].

When 7₁ was isolated by preparative vapor phase chromatography at temperatures around 120°, there was obtained 7₁ plus a second material (pmr analysis). This problem was surmounted by making recourse to a 1 ft x 0.25 in. chromatography column at temperatures not exceeding 75°, and at a fast flow rate (350 cc/min). Semibullvalene 7₁ was then obtained pure. Thus semibullvalene 7₁ gives evidence of thermal instability. Unfortunately, insufficient 7₁ was available for conversion to the unknown substances [see Part II, for thermal rearrangement of 2,8-tetramethylenesemibullvalene (66)].

Semibullvalene 7₁ was characterized by its accurate mass (calcd m/z 172.1252, obs 172.1254) and spectral properties. The ultraviolet spectrum exhibits a shoulder on strong end absorption at 258 nm (ε 3600). The pmr spectrum (Figure 4) in CDCl₃ consists of absorptions at δ 4.98 (2, olefinic), 3.78-3.90 (2, cyclopropyl-olefinic), 2.90-3.10 (1, H₅), 2.78 (1, H₁), 2.38-2.65 (4, allylic), and 1.40-2.10 (6, methylene). The time-averaged protons H₄ and H₆ appear in the δ 4 region, again denoting an almost equal distribution of isomers. Further discussion will follow in the next section.

From the pmr results of the above three examples, it is clear that the effect of varied 2,8-annulation on the semibullvalene nucleus is not merely strain related.
In a final effort to gain insight into the factors which effect the equilibrium of 36, semibullvalenes 97 and 112 were prepared. The successful synthesis of 8-oxa[4.3.2]propella-2,4,10-triene (86) is depicted in Scheme VIII.

3-Carbomethoxytetrahydrofuran-4-one (74), prepared according to the procedure of Granturco, Friedel, and Giammarino in 56% yield, was treated with sodium cyanide under acidic conditions to afford the corresponding cyano hydrin which was dehydrated as before. The resulting cyano ester 75, isolated in 82% yield, was hydrolyzed in concentrated hydrochloric acid to diacid 76 (78%) and dehydrated with acetic anhydride. Although successful, the dihydrofuran anhydride preparation was not pursued further because of product instability. To avoid this problem, diacid chloride 77 was prepared in 74% yield by refluxing diacid 76 in thionyl chloride. This procedure also gave small amounts of 72 which remained as a contaminant in the subsequent cycloaddition and reduction reactions. The reaction of 77 with 1,3-butadiene was performed in a sealed glass vessel at 105° for 12 hr. The gross structure of 78 was ascertained by its infrared (1770 cm⁻¹) and pmr spectra [CDCl₃, δ 5.7 (s, 2, olefinic), 4.16 (ABq, J_AB = 9 Hz, Δν_AB = 50.2 Hz, 4, -CH₂O-), and 2.64 (m, 2, allylic)]. Its reduction with lithium aluminum hydride in tetrahydrofuran afforded diol 80 in 92% yield. Dimesylate 81 proved to be a white crystalline solid whose methylene protons α to oxygen display an AB quartet centered at δ 3.85 (J_AB = 8.8 Hz, Δν_AB = 11.7 Hz).
Scheme VIII

\[ \text{HOCH}_2\text{COMe} \xrightarrow{1) \text{NaH/THF}} \stackrel{\text{2) OMe}}{\text{DMSO}} \xrightarrow{(56\%)} \text{T3} \]

\[ \text{T3} \xrightarrow{1) \text{HCN}} \xrightarrow{2) \text{SOCl}_2/\text{pyridine}} \xrightarrow{(82\%)} \text{T5} \]

\[ \text{HO}_2\text{C=CO}_2\text{H} \xrightarrow{\text{SOCl}_2} \xrightarrow{(74\%)} \text{T6} \]

\[ \text{T6} \xrightarrow{\text{Ac}_2\text{O}} \xrightarrow{(80\%)} \text{T9} \]

\[ \text{T9} \xrightarrow{1,3\text{-butadiene}} \xrightarrow{(95\%)} \text{T7} \]

\[ \text{T7} \xrightarrow{\text{LiAlH}_4} \xrightarrow{(92\%)} \text{T8} \]
Scheme VIII (Continued)

80

\[ \text{CH}_2\text{OH} \overset{\text{CH}_3\text{SO}_2\text{Cl}}{\text{pyridine}} (96\%) \rightarrow \text{CH}_2\text{OSO}_2\text{CH}_3 \]

81

\[ \text{CH}_2\text{OSO}_2\text{CH}_3 \overset{\text{Na}_2\text{S}}{\text{DMSO}} (85\%) \rightarrow \]

82

\[ \text{1) NCS} \]

\[ \text{2) [O]} \]

\[ (94\%) \]

83

\[ 85 \]

\[ \text{Br}_2 \] (67%)

86

84

\[ \text{Cl} \overset{\text{t-BuOK}}{\text{THF}} (39\%) \rightarrow \]

85

\[ 86 \]

\[ \text{1) Br}_2 \]

\[ \text{2) LiCl, Li}_2\text{CO}_3 \text{HMPA} \]
Cyclization of \overset{81}{\rightarrow} to oxathiapropellene \overset{82}{\rightarrow} was effected in 85% yield with dehydrated sodium sulfide in distilled dimethyl sulfoxide (DMSO). The pmr spectrum in CDCl$_3$ of this white solid is most informative: $\delta$ 5.72 (br t, $J = 2$ Hz, 2, olefinic), 3.76 (ABq, $J_{AB} = 9$ Hz, $\Delta
\nu_{AB} = 9.2$ Hz, 4, -CH$_2$O-), 2.86 (ABq, $J_{AB} = 12$ Hz, $\Delta
\nu_{AB} = 7.1$ Hz, 4, -CH$_2$S-), and 2.22 (m, 4, allylic). Sulfide \overset{82}{\rightarrow} was also converted to its more crystalline sulfone, the latter also displaying two sets of AB quartets: $\delta$ 3.79 ($J_{AB} = 9$ Hz, $\Delta
\nu_{AB} = 22.8$ Hz, 4, -CH$_2$O-) and 3.13 ($J_{AB} = 13.3$ Hz, $\Delta
\nu_{AB} = 15.4$ Hz, 4, -CH$_2$SO$_2$-). This cyclization reaction was found to give (vide infra) the double bond isomer \overset{87}{\rightarrow} in varying amounts (0-34%). This material, found to be inseparable from thia-

\[ \overset{87}{\rightarrow} \]

propellane \overset{82}{\rightarrow} (elution chromatography, crystallization, sublimation), displays a pmr spectrum similar to the symmetrical isomer \overset{82}{\rightarrow}. Apparently
is the result of a prototropic shift under rather mild conditions. The base could be sulfide ion whose basicity would likely vary from reaction to reaction depending upon solvation (level of residual hydration for example). That protonation can occur at C₃ parallels the selectivity observed during the NBS bromination of propellane sulfones, e.g. 88. Why isomerization prevails in this system and not in the others examined is not known with certainty. Whether this phenomenon is unique to the solvent system (DMSO instead of HMPA) or substrate remains unanswered. Contamination by 87 did not interfere with subsequent reactions except to lower the yield of the bromination-bisdehydrobromination step, because dibromide 89 gives monobromides 90 and/or 91
whose boiling points are significantly higher than that of triene 86.

Treatment of 8-oxa-11-thia[4.3.3]propell-3-ene (82) with one equivalent of recrystallized NCS afforded the α-chloro sulfide which was immediately oxidized with two equivalents of monoperphthalic acid in ether to afford a mixture of isomeric α-chloro sulfone 84a and 84b in 94% yield. The pmr spectrum (CDCl₃) of the mixture so obtained displays inter alia two >CHCl singlets at δ 4.92 and 4.70 (1:2, respectively). By analogy, the major isomer is assigned the chlorine syn to the five-membered ring (84a). The isomers were not separated.

Exposure of 84 to powdered potassium tert-butoxide in refluxing tetrahydrofuran afforded propelladiene 85 in 39% yield. The pmr spectrum of 85 in CDCl₃ consists of absorptions at δ 5.94 (s, 2, cyclobutenyl), 5.80 (dd, J = 3, 2.5 Hz, 2, olefinic), 3.47 (ABq, J_AB = 9.3 Hz, \( \Delta v_{AB} = 2.2 \text{ Hz, 4, } -\text{CH}_2\text{OH}^- \)), and 2.12 (m, 4, allylic). Purification by preparative gas-liquid chromatography on a Carbowax column afforded diene 85 as a clear liquid together with diene 92. The latter ether was characterized by its elemental analysis, spectral properties (see
Experimental), and independent synthesis (Scheme IX).

Scheme IX

\[
\begin{align*}
\text{85} & \xrightarrow{\text{NBS}} \text{Br} & \text{LiAlH}_4 & \xrightarrow{\text{ether}} \\
\end{align*}
\]

The allylic bromination of diene \textit{85} with NBS in the presence of azobisisobutyronitrile (AIBN) as initiator afforded bromide \textit{93} plus a significant amount of starting material. Without purification, this mixture was treated with lithium aluminum hydride in refluxing ether. Diene \textit{92} was isolated in a modest 27\% yield.

Propelladiene \textit{85} was treated with one equivalent of bromine in cold (-70\°) methylene chloride to afford the dibromide as a viscous
liquid. Without purification, this dibromide was treated with lithium chloride and lithium carbonate in dry HMPA to give oxapropellatriene \(^{86}\) in 67\% yield. The ultraviolet spectrum (isooctane) of \(^{86}\) consists of maxima at 265 (e 2740), 231 (1480), 225 (1680), and 218 nm (1720) and the pmr spectrum is consistent with the integrity of the cyclobutene ring \([\delta 5.87 (s, 2)]\).

The instantaneous cycloaddition of triene \(^{86}\) to N-methyltriazolinedione in cold (-70\°) acetone afforded adduct \(^9\) in 93\% yield (Scheme X). N-Methyltriazolinedione was chosen as the dienophile because it likewise is a powerful dienophile, its adducts are more soluble, and the byproduct from the hydrolysis-oxidation step is volatile methylamine rather than aniline. Methylurazole diene \(^9\), a stable white crystalline solid, underwent facile photocyclization under triplet-sensitized (acetone) conditions to provide 9,10-diazabishomocubane isomer \(^{95}\) in 58\% yield after chromatography and crystallization.

The characterization of \(^{95}\) is based on its elemental analysis and its pmr spectrum in CDCl\(_3\) which consists of multiplets centered at \(\delta 5.03\) (2, >C\(\equiv\)N<), 3.47-3.75 (2, methine), and 3.02-3.25 (2, methine); an AB quartet at 3.85 (\(J_{AB} = 11\) Hz, \(\Delta\nu_{AB} = 31.3\) Hz, 4, -CH\(_2\)O-); and a singlet at 3.07 (3, >NCH\(_3\)).

Silver(I)-catalyzed rearrangement of \(^{95}\) was attempted in the silver perchlorate-anhydrous benzene system. After refluxing for seven days, starting material was recovered (40\%) unchanged. Recourse was next made to silver nitrate in isopropyl alcohol-water (4:1).
Again the starting material was recovered (100%). Ultimately, 9,10-diazabishomocubane 95 and silver nitrate were dissolved in dioxane-water (4:1) and heated at 130° in a sealed tube for 4 days. The rearrangement proceeded to completion with isolation of snoutane 96 in 65% yield. This white crystalline solid was characterized by its elemental analysis and spectral properties.

The hydrolysis of 96 was accomplished in refluxing isopropyl alcohol and sodium hydroxide under argon. After pH adjustments had been made at 0° and the solution diluted, MnO2 was added in one portion. Nitrogen evolution was immediate. Careful processing furnished semibullvalene 97 as a low melting solid in 70% yield. This oxygen sensitive olefin displays an atypical ultraviolet spectrum (isooctane), 242 (ε 2800) and 233 sh nm (2400), but an accurate mass (calcd m/e 146.0732, obs 146.0733) and pmr spectrum (Figure 5) (CDCl3) fully consistent with structure 97: 6.38 (dd, J3,4 = J6,7 = 5.2 Hz, J4,5 = J5,6 = 2 Hz, 2, H4 and H6), 5.26 (d, J3,4 = J8,7 = 5.2 Hz, 2, H3 and H7), 4.2 (ABq, JAB = 9.5 Hz, ΔνAB = 3.95 Hz, 4, -CH2O-), 3.35 (dt, J3,5 = 7.1 Hz, J4,5 = J5,6 = 2 Hz, 1, H5), and 2.62 (d, J1,5 = 7.1 Hz, 1, H1).

Confirmation of the gross structural features was achieved by catalytic hydrogenation in anhydrous tetrahydrofuran over 5% rhodium on carbon. After the uptake of two equivalents of hydrogen, the solution was diluted with acetic acid and stirred under hydrogen for 5 hours. The saturated ethers 98 and 99 were isolated in a 1:1 ratio.
One of them (28) proved to be C\textsubscript{10}H\textsubscript{14}O in nature, while the second component was a white solid identified as 29 by direct comparison with an authentic sample.

The preparation of 29 began with the known keto alcohol 100 (Scheme XI). Treatment of this keto alcohol with lithium aluminum hydride according to the procedure of Mercier, Soucy, Rosen, and Deslongchamps afforded diol 101 in quantitative yield. This diol was then converted to dimethanesulfonate ester 102 by the sulfene method (methanesulfonyl chloride in triethylamine at 0\textdegree)\textsuperscript{61,62} in 49% yield. Olefin 102 was then reduced with lithium aluminum hydride to tetrahydrotriquinacene (103).\textsuperscript{63} The pmr spectra of 102 and 103 were compared with authentic samples. Diol 104 was obtained in 91% yield by treatment of 103 with excess ozone followed by a reductive workup;\textsuperscript{64} ir (neat) 3290 and 2900 cm\textsuperscript{-1} and pmr spectra [CDCl\textsubscript{3}, 6 4.32 (br 2, -OH), 3.74 (AB\textsubscript{4}, J\textsubscript{AB} = 10 Hz, \Delta v\textsubscript{AB} = 6.9 Hz, 2, -CH\textsubscript{2}O-), 3.62 (s, 2, -CH\textsubscript{2}O-), and 0.98-2.78 (series of multiplets, 12, methines and methylenes)]. Preparation of ether 29 was realized by adaptation of Agosta's method.\textsuperscript{65} When treated in pyridine with one equivalent of tosyl chloride for 24 hr, 104 was transformed to the monotosylate which was cyclized with excess sodium hydride in anhydrous tetrahydro-
The successful synthesis of this isomeric to thiobullvalene is outlined in Schemes XII and XIII. The $\pi^1 + \pi^2$ cycloaddition of ethyl ethylene-tetracarboxylate and 1,3-butadiene was carried out in an autoclave at 170-180$^\circ$ for 10 hr according to the procedure of Alder and Ricker. Treatment of tetraester with lithium aluminum hydride in refluxing
Scheme XII

\[
\begin{align*}
\text{EtO}_2\text{C} & \quad \text{CO}_2\text{Et} \\
\text{EtO}_2\text{C} & \quad \text{CO}_2\text{Et} \\
& \quad \xrightarrow{1,3\text{-butadiene} \ (77\%)} \quad \xrightarrow{\text{LiAlH}_4 \ (82\%)} \\
& \quad \xrightarrow{(\text{CH}_2\text{OH})_2} \\
& \quad \xrightarrow{(\text{CH}_2\text{OH})_2} \\
& \quad \xrightarrow{\text{CH}_2\text{SO}_2\text{Cl} \quad \text{pyridine} \ (83\%)} \\
& \quad \xrightarrow{(\text{CH}_2\text{OSO}_2\text{CH}_3)_2} \\
& \quad \xrightarrow{\text{Na}_2\text{S} \quad \text{DMF} \ (75\%)} \\
& \quad \xrightarrow{(\text{CH}_2\text{OSO}_2\text{CH}_3)_2} \\
& \quad \xrightarrow{\text{t-BuOK} \quad \text{THF} \ (50\%)} \\
& \quad \xrightarrow{(\text{CH}_2\text{OSO}_2\text{CH}_3)_2} \\
& \quad \xrightarrow{\text{LiAlH}_4 \quad \text{ether} \ (62\%)} \\
& \quad \xrightarrow{(\text{CH}_2\text{OSO}_2\text{CH}_3)_2} \\
& \quad \xrightarrow{\text{Br}_2 \quad \text{LiCl, Li}_2\text{CO}_3 \quad \text{HMPA} \ (81\%)} \\
\end{align*}
\]
tetrahydrofuran for 4 days afforded tetraol 107 in 82% yield. Conversion of 107 to tetramesylate was accomplished in 83% yield by the procedure of Buchta and Billenstein. Cyclization of tetramesylate 108 to 8,11-dithia[4.3.3]propell-3-ene (109) was effected in 75% yield by the use of a dehydrated solution of sodium sulfide nonahydrate in dimethylformamide (DMF). The pmr spectrum of 109 compared favorably with that reported. This sublimed white solid was treated with one equivalent of NCS to afford the α-chloro disulfide as a waxy solid, which was immediately oxidized with four equivalents of monoperphthalic acid in ether to yield a mixture of α-chloro disulfones 110. Analysis of this inseparable mixture by pmr as before showed 110a to 110b to be present in equimolar amounts. Further support for structure 110 was gained from its elemental analysis and infrared spectrum in CH₂Cl₂ [1340, 1325, and 1120 cm⁻¹].

\[
\begin{align*}
\text{Cl} & \quad \text{SO}_2 \\
\text{SO}_2 & \quad 110a \\
\delta & \quad 4.9
\end{align*}
\]

\[
\begin{align*}
\text{Cl} & \quad \text{SO}_2 \\
\text{SO}_2 & \quad 110b \\
\delta & \quad 5.5
\end{align*}
\]

Treatment of the α-chloro disulfone mixture with powdered potassium tert-butoxide in tetrahydrofuran afforded diene sulfone 111 (50%), the gross structure of which was determined by its elemental analysis and spectral properties. The infrared spectrum (CH₂Cl₂) of 111 displays...
intense sulfone bands at 1305, 1130, and 1112 cm\(^{-1}\), while the pmr spectrum (CDCl\(_3\)) shows the presence of cyclobutenyl protons [\(\delta 6.0 (s, 2)\)]; olefinic protons [5.84 (m, 2)], protons \(\alpha\) to sulfone [3.12 (ABq, \(J_{AB} = 14\) Hz, \(\Delta\nu_{AB} = 15.8\) Hz, 4)], and allylic protons [2.3 (br s, 2)]. Treatment of this sulfone with bromine afforded the white crystalline 114. However, bisdehydrobromination of 114 with lithium chloride and lithium carbonate in HMPA did not afford sulfone 115 or recovered 114. This problem was circumvented by reducing sulfone 111 with an excess of lithium aluminum hydride in refluxing ether to sulfide 112 in 62% yield. Treatment of 112 in cold (-70°) methylene chloride with one equivalent of bromine afforded the corresponding dibromide. This viscous liquid was immediately treated with lithium chloride and lithium carbonate in HMPA to afford in 81% yield 8-thia-[4.3.2]propella-2,4,10-triene (113), which displays the expected ultraviolet maxima (iso-octane) at 264 (\(\varepsilon 2520\)), 229 (2100), and 223 nm (2270). Further evidence for structure 113 is gained from the pmr spectrum (CDCl\(_3\)): \(\delta 5.91\) (br t, \(J = 1.3\) Hz, 4, olefinic), 5.74 (s, 2, cyclobutenyl), and 2.56 (ABq, \(J_{AB} = 12\) Hz, \(\Delta\nu_{AB} = 18.4\) Hz, 4, -\(\text{CH}_2\text{S}-\).
Cycloaddition of triene 113 in cold acetone (-70°) with N-methyl-triazolinedione afforded adduct 116 in 93% yield as a white crystalline solid, characterization of which is based on its elemental analysis, pmr spectrum in CDCl₃ which displays a cyclobutenyl singlet at 6 5.94 and an N-methyl singlet at 3.02, its infrared spectrum (KBr) which displays carbonyl bands at 1775 and 1710 cm⁻¹, and its
ready sensitized (acetone) photocyclization to cubyl isomer \( \text{117} \) (89\% yield, Scheme XIII).

Bond reorganization of \( \text{117} \) to \( 9,10\)-diazasnoutane \( \text{118} \) was attempted in silver perchlorate-anhydrous benzene solution. After a short reflux period a precipitate was formed. This solid, the assumed sulfonium salt \( \text{120} \), was isolated in 90\% yield and found to be insoluble in all common organic solvents and water. The solid did, however, dissolve in aqueous ammonia with regeneration of \( \text{117} \) in 57\% yield. A solution of \( \text{117} \) and silver nitrate in refluxing isopropyl alcohol-water (4:1) afforded only starting material. When heated with a solution of silver nitrate in dioxane-water (4:1) at 130° for 4 days (sealed tube) \( \text{117} \) was successfully isomerized to \( \text{118} \) in 62\% yield. This white solid was characterized by its elemental analysis and spectral properties.

Application of the mild hydrolysis and oxidation sequence described earlier afforded thiasemibullvalene \( \text{119} \) in 44\% yield after bulb to bulb purification (10⁻³ torr). The semibullvalene structure was verified by its accurate mass (calcd \( m/e \) 162.0503, obs 162.0506), ultraviolet
spectrum in isooctane [240 nm (ε 1900)], and pmr spectrum (Figure 6) in CDCl₃ [60 MHz, δ 5.22-5.41 (m, 4, olefinic), 3.4 (ABq, J_AB = 11.8 Hz, Δν_AB = 9.9 Hz, 4, -CH₂S⁻), 3.18-3.4 (m, 1, H₅), and 2.98 (d, J = 6.8 Hz, 1, H₄)]. At 100 MHz in CS₂, H₃,H₇ and H₄,H₆ were resolved: δ 5.33 (dd, J = 4.5, 2.5 Hz, 2, H₄, H₆) and 5.2 (d, J = 4.5 Hz, 2, H₃, H₇). Further discussion of the pmr and cmr spectra will follow in the next section.

In efforts directed toward the preparation of semibullvalene sulfo­

dene 121, 119 was treated with two equivalents of m-chloroperbenzoic

acid (MCPBA) in chloroform. The resulting dark solution did not

afford 121 or recovered 119. On the basis of this result, the prepara­

tion of sulfone 121 or a sulfoxide from oxidation of 119 was abandoned.

\[ \text{119} \]

\[ \text{MCPBA} \]
Attention was next turned to the stable crystalline N-methylura-
zo 118. Treatment of this sulfide in chloroform with one equivalent

\[
\begin{align*}
[0] & \quad \text{[O]} \\
\text{118} & \quad \text{122} & \quad \text{123}
\end{align*}
\]

of MCPBA according to the procedure of Johnson \(^{71}\) afforded two epimeric
sulfoxides. The \(\text{CHNN}^+\) signals at \(\delta 5.22\) and \(5.07\) integrated in a
ratio of 1 to 3.5. The two compounds were separated by preparative
thick layer chromatography and individually analyzed for \(\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_3\text{S}\). Further support for structures 122 and 123 was gained from their in-
frared spectra (KBr), which exhibited carbonyl stretching frequencies
at 1760 and 1700 cm\(^{-1}\) and an intense sulfoxide band at 1035 cm\(^{-1}\).
The syn and anti relationship of the sulfoxide oxygen to the proximal
cyclopropyl proton was determined by pmr (Table IV).

In order to correctly assign the geometrical relationship of
the sulfoxide group in 122 and 123, the sulfone snoutane 124 was pre-
pared. Oxidation of 118 with two equivalents of MCPBA afforded 124
in 82% yield. The gross structural features of 124 were determined
by elemental analysis and spectral properties. The infrared spectrum
Table IV. 

<table>
<thead>
<tr>
<th>Compound</th>
<th>&gt;CHN&lt;</th>
<th>-CH₂S-</th>
<th>-CH₂S-</th>
<th>&gt;NCH₃</th>
<th>cyclopropyl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5.03</td>
<td>3.08</td>
<td>3.08</td>
<td>2.46 (d, J = 4 Hz, 1)</td>
<td>1.84-2.17 (br m, 3)</td>
</tr>
<tr>
<td>[Diagram]</td>
<td>(br t, J = 3 Hz)</td>
<td>(s)</td>
<td>(s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.07</td>
<td>3.22</td>
<td>3.07</td>
<td>2.84 (d, J = 4.5 Hz, 1)</td>
<td>1.81-2.4 (br m, 3)</td>
</tr>
<tr>
<td>[Diagram]</td>
<td>(dd, J = 3.8, 2.5 Hz)</td>
<td>(br s)</td>
<td>(s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>&gt;CHN&lt;</td>
<td>-CH₂S-</td>
<td>-CH₂S-</td>
<td>&gt;NCH₃</td>
<td>cyclopropyl</td>
</tr>
<tr>
<td>----------</td>
<td>-------</td>
<td>--------</td>
<td>--------</td>
<td>------</td>
<td>-----------</td>
</tr>
<tr>
<td><img src="123" alt="Image" /></td>
<td>5.22 (dd, $J = 3.8$, 2.1 Hz)</td>
<td>3.22 (s)</td>
<td>3.05 (s)</td>
<td>1.87-2.34 (br m, 4)</td>
<td></td>
</tr>
<tr>
<td><img src="124" alt="Image" /></td>
<td>5.11 (t, $J = 2.5$ Hz)</td>
<td>3.38 (ABq, $J_{AB} = 15$ Hz)</td>
<td>3.04 (s)</td>
<td>1.99-2.44 (br m, 4)</td>
<td></td>
</tr>
</tbody>
</table>

$\Delta \nu_{AB} = 41$ Hz
(KBr) shows strong sulfone bands at 1300, 1155, and 1135 \, \text{cm}^{-1},
while the pmr spectrum (CDCl$_3$) shows inter alia an AB quartet at $\delta$ 3.38
($J_{AB} = 15$ Hz, $\Delta\nu_{AB} = 41$ Hz, $-\text{CH}_2\text{SO}_2^-$).

Examination of Table IV reveals that sulfoxide 123 must be of syn
stereochemistry because the cyclopropyl absorptions closely resemble
those of sulfone 124 which necessarily has a syn S=O bond. Also,
the cyclopropyl region of sulfoxide 122 closely resembles that of
starting sulfide 118. Of particular importance is the fact that the
cyclopropyl proton over the tetrahydrothiophene ring is a distinct
doublet ($J \sim 4$ Hz) in both 118 and 122. Thus the main isomer from
MCPBA oxidation of thiasnoutane 118 is anti sulfoxide 122. According
to Johnson's work, oxidations of sulfides with sodium meta-periodate
afford a syn to anti ratio opposite to that encountered by MCPBA oxida-
tions. To see if 123 would be formed in predominant quantities under
such conditions, 118 was oxidized with sodium meta-periodate in
aqueous methanol. A syn to anti sulfoxide ratio of 1 to 2.4 was
thereby realized.
With sulfoxide 122 and sulfone 124 available, the preparation of
the corresponding semibullvalenes was next attempted. Under the
conditions reported previously, sulfoxide 122 was hydrolyzed with
base and oxidized with manganese dioxide. The resulting workup did
not afford 125.

![Diagram of the chemical structures](image)

As a final effort to prepare thiasemibullvalene 119 in one of its
oxidized forms, sulfone 124 was subjected to hydrolysis and oxidation.
The workup did not afford sulfone 121, but rather the C_{10}H_{10} hydro-
carbon 126 (calcd m/e 130.0782, obs 130.0785). The ultraviolet spectrum
(isooctane) consisted of two maxima at 250 sh (ε 6400) and 219 nm
(26,000). The strongest evidence in support of structure 126 is its
pmr [CDCl₃, δ 6.02 (br s, 4, olefinic), 5.02 (d, J = 1.4 Hz, 2, exo-
methylene), 4.96 (d, J = 1.8 Hz, 2, exomethylene), 4.02 (d, J = 6 Hz,
1, H₅), and 3.82 (m, 1, H₁)] and cmr spectra [CDCl₃ with TMS as
internal standard, 156.6 (C₂, C₈), 139.5 and 133.0 (olefinic), 105.0
(C₉, C₁₀), 58.5 and 48.6 ppm (bridgeheads)].
Olefin 126 must be produced by a cheletropic extrusion of sulfur dioxide from sulfone semibullvalene 121. That the elimination proceeds with unprecedented facility was demonstrated when the MnO₂ reaction and workup were accomplished at temperatures not exceeding 25°.

Farrant and Feldmann have shown that 1,6-dimethylene-cyclohepta-2,4-diene (128) reacts with tetracyanoethylene (TCNE) and dimethylazodicarboxylate in a 8+2 cycloaddition process to give adducts 127 and
Tetraene 126 could also react in this manner to afford a diaza semibullvalene 130. Treatment of olefin 126 in acetone at 0° with one equivalent of N-methyltriazolinedione afforded some unreacted 126 and solid material which was not 130. A more detailed study of this and related reactions appears deserving of further investigation.

**Nmr and Cmr Spectra.** With the successful synthesis of several representative members of the 36a & 36b series, attention was directed to a quantitative evaluation of the changes in equilibrium position which accompany structural modification of the bracketing unit. Since the pentamethylene derivative (71) was found to exist as a nearly equitable
distribution of valence isomers at room temperature and to exhibit a strong temperature dependence of the equilibrium constant, this hydrocarbon readily accommodated variable-temperature pmr studies and was the first to be investigated in detail. Under conditions of fast exchange (\( < 40^\circ \)) in deuteriochloroform, the pmr spectrum (Figure 4) consists of a doublet at \( \delta 4.98 \) arising from the permanently olefinic protons \( H_3, H_7 \), an equilibrium-diagnostic multiplet centered at 3.75 due to \( H_4, H_6 \), a second multiplet at 3.00 attributable to \( H_5 \), and a doublet at 2.78 provided by \( H_1 \). The equilibrium-dependent allylic protons of the bracket (area 4) appear at 2.38-2.65 and the remaining six methylene protons are responsible for the envelope at 1.40-2.10.

Two sets of low temperature experiments were carried out. The first, undertaken with the collaboration of Professor J. Lambert and L. Greifenstein, was conducted at 90 MHz in \( \text{CF}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2 \) over the range \(-27^\circ \) to \(-120^\circ \) (Figure 1). Gradual cooling of the sample resulted initially in retardation of the rate of Cope rearrangement to that of the pmr time scale, and ultimately down to the slow-exchange level where direct spectral observation of two nondegenerate semibullvalene isomers proved possible for the first time. The large structural difference between \( H_4, H_6 \) and \( H_4', H_6' \) causes their average resonance to broaden at \(-51^\circ \), pass through coalescence at \(-85.5^\circ \), and then separate into two distinct peaks at \(-120^\circ \) with the olefinic pair of \( 7_{1b} \) appearing at 5.59 and the cyclopropyl pair of \( 7_{1a} \) at 2.34. The permanently olefinic protons of the two valence isomers likewise give separate
Figure 1. The proton magnetic resonance spectrum of pentamethylene-semibullvalene 71 as a function of temperature in CF$_2$Cl$_2$/CD$_2$Cl$_2$. The temperatures for the left column from the top are -27, -51, -66, and -71$^\circ$. The temperatures for the right column from the top are -85.5, -100, -110, and -120$^\circ$. A small impurity resonance is present at $\delta$ 5.3, and a sharp impurity resonance at 5.0; these peaks were temperature independent.
slow-exchange peaks at 5.19 (H₃, H₇) and 4.94 (H₃', H₇'). Complete pro-
ton assignment at the lowest temperature clearly showed the more
populous isomer to be 71b. Integration of the H₃, H₇ and H₃', H₇' peaks
denoted that at -120° there exists 84% of 71b and 16% of 71a, corre-
sponding to a ΔG° of 505 cal/mol. Given the slow-exchange chemical
shifts of H₄, H₆ and H₄', H₆' (Δν = 290.6 Hz) and the isomer populations,
the free energy of activation was determined by complete lineshape
analysis at the coalescence temperature to be 8.9 kcal/mol (71b to
71a) or 8.5 kcal/mol (71a to 71b).

These ΔG° values for Cope rearrangement are larger than that
determined experimentally for octamethylsemibullvalene (6.4 kcal/mol
at -141°)⁷⁶ and semibullvalene (5.5 kcal/mol at -140°)²² and are more
closely aligned in magnitude to the ΔG°'s found for the degenerate
rearrangements of barbaralane (7.8 kcal/mol at -77°), 9-methylenebar-
baralane (9.5 kcal/mol at -89.5°), dihydrobullvalene (9.5 kcal/mol at
-40°), and barbaralone (10.5 kcal/mol at -41°, Table I). Thus, the
energy advantage which is normally acquired in such systems by shorten-
ing of the bridge between C₁ and C₅ to the point where these atoms are
directly bonded is offset to some degree by the presence of the penta-
methylene bracket which joins C₂ to C₃.

The results of a comparable study in CF₃Cl/CD₂Cl₂/TMS (1:1:1)
solution at 100 MHz within the temperature limits -30.1° and -84.8°
are summarized in Table V. The mole fraction of 71b and the K⁰ value
at each temperature were computed on the basis of the equations
<table>
<thead>
<tr>
<th>Temp, °C</th>
<th>Chem Shift $H_4,H_5$ (δ)</th>
<th>Mol Fraction $Tlb$</th>
<th>$K_{eq}$ ($Tla/Tlb$)</th>
<th>$\ln K_{eq}$</th>
<th>$\Delta G°$, cal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>-30.1</td>
<td>4.26</td>
<td>59.1</td>
<td>0.692</td>
<td>-0.368</td>
<td>178</td>
</tr>
<tr>
<td>-45.2</td>
<td>4.40</td>
<td>63.4</td>
<td>0.577</td>
<td>-0.550</td>
<td>249</td>
</tr>
<tr>
<td>-54.3</td>
<td>4.47</td>
<td>65.5</td>
<td>0.527</td>
<td>-0.641</td>
<td>279</td>
</tr>
<tr>
<td>-66.3</td>
<td>4.56</td>
<td>68.3</td>
<td>0.464</td>
<td>-0.768</td>
<td>315</td>
</tr>
<tr>
<td>-71.8</td>
<td>4.61</td>
<td>69.8</td>
<td>0.433</td>
<td>-0.837</td>
<td>335</td>
</tr>
<tr>
<td>-74.8</td>
<td>4.66</td>
<td>71.4</td>
<td>0.401</td>
<td>-0.924</td>
<td>360</td>
</tr>
<tr>
<td>-78.8</td>
<td>4.69</td>
<td>72.3</td>
<td>0.383</td>
<td>-0.960</td>
<td>370</td>
</tr>
<tr>
<td>-81.8</td>
<td>4.72</td>
<td>73.2</td>
<td>0.366</td>
<td>-1.005</td>
<td>382</td>
</tr>
<tr>
<td>-84.8</td>
<td>4.76</td>
<td>74.5</td>
<td>0.342</td>
<td>-1.073</td>
<td>401</td>
</tr>
</tbody>
</table>
\[ \delta_m = \rho \delta \nu + (1 - \rho) \delta \zeta \]
\[ \rho = \frac{(\delta_m - \delta \zeta)}{(\delta \nu - \delta \zeta)} \]
\[ K_{eq} = \rho/(1 - \rho) \]

where \( \delta_m \) is the observed chemical shift of that pair of protons undergoing rapid exchange between the \( H_4, H_6 \) and \( H_4', H_6' \) sites at the given temperature, \( \delta \nu \) and \( \delta \zeta \) are the chemical shifts of \( H_4, H_6 \) and \( H_4', H_6' \), respectively, at their slow-exchange limits (-120°), and \( \rho \) is the mole fraction of one of the isomers (\( 71b \) in this instance). The enthalpy (\( \Delta H^0 = 1130 \text{ cal/mol} \)) and entropy (\( \Delta S^0 = 43.9 \text{ e.u.} \)) of this semibullvalene system were obtained from the data in Table V by plotting ln \( K_{eq} \) vs \( 1/T \) and deriving by the method of least squares the slope \((-\Delta H^0/R)\) and intercept \((\Delta S^0/R)\) values.

When eq 1 was applied to the 40° pmr spectra (60 MHz) of all five annulated semibullvalenes in deuteriochloroform solution, the approximate mole fraction and \( \Delta G^0_{313} \) terms of the series for that temperature became readily accessible. These data are collected in Table VI for the purpose of direct comparison. Thereby revealed is the fact that 2,5-pentamethylene bridging acts on the energy of the semibullvalene moiety to favor form \( 71b \) at low temperature, but to crossover and stabilize valence isomer \( 71a \) in the vicinity of 17° and above. It is therefore obvious from these findings that the assumedly lesser bracketing strain in this hydrocarbon is not exploited in a manner such as to
Table VI. Pmr Data (60 MHz, CDCl₃), Computed Equilibrium Constants ($K_{eq}$), and Gibbs Free Energy Values ($\Delta G^\circ$) for the Annulated Semibullvalenes (40°C).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chem Shift H₄,H₆ (€)</th>
<th>Mol Fraction $\delta$</th>
<th>$K_{eq}$ (36a/36b)</th>
<th>$\Delta G^\circ$ cal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>4.21</td>
<td>57</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.70</td>
<td>10</td>
<td>9.00</td>
</tr>
</tbody>
</table>
Table VI. (Continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chem Shift $\delta$</th>
<th>Mol Fraction</th>
<th>$K_{eq}$</th>
<th>$\Delta G^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Diagram 1]</td>
<td>3.75</td>
<td>42</td>
<td>1.38</td>
<td>-200</td>
</tr>
<tr>
<td>![Diagram 2]</td>
<td>5.58</td>
<td>99.7</td>
<td>$3 \times 10^{-3}$</td>
<td>3600</td>
</tr>
<tr>
<td>![Diagram 3]</td>
<td>5.25</td>
<td>89.5</td>
<td>$1.2 \times 10^{-1}$</td>
<td>1320</td>
</tr>
</tbody>
</table>
reveal itself by excessive weighting in the \(7_{1a}\) direction throughout the temperature span examined. In striking contrast, tetramethylene derivative 66 (Figure 3) conforms to the established preference of alkyl groups for bonding to \(sp^2\) rather than \(sp^{2.25}\)-hybridized carbon in structurally related homotropolilidene systems. \(^{18,25,81}\) This semibullvalene expectedly exhibits temperature-dependent pmr behavior, but of a very weak order. Consequently, further changes in ground state equilibria with changing T were too small to measure accurately.

This same difficulty persisted in the trimethylene system 57 but to a somewhat attenuated degree. Its pmr spectrum (40°, Figure 2) is characterized by a 2:2:2:4:2 ratio of protons, the relevant chemical shifts of which correspond closely to those of semibullvalene. Accordingly, a more equitable distribution of the two valence isomers exists in this instance at this temperature (see Table VI). Variable-temperature studies in carbon disulfide solution from +45° to -91° likewise revealed a crossover in the preferred direction of equilibrium but in the reverse sense from that of the pentamethylene case and to a less dramatic extent (Table VII). Here the \(\Delta H^0\) value is -315 cal/mol, with \(\Delta S^0\) equal to -1.29 e.u.

Replacement of the central carbon atom of the trimethylene bridge with an oxygen atom produces a marked shift in the equilibrium. This is demonstrated in the room temperature pmr spectrum where the chemical shift of the time-averaged protons \(H_4, H_6 (\delta 5.58)\) indicates the presence of nearly 100% of tautomer 97b. Due to the symmetry of this
Table VII. Low Temperature Pmr Data (60 MHz, CS$_2$), Computed Equilibrium Constants ($K_{eq}$), and Gibbs Free Energy Values ($\Delta G^\circ$) for the Fluxional System $57b \leftrightarrow 57a$.

<table>
<thead>
<tr>
<th>Temp, °C</th>
<th>Chem Shift, H$_4$,H$_6$ (δ)</th>
<th>Mol Fraction</th>
<th>$K_{eq}$ ($57a/57b$)</th>
<th>ln$K_{eq}$</th>
<th>$\Delta G^\circ$, cal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>-45</td>
<td>4.08</td>
<td>53.5</td>
<td>0.869</td>
<td>-0.140</td>
<td>88</td>
</tr>
<tr>
<td>-29</td>
<td>3.96</td>
<td>49.8</td>
<td>1.00</td>
<td>0.000</td>
<td>0</td>
</tr>
<tr>
<td>-56</td>
<td>3.92</td>
<td>48.6</td>
<td>1.06</td>
<td>0.058</td>
<td>-25</td>
</tr>
<tr>
<td>-91</td>
<td>3.77</td>
<td>44.0</td>
<td>1.27</td>
<td>0.239</td>
<td>-86</td>
</tr>
</tbody>
</table>

Like the oxasemibullvalene 97, the thiasemibullvalene was found to experience pronounced weighting in the $\underline{36b}$ direction (Figure 6). However, the effect is somewhat less dramatic, isomer 119b now dominating by a level of only 90%. This happens to be an isomer ratio opposite to that experienced by 2,8-tetramethylenesemibullvalene (66). Unlike semibullvalene 66, thiasemibullvalene 119 was weakly temperature dependent, showing an increase in isomer 119b as the temperature was
H₄, H₆ ₉ 5.58
H₃, H₇ ₉ 5.26

-CH₂O- ₉ 4.2
H₅ ₉ 3.35
H₁ ₉ 2.62

J₁,₂ = 0  J₂,₄ = 5.2 Hz  J₄,₅ = 2 Hz  J₅,₆ = 2 Hz  J₆,₇ = 5.2 Hz
J₁,₄ = 0  J₃,₅ = ~ 0  J₄,₆ = 0  J₅,₇ = ~ 0
J₁,₅ = 7.1 Hz  J₃,₆ = 0  J₄,₇ = 0
J₁,₆ = 0  J₃,₇ = 0
J₁,₇ = 0

lowered (-120°, CS₂) and a decrease in isomer 119b as the temperature was raised (+100°, C₂Cl₄, Table VIII). By plotting ln Kₑq vs 1/T (CS₂ values only) the values ΔH° ~ 0 and ΔS equal to -5.78 e.u. were obtained.

The valence isomeric equilibria of semibullvalene and several of the annulated derivatives have also been investigated by cmr spectroscopy. The spectra were recorded at room temperature and all chemical shifts assigned as summarized in Table IX. The properties of the
Table VIII. Variable Temperature Pmr Data (100 MHz, CS₂ for room temperature and below, C₂Cl₄ for above room temperature), Computed Equilibrium Constants (Kₑₜ), and Gibbs Free Energy Values (ΔG⁰) for the Fluxional System 119b ↔ 119a.

<table>
<thead>
<tr>
<th>Temp, °C</th>
<th>Chem Shift H₄,H₆ (δ)</th>
<th>Mol Fraction 119b (119a/119b)</th>
<th>Kₑₜ</th>
<th>ln Kₑₜ</th>
<th>ΔG⁰ cal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>5.25</td>
<td>89.8</td>
<td>0.114</td>
<td>-2.18</td>
<td>1620</td>
</tr>
<tr>
<td>80</td>
<td>5.29</td>
<td>90.8</td>
<td>0.101</td>
<td>-2.29</td>
<td>1610</td>
</tr>
<tr>
<td>68.5</td>
<td>5.30</td>
<td>91.1</td>
<td>0.0977</td>
<td>-2.33</td>
<td>1580</td>
</tr>
<tr>
<td>51</td>
<td>5.32</td>
<td>91.7</td>
<td>0.0905</td>
<td>-2.40</td>
<td>1550</td>
</tr>
<tr>
<td>32.5</td>
<td>5.33</td>
<td>92.0</td>
<td>0.0870</td>
<td>-2.44</td>
<td>1480</td>
</tr>
<tr>
<td>-19</td>
<td>5.38</td>
<td>93.5</td>
<td>0.0695</td>
<td>-2.67</td>
<td>1350</td>
</tr>
<tr>
<td>-43</td>
<td>5.41</td>
<td>94.5</td>
<td>0.0582</td>
<td>-2.84</td>
<td>1300</td>
</tr>
<tr>
<td>-69</td>
<td>5.44</td>
<td>95.4</td>
<td>0.0482</td>
<td>-3.03</td>
<td>1250</td>
</tr>
<tr>
<td>-78</td>
<td>5.45</td>
<td>95.7</td>
<td>0.0449</td>
<td>-3.10</td>
<td>1200</td>
</tr>
<tr>
<td>-110</td>
<td>5.48</td>
<td>96.6</td>
<td>0.0352</td>
<td>-3.35</td>
<td>1090</td>
</tr>
<tr>
<td>-120</td>
<td>5.49</td>
<td>96.9</td>
<td>0.0320</td>
<td>-3.44</td>
<td>1050</td>
</tr>
</tbody>
</table>
Table IX. Summary of Cmr Data (CDCl₃, ambient temperature).

<table>
<thead>
<tr>
<th>Compound</th>
<th>C₁</th>
<th>C₂,C₈</th>
<th>C₃,C₇</th>
<th>C₄,C₆</th>
<th>C₅</th>
<th>α</th>
<th>β</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Semibullvalene</td>
<td>50.0</td>
<td>86.5</td>
<td>120.4</td>
<td>86.5</td>
<td>50.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>66a 66b</td>
<td>56.4</td>
<td>145.7</td>
<td>115.5</td>
<td>41.3</td>
<td>48.1</td>
<td>30.3</td>
<td>26.2</td>
<td>--</td>
</tr>
<tr>
<td>7la 7lb</td>
<td>59.6</td>
<td>109.1</td>
<td>121.4</td>
<td>82.2</td>
<td>52.4</td>
<td>30.0</td>
<td>28.0</td>
<td>29.0</td>
</tr>
<tr>
<td>119a 119b</td>
<td>53.1</td>
<td>73.2</td>
<td>123.3</td>
<td>119.3</td>
<td>52.9</td>
<td>31.7</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>97a 97b</td>
<td>53.6</td>
<td>61.7</td>
<td>121.0</td>
<td>127.6</td>
<td>52.8</td>
<td>63.4</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

a In ppm downfield from TMS.

b Relates to the carbon atoms of the belt with the α position being most proximal to the semibullvalene nucleus.

c These values may be interchanged.

d These values may be interchanged.
parent hydrocarbon which comprise only three widely spaced signals are fully reconcilable with a rapidly equilibrating pair of degenerate isomers. With these chemical shifts as guidelines, those of the tetramethylene bridged system $\text{66}_1$ are seen to be characterized by a high-field position for $H_4, H_5$ and a low-field position for $H_2, H_6$. The central carbon atoms must therefore be less cyclopropanoid and the peripheral carbons less olefinic on a time average basis than the respective centers in semibullvalene. As one progresses downward in Table IX, this trend is seen to reverse itself. These shift considerations confirm the earlier conclusions derived from pmr studies that the tautomer disposition of the tetramethylene bridged semibullvalene lies heavily in the $\text{36a}$ direction, the pentamethylene case at an intermediate position, and the thia- and oxasemibullvalene heavily in the $\text{36b}$ direction.

In this study the synthesis of 2,8-annulated semibullvalenes $\text{36}_2$ and of new $[4,2,x]$propellanes has been achieved. The Diels-Alder, Ramberg-Bäcklund, and silver(I)-catalyzed reactions have been the backbone of the synthetic scheme, whereas variable-temperature pmr has been the tool employed to analyze the Cope equilibrium. The variable temperature phenomena observed do not serve to prove or disprove earlier results or predictions, but only to provide possible guidelines for future annulation work in degenerate systems. Throughout the following discussion, entropy contributions from possible differences in solvation of the two isomers will not be mentioned specifically.
Although, these medium effects should be of a low order of magnitude in the \( \text{36a} \neq \text{36b} \) equilibrium, they should not be ignored altogether. A reliable value for the equilibrium imbalance arising from alkyl substitution of the semibullvalene ring at C_2 is extractable from the behavior of the 2(4)-methylsemibullvalene (131). Here the methyl group, which is almost certainly electron-releasing relative to hydrogen, is seen to exert an electrical effect within the molecule which alters the relative potential energies in such a way as to favor 131a by approximately 1 kcal/mol at 40°. In this instance, the free energy difference lies in the expected direction. Placement of a second methyl group at C_2 should approximately double

\[
\text{131a} \quad \text{131b}
\]

the value of \( \Delta G^0 \), barring unforeseen steric problems of meaningful magnitude. Extrapolation of this analysis to an annulated semibullvalene of type \( \text{36a} \neq \text{36b} \) in which the 'belt' is not excessively truncated predicts that valence tautomer \( \text{36a} \) should be highly (> 95%) favored if all other factors are equal.

However, the fact that alkyl chains are 'mobile substituents' must be reckoned with. This means that intramethylene rotations and
rotations of the sidechain about the bond connecting it to the host molecular framework, in tandem with steric crowding, strain factors, and electronic demand, have a direct effect on the internal mobility of the molecule. In other words, the particular characteristics of a given alkyl chain can greatly affect its overall contribution to entropy.

The tetramethylenesemibullvalene $66$ is an interesting case in point. At $40^\circ$ in CDCl$_3$, isomer $66a$ is seen to be present to the extent of approximately $90\%$. Additionally, its pmr spectra are weakly temperature-dependent, a finding which signifies that $\Delta H^o$ approaches zero and consequently $\Delta S^o \approx -T\Delta F^o$. Entropy control prevails throughout the entire temperature range examined and $66a$ convincingly dominates the equilibrium, likely because it has access to a wider variety of translational, rotational, and vibrational motions (or conformations) than does $66b$. However, the four methylene groups seemingly do introduce some strain relative to the hypothetical $2,8$-dimethylsemibullvalene model such that the concentration of $66a$ is energetically precluded from exceeding the $90\%$ level at $40^\circ$.

Unlike the situation prevailing in tetramethylenesemibullvalene $66$, a trimethylene bridge necessarily places added strain on the semibullvalene nucleus. In order to understand the results, it is helpful to consider the factors which contribute to $\Delta H^o$ and $\Delta S^o$. The group contributions which comprise the $\Delta H^o$ term in isomers $57a$ and $57b$ may cancel, since each isomer contains a cis-divinylcyclopropane moiety. Though isomer $57a$ contains a more strained bicyclo[4.3.1]dec-1,5-
<table>
<thead>
<tr>
<th>Semibullvalene</th>
<th>$\Delta H^\circ$, kcal/mol</th>
<th>$\Delta S^\circ$, e.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\equiv$</td>
<td>$-0.3$</td>
<td>-1.3</td>
</tr>
<tr>
<td>57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\equiv$</td>
<td>$\sim 0$</td>
<td>ca +4.4</td>
</tr>
<tr>
<td>66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\equiv$</td>
<td>+1.13</td>
<td>+5.9</td>
</tr>
<tr>
<td>71</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table X. (Continued)

<table>
<thead>
<tr>
<th>Semibullvalene</th>
<th>$\Delta H^\circ$, kcal/mol</th>
<th>$\Delta S^\circ$, e.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Diagram 1" /> $\xrightarrow{97}$ <img src="image2" alt="Diagram 2" /></td>
<td>$\sim 0$</td>
<td>ca -11</td>
</tr>
<tr>
<td><img src="image3" alt="Diagram 3" /> $\xrightarrow{119}$ <img src="image4" alt="Diagram 4" /></td>
<td>$\sim 0$</td>
<td>ca -8.8</td>
</tr>
</tbody>
</table>
diene unit (A), it does have olefin substitution not found in 57b. Thus, depending on the balance between these opposing forces (strain vs alkyl stabilization) in A, an estimate of the magnitude of $H_a^0 - H_b^0$ is assumed to be near zero or slightly positive. For the oxa- and thia-semibullvalenes this is indeed the case, but not for 2,8-trimethylene-semibullvalene (57, Table X).

As concerns entropy, one must consider the molecule as a whole. In isomer 57b, it can be seen that the cyclopropane unit acts as a 'fulcrum' for translational, rotational, and vibrational motions of
the trimethylene bridge and semibullvalene nucleus. However, in 57a the molecule is constrained, i.e. the short trimethylene unit probably restricts translational freedom of the semibullvalene nucleus which in turn likely reduces the translational and rotational freedom of the trimethylene bridge. Consequently, isomer 57b should have more degrees of freedom than 57a; thus a negative $\Delta^0$ for the system. This corresponds to the behavior encountered for 57, 97, and 119 (Table X).

The fact that lowering the temperature in the trimethylene system shifts the equilibrium towards 57a suggests that electron release stabilization of an alkyl group on an olefin provides sufficient stabilization to overcome the strain disadvantages mentioned above. Replacement of this electron releasing group with an electron withdrawing group, e.g. $\text{-CH}_2\text{OR (}\sigma^+ = 0.52\text{ for CH}_3\text{OCH}_2\text{-) or -CH}_2\text{SR should reverse this equilibrium, and in fact it does.}$

Expansion of the bridge to five methylene carbons generates a complex situation which precludes a simple analysis as in the trimethylene case. In this case the enthalpy and entropy terms appear to be large. This is an example where $\Delta H^0$ and $\Delta S^0$ vary in a compensating manner, the large change in enthalpy being accompanied by a large change in the temperature-entropy term. This phenomenon has earlier been referred to by Leffler as an isoequilibrium relationship. At the lower temperatures where enthalpy control operates isomer 71b is favored, presumably as the result of more favorable bond strength contributions. However, the true causative factors underlying the
preferential attachment of the \( \alpha \)-methylene groups to \( \text{sp}^2 \) rather than \( \text{sp}^2 \)-hybridized carbon in this instance remain elusive. With heating, entropy control sets in and \( \text{Jla} \) becomes dominant as a likely consequence of a higher level of strain (from nonbonded interactions and the like) in the various conformations available to \( \text{Jlb} \).

In summary, the varied ground-state behavior of the annulated semibullvalenes provides an unusually clear example of the caution which must be exercised in equating a diminution in "bracketing strain" with direction of equilibrium. Earlier studies of this phenomenon (Table II) have uniformly succeeded in their predictability, i.e., in equating favored bicyclic character with an increase in bridge size, because of the unusually large equilibrium displacements toward the minimum number of ring constraints which already exist in the parent non-bridged systems. However, when a two fold-degenerate host molecule such as semibullvalene is involved, similar unidirectionally weighted equilibrium imbalances are not present and the quite subtle libration effects of the various aliphatic chains which comprise the bracket are consequently revealed with utmost clarity.
Figure 2. The 100 MHz pmr spectrum of 2,8-trimethylenesemibullvalene (57) in CDCl$_3$ at 500 Hz sweep width.

Figure 3. The 100 MHz pmr spectrum of 2,8-tetramethylenesemibullvalene (66) in CDCl$_3$ at 500 Hz sweep width.

Figure 4. The 100 MHz pmr spectrum of 2,8-pentamethylenesemibullvalene (71) in CDCl$_3$ at 500 Hz sweep width.

Figure 5. The 100 MHz pmr spectrum of oxasemibullvalene 97 in CS$_2$ at 500 Hz sweep width.

Figure 6. The 100 MHz pmr spectrum of thiasemibullvalene 119 in CS$_2$ at 500 Hz sweep width.
RESULTS AND DISCUSSION

Part II. Rearrangements of 2,8-Tetramethylenesemibullvalene

The special geometry of semibullvalene, renowned for its ability to markedly enhance the rate of degenerate Cope rearrangement (lifetime of an isomer is less than $3 \times 10^{-7}$ sec at $0^\circ$) has provoked investigation of varied synthetic approaches to the hydrocarbon, detailed structural (electron diffraction) and orbital sequencing (EE) studies, low temperature pmr measurements, and theoretical assessment of its possible neutral homoaromatic character. However, the potentially intriguing chemical consequences of such a continuous cyclic array of six peripheral $\sigma$ interacting electrons has not yet received the full attention it merits.

Aspects of the chemical behavior of 2,8-tetramethylenesemibullvalene (66) are described below. This annulated semibullvalene was selected as the prototypical member of the bridged semibullvalenes because of its availability in gram quantities and its relatively good stability towards oxygen.

Thermochemical Behavior. Zimmerman's early reports concerning semibullvalene (29) and certain of its methylated derivatives demonstrated the photochemical (triplet) reactivity of these systems. He isolated cyclooctatetraene (133) from the irradiation of semibullvalene
and proposed the intermediacy of bicyclo[3.3.0]octanediyl 132. However, the pyrolysis of semibullvalene had not been studied.

When olefin 29 was slowly vaporized into a nitrogen stream and passed through a quartz reactor packed with quartz chips at 427° and

Scheme XIV
30 mm pressure (contact times of 1-3 sec) cyclooctatetraene (133) was formed in 59% yield (Scheme XIV). This yellow hydrocarbon was characterized by pmr and ir spectral comparisons with an authentic sample. As depicted in Scheme XIV, the transformation is most likely proceeding by pathways a and/or b. In order to distinguish between these two mechanisms, 1,5-dimethylsemibullvalene (142) was prepared (Scheme XV).

The synthesis of 142 began with the condensation of ethyl acetone-dicarboxylate (137) and 2,3-butanedione (136) according to the procedure of Weiss and Edwards. Tetraester 138 (96% yield) was hydrolyzed and decarboxylated in acidic ethanol to give dione 139 ($\nu_{\text{max}}^{\text{CHCl}_3} 1740$ cm$^{-1}$) in 89% yield. Reduction of 1,5-dimethylbicyclo[3.3.0]octane-3,7-dione (139) with lithium aluminum hydride in refluxing anhydrous ether led to diol 140 in 97% yield. This diol had already been characterized by Baldwin and Kaplan. Following a literature procedure, the diol was dehydrated by pyrolysis of the intermediate dixanthate to afford a mixture of dienes 141, whose allylic bromination with two equivalents of recrystallized NBS in refluxing carbon tetrachloride gave a mixture of dibromides. Direct debromination with $\text{LiH}$ in anhydrous ether furnished semibullvalene 142 in 36% yield. The pmr spectrum of 142 in CDCl$_3$ consists of three signals at $\delta$ 5.40 (br s, 2, olefinic), 4.10 (m, 4, time-averaged protons), and 1.00 (s, 6, methyl).

Pyrolysis of 1,5-dimethylsemibullvalene (142) in the same quartz reactor as above at 590° and 30 mm afforded an isomeric pale yellow liquid in 76% yield. That the structure of this C$_{10}$H$_{12}$ hydrocarbon was
Scheme XV

\[
\text{Scheme XV}
\]

\[
\begin{align*}
\text{CH}_3\text{C}(-\text{C}_2) + 2(\text{EtO}_2\text{CCH}_2)_2\text{C}=\text{O} & \xrightarrow{\text{H}_2\text{O}, \text{pH 7}} (\text{96%}) \\
\end{align*}
\]

\[
\begin{align*}
\text{EtO}_2\text{C} & \text{CH}_3 \text{CO}_2\text{Et} \\
\text{EtO}_2\text{C} & \text{CH}_3 \text{CO}_2\text{Et} \\
\end{align*}
\]

\[
\begin{align*}
\text{EtOH} & \xrightarrow{\text{H}^+} (89\%) \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \text{CH}_3 \\
\text{CH}_3 & \text{CH}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{LiAlH}_4 & \xrightarrow{\text{97%}} \text{HO}^- \text{O} \\
\text{HO}^- \text{O} & \xrightarrow{\text{97%}} \text{HO}^- \text{O} \\
\end{align*}
\]

\[
\begin{align*}
1) \text{NaH} & \\
2) \text{CS}_2 & \\
3) \text{MeI} & \\
4) \Delta & (64\%) \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \text{CH}_3 \\
\text{CH}_3 & \text{CH}_3 \\
\end{align*}
\]

\[
\begin{align*}
1) \text{NBS} & \\
2) \text{Li}^{+} & (56\%) \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \text{CH}_3 \\
\text{CH}_3 & \text{CH}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \text{CH}_3 \\
\text{CH}_3 & \text{CH}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{141} & \\
\text{142} & \\
\end{align*}
\]
followed from elemental analysis and the pmr spectrum (CDCl₃) which consists of two absorptions in the olefinic region at δ 5.68 and 5.53 (6 protons) and a sharp singlet at 1.72 (6 protons). The ultraviolet [λ max = 280 sh nm (ε 222)] and infrared absorptions of this product were not those of the 1,2-, 1,3-, or 1,4-dimethylcyclooctatetraenes. Treatment with tetracyanoethylene in refluxing ethyl acetate gave adduct 145, pmr analysis of which requires the product to be that derived from (4+2) cycloaddition to 151 (Scheme XVI). Thus, bridgehead proton H₆ appears as a multiplet centered at δ 3.6 whereas H₁ (3.80) is seen as a doublet of doublets (J = 7.0 and 3.0 Hz). The protons at positions 2 and 5 appear as broad overlapping multiplets at 3.13 and the olefinic hydrogens give rise to doublet (J = 7.0 Hz, 6.00, H₆) and multiplet patterns (5.61, H₄). Scheme XVI shows that 1,5-dimethylcyclooctatetraene (144) must necessarily arise from bicyclo[3.3.0]octanediyl biradical 143.

Strict adherence of 2,8-tetramethylenesemibullvalene (66) to rearrangement by this mechanism would lead to the severely strained 1,3-tetramethylcyclooctatetraene (152). It was therefore of interest to
examine the consequence of such steric strain on the course of the thermally-promoted bond reorganization. In gas phase experiments conducted at 460-500° and 1.5 mm, \(66\) did afford a cyclooctatetraene product in 69% yield. This material was identified, however, as the known 1,2-tetramethylene derivative on the basis of its characteristic infrared and pmr absorptions and conversion to the TCNE adduct \(154\) of established structure. The isolation of this particular product

\[
\begin{align*}
\text{66} & \xrightarrow{\Delta} \frac{69\%}{(69\%)} \\
\text{153} & \xrightarrow{\text{TCNE}} \begin{array}{c}
\text{154} \\
(\text{CN})_2 \\
(\text{CN})_2
\end{array}
\end{align*}
\]

necessitates that the 1,3-tetramethylene chain in \(66\) undergo concurrent translocation in a fashion which eventuates in its vicinal attachment
to the medium ring in 152.

Having observed this somewhat unusual rearrangement, further insight into its mechanism was desired. For this purpose, the 1,5-dideuterio derivative 159 was prepared (Scheme XVII).

Scheme XVII

\[
\begin{align*}
\text{155} & \xrightarrow{\text{hv, acetone}} \text{156} \\
\text{156} & \xrightarrow{\text{MnO}_2} \text{157}
\end{align*}
\]
The synthesis of 159 followed the same methodology as for the protio compound. Treatment of a cold (-70°) solution of 11,12-dideutero[4.4.2]propella-2,4,11-triene (155) with N-phenyltriazoline-dione afforded adduct 156 in 74% yield. The pmr spectrum (CDCl₃) of this adduct contains the reported absorptions except for the lack of the cyclobutene singlet at δ 5.95. Irradiation of an acetone solution of 156 with a 200-W Hanovia lamp through Vycor afforded the 9,10-diazabishomocubane derivative 157 in 98% yield. Again the pmr spectrum (CDCl₃) denotes the location of isotopic labeling. Skeletal rearrangement of 157 to 158 was accomplished in quantitative yield by refluxing in the dark a solution of 157 and silver nitrate in methanol-water (4:1) for 48 hr. Mild hydrolysis and oxidation as described in Part I afforded labeled semibullvalene 159 in 53% yield. The pmr spectrum lacks absorptions at δ 2.56-3.09 as expected from the presence of deuterium at the 1 and 5 positions.

In this instance, thermal isomerization was conducted at somewhat lower temperatures (460° and 1.5 mm; contact time ca 1 sec) than those originally employed for two reasons. First, incomplete conversion of 159 to 160 occurs under these conditions and consequently it is possible to recover semibullvalene and search for isotopic scrambling in the starting material. None was observed by pmr analysis. Secondly, these conditions are sufficiently subdued that deuterium migration likewise does not operate in the annulated cyclooctatetraene product 160. The samples of 1,2-tetramethylenecyclooctatetraene-d₈ obtained from pyrolysis of 159 were separated from the semibullvalene by preparative
vapor phase chromatography and converted individually to their TCNE adducts. Specific location of the deuterium atoms directly in 160 is
not readily achievable by pmr techniques because its olefinic protons appear as closely spaced multiplets at both 60 and 100 MHz. The selection of TCNE as dienophile was predicated on the fact that it reacts exclusively under mild conditions with that valence isomer of 153 having the cycloalkane ring fused to the cyclobutene moiety. The pmr spectra of the adducts revealed the absence of both an $sp^3$-bound proton in the cyclobutene ring and a hydrogen from the pair $H_7,H_8$. Thus, the problem became one of distinguishing between 161 and 162.

Resolution of this question was made possible by LAUQCOON III computer simulation of the 100 MHz pmr spectra of these isomeric adducts. The parameters employed are summarized in Table XI and the $H_1,H_6$ region is depicted in Figure 7. By this technique, one sees that the combined absorption due to $H_1$ and $H_6$ differs markedly in the two compounds and that the spectra of the isolated product conform uniquely to that pattern computed for 161. Consequently, the annulated cyclooctatetraene derived from thermal rearrangement of 159 is isotopically substituted predominantly, and perhaps exclusively, as in 160.

The 1,4-disposition of the deuterium atoms in 160 requires that $C_1$ in 159b & 159a ultimately become transposed with one of the adjacent bridgehead carbon atoms. One possible mechanism involves homolytic cleavage of a strained cyclopropyl bond in the only mode which can possibly give rise to two allylically stabilized radical centers. The ensuing intermediate (163) could then experience bond reorganization with formation of the 2,8-bridged bicyclo[4.2.0]octatriene 165 (Scheme
Table XI. Parameters used in the LAOCOON III computer simulation of 154.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2, H_5$</td>
<td>6.334</td>
</tr>
<tr>
<td>$H_1, H_6$</td>
<td>4.02</td>
</tr>
<tr>
<td>$H_7, H_8$</td>
<td>6.485</td>
</tr>
</tbody>
</table>

![Chemical Structure]

$J_{1,2} = 3.5$ Hz  $J_{2,5} = 6.0$ Hz  $J_{5,8} = 3.5$ Hz  $J_{6,7} = 6.6$ Hz  $J_{7,8} = 8.0$ Hz

$J_{1,5} = 0.00$  $J_{2,6} = 0.00$  $J_{5,7} = 0.5$  $J_{6,8} = 1.2$

$J_{1,6} = 0.5$  $J_{2,7} = 0.0$  $J_{5,8} = 0.0$

$J_{1,7} = 1.2$  $J_{2,8} = 0.5$

$J_{1,8} = 6.6$
Figure 7. Experimental (A,B) and computer simulated (C,D) partial 100-MHz pmr spectra of (A) the 1,2-tetramethylenecyclo-octatetraene-TCNE adduct; (B) and (D) the 2,7-\textsuperscript{d\textsubscript{2}} derivative 161; and (C) the 2,8-\textsuperscript{d\textsubscript{2}} derivative 162.
XVIII). This conversion could operate by way of a simple 1,2-alkyl shift in **163** or less directly by homolytic cleavage of the sym-

Scheme XVIII

![Diagram of chemical reactions and structures](image-url)
metrically disposed central \( \sigma \) bond to give 1,3-tetramethylenecyclo-
ctatetraene (164) and its subsequent valence isomerization. Our data
do not, of course, permit a possible distinction to be made between
these two rationalizations. Suffice it to say that the findings are
not incongruent with the initial formation of 164, and the driving
force for its conversion to 165 is fully anticipated from its excessive
ground state strain. Intramolecular Diels-Alder bonding in 165 to
give bishomobenzene 166 and ultimately 167 parallels the intermediacy
of such tetracyclo[4.2.0.0\(^2\).0\(^5\).0\(^7\)]octenes in the pyrolytic conversion
of bicyclo[4.2.0]octatrienes to cyclooctatetraenes and in the
thermal rearrangement reactions of cyclooctatetraenes.

Photoisomerization. As discussed earlier, Zimmerman and coworkers
have determined that semibullvalene and 1,3,5,7-tetramethylsemibull-
valene (168) are capable of acetone-sensitized photorearrangement to

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{CH}_3 \\
\text{H}_3\text{C} & \quad \text{CH}_3 \\
\text{H}_3\text{C} & \quad \text{CH}_3
\end{align*}
\]

\( \xrightarrow{\text{hv, acetone}} \)

\[
\begin{align*}
\text{CH}_3 & \\
\text{CH}_3 & \\
\text{CH}_3 & \\
\text{CH}_3 & \\
\text{CH}_3 & \\
\text{CH}_3 & \\
\text{CH}_3 & \\
\text{CH}_3 &
\end{align*}
\]

168 169
cyclooctatetraene and 169, respectively. In agreement with these find-
ings, an acetone solution of 1,5-dimethylsemibullvalene (142) upon irra-
diation led to 1,5-dimethylocyclooctatetraene (144). From considerateion
of the alternating carbon substitution pattern in 169 and the isolation of 144 from 142, direct analogy with the thermal isomerization pathway is seen. This may be due to close approach of excited and ground states which facilitates intersystem crossing of electronically excited bicyclo[3.3.0]octanediyl biradicals to lower vibrational levels followed by ring opening. However, the limited number of examples studied to this time does not yet allow for sweeping mechanistic conclusions.

Owing to the structural restrictions inherent in 66 which lead directly to modification of the reactivity of 163, perturbation of one or more of the photochemical steps can be anticipated if such an intermediate does in fact intervene. We therefore examined the excited state behavior of this annulated semibullvalene. No cyclooctatetraenes were produced; rather, the first example of an intriguing semibullvalene-semibullvalene rearrangement was encountered.

Direct irradiation of 66 in cyclohexane through quartz with 2537 Å incident light gave rise to a multitude of products, none of which was formed at a dominant concentration level. In contrast, when the
triplet-sensitized irradiation of \( \text{66} \) was carried out in acetone solution at 3000 \( \text{R} \) (Pyrex optics) and followed by intermittent vpc analysis, a single new substance made its appearance rather quickly. With increasing time, the peak associated with this product gradually decayed and several new minor components were seen. Considerable polymer formation was also in evidence. For preparative scale work a bank of seven Pyrex test tubes, each containing 23.6 mg of \( \text{66} \) dissolved in degassed acetone, was irradiated for 2 hr in a Bayonet reactor equipped with a 'merry-go-round' device. Isolation by preparative vapor phase chromatography returned 40% of unreacted \( \text{66} \) and gave 6.2% of the new hydrocarbon. This air-sensitive compound was found to be isomeric with \( \text{66} \) by accurate mass measurement (parent ion at \( m/e \) 158,1098). Its ultraviolet spectrum consists of a shoulder at 235 nm (\( \varepsilon \) 3200) on the end of an intense end absorption, the similarity of which to the electronic properties of \( \text{66} \) and other alkyl substituted semibullvalenes proving to be particularly striking (cf. Table III). The 100 MHz pmr spectrum in CDCl\(_3\) at 35\( ^\circ \) shows a total of three olefinic protons, one appearing as a doublet at 6 5.6 (\( J = 6 \text{ Hz} \)), the second as a doublet of doublets (\( J = 6 \text{ and } 2 \text{ Hz} \)) centered at 5.34, and the third as a broadened singlet at 4.9. In addition, three cyclopropyl protons are present, two of which are allylic (2.86, d, \( J = 5 \text{ Hz} \)) and the other more shielded (2.60 t, \( J \approx 6 \text{ Hz} \)). Also, the tetramethylene chain is now positioned such that one methylene group is allylic (2.36, m, 2H) by comparison to the other three (1.2-1.9, m, 6H). Double resonance studies showed the olefinic hydrogens not to be strongly
coupled to the higher field protons, but did give evidence of spin-spin interaction between the olefinic proton at 5.34 (collapse to a doublet with $J = 6.1$ Hz) and the cyclopropyl hydrogens at 2.86. Variable temperature measurements from +35°C to -92°C witnessed major changes in the 5.6 (downfield shifting) and 2.86 (migration to higher field) doublets.

This temperature dependent behavior likewise is fully compatible with a semibullvalene structural assignment. The presence of three rather than four olefinic protons and the unsymmetrical nature of the tetramethylene bridge serve to rule out 170 as the correct structure. A comparison of the remaining tetramethylene semibullvalene possibilities 171 and 172 shows that only isomer 172 is compatible with the data. Thus, for semibullvalene 171 to be consistent with the nmr data, the major isomer must be 171a, the consequence of which is inconsistent with the proven preference for alkyl substitution on $sp^2$ carbon. Also for isomer 171a to be the major contributor to
the observed pmr spectrum, one must postulate superimposed chemical shifts of $H_5$ and $H_6$, a premise which is unlikely due to the fact $H_6$ is an allylic-cyclopropyl methine proton while $H_5$ is merely a cyclopropyl methine proton. Finally, as the temperature of the system is decreased, $H_6$ (assumedly at $\delta 5.6$) is forced to become more olefinic in character (downfield shifting) while the $C_5$-$H$ and $C_6$-$H$ bonds must necessarily gain $p$ character. This means that the concentration level of 172a must increase with a drop in temperature, a consequence of which is that $H_2$ (assumedly at $\delta 4.9$) should shift to lower field to an extent approximating the displacement of the $H_6$ signal. It does not. Any question that the bridging be of some other type is reasonably removed upon comparison of the low field segments of the pmr spectra (60 MHz) of the photoproduct and 2(4)-methylsemibullvalene (131), the near superimposability of which at the appropriate temperatures is indeed remarkable (Figure 8). This assignment of structure is further substantiated by the finding that $H_6$ ($\delta 2.86$) spin interacts to the extent of 2 Hz with $H_7$ ($5.34$) and $H_4$ ($2.86$) at approximately the same level with $H_3$ ($4.9$). The increase in olefinic character at $C_6$ ($\delta 5.6$)
Figure 8. Pmr spectra (60 MHz) of (top) 2(4)-methylsemibullvalene and (bottom) 1,2-tetramethylenesemibullvalene (172) in CS$_2$ solution. The spectra were recorded at -101° and +35°, respectively, to equalize as much as possible the concentration gradients of the two valence isomers in the samples.
coupled with added cyclopropyl character at \( C_4 \) and \( C_6 \) (2.86) with decreasing temperature conforms plausibly with the gradual added concentration advantage expected for \( \text{172b} \) under these conditions. \(^{13b, ^{25}}\)

Interestingly, the photoisomerization of \( \text{66} \) again results in the permutation of a 1,3-bridged tetramethylene system to one that incorporates a 1,2-annulated framework. However, in this particular instance the novel and unprecedented conversion of one semibullvalene isomer to another has occurred. For the purpose of mechanistic deduction, recourse was again made to dideuterio derivative \( \text{159} \), which for this particular series of experiments was labeled to the extent detailed in structure \( \text{173} \) (pmr analyses). The rearranged semibullvalene isolated from sensitized photoisomerization of \( \text{173} \) was subjected to quantitative pmr integration at 100 MHz and determined to be isotopically substituted as in \( \text{174} \). Several significant points thereby emerge. Firstly skeletal bond reorganization operates in a manner such as to preclude the entry of deuterium at position 3. Secondly, although a sizeable fraction of the isotope attached to the original bridgehead sites in \( \text{173} \) turns up bonded to \( C_7 \) and \( C_8 \) in \( \text{174} \), dilution
does occur in a way that leads to a near equitable smaller influx of deuterium at C₄, C₅, and C₆. Since any combination which relates a methine group from the first set (53% D) to a methine of the second set (16-17% D) gives rise to a fractionation factor of at least 3.1, it becomes clear that a single intermediate cannot be involved because the number is too large to originate from conventional secondary deuterium isotope effects. Recovered $^{173}$ appeared not be isotopically scrambled (pmr analysis).

Two mechanisms seem especially reasonable, and these are outlined in Scheme XIX. Both are initiated by vinyl-vinyl bonding of the di-$\pi$-methane moiety in $^{159}$ with formation of biradical $^{176}$. Relocation of the odd electron density in this intermediate is capable of leading via $^{175}$ or $^{177}$ and then $^{178}$ to $^{180}$ in which the deuterium distribution is necessarily at C₇ and C₈. The predominance of isotopic labelling at these sites in the photoproduct supports the assumption that this pathway may be dominant. Alternatively, $^{175}$ and $^{177}$ can undergo cyclopropane ring opening with formation of barrelene $^{179}$. The structural features of this triene are such that it can expectedly serve as the precursor to annulated semibullvalenes $^{180-182}$. The inequality in the levels of isotopic substitution at C₄, C₅, and C₆ (of $^{174}$) in the photoproduct is considered to perhaps arise from a fortuitous combination of experimental error, isotope effects, and/or somewhat less than fully equitable deuterium labeling in the two bridgehead positions of the starting material.
Scheme XIX

\[ \text{hv, sens di-π-methane} \]

\[ 159a \rightarrow 159b \]

\[ \text{hv, sens di-π-methane} \]

\[ 175 \rightarrow 176 \rightarrow 177 \]

\[ \text{hv, sens di-π-methane} \]

\[ 178 \rightarrow 179 \rightarrow 180 \]

\[ 181 \]

\[ 182 \]

\( \text{denotes deuterium} \)
In attempts to independently establish the photolability of 179 a rather exhaustive, although ultimately unsuccessful study of its preparation in unlabeled form was undertaken. We have found, for example, that the α-pyrone, 5,6,7,8-tetrahydrocoumarin (183), is capable of double Diels-Alder reaction with such dienophiles as maleic anhydride, ethyl acrylate, and methyl vinyl ketone with formation of adducts 184, 185a, and 185b, respectively. However, intensive investigation of established and new methods for conversion of these different types of sidechain to internal double bonds were uniformly unrewarding. Attempts to interrupt the photoisomerization of 66 in its very early stages also did not serve to provide indication of the barrelene.

Despite the unavailability of 179 (as the d0 or d2 species), sufficient precedent is now available in the form of aromatic fused barrelenes as well as the parent hydrocarbon to be of the conviction that this bridged triene will also be especially prone to triplet excited state di-π-methane rearrangement.
The rearrangement prompted by alumina, magnesium bromide, and rhodium dicarbonyl chloride dimer. The recent recognition that strained molecules are subject to rearrangement when treated under very mild conditions with various metal catalysts has played an important role in broadening our understanding of the reactivity of these systems. Semibullvalene has recently been shown to react with transition metal complexes. Tungsten hexacarbonyl and silver nitrate form weak complexes which merely perturb the fluxional system while leaving the divinylcyclopropane system unchanged, while diiron nonacarbonyl is more drastic and prefers to insert iron into carbon-carbon σ-bonds. Dibenzosomibullvalene (186) gives the simple insertion product ferre-

\[
\begin{align*}
\text{186} & \quad \text{Fe}_2(\text{CO})_9 \quad \text{187} \\
\text{22} & \quad \text{Fe}_2(\text{CO})_9 \quad \text{188} \quad \text{189}
\end{align*}
\]
tane 187, while semibullvalene (29) reacts to give σ-π-allylic complex 189, presumably through intermediate 188.

Based on the work of Löffler and Schröder, annulated semibullvalene 66 was treated with mercuric bromide in ether and an intractable tarry residue resulted. This suggested that utilization of a less powerful catalyst was in order. Subsequent studies involving the use of slurried activity I alumina (neutral or basic) in pentane revealed a capacity of 66 for rapid and quantitative conversion to a single new substance under these conditions. Subsequently, chromatographic elution of 66 through a column of alumina supplanted the earlier method as the procedure of choice for preparative scale work.

The product was a colorless oil whose temperature independent pnr (Figure 11) shows the presence of four olefinic protons at δ 5.95 (s, 2), 5.67 (m, 1), and 5.15 (m, 1), two protons of intermediate chemical shift (complex multiplet at 3.42-4.08), and eight more shielded hydrogens (broad manifold in the 1.0-2.9 region). The electronic spectrum in isooctane which consists of three maxima at 256 (ε 14,000), 243 (14,000), and 262 sh nm (5600) serves to establish the presence of a heteroannular 1,3-diene unit. The isomeric nature of the hydrocarbon was established by elemental analysis and mass spectral molecular weight determination.

The inability of the rearrangement product to react with N-phenyl-triazolinonedione suggested that the chromophore was a rigid σ-trans diene and the possibility was considered that the overall structure was
Confirmation of this assignment was obtained by catalytic hydrogenation of \( \text{190} \) over 5% rhodium on carbon in tetrahydrofuran-glacial acetic acid solution to afford the perhydro derivative \( \text{191} \), whose high resolution infrared and 100 MHz pmr spectra were superimposable upon those of the reduction product of \( \text{66} \) and \( \text{192} \).

That the bond reorganization involved in the isomerization of \( \text{66} \) to \( \text{190} \) does not involve unexpected deep-seated bond migration became evident when \( \text{192} \) was subjected to the identical reaction conditions. A priori, one would anticipate \( \text{193} \) to contain the indicated deuterium labeling pattern if a minimum number of bonds were being cleaved. The isotopically substituted product was seen to give a pmr spectrum similar to that of \( \text{190} \) except for the complete absence of the two-proton multiplet at \( \delta \) 3.42-4.08, simplification of the 5.67 signal to a triplet, and slight alteration of fine structure in the broad high field multiplet. Any possibility that the deuterium atoms are positioned
elsewhere than at the bridgehead sites is not supported by the spectral data.

Although alumina is most efficient in effecting this isomerization, magnesium bromide and rhodium dicarbonyl chloride dimer were also found to promote the identical structural change. Thus, an ethereal solution of anhydrous MgBr₂, prepared by reaction of 'reagent grade' magnesium with 1,2-dibromoethane, effected complete conversion of 66 to 190 after 15 min at room temperature. However, substitution of triply sublimed magnesium for the somewhat less pure metal led to a total inability to effect rearrangement. A minor metal contaminant, such as iron, copper, and the like which is present in the 'reagent grade' material, is therefore presumed responsible for promoting the isomerization. Although this point was not exhaustively examined, the finding did suggest that some transition metals should be particularly effective. Indeed, when 66 was treated with a catalytic quantity of rhodium dicarbonyl chloride dimer in chloroform, the identical rearrangement was evidenced. But because concomitant decomposition of the semi-bullvalene also operates under those conditions, this method is not recommended for the preparation of 190.
Speculation of a mechanistically plausible path for this isomerization centers about initial oxidative addition of the metal atom into the peripheral cyclopropyl bond of the predominant valence isomer (159a) or directed electrophilic attack at C₄ or C₆ (Scheme XX). One

Scheme XX

• denotes deuterium
hypothetical route leads directly to 195, while the other requires subsequent heterolytic opening of that strained four-membered ring which contains the metal. A feasible conversion of 195 to product triene is illustrated without belaboring the details.

In ancillary studies, it was noted that benzosemibullvalene and 1,5-dimethylsemibullvalene are not prone to rearrangement with the above catalyst systems. On the other hand, annulated hydrocarbon 66 also undergoes the predescribed structural change when treated with anhydrous p-toluenesulfonic acid in dry benzene. A second product is now simultaneously formed in 10% relative yield, the structure of which proved to be identical with that of the compound formed exclusively upon silver-catalyzed rearrangement (vide infra). p-Toluene-sulfonic acid is seemingly unique in the sense that it represents the only reagent studied which would partition 66 simultaneously along two rearrangement channels.

Silver(I)-Catalyzed Isomerization. The unique ability of silver(I) ion to promote unparalleled rearrangement of bicyclo[1.1.0]butanes and cubyl systems has been amply demonstrated. Its intrinsic electronic properties induce structural perturbations which are not frequently matched by other catalysts. This general characteristic of Ag⁺ is demonstrated by the reaction of 66 with catalytic amounts of anhydrous silver perchlorate in dry benzene. After 30 min at room temperature, a single new isomeric compound was produced. The colorless oil (in isooctane) displays an intense ultraviolet maximum at 243 nm.
revealing thereby the presence of a heteroannular 1,3-diene system. Noteworthy pmr features (Figure 9) are the five olefinic protons seen as a trio of multiplets at δ 5.85-6.20 (2H), 5.60-5.84 (2H), and 5.44-5.60 (1H), one doubly allylic hydrogen (2.75-3.05, m), and a pair of allylic protons (2.05-2.45, m). The hydrocarbon was unreactive toward N-phenyltriazolinedione, tetracyanoethylene, and rhodium dicarbonyl acetonilactonate. Epoxidation with m-chloroperbenzoic acid at 0° gave three thermally labile epoxides which defied characterization. These data together with double resonance decoupling experiments were compatible with the structural features of 197 and 198.

![Structures 197 and 198](image)

Catalytic hydrogenation served to distinguish between these possibilities. When the isomerization product was reduced with 5% palladium on carbon in absolute ethanol, ethyl acetate, or tetrahydrofuran, two C12H20 compounds were produced in a constant ratio of 6.5:1. Because saturation of the double bonds in 198 can give rise only to a single hexahydro product, this triene can now be dismissed as the correct structure.
That 197 did indeed possess the indicated tricyclic skeleton was confirmed by the independent synthesis of its perhydro derivatives (201 and 202, Scheme XXI). One of the isomers had been previously described by Haworth and coworkers, but unfortunately its infrared spectrum proved to be no longer available. However, catalytic hydrogenation of dienone 199 and subsequent Wolff-Kishner reduction of 200 furnished the same two hydrocarbons in a 1:1.3 ratio. The high resolution infrared and 100 MHz pmr spectra of the first components from the two reductions were superimposable. Elucidation of the relative stereochemistry of the isomeric pair was not attempted.

The analogous rearrangement of 199 led to the dideuterated counterpart of 197. The most revealing features of its 100 MHz pmr spectrum (Figure 10) were the absence of two olefinic protons, one each from the δ 5.85-6.20 and 5.60-5.84 sets of 197, and simplification of the doubly allylic bridgehead hydrogen signal to a broadened triplet. Upon double irradiation of the C₃ methylene region (δ 1.8), the bridgehead proton absorption collapsed to a doublet (J = 6 Hz). The 4,6-d₂ and 3,7-d₂ isomers (cf 197 for numbering) could thereby be excluded. Because the high field olefinic signal due to H₃ remains present, labeling at that site is also precluded. If the deuterium atoms were positioned at the 4,7 or 3,6 sites, then H₃ and H₇, respectively, should be displayed as unsplit or very weakly coupled peaks. This is not seen. To distinguish between the remaining two alternatives (203 and 204), information compiled from spin decoupling studies on
Scheme XXI

\[ \text{Compound A} \xrightarrow{\text{CHO, base}} \text{Compound B} \xrightarrow{\text{Zn(Hg)}_x, H^+} \text{Compound C} \]

\[ \begin{align*}
1) & \text{CsHsN'HCl} \\
2) & \text{NaH} \\
3) & \text{CeHsCHgCl} \\
\end{align*} \]

\[ \begin{align*}
\text{Compound B} \xrightarrow{\text{LIAIH}_4} \text{Compound D} \xrightarrow{\text{TsCl}} \text{Compound E} \xrightarrow{\text{H}_2/\text{Pd-C}} \text{Compound F} \\
\end{align*} \]

\[ \begin{align*}
\text{t-BuOK} & \xrightarrow{\text{t-BuOH}} \text{Compound G} \\
\text{H}_2 \xrightarrow{\text{Pd-C}} \text{Compound H} \xrightarrow{\text{KOH}} \text{Compound I} \\
\end{align*} \]

\[ \begin{align*}
\text{Compound G} & \xrightarrow{\text{H}_2} \text{Compound J} \\
\text{Compound H} & \xrightarrow{\text{H}_2\text{NNH}_2} \text{Compound K} \\
\end{align*} \]

\[ \begin{align*}
\text{Compound L} \xrightarrow{\text{H}_2/\text{Pd-C}} \text{Compound M} \\
\end{align*} \]
together with literature data for the parent bicyclo[3.2.1]octa-2,6-diene system was submitted to LAOCOON III computer simulated analysis. Although a close spectral match was achieved for 197 and 203, several minor differences in signal intensities discouraged us from concluding only on this basis that 203 was the actual isomerization product.

A definitive resolution of the question was achieved by cmr spectroscopy. Table XII gives the carbon chemical shifts for 2-methylenebicyclo[3.2.1]oct-3-ene (205) and 2-methylenetetacyclo[3.2.1]octa-3,6-diene (206), the additional double bond in the latter causing C2 and C4 to appear at somewhat higher field. A similar phenomenon is
Table XII. Cmr Chemical Shift Data.

<table>
<thead>
<tr>
<th>Compound</th>
<th>C₂</th>
<th>C₃,C₄</th>
<th>C₆,C₇</th>
<th>C₉</th>
<th>Tetrahedral carbons</th>
</tr>
</thead>
<tbody>
<tr>
<td>205</td>
<td>153.0</td>
<td>127.2, 138.1</td>
<td>-------</td>
<td>106.2</td>
<td>31.2, 34.0, 36.3, 37.6, 43.3</td>
</tr>
<tr>
<td>206</td>
<td>144.5</td>
<td>126.1, 130.7</td>
<td>134.4, 138.4</td>
<td>110.3</td>
<td>40.7, 44.9, 48.6</td>
</tr>
<tr>
<td>197</td>
<td>137.7</td>
<td>126.0, a</td>
<td>133.3, 136.1</td>
<td>125.4 a</td>
<td>20.4, 26.1, 32.6, 41.4, 48.6, 50.4</td>
</tr>
<tr>
<td>203</td>
<td>137.7</td>
<td>126.0, a</td>
<td>132.0</td>
<td>b</td>
<td>125.4 a</td>
</tr>
</tbody>
</table>

*May be interchanged.

*Signals greatly diminished and split due to C-D coupling.*
observed in the bridged system \( \text{127} \), the alkyl chain further perturbing \( \text{C}_2 \) and \( \text{C}_3 \) in the expected manner. In the deuterium labeled product, significant loss of signal for the 136.1 and 133.3 ppm peaks is seen as a result of C-D coupling at \( \text{C}_6 \) and \( \text{C}_7 \). Structural assignment \( \text{203} \) is thereby confirmed.

A grossly reasonable but untested mechanism for the rearrangement of \( \text{159} \) to \( \text{203} \) involves initial bonding of Ag\(^+\) to a permanently olefinic carbon of the semibullvalene nucleus (Scheme XXII). Either of the resulting homoallylic cations (\( \text{207} \) or \( \text{209} \)) can converge by minimum electron redistribution pathways to dicyclopropylcarbinyl species \( \text{208} \), the inherent stabilization in which is difficult to assess but may be sufficient to dismiss \( \text{207} \) and \( \text{209} \) as true intermediates. The hypothetical mechanism is completed by proton loss from \( \text{208} \) to give triene \( \text{210} \), protolytic cleavage of the C-Ag bond in which provides suitably labeled product and regenerates the catalytic agent.

The semibullvalene nucleus has for the last sixteen years been a molecule of theoretical interest. Its unique structural features which enhance the Cope rearrangement have been exhaustively discussed in Part I. The work described in this section has demonstrated that this \( \text{C}_6\text{H}_9 \) framework can also be of synthetic use. The gas phase pyrolysis experiments have demonstrated the stereospecific formation of substituted cyclooctatetraenes, in particular the conversion of a \( \text{m,n}-\text{dialkylsemibullvalene} \) to a \( \text{m,n}-\text{dialkylcyclooctatetraene} \). Another example is semibullvalene \( \text{211} \).
Scheme XXII

\[ \text{Scheme XXII} \]

\[ \begin{align*}
\text{159a} & \xrightarrow{\text{Ag}^+} \text{207} \\
\text{208} & \xleftarrow{\text{Ag}^+} \text{209} \\
\text{210} & \xrightarrow{\text{Ag}^+} \text{203}
\end{align*} \]

- denotes deuterium
The photolysis work has laid the foundation for the study of degenerate photoisomerizations of semibullvalenes, a possible synthetic method for obtaining otherwise inaccessible semibullvalenes. That the parent system could be easily studied in this reaction is witnessed by the preparation of the dideuterio derivative 212 (prepared in an analogous manner as 1,5-dimethylsemibullvalene, Scheme XV, except for the substitution of LiALD₄ for LiALH₄). If the mechanism in

Scheme XIX operates to any significant extent then pmr analysis will show deuterium scrambling.

The latent reactivity of the semibullvalene nucleus towards mild Lewis acids is no doubt facilitated by alkyl substitution at suitable points in the molecular framework, since proton loss from these groups
is evidenced. The most striking behavior in these reactions is their specificity. Alumina and related catalysts give rise to a $\text{C}_{12}\text{H}_{14}$ isomer with a bicyclo[3.3.0]octane framework, while silver(I)-catalysis produces an isomer with a bicyclo[3.2.1]octane structure. No doubt this is just another example of the intrinsic ability of silver(I) ion to promote unique molecular rearrangements.
Figure 9. The 100 MHz pmr spectrum of 197 in CDCl₃ at 1000 Hz sweep width.

Figure 10. The 100 MHz pmr spectrum of 203 in CDCl₃ at 1000 Hz sweep width.

Figure 11. The 100 MHz pmr spectrum of 190 in CDCl₃ at 1000 Hz sweep width.
EXPERIMENTAL

Melting points were determined in open capillaries with a Thomas-Hoover apparatus and are corrected, while boiling points are uncorrected. Proton magnetic resonance spectra were obtained on Varian A60-A, Varian HA-100, and Jeolco MH-100 instruments, while carbon magnetic resonance spectra were obtained with a Bruker 90 spectrometer. Apparent splittings are given in all cases. Infrared spectra were recorded on Perkin Elmer model 137 and 467 instruments, whereas mass spectra were recorded on an AEI-MS9 spectrometer at an ionizing potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. The drying of organic solutions was accomplished with magnesium sulfate unless otherwise indicated. Hexamethylphosphoramide (HMPA) and dimethyl sulfoxide (DMSO) were dried before use by distillation over calcium hydride and storage over molecular sieves. The following tubular aluminum columns were employed in the preparative glpc separations: A, 4 ft x 0.25 in. 5% SF-96 on 60/80 mesh Chromosorb G; B, 1 ft x 0.25 in. 5% SF-96 on 60/80 mesh Chromosorb G; C, 3 ft x 0.25 in. 5% Carbowax 20M on 60/80 mesh Chromosorb G; D, 6 ft x 0.25 in. 5% Carbowax 20M on 60/80 mesh Chromosorb G; E, 5 ft x 0.25 in. 5% SE-30 on 60/80 mesh Chromosorb G; F, 5 ft x 0.25 in. 5% PME (5-ring) on 60/80 mesh Chromosorb G; G, 3.5 ft x 0.25 in. 5% PME (5-ring) on 60/80 mesh Chromosorb G; H, 11.5 ft x 0.25 in. 8% Carbowax 20M on 60/80 mesh Chromosorb G.
To a stirred solution of ethyl cyclopentanone-2-carboxylate (117 g, 0.750 mol) in 250 ml of ether was added 146 g (2.25 mol) of potassium cyanide. After the mixture had been cooled in an ice bath, 207 ml (2.25 mol) of concentrated hydrochloric acid was added over a period of 1 hr under nitrogen, and stirring was maintained for 1 hr at 0° and for 1/4 hr at ambient temperature. After the residual hydrogen cyanide had been removed by entrainment with nitrogen, the yellow organic layer was separated and the aqueous phase was washed with ether (3 x 150 ml). The combined organic layers were washed with sodium carbonate solution, water, and brine. After drying and ether removal, the crude cyanohydrin was dissolved in 178 g of cold pyridine and treated with 268 g (2.25 mol) of thionyl chloride during 1 hr at 0° under nitrogen. After the solution had been stirred at room temperature for 12 hr, it was carefully poured into 3 liters of ice and water and extracted with ether (6 x 200 ml). After processing as above, the residual oil was distilled to give 112.8 g (91%) of ethyl 1-cyanocyclopentene-2-carboxylate, bp 84-85° (0.5 mm) [lit. bp 132° (11 mm)]; ν\text{max} \text{cm}^{-1} 2950, 2225, 1725, 1220, and 764 cm\textsuperscript{-1}.

A 60.0-g sample (0.364 mol) of this cyano ester was added to 100 ml of concentrated hydrochloric acid and the resulting mixture was refluxed with stirring for 2 hr. Water (100 ml) was introduced and reflux...
was resumed for an additional 2.5 hr. The diacid was collected by filtration and dried over potassium hydroxide at 0.1 mm. There was obtained 49.0 g (86.4%) of cyclopentene 1,2-dicarboxylic acid, mp 174.5-176.5° (lit mp 178°); $\delta_D^{35}$ 2.88 (t, $J = 7$ Hz, 4, allylic) and 1.94 (m, 2, methylene).

A solution of 78 g (0.5 mol) of the diacid in 200 ml of acetic anhydride was heated at reflux with stirring for 4 hr. After cooling, the solution was removed by distillation at 10 mm and the residue was subsequently fractionated to give 64.2 g (93.0%) of the white crystalline anhydride, bp 92-94° (0.3 mm), mp 178-180° [lit bp 130° (5 mm)]; $\nu_{\text{max}}^{\text{CHCl}_3}$ 3000, 1850, 1775, 1670, 1320, 1085, and 874 cm$^{-1}$.

A mixture of 27.6 g (0.20 mol) of cyclopentene 1,2-dicarboxylic anhydride ($\text{I}$), 20 ml of dioxane, and 147 g (2.73 mol) of butadiene was heated in a heavy wall sealed glass vessel at 120° for 12 hr. The cooled reaction mixture was evaporated to remove the volatiles and the residue was crystallized from chloroform-hexane to furnish 35.5 g (92.1%) of $\text{I}_5$, mp 117-118° (lit mp 122° from hexane); $\nu_{\text{max}}^{\text{CHCl}_3}$ 2950, 1850, 1790, 1450, and 970 cm$^{-1}$; $\delta_{\text{CDCl}_3}^{\text{TMS}}$ 6.04 (pent, $J = 1.8$ Hz, 2, olefinic) and 1.68-3.00 (br m, 10, allyl and methylenes).

cis-1,6-Bis(hydroxymethyl)bicyclo[4.3.0]non-3-ene ($\text{I}_6$). To a slurry of 38 g (1 mol) of lithium aluminum hydride in 1.5 liters of anhydrous tetrahydrofuran was added dropwise under nitrogen a solution of $\text{I}_5$ (129 g, 0.667 mol) in 1 liter of the same solvent and the mixture was refluxed for 6 hr. With ice cooling, 38 g of water, 38 ml of 30% sodium
hydroxide solution, 114 ml of water, and 5 g of anhydrous magnesium sulfate were added sequentially. The inorganic salts were filtered and twice leached with 500 ml of refluxing ether. The combined organic layers were dried and evaporated, and the residue recrystallized from chloroform-hexane to give 114.2 g (94.0%) of \( \text{46} \), mp 173-177° (lit mp 158-160° from hexane); \( \nu_{\text{max}}^{\text{CHCl}_3} \) 3400, 2960, 1065, and 1030 cm\(^{-1}\); \( \delta_{\text{TMS}}^{\text{CDCl}_3} \) 5.59 (m, 2, olefinic), 4.53 (s, 2, -OH), 3.52 (ABq, \( J_{AB} = 12.2 \) Hz, \( \Delta \nu_{AB} = 8.2 \) Hz, 4, -CH\(_2\)O-), 2.03 (m, 4, allyl), and 1.63 (br s, 6, methylenes).

cis-1,6-Bis(methanesulfonyloxymethyl)bicyclo[4.3.0]non-3-ene (47). A mechanically stirred, cold (-10°) solution of 250 g (2.0 mol) of methanesulfonyl chloride in 1 liter of pyridine was treated dropwise with a solution of \( \text{46} \) (117.2 g, 0.644 mol) in 500 ml of the same solvent. After being stirred at -5° for 3.5 hr, the mixture was treated with sufficient ice to destroy the excess sulfonyl chloride and 10% hydrochloric acid was added until distinctly acidic. The solution was allowed to stand at 0° for 1 hr, whereupon the precipitate was filtered, washed with cold water, and dried in vacuo over phosphorus
pentoxide. There was obtained 218 g (100%) of \( \text{I} \), mp 74.0-74.5° (from chloroform-hexane); \( \nu_{\text{max}}^{\text{CHCl}_3} \) 2950, 1650, 1450, 1340, 1160, and 940 cm\(^{-1}\); \( \delta_{\text{TMS}}^{\text{CDCl}_3} \) 5.65 (m, 2, olefinic), 4.15 (s, 4, \(-\text{CH}_2\text{O}-\)), 3.00 (s, 6, methyl), 2.15 (br s, 4, allyl), and 1.77 (br s, 6, methylene).

**Analytical data**

Calcd for C\(_{13}\)H\(_{22}\)O\(_5\)S\(_2\): C, 46.11; H, 6.55; S, 18.91.

Found: C, 46.17; H, 6.75; S, 18.75.

8-Thia[4.3.3]propell-3-ene (k8). Into a 2-liter three-necked flask fitted with a mechanical stirrer and distillation head was placed 98.2 g (0.95 mol) of freshly recrystallized (ethanol) sodium sulfide nonahydrate and 500 ml of anhydrous HMPA. Dehydration was achieved by distillation of the HMPA at 15 mm until the temperature of the distillate reached 135°. The dull blue solution was cooled to 40°, 105.6 g (0.313 mol) of \( \text{I} \) was added, and the mixture was heated at 120° with stirring for 18 hr. It was subsequently cooled in ice, diluted with 500 ml of water, and extracted with pentane (5 x 300 ml). The combined organic layers were washed with water (6 x 200 ml) and brine, dried, and evaporated. The viscous red liquid was redissolved in pentane (1 liter) and the solution passed through a column of neutral activity I alumina. Evaporation of the eluate afforded 53.7 g (95.4%) of \( \text{k8} \) as a white solid, mp 88-92°; \( \nu_{\text{max}}^{\text{CHCl}_3} \) 2950, 1645, 1450, 1435, 1420, and 1120 cm\(^{-1}\); \( \delta_{\text{TMS}}^{\text{CDCl}_3} \) 5.65 (t, \( J = 1.8 \) Hz, 2, olefinic), 2.78 (ABq, \( J_{\text{AB}} = 11 \) Hz,
\[ \Delta v_{AB} = 6.9 \text{ Hz}, 4, -\text{CH}_2\text{S}-, 2.12 (\text{m, 4, allyl}), \text{ and } 1.75 (\text{m, 6, methylenes}). \]

Oxidation of a small sample of this sulfide with two equivalents of m-chloroperbenzoic acid afforded the more crystalline sulfone 51, mp 136.5-137.5° (from hexane);

\[ \nu_{\text{max}} \text{CHCl}_3 2900, 1670, 1410, 1290, 1130, \text{ and } 1110 \text{ cm}^{-1}; \delta_{\text{TMS}} \text{CDCl}_3 5.76 \]

(\( \text{t, J} = 2.4 \text{ Hz}, 2, \text{ olefinic} \)), 3.07

(\( \text{s, 4, } -\text{CH}_2\text{SO}_2- \)), 2.23 (br s, 4, allyl), and 1.86 (br s, 6, methylenes).

**Anal.** Calcd for C_{11}H_{10}O_{2}S: C, 62.61; H, 7.60; S, 15.11.

**Found:** C, 62.38; H, 7.68; S, 15.04.

7-Chloro-8-thia[4,3,3]propell-3-ene 8,8-Dioxide (49). To a solution of 8.2 g (45.6 mmol) of 8 in 50 ml of carbon tetrachloride chilled to 0° was slowly added 6.4 g (47.8 mmol) of N-chlorosuccinimide. The mixture was refluxed for 6 hr, cooled, filtered, and evaporated. The residual \( \alpha \)-chloro sulfide was dissolved in 100 ml of ether and cooled to 0°. To this stirred solution was added dropwise a standardized ethereal solution containing 95.6 mmol of monoperphthalic acid and stirring at room temperature was maintained for 12 hr. The precipitated phthalic
acid was removed by filtration and the filtrate was washed with 0.5 N sodium hydroxide solution, water and brine, dried, and evaporated. There remained 10.9 g (97.7%) of 49 as a white solid, mp 107-117°. Integration of the >CHCl absorptions of the isomeric pair of α-chloro sulfones (δ 4.83 and 4.73) revealed the isomer distribution to be 39:61.

The major isomer, 49a (chlorine syn to the cyclopentane ring), was obtained in pure form by elution chromatography on silica gel (ether-petroleum ether mixtures), mp 126-128° (from hexane); δCDCl3

5.76 (m, 2, olefinic), 4.68 (s, 1, >CHCl), 3.05 (br s, 2, -CH2SO2-),
and 1.53-2.31 (br m, 10, allylic and methylenes).

Found: C, 53.60; H, 6.12; S, 12.88.

[4.3.2]Propella-3,10-diene (50). To an ice-cold magnetically stirred solution of 5.0 g (20.3 mmol) of 49 in 175 ml of anhydrous tetrahydrofuran was added 9.9 g (88.3 mmol) of commercial powdered potassium t-butoxide in one portion under nitrogen. The mixture was stirred at room temperature for 1 hr, heated at reflux for 3 hr, cooled in ice, and treated with water. Extraction with pentane, followed by washing of the combined organic layers with water and brine, drying, and careful solvent removal by distillation at atmospheric pressure through a 6-in.
metal helix-packed column gave a residual oil. If this material was subjected to distillation at reduced pressure, 1.25 g (41%) of 50, bp 67° (10 mm) was obtained; \( \nu_{\text{max}} \) 3040, 2930, 1650, 1450, 1095, 975, 883, 825, and 755 cm\(^{-1}\); \( \delta_{\text{TMS}} \) 5.72 (m, 4, olefinic), 0.9-2.47 (continuous series of multiplets, 10, allylic and saturated methylenes).

**Anal.** Calcd for C\(_{11}\)H\(_{14}\): C, 90.34; H, 9.66.

**Found:** C, 90.28; H, 9.60.

If the oil is subjected to chromatography on silica gel instead, there can be isolated in addition to 50, the \( \alpha-t \)-butoxy sulfone 53, mp 76-77° (from hexane) in 37% yield; \( \nu_{\text{max}} \) \( \text{CHCl}_3 \) 2950, 1475, 1375, 1300, 1155, 1090, and 883 cm\(^{-1}\); \( \delta_{\text{TMS}} \) 5.61 (m, 2, olefinic), 4.52 (s, 1, >CHO-), 3.04 (ABq, \( J_{AB} = 13 \) Hz, \( \Delta\nu_{AB} = 7.5 \) Hz, 2, \(-\text{CH}_2\text{SO}_2-\)), 1.84-2.30 (br m, 10, allylic and saturated methylenes), and 1.31 (s, 9, \( t \)-butyl).

**Anal.** Calcd for C\(_{15}\)H\(_{24}\)O\(_3\)S: C, 63.32; H, 8.51; S, 11.28.

**Found:** C, 63.22; H, 8.56; S, 11.37.

\[ \text{[4.3.2]Propella-2,4,10-triene (52).} \] Pyridinium hydrobromide perbromide (3.90 g, 12.2 mmol) was added in one portion to a magnetically stirred solution of 1.62 g (11.1 mmol) of 50 in 30 ml of carbon tetrachloride-acetic acid (1:1) and the mixture was stirred at room temperature with
protection from the atmosphere for 12 hr. The reaction mixture was
diluted with ether and washed sequentially with water, 0.5 N sodium
hydroxide solution, saturated sodium bicarbonate solution, water, 10% sodium thiosulfate solution, water, and brine. Drying and solvent re-
moval in vacuo (no heat) left 2.86 g (87%) of dibromide as a viscous
pale reddish oil which was used without further purification.

A solution of 10.24 g (33.5 mmol) of this dibromide in 300 ml of
dry HMPA was treated with 28.2 g (0.664 mol) of anhydrous lithium
chloride (both lithium salts were dried over phosphorus pentoxide in
vacuo before use) and 35.6 g (0.482 mol) of anhydrous lithium carbonate
and the slurry was heated at 95-100° with magnetic stirring under
nitrogen for 25 hr. After cooling, the slurry was diluted with water
and extracted with pentane. The combined organic layers were washed
with water and brine, dried, and passed through a neutral activity I
alumina column. Careful solvent removal by distillation at atmospheric
pressure through a 6-in. metal helix-packed column and removal of
the remaining traces of solvent at 20° and 20 mm gave 3.43 g (73%) of
52; \( \lambda_{\text{\text{cyclohexane}}} \ 266 \ (\epsilon \ 3380), \ 231 \ (\epsilon\ 1710), \) and \( \lambda_{\text{\text{max}}} \ 225 \ \text{nm} \ (\epsilon\ 2000); \ \nu_{\text{max}} \ 2900, \ 1445, \ 1395, \ 1220, \ 1095, \ 949, \ 763, \) and \( \\text{700 cm}^{-1}; \ \delta_{\text{CDCl}_3} \ 5.71-5.78 \)
(m, 6, olefinic) and 0.99-1.79 (br m, 6, methylenes).

Anal. Calcd for C\textsubscript{11}H\textsubscript{12}: C, 91.61; H, 8.39.

Found: C, 91.45; H, 8.54.
6,7-Dihydro-N-phenyl-1,4:4a,7a-dietheno-5H-cyclopenta[d]pyridazine-2,3(1H,4H)-dicarboximide (54). A cold (-78°) magnetically stirred solution of 52 (562 mg, 3.90 mmol) in 50 ml of acetone was treated dropwise with a solution containing 685 mg (3.91 mmol) of N-phenyltriazolinedione in 25 ml of acetone. The solution was allowed to warm to room temperature where it was kept for 1 hr and then refluxed until the red color faded. Solvent removal left a yellowish solid which was chromatographed on neutral activity I alumina. Elution with 30% chloroform in ether afforded 1.07 g (86%) of adduct 54 as a white solid, mp 253.0-253.5° (from acetone-hexane);

\[
\nu_{\text{max}}^{\text{CHCl}_3} 2930, 1770, 1710, 1490, 1400, 1260, 1135, \text{ and } 1075 \text{ cm}^{-1}; \delta_{\text{TMS}}^{\text{CDCl}_3} 7.41 (s, 5, aromatic), 6.24 (t, J = 3.8 Hz, olefinic), 5.86 (s, 2, cyclobutene), 4.87 (br t, J = 3.8 Hz, 2, >C\text{HN}<), and 1.50-2.08 (br m, 6, methylenes).
\]

**Anal.** Calcd for C19H17N3O2: C, 71.44; H, 5.37; N, 13.17.

Found: C, 71.19; H, 5.36; N, 13.05.

Tetrahydro-N-phenyl-6H-1,5a,2,5-ethanediylidenedecyclobuta[c]cyclopenta-[d]pyridazine-3,4(1H,5H)-dicarboximide (55). A solution of 1.05 g (3.22 mmol) of 54 in 350 ml of deoxygenated acetone was irradiated under a nitrogen atmosphere with a 200-W Hanovia lamp fitted with a Vycor filter for 2 hr. Solvent evaporation in vacuo left a yellow
crystalline solid which was chromatographed on neutral activity I alumina. Elution with 20% chloroform in ether gave 995 mg (92%) of 55 as a white crystalline solid, mp 203.5-204.5° (from acetone-hexane); \( \nu_{\text{max}}^{\text{CHCl}_3} \) 2990, 1775, 1700, 1510, 1420, 1325, and 1130 cm\(^{-1}\);

\[ \delta_{\text{TMS}}^{\text{CDCl}_3} 7.26-7.70 \text{ (br m, 5, aromatic), 4.96 (t, } J = 3 \text{ Hz, 2, >CHN<),} \]
\[ 3.43-3.71 \text{ (br m, 2, methine), 2.91 (br t, } J = 3 \text{ Hz, 2, methine), and 1.80 (br s, 6, methylene).} \]

**Anal.** Calcd for C\(_{18}\)H\(_{17}\)N\(_3\)O\(_2\): C, 71.44; H, 5.37; N, 13.17.

Found: C, 71.31; H, 5.45; N, 13.12.

Octahydro-N-phenyl-2H-cyclopenta[1,3]cyclopropa[1,2,3-cd]cyclopropa-
[gh]pentalene-1,5-biimine-6,7-dicarboximide (56). A 1.10 g (3.45 mmol) sample of 55 was dissolved in 300 ml of 0.2 N silver perchlorate-anhydrous benzene solution and the reaction mixture was refluxed with protection from light and atmospheric moisture (N\(_2\) atmosphere) for 108 hr with magnetic stirring. The solvent was removed in vacuo and the resulting off-white solid was leached with chloroform. The combined filtrates
were washed with water and brine, dried, and evaporated. The yellow oil so obtained was triturated with benzene to furnish 948 mg (86%) of 56 as a white crystalline solid, mp 169.5-170.5°C (from ether-hexane); $\nu_{\text{max}}^{\text{CHCl}_3}$ 2950, 1775, 1700, 1500, 1410, and 918 cm$^{-1}$; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.24-7.68 (br m, 5, aromatic), 4.96-5.11 (m, 2, $>\text{CH}_2<$), 1.88-2.04 (m, 6, methylene), and 1.38-1.82 (br m, 4, cyclopropyl).

**Anal.** Calcd for C$_{18}$H$_{27}$N$_3$O$_2$: C, 71.44; H, 5.37; N, 13.17.

Found: C, 71.08; H, 5.46; N, 13.44.

2a, 6, 7, Tb-Tetrahydro-5H-cyclopenta[1,3]cyclopropa[1,2,3-cd]pentalene (57b) $\rightarrow$ 3, 4, 5a, 5b, 5e, 5d-Hexahydro-2H-benzo[cd]cyclopropa[gh]pentalene (57a). A mixture of 1.073 g (3.37 mmol) of 56, 2.11 g (32.7 mmol) of potassium hydroxide (86.6%), and 30 ml of 2-propanol was heated to reflux for 1 hr. Upon cooling to 0°C, 3 N hydrochloric acid was added to pH 2.

The resulting violet mixture was stirred for 5 min at which point 3 N ammonium hydroxide was added at 0°C until a pH of 8 was attained. The deep bourbon colored solution was stirred for 5 min and chloroform (10 ml) together with pentane (30 ml) were added. Activated manganese dioxide (2.24 g, 28.0 mmol) was added in one portion (immediate effervescence) and the mixture was stirred at room temperature for 3 hr.
After filtration, the filtrate was washed with water (3 x 50 ml) and brine (60 ml), dried over anhydrous sodium sulfate, and carefully concentrated by distillation through a Vigreux column. Preparative vpc purification on column A at $70^\circ$ afforded 94 mg (19.4%) of the semibullvalene as a colorless liquid; $\lambda_{\text{max}}$ isooctane 240 sh nm ($\epsilon 4600$); $\nu_{\text{max}}$ neat 2950, 1625, 1450, 914, 832, and 742 cm$^{-1}$; $\delta_{\text{TMS}}$ CDCl$_3$ 4.99 (m, 2, H$_3$, H$_7$), 4.12-4.26 (m, 2, H$_4$, H$_8$), 2.73-2.93 (m, 2, bridge protons), and 1.54-2.26 (br m, 6, methylenes). Spin decoupling: saturation of the 4.99 signal collapsed the peak at 4.12-4.26 to a doublet while double irradiation of the 4.12-4.26 signal collapsed the 4.99 absorption to a singlet and slightly affected the 2.73-2.93 multiplet; calcd m/e 144.0939, observed 144.0941.

Hydrogenation of 2a,6,7,7b-Tetrahydro-5H-cyclopenta[1,3]cyclopropa[1,2,3-ed]pentalene (57b) $\equiv$ 3,4,5a,5b,5c,5d-Hexahydro-2H-benzo[cd]-cyclopropa[gh]pentalene (57a). A 58.3-mg sample (0.40 mmol) of the semibullvalene dissolved in 100 $\mu$l of anhydrous tetrahydrofuran was introduced via syringe into a hydrogen flask containing 10 ml of the same solvent and 150 mg of prereduced 5% rhodium on carbon. Hydrogen uptake was immediate and after 30 min the catalyst was separated. The filtrate was partitioned between pentane and water and the organic phase was dried and carefully distilled through a 6-in. Vigreux column to remove solvent. The concentrate was subjected to preparative
vpc separation (column A, 60°). Two products were isolated, the more rapidly eluted ($t_{\text{ret}} = 16$ min) being characterized as 63; $^1$H NMR (250 MHz, CDCl$_3$, TMS) 2.5 (br m, 1), 1.37-1.93 (br m, 12), and 1.26 (br m, 3); calcd m/e 148.1252, observed 148.1249.

The product of longer retention time (27.5 min) was a white solid, mp 49-52° (lit mp 50°), and was identified as 62 by direct comparison with an authentic sample; $^{13}C$ NMR (294.10, 1450, and 900 cm$^{-1}$, CDCl$_3$, TMS) 1.52 (br envelope); calcd m/e 150.1408, observed 150.1406.

Anal. Calcd for C$_{11}$H$_{18}$: C, 87.92; H, 12.08.

Found: C, 87.90; H, 11.92.

2a,5,6,7,8,8b-Hexahydrobenzo[1,5]cyclopropa[1,2,3-cd]pentalene (66a) #

2,3,4,5,6a,6b,6c,6d-Octahydrocyclohepta[cd]cyclopropa[gh]pentalene (66b).

This semibullvalene was prepared in exactly the same manner as 57, to afford 66 in a 60% yield after preparatory gcpc purification.

6,7,8,9-Tetrahydro-N-phenyl-1,4:4a,9a-dietheno-5H-cyclohepta[d]pyridazine-2,3(1H,4H)-dicarboximide (68). A solution of 41.5 mg (0.241 mmol) of 67 in 10 ml of ethyl acetate was treated dropwise at room tempera-
ture with a solution containing 42.6 mg (0.243 mmol) of N-phenyl-triazolinedione in 10 ml of ethyl acetate under nitrogen. After the red solution had been refluxed for 18 hr under nitrogen, 5 ml of ethanol was added, the pale yellow solution was allowed to cool to room temperature, and the solvent was removed in vacuo. The yellow oil so obtained was chromatographed on silica gel (elution with methylene chloride) to afford 78.4 mg (94%) of 68 as a white solid, mp 240.0-241.5° (from methylene chloride-hexane); ν<sub>max</sub><sup>CHCl<sub>3</sub></sup> 2900, 1770, 1700, 1600, 1260, and 908 cm<sup>-1</sup>; δ<sub>TMS</sub><sup>CDCl<sub>3</sub></sup> 7.48 (br s, 5, aromatic), 6.28 (t, J = 4 Hz, 2, olefinic), 5.96 (s, 2, cyclobutene), 4.60 (t, J = 4 Hz, 2, >CHN<), and 1.50-2.30 (m, 10, methylene).

Anal. Calcd for C<sub>21</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub>: C, 72.60; H, 6.09; N, 12.09.
Found: C, 72.38; H, 6.07; N, 12.08.

Hexahydro-N-phenyl-6H-1,5a,2,5-ethanediylidenecyclobuta[c]cyclohepta[d]pyridazine-3,4(1H,5H)-dicarboximide (69). A solution of 1.50 g (4.33 mmol) of 68 in 350 ml of acetone was deaerated with nitrogen and irradiated with a 200-W Hanovia lamp (Vycor filter) for 2 hr. The solvent was removed in vacuo and the residual solid was chromatographed on neutral activity I alumina
(elution with 10% chloroform in benzene) to furnish 1.0 g (67%) of 69 as a white crystalline solid, mp 227.5-228.5° (from methylene chloride-hexane); \( \nu_{\text{max}}^{\text{CHCl}_3} \) 2900, 1769, 1700, and 1410 cm\(^{-1}\); \( \delta^{\text{CDCl}_3} \) 7.1-7.6 (br m, 5, aromatic), 4.6 (br t, \( J = 4 \) Hz, 2, >\( \text{CHN}< \)), 3.5 (m, 2, methine), 2.84 (t, \( J = 3 \) Hz, 2, methine), and 1.2-2.1 (m, 10, methylenes).

**Anal. Calcd for C$_{21}$H$_{21}$N$_3$O$_2$:** C, 72.60; H, 6.09; N, 12.09.

**Found:** C, 72.74; H, 6.08; N, 12.02.

Decahydro-N-phenyl-2H-cyclohepta[1,3]cyclopropa[1,2,3-cd]cyclopropa-[gh]pentalene-1,7-bilimine-8,9-dicarboximide (70). A solution containing 740 mg (2.13 mmol) of 69, 30 g (176 mmol) of silver nitrate, and 200 ml of isopropyl alcohol-water (4:1) was refluxed with magnetic stirring for 16 days in the absence of light, cooled, and diluted with methylene chloride. The organic phase was washed with water and brine, dried, and evaporated. Recrystallization of the residue from methylene chloride-hexane afforded 487 mg (66%) of 70 as a white crystalline solid, mp 156-157°; \( \nu_{\text{max}}^{\text{CHCl}_3} \) 2900, 1750, 1700, 1400, 1130, and 909 cm\(^{-1}\); \( \delta^{\text{CDCl}_3} \) 7.23-7.68 (br m, 5, aromatic), 4.70-4.91 (m, 2, >\( \text{CHN}< \)), and 1.10-2.17 (m, 14, cyclopropyl and methylenes).

**Anal. Calcd for C$_{21}$H$_{21}$N$_3$O$_2$:** C, 72.60; H, 6.09; N, 12.09.

**Found:** C, 72.72; H, 6.09; N, 12.11.
2a,6,7,8,9,9b-Hexahydro-5H-cyclohepta[1,3]cyclopropa[1,2,3-cd]pentalene (71b) \[ \overset{\text{H}}{\text{C}} \] 3,4,5,6,7a,7b,7c,7d-Octahydro-2H-cycloocta[cd]cyclopropa[gh]-
pentalene (71a). A mixture of 281 mg (0.81 mmol) of 70, 719 mg (11.2
mmol) of potassium hydroxide (86.6%), and 15 ml of 2-propanol
was heated at reflux for 1 hr under completely anaerobic conditions,
cooled to 0°C, and treated slowly with 3 N hydrochloric acid until a pH of 2 was reached.
The acidic solution was stirred for 5 min and the pH was adjusted to 8
with 3 N aqueous ammonia. Pentane (10 ml) and methylene chloride (10
ml) were carefully introduced, followed by 802 mg (9.22 mmol) of active
manganese dioxide. After this mixture had been stirred at room tempera-
ture for 4.5 hr, it was filtered through Celite, washed with water and
brine, dried over anhydrous sodium sulfate, and evaporated in vacuo to
afford a yellow mixture. Filtration afforded 100 mg (0.312 mmol) of
white solid which was identified as 72; \( \nu_{\text{max}}^{\text{CHCl}_3} \) 3180, 2980, 2880, 1770,
1600, 1540, 1450, 1320, 1110, and 911 cm\(^{-1}\); \( \delta_{\text{TMS}}^{\text{CDCl}_3} \) 8.6 (br s, 1,
>NNH<), 6.8-7.6 (series of multiplets, 5, aromatic), 4.78 (d, J = 5
Hz, 1, >CHNH<), 3.78 (br, 1, >NH), 3.58 (d, J = 5 Hz, 1, >CHNNH<), and
0.6-2.2 (m, 13, cyclopropyl and methylenes); calcd m/e 321.1844, ob-
served 321.1844. Preparative vpc isolation of the filtrate (column B3,
column temperature 65°; detector temperature 95°, injector temperature 75° flow rate = 350 cc/min) yielded 54.4 mg (64% based on unrecovered 72) of the semibullvalene as a very light yellow oil; λ_{max}^\text{isoctane} 238 nm (ε 3600); λ_{max}^\text{neat} 3040, 2900, 1430, 1325, 1250, 935, 860, 800, 732, and 722 cm⁻¹; δ_{TMS}^{CDCl₃} (35°) 4.98 (d, J = 2.7 Hz, 2, olefinic), 3.78-3.90 (m, 2, cyclopropyl-olefinic), 2.90-3.10·(m, 1, outer methine), 2.78 (d, J = 6 Hz, 1, inner methine), 2.38-2.65 (m, 4, allylic), and 1.40-2.10 (m, 6, methylene); calcd m/e 172.1252, observed 172.1254.

3-Carbomethoxytetrahydrofuran-4-one (74). A mixture of 70% glycolic acid (456 g, 4 mol) in 400 ml of benzene was dehydrated by azeotropic distillation (Dean-Stark trap).

The anhydrous mixture was diluted with 600 ml of methanol and 4 ml of concentrated sulfuric acid and refluxed for 36 hr under nitrogen. The resulting yellow solution was neutralized with sodium bicarbonate and distilled to afford 283 g (79%) of methyl glycolate, bp 76-82°/60-65 mm (lit 76-80°/60-65 mm).

To a gray mixture of pentane-washed sodium hydride (57% on mineral oil, 50.5 g, 1.2 mol) in 1 liter of anhydrous tetrahydrofuran was added at reflux 108 g (1.2 mol) of methyl glycolate (73) under nitrogen. After the hydrogen evolution had ceased, the stirred, ice-cold solution was diluted with a solution of distilled methyl acrylate (110.3 g, 1.24 mol) in 400 ml of dry DMSO and stirred overnight at room temperature.
The dark solution was again cooled (0°), quenched with 500 ml of cold 2 N hydrochloric acid, and diluted to a volume of 3 liters with water. The organic layer was separated and dried while the aqueous layer was continuously extracted with ether (20 hr). The combined organic solvents were removed in vacuo to afford after fractional distillation 97.2 g (56%) of 74, bp 70-75°/1 mm (lit. bp 57-58°/0.15 mm); $\nu_{\text{max}}^{\text{neat}}$ 1770 and 1730 cm$^{-1}$.

3-Carbomethoxy-4-cyano-2,5-dihydrofuran (75). To a stirred solution of sodium cyanide (1.12 g, 2.3 mol) in 100 ml of water was added 110 g (0.76 mol) of 74 in 1 liter of ether. After this mixture had been cooled in an ice bath, 132 ml of 18 N sulfuric acid was added over a period of 1.5 hr. After stirring the room temperature solution overnight, the excess hydrogen cyanide was removed under reduced pressure. The organic solution was decanted from the salts which were washed twice with benzene. After drying and solvent removal, the crude cyanohydrin ($\nu_{\text{max}}^{\text{neat}}$ 3400 and 1730 cm$^{-1}$) was dissolved in 182 g of cold pyridine and treated with 274 g (2.3 mol) of thionyl chloride during 1.5 hr at 0° under nitrogen. The resulting red solution was warmed to room temperature, stirred for 6 hr, slowly poured into 1.5 liters of ice and water, and extracted with benzene. The combined extracts were dried and concentrated in vacuo to afford after short path distillation (80°/
0.6 mm) 96 g (82%) of light yellow solid. Further purification by recrystallization (ether) afforded white crystals, mp 71-72°C; \( \nu_{\text{CHCl}_3} \) max 3020, 2960, 2860, 2240, 1740, 1295, and 1278 cm\(^{-1}\); \( \delta_{\text{TMS}} \) 4.9 (s, 4, -CH\(_2\)-) and 3.86 (s, 3, -OCH\(_3\)).

Anal. Calcd for C\(_7\)H\(_7\)NO\(_3\): C, 54.90; H, 4.61.

Found: C, 55.21; H, 4.74.

2,5-Dihydrofuran-3,4-dicarboxylic Acid (75). A solution of crude 75 (83.5 g, 0.546 mol) in 500 ml of concentrated hydrochloric acid was heated to reflux to afford a tan solid. Continued heating afforded a brown solution which was diluted with 300 ml of water and refluxed for an additional hour. Filtration of the ice-cold mixture afforded 67.4 g (78%) of 75, mp 179-188°C.

In a similar manner, 15.3 g (0.1 mol) of recrystallized 75 was converted to 13.1 g (83%) of 75, mp 191-195°C. Recrystallization from ethyl acetate afforded white crystals, mp 191-195°C.

Anal. Calcd for C\(_8\)H\(_9\)O\(_3\): C, 45.58; H, 3.83.

Found: C, 45.54; H, 3.90.

2,5-Dihydrofuran-3,4-dicarboxylic Anhydride (79). A solution of 76 (700 mg, 4.43 mmol) in 15 ml of acetic anhydride was refluxed for 3.5 hr, cooled, and removed of acetic anhydride in vacuo. Kugelrohr distillation (100-150°C/0.2 mm) afforded 500 mg (80.5%) of white solid. Further
purification by sublimation (80°/0.02 mm, mp 117-121°) or by crystallization (chloroform, mp 135-138°) afforded material which darkened after standing on the shelf; $\nu_{\text{max}}^{\text{CHCl}_3} 1860$ and $1790\text{ cm}^{-1}$; $\delta^{\text{CDCl}_3} 4.9$ (s); calcd m/e 140.0109, observed 140.0112.

3,4-Bis(chloroformyl)-2,5-dihydrofuran ($\mathbf{77}$). A mixture of crude $\mathbf{76}$ (2.0 g, 12.6 mmol) in 10 ml of thionyl chloride was slowly warmed to reflux. After the diacid had dissolved, reflux was continued for an additional 2 hr. The usual workup afforded 1.8 g (74%) of $\mathbf{77}$ as a yellow liquid, bp 80°/0.5 mm; $\nu_{\text{max}}^{\text{neat}} 1770\text{ cm}^{-1}$ (br); $\delta^{\text{CDCl}_3} 5.8$ (s).

The pmr spectrum also showed the presence of $\mathbf{72}$ (11%).

cis-1,6-Bis(chloroformyl)-8-oxabicyclo[4.3.0]non-3-ene ($\mathbf{78}$). A mixture of $\mathbf{77}$ (1.8 g, 9.25 mmol), 10 ml of benzene, a few crystals of hydroquinone, and 10 ml of butadiene was heated in a heavy wall sealed glass vessel at 105° for 12 hr. The cooled reaction mixture afforded
after distillation 2.2 g (95%) of 78, bp 120°/0.3 mm, as a liquid
which solidified upon standing; ν\text{neat} \text{max} 1780 cm\(^{-1}\), 8\text{CDCl}_3 5.7 (s, 2, olefinic), 4.16 (ABq, J\text{AB} = 9 Hz, Δν\text{AB} = 50.2 Hz, 4, -CH_2O-), and 2.64
(m, 2, allylic).

The pmr spectrum also contained absorptions due to the adduct of
79.

cis-1,6-Bis(hydroxymethyl)-8-oxabicyclo[4.3.0]non-3-ene (80). To a
refluxing slurry of lithium aluminum hydride (0.57 g, 15 mmol) in
20 ml of anhydrous tetrahydrofuran was added dropwise under nitrogen
2.2 g (8.87 mmol) of crude 78 in
15 ml of the same solvent and the
mixture was refluxed for 2.5 hr. After quenching the stirred, ice-cold
slurry with a saturated sodium sulfate solution, the white salts were
removed by filtration and leached with hot tetrahydrofuran. The com-
bined filtrates were dried and evaporated to afford 1.5 g (92%) of 80
as a yellow solid, mp 181.5-185°. Further purification by recrystalli-
zation (chloroform-ether-hexane) afforded white needles, mp 193-195°;
ν\text{KBr} 3340 (br), 3035, and 2890 cm\(^{-1}\); 8\text{CDCl}_3 5.66 (m, 2, olefinic),
4.6 (br s, 2, -OH), 3.72 (ABq, J\text{AB} = 9 Hz, Δν\text{AB} = 18.3 Hz, 4, -CH_2O-),
3.64 (br s, 4, -CH_2OH), and 1.9-2.36 (br m, 4, allylic).
cis-1,6-Bis(methanesulfonyloxymethyl)-8-oxabicyclo[4,3,0]non-3-ene (81).  

A mechanically stirred cold (-10°) solution of methanesulfonyl chloride (195 g, 1.7 mol) in 1.5 liters of pyridine was treated dropwise with a solution of 103.2 g (0.562 mol) of recrystallized 80 in 1 liter of the same solvent under a nitrogen blanket. After being stirred at -5° for 3 hr, the mixture was quenched with sufficient ice to destroy the excess sulfonyl chloride and diluted to ca 7 liters with cold 10% hydrochloric acid (pH 1). The solution was allowed to stand at 0° for 1-2 hr, whereupon the precipitate was filtered, washed with cold water, and dried in vacuo (0.02 mm) at room temperature for 24 hr. There was obtained 183.7 g (96%) of 81, mp 103-104.5°. Further purification by recrystallization (chloroform-ether) afforded white crystals, mp 106.5-107°; νKBr 1345, 1170, 945, 843, and 830 cm⁻¹; νCDCl3 5.74 (br t, J = 1.5 Hz, 2, olefinic), 4.25 (s, 4, -CH₂SO₂Me), 3.85 (ABq, JAB = 8.8 Hz, ΔνAB = 11.7 Hz, 4, -CH₂-O-), 3.06 (s, 6, -O₂SO₂CH₃), and 2.26 (br s, 4, allylic).

Anal. Calcd for C₁₂H₂₀O₇S₂:  C, 42.34; H, 5.92; S, 18.84.

Found:  C, 42.23; H, 5.90; S, 18.82.

8-Oxa-11-thia[4,3,3]propell-3-ene (82). A mixture of recrystallized (ethanol) sodium sulfide nonahydrate in 3 liters of DMSO was dehydrated by means of vacuum distillation (maximum distillate temperature 85°/50
To this cooled yellow mixture was added 291 g (0.856 mol) of recrystallized \( \text{II} \) in one portion under nitrogen and the mixture was heated to 120° for 18 hr. The mixture was again cooled (0°), diluted to a volume of 4 liters with cold water, and extracted with ether (7 x 500 ml). The combined ethereal extracts were washed with brine, dried, and concentrated in vacuo to afford a clear liquid which after column chromatography on neutral activity I alumina (ether elution) amounted to 133 g (85%) of solid, mp 82-85°. A small portion of this solid was sublimed at 100°/25 mm to afford \( \text{III} \) as a white solid, mp 93.5-95.5°; \( \nu_{\text{CHCl}_3} \) 2920, 2860, 1430, and 1035 cm\(^{-1}\); \( \delta_{\text{TMS}} \) 5.72 (br t, J = 2 Hz, 2, olefinic), 3.76 (ABq, \( J_{AB} = 9 \) Hz, \( \Delta \nu_{AB} = 9.2 \) Hz, 4, -CH\(_2\)O-), 2.86 (ABq, \( J_{AB} = 12 \) Hz, \( \Delta \nu_{AB} = 7.1 \) Hz, 4, -CH\(_2\)S-), and 2.22 (m, 4, allylic); calcd m/e 182.0765, observed 182.0768.

Oxidation of a small sample of the sublimed sulfide with two equivalents of a standardized monoperphthalic acid solution afforded the more crystalline sulfone, mp 154.5-155.5° (chloroform-hexane); \( \nu_{\text{CHBr}} \) 2860, 1320, 1300, 1230, 1174, 1123, 938, 711, 705, and 485 cm\(^{-1}\); \( \delta_{\text{TMS}} \) 5.86 (m, 2, olefinic), 3.79 (ABq, \( J_{AB} = 9 \) Hz, \( \Delta \nu_{AB} = 22.8 \) Hz, 4, -CH\(_2\)O-), 3.13 (ABq, \( J_{AB} = 13.3 \) Hz, \( \Delta \nu_{AB} = 15.4 \) Hz, 4, -CH\(_2\)SO\(_2\)-), and
2.10-2.60 (series of multiplets, \( \Delta \), allylic).

\textbf{Anal.} Calcd for C_{10}H_{15}O_{3}S: C, 56.05; H, 6.59; S, 14.96.
Found: C, 55.90; H, 6.47; S, 14.85.

7-Chloro-11-oxa-8-thia[4.3.3]propell-3-ene 8,8-Dioxide (84). To a solution of 27.3 g (150 mmol) of 82 in 225 ml of ice-cold carbon tetrachloride was added 21.0 g (157.5 mmol) of recrystallized N-chlorosuccinimide in one portion under nitrogen. After stirring at 0° for an additional 30 min, the solution was allowed to warm to room temperature for 2 hr. Removal of the succinimide and evaporation of the solvent afforded a waxy residue which was dissolved in 1 liter of anhydrous ether. To this ice-cold ethereal solution was added dropwise a standardized ethereal solution containing 0.315 mol of monoperphthalic acid under nitrogen. After this solution had been stirred at room temperature overnight, the precipitated phthalic acid was removed by filtration and the filtrate was washed with 0.5 N sodium hydroxide solution, brine, and dried. Solvent removal in vacuo afforded 35 g (94%) of 84 as a viscous oil; \( \nu_{\text{max}}^{\text{CHCl}_3} \) 1330, 1150, 1130, and 1060 cm\(^{-1}\); \( \delta_{\text{TMS}}^{\text{CDCl}_3} \) 5.89 (m, 2, olefinic), 4.92 and 4.70 (s, 1, \( \sim \text{CHCl} \), ratio 1:2, respectively, see text for assignment of configuration), 3.08-4.33 (continuous series of multiplets, 7, \(-\text{CH}_2\text{O}-\) and \(-\text{CH}_2\text{SO}_2\text{O}^+\)), and 2.3 (br s, 4, allylic); calcd m/e 248.0274, observed 248.0277. The pmr spectrum contained added absorptions due to the presence of \( \delta_{\text{TMS}} \) in 82.
8-Oxa[4,3.2]propella-3,10-diene (85). To an ice-cold mechanically stirred solution of 84 (35 g, 141 mmol) in 2 liters of anhydrous tetrahydrofuran was added 63.0 g (0.564 mol) of commercial powdered potassium t-butoxide in one portion under nitrogen. After stirring for 30 min at 0°, the solution was refluxed for 4 hr. The cooled dark solution was diluted with 2 liters of cold water and extracted with pentane (8 x 200 ml). The combined extracts were washed with brine, dried, and concentrated in vacuo to afford a viscous oil, which after vacuum distillation afforded 8.1 g (39%) of 85 as a clear liquid, bp 72°/5 mm. Further purification by preparatory glpc on column C at 85° (100 cc/min), t<sub>ret</sub> = 18 min, afforded 85 as a clear liquid; ν<sub>max</sub> 3300, 2910, 2830, 1080, 1035, and 779 cm<sup>-1</sup>; δ<sub>CDCl<sub>3</sub></sub> 5.94 (s, 2, cyclobutenyl), 5.80 (dd, J = 3, 2.5 Hz, 2, olefinic), 3.47 (ABq, J<sub>AB</sub> = 9.3 Hz, Δν<sub>AB</sub> = 42.2 Hz, 4, -CH<sub>2</sub>O-), and 2.12 (m, 4, allylic).

Anal. Calcd for C<sub>10</sub>H<sub>12</sub>O: C, 81.04; H, 8.16.

Found: C, 80.65; H, 8.49.

There was also obtained isomer 92 in 14% yield, t<sub>ret</sub> = 14 min; ν<sub>max</sub> 3025, 2920, 2835, 1040, 928, 873, and 780 cm<sup>-1</sup>; δ<sub>CDCl<sub>3</sub></sub> 5.99 (ABq, J<sub>AB</sub> = 2.5 Hz, Δν<sub>AB</sub> = 18.6 Hz, 2, cyclobutenyl), 5.6-6.08 (br m, 2, olefinic), 3.88 (dd, J = 9.5, 5 Hz, 2, -CH<sub>2</sub>O-), 3.06 (d, J = 9.5 Hz, 2, -CH<sub>2</sub>O-), 1.7-2.2 (br m, 3, methylene), 1.1-1.45 (m, 1, methylene); calcd m/e 148.0888, observed 148.0891.
8-Oxa[4,3,2]propella-2,10-diene (92). A mixture of pure 85 (48.6 mg, 0.328 mmol), 4 ml of carbon tetrachloride, 58.7 mg (0.33 mmol) of recrystallized N-bromosuccinimide, and a few granules of azobisisobutyronitrile (AIBN) was placed in a preheated oil bath (100°) and refluxed under argon. After initiation, the mixture was refluxed for an hour, cooled, filtered, and the filtrate was concentrated in vacuo to afford a clear oil. The pmr spectrum showed the presence of 85 and a broad >CHBr absorption at δ 4.2-4.8. Without further purification this oil was dissolved in 10 ml of anhydrous ether, to which was added 38 mg (1 mmol) of lithium aluminum hydride under argon. After refluxing this gray-white mixture overnight, it was cooled and quenched with a saturated sodium sulfate solution. The white salts were removed by filtration and leached with hot ether. The dried filtrate was concentrated in vacuo and subjected to preparatory glpc on column D at 130° to afford two components; the first $t_{ret} = 17$ min, 13 mg (27%), compared exactly with 92 (gc retention time, ir, and pmr); and the second, $t_{ret} = 21$ min, 18.1 mg, was starting material (gc retention time and pmr).
To a solution of distilled \(85\) (2.2 g, 14.8 mmol) in cold \(-70^\circ\) methylene chloride was slowly added under nitrogen 15.1 mmol of bromine in methylene chloride. After warming to room temperature, the solvent was removed in vacuo to afford 4.8 g of yellow semisolid which was used without further purification.

A solution of this dibromide in 100 ml of anhydrous HMPA was treated with 6.3 g (0.148 mol) of lithium chloride and 11.0 g (0.148 mol) of lithium carbonate and the stirred slurry was heated at \(90^\circ\) for 16 hr under nitrogen. After cooling, the slurry was diluted with water and extracted several times with pentane. The combined extracts were washed with brine, dried, and passed through a neutral activity I alumina column to afford after vacuum distillation 1.46 g (67\%) of \(86\) as a clear oil. Further purification by preparatory glpc on column C at \(85^\circ\) (100 cc/min) afforded one peak, \(t_{\text{ret}} \approx 20\) min, bp \(76^\circ/6\) mm;

\[\begin{align*}
\lambda_{\text{isoctane}} & 265 (\epsilon 2740), 231 (1480), 225 (1680), \text{and 218 nm (1720);} \\
\nu_{\text{max}}^\text{neat} & 3300, 2955, 2830, 1193, 1080, 1025, 923, 778, 723, \text{and 678 cm}^{-1}; \\
\delta^\text{CDCl}_3 & 5.87 (s, 2, \text{cyclobutenyl}), 5.63-6.07 (m, 4, \text{olefinic}), \text{and 3.48 (ABq, } J_{\text{AB}} = 9.5 \text{ Hz, } \Delta \nu_{\text{AB}} = 47.6 \text{ Hz, 4, } \text{-CH}_2\text{-}).
\end{align*}\]

**Anal.** Calcd for \(C_{10}H_{10}O\): C, 82.16; H, 6.90.

Found: C, 81.99; H, 7.09.
N-Methyl-5H,7H-1,4:4a,7a-dithieno[3,4-d]pyridazine-2,3(1H,4H)-
dicarboximide (94). A cold (-78°) magnetically stirred solution of
pure 86 (4.0 g, 27.4 mmol) in 100 ml of acetone was treated dropwise
with a solution of 3.1 g (27.4 mmol) of N-methyltriazolinedione in 40
ml of acetone. The resulting reddish-pink solution was warmed
to ambient temperature, refluxed
in the presence of a few milliliters of absolute ethanol, and then
cooled to room temperature. After the removal of the solvents in vacuo,
the light orange solid was dissolved in a minimal amount of chloroform
and filtered through a silica gel column (chloroform elution) to
afford 6.6 g (93%) of white solid, mp 191-196°. Further purification
by recrystallization (chloroform-ether) afforded a white solid, mp
197.5-199°; $\nu_{\text{max}}^\text{KBr}$ 2970, 2865, 1770, 1705, 1460, 1395, 1192, 1035, and
810 cm$^{-1}$; $\delta_{\text{CDCl}_3}^{\text{TMS}}$ 6.26 (dd, $J = 4.5$, 3 Hz, 2, olefinic), 6.06 (s, 2,
cyclobutenyl), 4.88 (dd, $J = 4.2$, 3.3 Hz, 2, $>\text{CHN}<$), 3.82 (s, 4, -CH$_2$O-),
and 3.02 (s, 3, >NCH$_3$).

Anal. Calcd for C$_{13}$H$_{13}$N$_3$O$_3$: C, 60.22; H, 5.05; N, 16.21.
Found: C, 59.98; H, 5.06; N, 16.22.

Dihydro-N-methyl-3H-3a,8,4,7-ethanediylidene-1H-cyclobuta[c]furo-
[3,4-d]pyridazine-5,6(4H,6aH)-dicarboximide (95). A solution of 94
(2.0 g) in 300 ml of acetone-benzene (1:1) was irradiated through
quartz under a nitrogen blanket with a 450-W Hanovia lamp filtered with a Corex filter for 2 hr. The solvents were removed in vacuo to afford crude 95. This procedure was repeated until 16 g of 94 had been irradiated. The crude 95 was chromatographed on neutral activity I alumina (petroleum ether-chloroform (3:1) elution) to yield after recrystallization (chloroform-ether) 9.3 g (58%) of white solid, mp 150-153°. Further purification by recrystallization afforded white crystals, mp 161.5-162.5° (hot bath); \( \nu_{\text{max}}^{\text{KBr}} \) 3015, 2845, 1762, 1700, 1467, 1265, 900, and 763 cm\(^{-1} \); \( \delta_{\text{CDCl}_3} \) 5.03 (dd, \( J = 4.4, 2.2 \text{ Hz} \), 2, \( >\text{CHN}< \)), 3.85 (ABq, \( J_{\text{AB}} = 11 \text{ Hz} \), \( \Delta \nu_{\text{AB}} = 31.3 \text{ Hz} \), 4, \(-\text{CH}_2\text{O}-\)), 3.47-3.75 (br m, 2, methine), 3.07 (s, 3, \( >\text{HCH}< \)), and 3.02-3.25 (m, 2, methine).

**Anal.** Calcd for C\( _{13} \)H\( _5 \)N\( _3 \)O\( _3 \): C, 60.22; H, 5.03; N, 16.21.

Found: C, 60.11; H, 5.02; N, 16.18.

Hexahydro-N-methyl-2H,4H-cyclopropa[3',4']pentalen0[1',6';1,3,2]cyclopropa[1,2-g]furan-1,5-bilimine-6,7-dicarboximide (96). A solution of recrystallized 95 (1.3 g, 5 mmol) in 160 ml of distilled and degassed dioxane containing 25.5 g (150 mmol) of silver nitrate in 40 ml of water was heated in a heavy wall sealed glass vessel at 130° (oil bath temperature) for 4 days in the dark. The cooled tube was carefully opened in a hood and the mixture was diluted with an equal
volume of 7 N aqueous ammonia, stirred, and filtered. The resulting clear yellow filtrate was concentrated to ca. 20 ml, extracted with chloroform (5 x 40 ml) and the combined chloroform extracts were washed with brine and dried. Removal of the solvent in vacuo afforded 1.1 g of a tan solid which was crystallized from chloroform-ether to yield 0.84 g (65%) of white material, mp 187-190°C. A small portion of 96 was further purified by recrystallization (chloroform-ether) to afford white crystals, mp 191-192°C (dec); \( \nu_{\text{KBr}}^{\text{max}} \) 2860, 2850, 1768, 1690, 1465, 1234, 1142, 1135, 1048, 1000, 942, 903, 800, 765, 676, and 540 cm\(^{-1} \); \( \delta_{\text{CDCl}_3} \) 5.06 (br t, \( J = 2.8 \text{ Hz} \), 2, >CHNK), 3.83 (ABq, \( J_{AB} = 9.2 \text{ Hz} \), \( \Delta \nu_{AB} = 19.7 \text{ Hz} \), 4, -CH2O-), 3.08 (s, 3, >NCH3), and 1.84-2.22 (br m, 4, cyclopropyl).

**Anal.** Calcd for C\(_{13}\)H\(_{13}\)N\(_3\)O\(_3\): C, 60.22; H, 5.05; N, 16.21.

Found: C, 60.01; H, 5.07; N, 15.94.

2a,7b-Dihydro-5H,7H-pentaleno[1',5':1,3,2]cyclopropan[1,2-c]furan (97b) at 2,4,5a,5b,5c,5d-Hexahydrocyclopropan[3,4]pentaleno[1,6-cd]pyran (97a).

A mixture of 96 (0.75 g, 2.9 mmol), 1.16 g (29 mmol) of sodium hydroxide, and 30 ml of degassed 2-propanol was refluxed for one hour under argon. The cooled (0°C) mixture was acidified to pH 1 with 3 N hydrochloric acid, basified again to pH 8 by slow addition of 3 N...
aqueous ammonia, and diluted with 20 ml of pentane-methylene chloride (1:1). To this clear solution was added 2.52 g (29 mmol) of activated manganese dioxide in one portion and stirring was continued at room temperature for 10 hr. After filtration, the clear filtrate was diluted with pentane, washed with water (3 x 40 ml), and dried by shaking with sodium chloride-anhydrous sodium sulfate (1:1). The excess solvent was carefully removed by atmospheric fractional distillation (argon purging of the solution) and the remaining clear liquid was purified by bulb to bulb transfer ($10^{-3}$ torr) at room temperature to afford 97 as a clear solid, 295 mg (70%), mp 23-25°; $\lambda_{\text{max}}^\text{isoctane}$ 242 (e 2800) and 233 sh nm (2400); $\nu_{\text{max}}^\text{neat}$ 2840, 1202, 1026, 912, 740, and 730 cm$^{-1}$; $^1$H NMR (CDCl$_3$): 5.58 (dd, $J_{3,4} = J_{6,7} = 5.2$ Hz, $J_{4,5} = J_{5,6} = 2$ Hz, 2, H$_4$ and H$_6$), 5.26 (d, $J_{3,4} = J_{6,7} = 5.2$ Hz, 2, H$_3$ and H$_7$), 4.2 (ABq, $J_{AB} = 9.5$ Hz, $\Delta\nu_{AB} = 3.95$ Hz, 4, -CH$_2$O-), 3.35 (dt, $J_{1,5} = 7.1$ Hz, $J_{4,5} = J_{5,6} = 2$ Hz, 1, H$_3$), and 2.62 (d, $J_{1,5} = 7.1$ Hz, 1, H$_1$); calcd m/e 146.0732, observed 146.0733.

Hydrogenation of 2a,7b-Dihydro-5H,7H-pentaleno[11'6':1,3,2]cyclopropa-
[1,2-c]furan (97b) @ 2,4,5a,5b,5c,5d-Hexahydrocyclopropa[3,4]pentaleno-
[1,6-cd]pyran (97a). A 110-mg sample (0.754 mmol) of 97 dissolved in
2 ml of anhydrous tetrahydrofuran was introduced via syringe into a hydrogenation flask containing 3 ml of the same solvent and 126 mg of prerduced 5% rhodium on carbon. After an uptake of ca 2 equivalents of hydrogen, 1 ml of glacial acetic acid was added and the mixture was stirred for an additional 5 hr. After filtration, the filtrate was diluted with pentane, washed with water, saturated sodium bicarbonate, water, and brine and dried. The solvent was removed by atmospheric distillation and the residue was subjected to preparatory glpc on column F at 115° to afford three major components. The first to elute (49%, \( t_{ret} = 22 \text{ min} \)) was characterized as

\[
\begin{align*}
\text{98} &; v_{\text{max}} \text{ neat} 3020, 2940, 2860, 1065, \\
&; 1022, \text{ and } 915 \text{ cm}^{-1}; \delta_{\text{TMS}} \text{CDCl}_3 3.78 \\
&; (\text{AB, } J_{\text{AB}} = 8.7 \text{ Hz}, \Delta v_{\text{AB}} = 9.2 \text{ Hz}, \\
&; 4, -\text{CH}_2\text{O}-), 2.5-2.83 \text{ (br m, 1, methine), and } 1.14-2.12 \text{ (series of} \\
\end{align*}
\]

multiplets, 9, methine and methylenes); calcd m/e 150.1044, observed 150.1047.

The second component (45%, \( t_{ret} = 30 \text{ min} \)) proved to be a white solid, mp 71-72°, and was identified as \text{29} by direct comparison with an authentic sample.

The third component (6%, \( t_{ret} = 38 \text{ min} \)) was not isolated.

**Tetrahydrotriquinacene (103).** To a slurry of lithium aluminum hydride (0.49 g, 12.8 mmol) in 30 ml of anhydrous tetrahydrofuran was added 2.1 g (2.8 mmol) of keto alcohol \text{100} in 10 ml of the above solvent under
After this slurry had been refluxed for 2 hr, it was cooled (0°) and quenched with a saturated sodium sulfate solution. The resulting white salts were removed by filtration and leached with hot tetrahydrofuran. After the filtrate had been dried, the solvent was removed in vacuo to afford 2.3 g of crude diol 101.

To an ice-cold stirred solution of crude diol in 20 ml of alcohol-free methylene chloride and 3.36 g (33.3 mmol) of triethylamine was added in four equal portions a solution of methanesulfonyl chloride (3.24 g, 28.2 mmol) in an equal volume of methylene chloride. The resulting white mixture was stirred at 0° for 30 min, quenched with water and the organic phase was washed with 10% hydrochloric acid, saturated sodium bicarbonate, and brine, and dried. After the solvent had been removed in vacuo, the yellow oil was crystallized from chloroform-ether to afford 2 g (49%) of 102 as white crystals. The pmr of 102 compared with authentic material.

To a slurry of lithium aluminum hydride (2.4 g, 62 mmol) in 50 ml of anhydrous ether was added a solution of this dimesylate (2.0 g, 6.2 mmol) in 15 ml of anhydrous tetrahydrofuran. After this mixture had been refluxed for 10-12 hr, it was cooled (0°) and treated with a saturated sodium sulfate solution. The white salts were removed by filtration and leached with hot ether. After the dried solvent had been carefully
removed by atmospheric fractional distillation, the residue was filtered through a Florisil column (pentane elution) to afford after the above workup a clear liquid. This liquid was subjected to preparatory glpc on column D at 100° to afford 103 as major peak, $t_{\text{ret}} = 11$ min, which was isolated in sufficient quantity for comparison with authentic material and to use in the ozonolysis reaction.

cis-2,8-Bis(hydroxymethyl)bicyclo[3,3,0]octane (104). To a 50-ml three-necked flask equipped with a stopper, gas inlet tube, condenser, and spinbar was added 198 mg (1.48 mmol) of 104 in 20 ml of chloroform. After cooling the solution to -20°, ozone was bubbled through the solution until the appearance of a bluish color was noted. The resulting turbid solution was purged with oxygen for 10 min and then diluted with 5 ml of 95% ethanol followed by a slurry of sodium borohydride (450 mg, 118 mmol) in 10 ml of 20% aqueous ethanol and stirring was continued overnight. The mixture was carefully hydrolyzed with 1 N hydrochloric acid and diluted with chloroform. The organic phase was washed with dilute hydrochloric acid, saturated sodium bicarbonate, and brine, dried, and evaporated to afford 130 mg of viscous oil. Back extraction of the salt-saturated aqueous phase with chloroform afforded another 100 mg of diol 104, 230 mg total (91%); $\nu_{\text{max}}^\text{neat}$ 3290 and 2900 cm$^{-1}$; $\delta^\text{CDCl}_3$ (crude) 4.32 (br, 2, -OH), 3.74 (ABq, $J_{AB} = 10$ Hz, $\Delta\nu_{AB} = 6.9$)
Hz, 2, -CH$_2$O-), 3.62 (s, 2, -CH$_2$O-), and 0.98-2.78 (series of multiplets, 12, methines and methylenes).

$1,3,3a,4,5,5a,6,7,7a,7b$-Decahydropentaleno[1,6-cd]pyran (99)\textsuperscript{85} To a solution of $104$ (230 mg, 1.35 mmol) in 5 ml of pyridine was added 257 mg (1.35 mmol) of tosyl chloride in one portion and the solution was magnetically stirred for 24 hr under argon. The solution was quenched with water, diluted with chloroform and the organic phase was washed with 1 N hydrochloric acid and brine, and dried. Removal of the solvent in vacuo afforded an oil which contained a trace amount of pyridine.

The pmr spectrum already showed the presence of 99, so without further delay the oil was dissolved in 40 ml of anhydrous tetrahydrofuran.

To this solution was added 75.5 mg (1.79 mmol) of pentane-washed sodium hydride (57% in mineral oil) under argon and the mixture was stirred at reflux overnight. The cooled, carefully quenched mixture was extracted several times with petroleum ether (30-60$^\circ$) and the combined extracts were washed with brine and dried. Removal of the solvent in vacuo (no heat) afforded a yellow liquid which was filtered through a small Florisil column (pentane elution). The condensed eluate was subjected to preparatory glpc on column E at 130$^\circ$ to afford 99, $t_{ret} = 9.5$ min (50 mg, 24%), as a white solid, mp 67-69$^\circ$; $\nu_{max}^{KBr}$ 2945, 2870, 2840, 1155, 1114, 867, and 742 cm$^{-1}$; $\delta^{CDCl_3}$ \textsuperscript{TMS} 3.85 (ABX, $J_{AB} =$
12 Hz, 4, -CH₂O-, 2.28-2.77 (br m, 2, methines), and 1.35-2.04 (m, 10, methines and methylenes).

**Anal.** Calcd for C₁₀H₁₄O: C, 78.89; H, 10.59.

**Found:** C, 79.03; H, 10.44.

1,1,2,2-Tetrakis(hydroxymethyl)cyclohex-4-ene (107). A mixture of ethyl ethylenetetracarboxylate (100 g, 0.317 mol), 1 g of hydroquinone, 100 ml of benzene, and 200 ml of butadiene was heated in an autoclave at 170-180° for 10 hr. The cooled solution was subjected to vacuum distillation to afford 90 g (77%) of 106 as a viscous light green liquid, bp 150°/0.3 mm (lit 149-151°/0.1 mm).

To a slurry of lithium aluminum hydride (30.8 g, 0.81 mol) in 1.5 liters of tetrahydrofuran was added at reflux 100 g (0.270 mol) of 106 in the above solvent (250 ml total) and mechanical stirring was continued for 4 days. The cooled mixture was carefully quenched with saturated sodium sulfate solution and the white salts were removed by vacuum filtration. After extraction of the salts with tetrahydrofuran for 4 days, the dried solvent was removed in vacuo to afford 45 g (82%) of 107, mp 271-273° (methanol-benzene) [lit mp 256-270° (methanol-benzene)].
1,1,2,2-Tetrakis(methanesulfonyloxymethyl)cyclohex-4-ene (108). This material was prepared according to the procedure by E. Buchta and S. Billenstein in 83% yield, mp 130-142° (mp 152-153.5° from benzene-hexane) (lit mp 154-156° from propanol).

\[
\text{(CH}_2\text{OSO}_2\text{CH}_3)_2
\]

108

8,11-Dithia[4.3.3]propell-3-ene (109). A mixture of recrystallized (ethanol) sodium sulfide nonahydrate (14.4 g, 60 mmol) in 700 ml of dimethylformamide (DMF) was dehydrated by vacuum distillation (maximum distillate temperature 65°/30 mm). To this room temperature mixture was added 10.3 g (20.0 mmol) of recrystallized 108 in 200 ml of dry DMF over a period of 30 min under nitrogen and mechanical stirring was continued at 130-140° for 40 hr. The cooled mixture was quenched with 1.5 liters of crushed ice and extracted with pentane-ether (1:1). The combined extracts were washed with water and brine, dried, and concentrated in vacuo. The residue was then chromatographed on neutral activity I alumina (ether-hexane (1:1) elution) to afford 2.98 g (75%) of 109 as a white solid whose pmr spectrum compared favorably with that reported. A small portion was sublimed (100°/30 mm) to afford a white solid, mp 116-118° (lit mp 108-112°).
7-Chloro-8,11-dithia[4.3.3]propell-3-ene 8,8,11,11-Tetraoxide (110).

To a solution of sublimed 109 (1.98 g, 10 mmol) in 15 ml of carbon tetrachloride was added 1.4 g (10.5 mmol) of recrystallized N-chlorosuccinimide and stirring was continued under nitrogen for 18 hr at room temperature. After filtration and solvent evaporation, the residue was diluted with 100 ml of ice-cold anhydrous ether and treated with a standardized ethereal solution containing 40.8 mmol of monoperphthalic acid under nitrogen. The room temperature solution was stirred for 5 hr and the precipitated phthalic acid was removed by filtration and washed with chloroform. The filtrate was concentrated in vacuo and the resulting solid was dissolved in chloroform. After washing this solution once with 0.5 N sodium hydroxide-brine (1:1) and drying, the solvent was removed in vacuo to afford 2.5 g (84%) of white solid, mp 260-275° dec (methylene chloride-ether); $\nu_{\text{max}}^{\text{CHCl}_3}$ 1340, 1325, and 1120 cm$^{-1}$; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.88 (br s, 2, olefinic), 5.5 and 4.9 (each is a singlet, 1, >CHCl, see text for configuration assignment), 3.1-3.9 (m, 6, -CH$_2$SO$_2$-), 2.4-2.8 (br m, 4, allylic).

Anal. Calcd for C$_{10}$H$_{18}$ClO$_4$S$_2$: C, 40.47; H, 4.42; S, 21.61.

Found: C, 40.45; H, 4.51; S, 21.23.

8-Thia[4.3.2]propella-3,10-diene 8,8-Dioxide (111). To a solution of 110 (0.82 g, 2.77 mmol) in 150 ml of cold (-70°) anhydrous tetrahydro-
furan was added under nitrogen 1.24 g (11.1 mmol) of commercial powdered potassium t-butoxide in one portion and stirring was continued for 2 hr while the solution warmed to room temperature. The water quenched solution was diluted with an equal volume of 50% brine and extracted with pentane. The combined extracts were washed with brine, dried, and concentrated in vacuo. The residue was chromatographed on neutral activity I alumina (increasing the chloroform concentration to 15% in ether) to afford 0.27 g (50%) of yellow solid, mp 105-108°. Further purification by recrystallization (methylene chloride-pentane) and sublimation (105°/25 mm) afforded a white solid, mp 110-111°; \( \nu_{\text{max}}^{\text{CHCl}_3} 1305, 1150, \text{ and } 1112 \text{ cm}^{-1} \); \( \delta_{\text{TMS}}^{\text{CDCl}_3} 6.0 \text{ (s, 2, cyclobutenyl)}, 5.84 \text{ (m, 2, olefinic)}, 3.12 \text{ (ABq, } J_{AB} = 14 \text{ Hz, } \delta_{AB} = 15.8 \text{ Hz, 4, } -\text{CH}_3\text{SO}_2^-\text{)}, \text{ and 2.3 (br s, 2, allylic).}

**Anal. Calcd for C_{10}H_{12}O_{2}S: C, 61.19; H, 6.17; S, 16.33. Found: C, 61.08; H, 6.24; S, 16.26.**

8-Thia[4.3.2]propella-3,10-diene (112). To a slurry of 3.8 g (0.1 mmol) of lithium aluminum hydride in 125 ml of ice-cold anhydrous ether was added under nitrogen 1.96 g (10 mmol) of recrystallized 111 in one portion and stirring at reflux was continued for 42 hr.
After quenching the cooled (0°) mixture with a saturated sodium sulfate solution, the white salts were removed by filtration and leached with hot chloroform-ether. The combined solvents were dried and evaporated in vacuo to afford an oil which when stored in ether overnight at 0° afforded 0.34 g of unreacted 111 and 1 g of crude sulfide. Kugelrohr distillation afforded 0.8 kg (62% yield based on reacted 111) of 112 as a clear liquid, bp 95°/4 mm; \( \nu_{\text{max}} \) \text{mm} 3300, 2900, 2825, 895, 764, 730, and 680 cm\(^{-1}\); \( \delta_{\text{CDCl}_3} \) 5.7-5.81 (m, 2, olefinic), 5.76 (s, 2, cyclobutenyl), 2.54 (ABq, \( \Delta \nu_{\text{AB}} = 12.6 \text{ Hz} \)), \( \Delta \nu_{\text{AB}} = 5 \text{ Hz} \), 4, -CH=\( \text{S} \)-), and 2.02-2.3 (m, 4, allylic); calcd m/e 164.0660, observed 164.0662.

8-Thia[4.3.2]propella-2,4,10-triene (113). To a solution of 112 (5 g, 30.4 mmol) in 100 ml of cold (-70°) methylene chloride was slowly added over a period of 5 hr 30.4 mmol of bromine in methylene chloride under nitrogen. Solvent removal in vacuo afforded a reddish viscous oil; \( \delta_{\text{CDCl}_3} \) 6.03 (ABq, \( \Delta \nu_{\text{AB}} = 2.8 \text{ Hz} \)), \( \Delta \nu_{\text{AB}} = 13 \text{ Hz} \), 2, cyclobutenyl), 4.42-4.84 (br m, 2, >CHBr), and 1.9-3.0 (br m, 8, methylene); calcd m/e 321.9028, observed 321.9032.

To a solution of the dibromide in 300 ml of dry HMPA was added 12.8 g (0.304 mol) of lithium chloride and 22.5 g (0.304 mol) of lithium carbonate and the stirred slurry was heated at 90° for 17 hr. After cooling, the slurry was diluted with water and extracted with pentane.
The combined extracts were washed with brine, dried, and evaporated in vacuo (no heat). The residue was then chromatographed on neutral activity I alumina (pentane-ether (1:1) elution) to afford after solvent removal 4 g (81%) of 113, bp 96°/5 mm. The pmr spectrum and glpc trace (column C at 125°) showed that the liquid was pure 113; \( \lambda_{\text{max}} \) isoctane 264 (e 2520), 229 (2100), and 223 nm (2270); \( \nu_{\text{max}} \) neat 3200, 2900, 2820, 1224, 1074, 1008, 765, 740, 691, and 650 cm\(^{-1}\); \( \delta_{\text{TMS}} \) CDCl\(_3\) 5.91 (br t, \( J = 1.3 \) Hz, 4, olefinic), 5.74 (s, 2, cyclobutenyl), and 2.56 (ABq, \( J_{AB} = 12 \) Hz, \( \Delta \nu_{AB} = 18.4 \) Hz, 4, -CH\(_2\)S-).

Anal. Calcd for C\(_{10}\)H\(_{10}\)S: C, 74.05; H, 6.22.

Found: C, 73.65; H, 6.35.

**N-Methyl-5H,7H-1,4:4a,7a-diethenothieno[3,4-d]pyridazine-2,3(1H,4H)-dicarboximide (116).** A solution of 3.5 g (21.6 mmol) of distilled 113 in 100 ml of cold (-70°) acetone was treated dropwise with a solution of 2.44 g (21.6 mmol) of N-methyltriazolinedione in 20 ml of the same solvent under nitrogen. The resulting reddish-pink solution was warmed to ambient temperature, refluxed in the presence of a few milliliters of absolute ethanol, and then cooled. Solvent removal in vacuo afforded a tan solid which was filtered through a silica gel column (chloroform elution) to afford 5.6 g (93%) of white solid, mp 227-228°. Further purification by recrystallization (chloroform-ether) afforded white needles, mp 227.5-
288°, $\nu_{KBr}^\text{max}$ 2930, 2920, 1775, 1710, 1460, 1394, 1190, 1000, 796, 789, 744, and 567 cm$^{-1}$; $^6$CDCl$_3$ 6.22 (dd, $J = 4.6, 3.3$ Hz, 2, olefinic), 5.94 (s, 2, cyclobutanyl), 4.77 (br t, $J = 3.8$ Hz, 2, >CHN<), 3.02 (s, 3, >NCH$_3$), and 2.87 (ABq, $J_{AB} = 12$ Hz, $\Delta\nu_{AB} = 37.8$ Hz, 4, -CH$_2$S-).

**Anal.** Calcd for C$_{13}$H$_{13}$N$_3$O$_2$S: C, 36.72; H, 4.76; S, 11.62.

**Found:** C, 36.38; H, 4.85; S, 11.34.

Dihydro-N-methyl-3H-3a,8,4,7-ethanediyldiene-1H-cyclobuta[c]thieno-[3,4-d]pyridazine-5,6(4H,6aH)-dicarboximide (117). A deaerated solution of 116 (2.0 g) in 300 ml of benzene-acetone (1:1) was irradiated through quartz with a 450-W Hanovia lamp fitted with a Corex filter for 2 hr under nitrogen. The solvents were removed in vacuo to afford crude 117. This procedure was repeated until 7.3 g of 116 had been irradiated. The crude 117 was chromatographed on neutral activity I alumina (petroleum ether-chloroform (3:1) elution) to yield 6.5 g (89%) of white solid, mp 175-180°. Further purification by recrystallization (chloroform-ether) afforded white crystals, mp 185-185.5°; $\nu_{KBr}^\text{max}$ 2980, 1750, 1690, 1463, 1308, and 538 cm$^{-1}$; $^6$CDCl$_3$ 4.95 (dd, $J = 4.6, 2.5$ Hz, 2, >CHN<), 3.42-3.79 (br m, 2, methine), 3.07 (s, 3, >NCH$_3$), 2.92-3.07 (m, 2, methine), and 2.92 (s, 4, -CH$_2$S-).

**Anal.** Calcd for C$_{13}$H$_{13}$N$_3$O$_2$S: C, 56.72; H, 4.76; N, 15.27.

**Found:** C, 56.41; H, 4.73; N, 15.13.
Hexahydro-N-methyl-2H,4H-cyclopropa[3',4']pentaleno[1',6':1,3,2]cyclo-
propa[1,2-c]thiophene-1,5-blimine-6,7-dicarboximide (118). A solution
of recrystallized 117 (1.38 g, 5
mmol) in 160 ml of distilled and
degassed dioxane containing
25.5 g (150 mmol) of silver nitrate
in 40 ml of water was heated in a
heavy wall sealed glass vessel at
130° (oil bath temperature) for 4
days in the dark. The cooled tube
was carefully opened in a hood 132
and the mixture was diluted with an equal volume of 7 N aqueous ammonia,
stirred, and filtered. The resulting clear yellow filtrate was con-
centrated to ca 20 ml, extracted with chloroform (5 x 40 ml), and the
combined chloroform extracts were washed with brine and dried. Removal
of the solvent in vacuo afforded 1.2 g of yellow solid which was cry-
stallized from chloroform-ether to afford 0.85 g (62%) of white solid,
mp 173-175°. Further purification by recrystallization from chloroform-
hexane provided white needles, mp 175-176.5° (dec); νKBrmax 2920, 1763,
1700, 1468, 1396, 1232, 797, and 748 cm⁻¹; δCDCl₃ 5.03 (br t, J = 3
Hz, 2, >CHN<), 3.08 (s, 7, -CH₂S- and >NCH₃), 2.46 (d, J = 4 Hz, 1,
cyclopropyl syn to sulfur ring), and 1.84-2.17 (br m, 3, cyclopropyl).

Anal. Calcd for C₁₃H₂₃N₃O₈S: C, 56.72; H, 4.76; N, 15.27.
Found: C, 56.64; H, 4.74; N, 15.22.
Hexahydro-N-methyl-2H,4H-cyclopropa[3',4']pentaleno[1',6':1,3,2]cyclo-
propa[1,2-ε]thiophene-1,5-biimine-6,7-dicarboximide anti-3-Oxide (122)
and Hexahydro-N-methyl-2H,4H-cyclopropa[3',4']pentaleno[1',6':1,3,2]-
cyclopropa[1,2-ε]thiophene-1,5-biimine-6,7-dicarboximide syn-3-Oxide
(123).

A. Oxidation with m-Chloroperbenzoic Acid. A solution of 346
mg (2.0 mmol) of m-chloroperbenzoic acid in 5 ml of chloroform was
added dropwise to a stirred, ice-cold
solution of 118 (550
mg, 2 mmol) in 20 ml
of chloroform and
stirring was continued
at room temperature
overnight (10 hr).
Solvent removal in
vacuo afforded a white solid whose pmr spectrum showed a syn to anti
sulfoxide ratio of 1/3.5 in the δ 5 region. The isomers were separated
by preparative tlc on silica gel (1% methanol in ethyl acetate, 6 elu-
tions) to afford three bands: \( R_f = 1, \) m-chlorobenzoic acid; \( R_f = 0.11, \)
411 mg (71%) of anti sulfoxide 122; and \( R_f = 0.04, \) 143 mg (25%) of
syn sulfoxide 123. Further purification of 123 by recrystallization
(methanol) afforded white crystals, mp above 260° (dec, sealed capil-
lary); \( v_{KBr}^{max} 2010, 1762, 1700, 1468, 1446, 1395, 1230, 1056, 796, \) and
749 cm\(^{-1}; \) \( ^1H NMR \) 5.07 (dd, \( J = 3.8, 2.5 \) Hz, 2, CHN\( \times 2 \)), 3.22 (br s, 4,
-CH$_2$S-), 3.07 (s, 3, >NCH$_3$), 2.84 (d, J = 4.5 Hz, 1, cyclopropyl syn to sulfoxide ring), and 1.81-2.4 (br m, 3, cyclopropyl).

**Anal.** Calcd for C$_{13}$H$_{13}$N$_2$O$_3$S: C, 53.61; H, 4.50; N, 14.43.

Found: C, 53.55; H, 4.55; N, 14.24.

Further purification of 122 by recrystallization (methanol) afforded white crystals, mp above 270° (dec, sealed capillary); $\nu_{\text{max}}$KBr 2975, 1755, 1690, 1460, 1393, 1038, and 748 cm$^{-1}$; $\delta$CDCl$_3$ 5.22 (dd, J = 3.8, 2.1 Hz, 2, >CHN<), 3.22 (s, 4, -CH$_2$S-), 3.05 (s, 3, >NCH$_3$), and 1.87-2.34 (br m, 4, cyclopropyl).

**Anal.** Calcd for C$_{13}$H$_{13}$N$_2$O$_3$S: C, 53.61; H, 4.50; N, 14.43.

Found: C, 53.53; H, 4.49; N, 14.48.

**B. Oxidation with Sodium meta-Periodate.** To a solution of 118 (275 mg, 1 mmol) in 20 ml of ice-cold methanol was added dropwise a solution of 0.225 g (1.05 mmol) of sodium meta-periodate in 10 ml of water and stirring was continued at room temperature overnight (12 hr). After filtration, the solvent was removed in vacuo to afford a white solid whose syn to anti sulfoxide ratio was 1/2.4 (pmr spectroscopy).

Hexahydro-N-methyl-2H,4H]-cyclopropa[3',4']pentaleno[1',6';1,3,2]cyclopropa[1,2-c]thiophene-1,5-biimine-6,7-dicarboximide 3,3-Dioxide (124). A solution of 730 mg (4.2 mmol) of m-chloroperbenzoic acid $^{134}$ in 5 ml of chloroform was added dropwise to a stirred, ice-cold solution of 118 (550 mg, 2.0 mmol) in 25 ml of chloroform. The clear solution was diluted to 50 ml with chloroform, washed with 0.5 N sodium hydroxide-
Evaporation in vacuo afforded a light yellow solid which was crystallized from chloroform-ether to afford 500 mg (82%) of white crystals, mp 189-190° (dec); ν\textsubscript{KBr} max 2990, 2950, 1765, 1695, 1462, 1318, 1300, 1155, 1135, and 470 cm\(^{-1}\); \(\delta\)\textsubscript{CDCl\(_3\)} 5.11 (t, J = 2.5 Hz, 2, >CHN<), 3.38 (ABq, \(J\textsubscript{AB} = 15\) Hz, \(\Delta\nu\textsubscript{AB} = 41\) Hz, 4, -CH\(_2\)SO\(_2\)-), 3.04 (s, 3, >NCH\(_3\)<), and 1.99-2.44 (br m, 4, cyclopropyl).

Anal. Calcd for C\(_{13}\)H\(_{13}\)N\(_3\)O\(_4\)S: C, 50.81; H, 4.26; N, 13.68.

Found: C, 50.60; H, 4.45; N, 13.41.

2a,7b-Dihydro-5H,7H-pentaleno[1',6':1,3,2]cyclopropa[1,2-e]thiophene (119b) \(\triangleq\) 2,4,5a,5b,5c,5d-Hexahydrocyclopropa[3,4]pentaleno[1,6-cd]-thiopyran (119a). A mixture of 118 (0.75 g, 2.73 mmol), 1.09 g (27.3 mmol) of sodium hydroxide, and 30 ml of degassed 2-propanol was refluxed for 1 hour under argon. The cooled (0°) mixture was acidified to pH 1 with 3 N hydrochloric acid, basified again to pH 8 by slow addition of
3 N aqueous ammonia, and diluted with 20 ml of pentane-methylene chloride (1:1). To this clear solution was added 2.37 g (27.3 mmol) of activated manganese dioxide in one portion and stirring was continued at room temperature for 6 hr. After filtration, the clear filtrate was diluted with pentane, washed with water (3 x 40 ml), and dried by shaking with sodium chloride-anhydrous sodium sulfate (1:1). The excess solvent was carefully removed by atmospheric fractional distillation (argon purging of the solution) and the remaining clear liquid was purified by bulb to bulb transfer (10⁻³ torr) at 50° to afford 119 as a clear liquid, 193 mg (44%); λisoctane max 240 nm (ε 1900); \( \lambda^\text{neat max} \) 3040, 2910, 2840, 1362, 748, 738, and 717 cm⁻¹; \( \delta^\text{CDCl₃ (40°)} \) 5.22-5.41 (m, 4, olefinic), 3.4 (ABq, \( \Delta\nu_{AB} = 7.9 \text{ Hz}, 4, -\text{CH}_2\text{S}- \)), 3.18-3.4 (m, 1, H₅), and 2.98 (d, \( J = 6.8 \text{ Hz}, 1, H_1 \)); calcd m/e 162.0503, observed 162.0506.

Attempted Preparation of 125. A mixture of 122 (500 mg, 1.72 mmol), 690 mg (17.2 mmol) of sodium hydroxide, and 20 ml of methanol was refluxed for 2 hr under argon. The cooled (0°) mixture was acidified to pH 1 with 3 N hydrochloric acid, basified again to pH 8 by slow addition of 3 N aqueous ammonia, and diluted with 20 ml of ether. To this dark solution was added 1.5 g (17.2 mmol) of activated manganese dioxide in one portion and stirring was continued at room temperature for 10 hr. After filtration, the yellow filtrate was diluted with ether, washed with water (1 x 40 ml), and dried by shaking with sodium chloride-anhydrous sodium sulfate (1:1). The excess solvent was quickly removed in vacuo (no heat) to afford a yellow solid whose pmr spectrum contained
a multitude of absorptions from $\delta$ 0.6 to 6. An attempted sublimation of the crude material at $10^{-3}$ torr (25-140°F) afforded ca 1 mg of liquid whose pmr spectrum was too dilute to allow characterization.

Attempted Preparation of 125. A mixture of 124 (500 mg, 1.63 mmol), 650 mg (16.3 mmol) of sodium hydroxide, and 20 ml of degassed 2-propanol was refluxed for 1 hour under argon. The cooled (0°F) mixture was acidified to pH 1 with 3 N hydrochloric acid, basified again to pH 8 by slow addition of 3 N aqueous ammonia, and diluted with 20 ml of ether. To this clear solution was added 1.4 g (16.3 mmol) of activated manganese dioxide in one portion and stirring was continued at room temperature for 10 hr. After filtration, the clear filtrate was diluted with pentane, washed with water (4 x 30 ml), and dried by shaking with sodium chloride-anhydrous sodium sulfate (1:1). The excess solvent was carefully removed by fractional distillation such that the pot temperature never exceeded 25°F (argon purging of the solution) and the remaining yellow liquid was transferred to a sublimation apparatus. Sublimation at room temperature ($10^{-3}$ torr, Dry-Ice cold finger) afforded 125 mg (59%) of 126 as a white solid, mp 0-1°F; $\lambda_{\text{max}}$ isoctane 250 sh (e 6400) and 219 nm (26,000); $\nu_{\text{max}}$ neat 3080, 3055, 2880, 1640, 892, 865, and 823 cm$^{-1}$; $\delta_{\text{CDCl}_3}$ 6.02 (br s, 4, olefinic), 5.02 (d, $J = 1.4$ Hz, 2, exomethylene), 4.96 (d, $J = 1.8$ Hz, 2, exomethylene), 4.02 (d, $J = 6$ Hz, 1, H$_5$), and 3.82 (m, 1, H$_1$); calcd m/e 130.0782, observed 130.0785.
Reaction of 126 with N-Methyltriazolinedione. A solution of 74.6 mg (0.66 mmol) of N-methyltriazolinedione in 0.5 ml of acetone was added dropwise to a stirred, ice-cold solution of 126 (85 mg, 0.65 mmol) in 1 ml of acetone under argon. The red color disappeared immediately. After the addition, the tan mixture was stirred for an additional 5 minutes while warming to room temperature. Solvent removal in vacuo afforded 140 mg of yellow material whose pmr spectrum showed the presence of starting material plus a multitude of other absorptions.

Pyrolysis of Semibullvalene. Freshly prepared semibullvalene (42.8 mg, containing 4.4% of 133) was slowly vaporized in a flow system of nitrogen into a quartz reactor packed with quartz chips heated to 427° under 30 mm of pressure. The yellow pyrolysate (25.3 mg, 59%) was collected in a Dry Ice-acetone cooled receiver. Pmr and ir analysis revealed this material to be composed of cyclooctatetraene (95%, $\delta_{CDCl_3}^{TMS}$ 5.75) and semibullvalene (5%, $\delta_{CDCl_3}^{TMS}$ 5.18, 4.20, and 3.00).

Tetraethyl 1,5-Dimethylbicyclo[3.3.0]octane-3,7-dione-2,4,6,8-tetra-carboxylate (138). A 3-l three-necked Morton flask was charged with a solution of ethyl acetonedicarboxylate (81 g, 0.4 mol) in 1.5 liters of distilled water, 17.6 g (0.205 mol) of 2,3-butanedione, and 6 drops
of 6 N sodium hydroxide (pH 7) and the yellow solution was vigorously stirred at room temperature for 36 hr. Filtration afforded 90.0 g (96%) of 138 as a white solid, mp 154-158° (lit 144-146°); νCHCl₃ max 1730 and 1665 cm⁻¹.

1,5-Dimethylbicyclo[3.3.0]octane-3,7-dione (139). A solution of 138 (90 g, 0.198 mol) in 500 ml of concentrated hydrochloric acid and 500 ml of absolute ethanol was slowly warmed to reflux and stirred for 48 hr. The cooled solution was washed with water, 20% sodium hydroxide solution, water, and brine, and dried. Solvent removal in vacuo afforded 29.2 g (89%) of 139 as a light yellow solid [lit mp 167-169° (sublimed)]; νCHCl₃ max 1740 cm⁻¹; δCDCl₃ 2.32 (s, 8, methylene) and 1.2 (s, 6, methyl).

3,7-Dihydroxy-1,5-dimethylbicyclo[3.3.0]octane (140). A solution of 139 (60.6 g, 0.365 mol) in 500 ml of anhydrous ether-tetrahydrofuran (4:1) was added dropwise to a refluxing slurry of lithium aluminum hydride (19 g, 0.5 mol) in 1 liter of anhydrous ether under nitrogen and mechanical stirring was continued for 2 hr at reflux. The reaction
was quenched by means of sequential addition of 19 ml of water, 19 ml
of 15% sodium hydroxide solution, and 57 ml of water. The white salts
were removed by filtration and leached with hot methylene chloride.
The filtrate was dried and concentrated in vacuo to afford 60.2 g (97%) of
140 as a white solid, mp 148-150.5° (from chloroform) (lit mp
141-145°).

1,5-Dimethylbicyclo[3.3.0]octa-2,6- and 2,7-dienes (141). A solution
of 140 (10 g, 59 mmol) in 150 ml of anhydrous tetrahydrofuran was
added dropwise to a mixture of 57% sodium hydride (7.41 g, 0.176 mol)
in the above solvent. The solution was refluxed for 6 hr; after two
hours at reflux 9.2 ml (153 mmol) of carbon disulfide was added by
syringe; after five hours at reflux 9.2 ml (153 mmol) of methyl iodide
was added by syringe. After cooling (0°) and quenching the excess
sodium hydride with water, the solution was diluted with dichloro-
methane and washed with water and brine, and dried. Solvent removal
afforded the red dixanthate which was immediately pyrolyzed at 160-220°
(760 mm) to afford a light yellow smelly liquid. Further purification
by fractional distillation afforded 5 g (64%) of dienes, bp 54-56°/30
mm; ν̄max 3000, 2900, 2860, 2800, 1630, 1440, and 960 cm⁻¹; δCDCl₃
5.36-5.52 (br m, 4, olefinic), 2.24 (m, 4, allylic), and 1.04, 0.98,
0.96 (all singlets, 6, methyls).
**1,5-Dimethylsemibullvalene** (142).

To a solution of 141 (9 g, 67.2 mol) in 200 ml of carbon tetrachloride was added 26.2 g (0.147 mol) of recrystallized N-bromosuccinimide and 0.5 g of azobisisobutyronitrile and the magnetically stirred mixture was placed in a preheated oil bath (100°) and refluxed for 2 hr after initiation. After filtration, the solvent was removed *in vacuo* to afford a viscous yellow liquid. This liquid was redissolved in ether and washed with water and brine and dried. Solvent removal *in vacuo* afforded 21 g of dibromide mixture which was divided into three portions. Each portion was treated with 73 g of 1/2 Li(Hg)\(_2\) in ether under argon. After stirring this mixture for 24 hr, the amalgam was removed by filtration and the filtrate was filtered through a silica gel column (pentane elution) to afford 3.2 g (36%) of 142, bp 30°/10 mm. Further purification by preparatory glpc on column E at 65° (injector and detector temperature 125°, 100 cc/min, \( t_{ret} = 10 \) min) afforded 142 as a clear liquid; \( \nu_{max} \) neat 3050, 2950, 1455, 1350, and 740 cm\(^{-1}\); \( \delta_{CDCl_3} \) 5.40 (br s, 2, olefinic), 4.10 (m, 4, time averaged protons), and 1.00 (s, 6, methyl).

**Pyrolysis of 1,5-Dimethylsemibullvalene.** A 95.1-mg sample of freshly purified 142 was passed through a quartz chip-packed quartz tube heated at 390° by entrainment in a stream of dry nitrogen at 30 mm. The
effluent material was collected at -78° in a small U-tube. There was obtained 73 mg (76%) of \( \text{I44} \) which was further purified by preparative glpc on column E at 60° to yield a light yellow material; \( \lambda_{\text{isoctane}} \)

280 sh nm (e 222); \( \nu_{\text{max}}^{\text{neat}} \) 2950, 1650, 1445, 1150, 815, and 725 cm\(^{-1}\); \( \delta_{\text{TMS}} \) CDCl\(_3\) 5.68 (m, 4, olefinic), 5.52 (m, 2, olefinic), and 1.72 (s, 6, methyl).

**Anal.** Caled for C\(_{10}\)H\(_{12}\): C, 90.91%; H, 9.09.

Found: C, 90.73%; H, 9.12.

**TCNE Adduct of 1,5-Dimethylcyclooctatetraene.** A solution of 12 mg (0.091 mmol) of \( \text{I44} \) and 128 mg (1 mmol) of tetracyanoethylene (TCNE) in 3 ml of ethyl acetate was refluxed under nitrogen for 12 hr, cooled, and diluted with ether. Subsequent processing involved washing with 10% sodium bisulfate solution, water, and brine. After drying and evaporation of solvent, the residual crystalline material was chromatographed on Florisil (methylene chloride elution) to furnish 13.1 mg (55.4%) of \( \text{I45} \) as a white crystalline solid, mp 179.5-180° (from methylene chloride-ether); \( \delta_{\text{TMS}}^{\text{acetone-d}} \) 6.0 (br d, \( J = 7 \) Hz, 1, \( H_3 \)), 5.61 (m, 1, \( H_4 \)), 3.80 (dd, \( J = 7, 3 \) Hz, 1, \( H_1 \)), 3.60 (m, 1, \( H_2 \)), 3.56 (d, 2, \( H_5 \)), 3.40 (d, 2, \( H_6 \)), 3.20 (d, 2, \( H_7 \)), 3.10 (d, 2, \( H_8 \)), 2.70 (s, 2, \( H_9 \)), 2.60 (s, 2, \( H_{10} \)), 2.50 (s, 2, \( H_{11} \)), 2.40 (s, 2, \( H_{12} \)).
3.13 (br s, 2, H₂, H₅), 1.95 (d, J = 2 Hz, 3, -CH₃₂), and 1.62 (m, 3, -CH₃₅).

**Anal.** Calcd for C₁₂H₁₂N₄: C, 73.83; H, 4.65.  
Found: C, 73.75; H, 4.71.

**Photolysis of 1,5-Dimethylsemibullvalene.** A degassed solution of 1/4₂ (47.5 mg, 0.36 mmol) in 1 ml of hexane and 1 ml of acetone was irradiated with a bank of lamps (2537 Å) through quartz for 4 hr. After filtering the solution through a silica gel column (pentane elution), the eluate was carefully concentrated and the residue was subjected to preparatory glpc on column E at 60° (150 cc/min). There was obtained 14.1 mg of starting material (t_ret = 8 min) and 13.6 mg (28.6%) of 1/4₄ (t_ret = 8 min). The ir and pmr of 1/4₄ compared exactly with that prepared by the pyrolysis method.

**Thermal Rearrangement of 66.** A 90-mg (0.57 mmol) sample of 66 was passed through a quartz chip-packed quartz tube heated at 500° by entrainment in a stream of dry nitrogen at 1.0 mm pressure. The residence time was 1-2 sec. The effluent material was collected at -78° in a small U-tube. There was obtained 62 mg (69%) of 15₃ which was purified further by preparative vpc at 80° (column A) and shown to exhibit spectra identical to those of an authentic sample.
N-Phenyltriazolinedione Addition to 155. To a magnetically stirred solution of 3.16 g (19.7 mmol) of 155 in 90 ml of acetone cooled to -78° was added dropwise an acetone solution of N-phenyltriazolinedione until a slight red color persisted. Solvent removal and chromatography on neutral activity alumina (chloroform-ether (1:9) elution) afforded 4.92 g (74.3%) of 156; $^\delta_{\text{CDCl}_3}$ 7.45 (m, 5, aromatic), 6.23 (t, $J = 4$ Hz, 2, olefinic), 4.63 (t, $J = 4$ Hz, 2, >CHN<), and 1.4-2.1 (br m, 8, methylenes). The cyclobutene singlet at 5.95 was lacking.

Photocyclization of 156. A solution of 4.92 g (14.6 mmol) of 156 in 700 ml of acetone was irradiated through Vycor with a 200-W Hanovia lamp for 2.5 hr. The yield of 157 after chromatography on neutral alumina (activity I, 20% chloroform in ether elution) was 4.82 g (98.0%); $^\delta_{\text{CDCl}_3}$ 7.50 (br m, 5, aromatic), 4.66 (t, $J = 3.5$ Hz, 2, >CHN<), 3.58 (m, 2, methine), and 1.4-2.0 (m, 8, methylenes). The methine multiplet at 2.98 was not in evidence.
Silver(I)-Catalyzed Rearrangement of 157. To a solution of 4.82 g (14.3 mmol) of 157 in 250 ml of methanol-water (4:1) was added 30.5 g (0.180 mol) of silver nitrate and the solution was refluxed in the dark for 48 hr. After dilution with water (350 ml), the solution was extracted with chloroform (2 x 250 ml) and the combined extracts were washed with water and brine, and dried. Removal of the solvent gave a yellowish oil which crystallized on standing. Elution of the crude product through an alumina column with chloroform-ether (1:3) gave a quantitative yield of white crystalline 158; \( \delta_{\text{CDCl}_3}^{\text{TMS}} \) 7.30-7.73 (br m, 5, aromatic), 4.88 (br t, \( J = 2.7 \text{ Hz} \), 2, >CHN<), 1.67-2.30 (br m, 6, proximate methylenes and cyclopropyl), and 0.92-1.50 (br m, 4, remote methylenes).

2a,5,6,7,8,8b-Hexahydrobenzo[1,3]cyclopropa[1,2,3-cd]pentalene-2a,8b-d\(_2\) (159b) \& 2,3,4,5,6a,6b,6c,6d-Octahydrocyclohepta[cd]cyclopropa[gh]-pentalene-6c,6d-d\(_2\) (159a). To a 100-ml three-necked flask was added 1.09 g (3.28 mmol) of 158, 25 ml of isopropyl alcohol, and 2.11 g (33 mmol) of potassium hydroxide and the mixture was blanketed with nitrogen. After being heated at reflux for 1 hr, the dark yellow solution was cooled to 0°, treated with 3 N hydrochloric acid until pH 2, and stirred for 5 min. The pH was then adjusted to 8 with 3 N ammonium
hydroxide and pentane (15 ml) together with methylene chloride (15 ml) were added. To this mixture was added 2.88 g (33 mmol) of activated manganese dioxide, stirring was maintained for 3 hr at 25°, and the insolubles were removed by filtration through Celite. The pale yellow filtrate was washed with water and brine, dried over anhydrous sodium sulfate, and carefully distilled at atmospheric pressure to remove solvents. Preparative vpc isolation at 85° (column A) furnished 280 mg (53.4%) of 159: \( \delta^\text{CDCl}_3 \) 4.82 (br s, 2, olefinic), 2.64 (br s, 2, cyclopropyl), 2.11-2.51 (br m, 4, allyl), and 1.18-1.78 (br m, 4, remote methylenes).

**Thermal Rearrangement of 159.** A freshly purified 280-mg sample of 159 was pyrolyzed as above at 460° and 1.5 mm. The collected liquid was subjected to preparative vpc at 95° (column G) to separate unreacted 159 (81 mg) from 160 (51 mg, 26%).

**TCNE Adduct of 160.** The deuterium labeled cyclooctatetraene 160 (51 mg, 0.319 mmol) and tetracyanoethylene (407 mg, 3.19 mmol) dissolved in
ethyl acetate (15 ml) were heated at reflux under nitrogen for 5 hr. The resulting light red solution was cooled, diluted with ether, washed with 10% sodium bisulfite solution, water, and brine, and dried. Solvent removal left a yellow solid which was chromatographed on Florisil (elution with methylene chloride) to give 40 mg (44%) of adduct \( \text{161} \) as a white solid; \( \delta^\text{acetone} \) \( \begin{align*} 6.5 & (\text{br d, } J = 8 \text{ Hz, 1, olefinic}), \\ 4.0 & (\text{dd, } J = 4.5 \text{ and } 2 \text{ Hz, 2, bridgehead}), \\ 3.3 & (\text{br m, 1, cyclobuteny} \text{ sp}^3 \text{ center}), \\ 1.84 & (\text{br m, 4, allyl}), \text{ and } 1.6 (\text{br m, 4, methylenes}). \end{align*} \) See text for further discussion of pmr data.

**Photoisomerization of 66.** Into each of seven base-washed 20-ml Pyrex test tubes was placed 23.6 mg of freshly purified 66 and 15 ml of reagent grade acetone. After each tube had been deaerated with a slow stream of dry nitrogen for 20 min, it was capped with a serum stopper and placed in a Rayonet 'merry-go-round' unit which was equipped with 3000 \( \lambda \) lamps. After the solutions had been irradiated for 2 hr, they were
combined, diluted with pentane, washed with water, 5% aqueous ammonium hydroxide, water, and brine, and dried. Careful removal of the major portion of the solvent by atmospheric distillation was followed by preparative vpc separation at 100° (column C). There was recovered 41.4 mg of unrearranged 175 and 7.7 mg (6.2%) of 172; \( \lambda_{\text{max}} \) of isooctane 235 sh nm (e 3200); \( \delta_{\text{TMS}}^{\text{CDCl}_3} \) 5.4 (d, \( J = 6 \) Hz, 1, \( H_6 \)), 5.14 (dd, \( J = 6, 2 \) Hz, 1, \( H_7 \)), 4.72 (br s, 1, \( H_3 \)), 2.75 (d, \( J = 5 \) Hz, 2, \( H_4, H_8 \)), 2.55 (t, \( J \approx 6 \) Hz, 1, \( H_5 \)), 2.3 (m, 2, allyl), and 1.2-1.9 (m, 6, methylenes); calcd m/e 158.1095, observed 158.1098.

Photoisomerization of 173. Into each of eight base-washed Pyrex test tubes was placed 25.2 mg of 173 and 10 ml of acetone. Irradiation as above for 2.5 hr and analogous workup gave 12.6 mg (8.4%) of 174 and 55 mg of recovered starting material; \( \delta_{\text{TMS}}^{\text{CDCl}_3} \) 5.4 (m, 0.47), 5.14 (d, \( J = 5 \) Hz, 0.47), 4.72 (br s, 1), 2.75 (d, \( J = 5 \) Hz, 1.69); 2.55 (t, \( J \approx 6 \) Hz, 0.83), 2.3 (m, 2), and 1.2-1.9 (m, 6).

Alumina-Promoted Rearrangement of 66. A 425-mg sample of 66 was slowly eluted (pentane) through a column of neutral activity I alumina (ca 300 g) and the eluate was carefully concentrated at atmospheric pressure to leave 417 mg of a new hydrocarbon identified as 190. An analytical sample was obtained by preparative vpc isolation at 80° (column C);
isoctane; λ max 236 (ε 14,000), 243 (14,000), and 262 sh nm (5600); δ CDCl₃

5.95 (s, 2, H₃, H₄), 5.67 (m, 1, H₇), 5.15 (m, 1, H₉), 3.42-4.08 (m, 2, H₂, H₆), and 1.0-2.9 (series of multiplets, 8, allylic and methylenes); calcd m/e 158.1095, observed 158.1093.

Anal. Calcd for C₁₂H₁₄: C, 91.08; H, 8.92.

Found: C, 91.13; H, 8.79.

Alumina-Promoted Rearrangement of 159. A partially polymerized sample of 159 (56 mg) was eluted through alumina (17 g) as before. Collection of monomeric rearranged product by preparative vpc methods furnished 10.8 mg of 123; δ CDCl₃

5.95 (s, 2), 5.67 (t, J = 7 Hz, 1), 5.15 (m, 1), and 1.0-2.9 (series of multiplets, 8).

Magnesium Bromide-Promoted Rearrangement of 66. A solution of anhydrous magnesium bromide in ether was prepared by the addition of 1.80 g (9.6 mmol) of 1,2-dibromoethane in 25 ml of ether dropwise to 0.25 g (10 mg-at) of reagent grade magnesium turnings in 75 ml of ether at the reflux temperature. After being heated for 6 hr, the solution was filtered and stored at 0° under nitrogen.

To a magnetically stirred solution of 22 mg (0.14 mmol) of 66 in 10 ml of anhydrous ether was added 10 ml of the above solution. After 15 min, water and pentane were added and the organic layer was separated,
washed, and dried. Removal of the solvent in vacuo left 190 in quantitative yield. Identification was made by spectral comparisons.

**Rhodium Dicarbonyl Chloride Dimer-Catalyzed Isomerization of 66.** To a solution of 40 mg of 66 in 300 μl of deuteriochloroform contained in an nmr tube was added 6 mg of rhodium dicarbonyl chloride dimer. The mixture was placed in a constant temperature bath maintained at 40° while protected from light and the pmr spectrum was periodically recorded. After a total of 114 hr, no signals due to 66 remained; vpc isolation gave 5 mg of 190 as the only volatile product.

**Catalytic Reduction of 190.** A mixture of 190 (38 mg), 5% rhodium on carbon (38 mg), and anhydrous tetrahydrofuran (5 ml) was exposed to a hydrogen atmosphere at ambient temperature. After the initial hydrogen consumption had subsided, glacial acetic acid (5 ml) was introduced via syringe and stirring was continued for 8 hr. The filtered solution was diluted with water, extracted with pentane, dried, and concentrated. Preparative vpc at 90° (column G) afforded two components in a ratio of 1:49. For the major product: calcd m/e 164, 1565, observed 164, 1567. This material was identical to the major reduction product of 66 and 192.
Silver(I)-Catalyzed Isomerization of 66. To a magnetically stirred solution of 145 mg (0.917 mmol) of 66 in 6 ml of anhydrous benzene was added dropwise 10 ml of 0.2 N silver perchlorate-benzene solution. After 30 min in the absence of light and atmospheric moisture, the solution was washed with dilute ammonium hydroxide solution, water, and brine, and dried. Careful solvent removal left a dark oil, preparative vpc of which at 80° (column A) afforded 65 mg (45%) of 197 as a colorless oil; λ_{max}^\text{isoctane} 243 nm (ε 12,000); δ_{\text{TMS}}^{\text{CDCl}_3} 5.8-6.25 (m, 2, H_4, H_8), 5.6-5.8 (m, 2, H_9, H_7), 5.44 (t, J = 3.2 Hz, 1, H_9), 2.73-3.05 (m, 1, H_5), 1.98-2.30 (m, 2, allyl), and 1.42-1.92 (m, 6, methylenes); calcd m/e 158.1095, observed 158.1095.

Anal. Calcd for C_{12}H_{14}: C, 91.08; H, 8.92.

Found: C, 90.87; H, 9.06.

Catalytic Hydrogenation of 197. A solution of 197 (51.1 mg) in absolute ethanol (7 ml) containing 153 mg of 5% palladium on carbon was hydrogenated at 1 atm for 1 hr. Vpc analysis revealed the formation of two products in a 6.5:1 ratio. The major component was isolated by preparative vpc (column H at 97°) and shown to be identical with the minor product from the Wolff-Kishner reduction of 200; calcd m/e 164.1565, observed 164.1567.
Reduction of 192. A solution containing 396 mg (2.3 mmol) of 192 in 20 ml of ethyl acetate was hydrogenated over 255 mg of 5% palladium on charcoal at 1 atm for 2 hr. Filtration and solvent removal left 354 mg (86.5%) of 200 as a colorless oil; $\nu_{\text{max}}^{\text{neat}}$ 1725 cm$^{-1}$.

Anal. Calcd for C_{12}H_{18}O: C, 80.85; H, 10.18.
Found: C, 81.22; H, 10.34.

Wolff-Kishner Reduction of 200. A 110-mg (0.621 mmol) sample of 200 was heated under nitrogen with 2.6 ml of triethylene glycol, 0.76 ml of hydrazine hydrate, and 102 mg of hydrazine dihydrochloride for 4 hr at 130°. Potassium hydroxide (340 mg) was added and the temperature was slowly raised to 210° while the volatile materials distilled through a 6-in. Vigreux column. After 3 hr at 200-210°, the reaction mixture was processed in accepted fashion and the residual oil was subjected to preparative vpc (column H at 97°). Two components in the ratio 1:1.3 were isolated in quantities sufficient for high resolution infrared and 100 Hz pmr analysis; $\delta_{\text{CDCl}_3}^{\text{TMS}}$ 2.1 (m, 1) and 0.8-2.0 (m, 19).
Anal. Calcd for C₁₂H₂₀ (mixture of isomers): C, 87.73; H, 12.27.

Found: C, 87.58; H, 12.27.

Silver(I)-Catalyzed Isomerization of 159. A 105-mg (0.651 mmol)

sample of 159 was treated as above

with 3.5 ml of 0.2 M silver perchlorate-benzene solution at ambient temperature for 1 hr. The

analogous workup gave 32 mg (30%) of 203; ⁶CDCl₃ 6.0 (dd, J = 8, 5

Hz, 1), 5.6 (d, J = 7.5 Hz, 1), 5.44 (t, J = 3.2 Hz, 1), 2.84 (t, J =

5 Hz, 1), 2.2 (br m, 2, allyl), and 1.4-2.0 (br m, 6, methylenes).
REFERENCES

1. (a) A. C. Cope and E. M. Hancock, J. Amer. Chem. Soc., 60, 2903 (1938); (b) A. C. Cope and E. M. Hardy, ibid., 62, 1441 (1940); (c) A. C. Cope, C. M. Hofmann, and E. M. Hardy, ibid., 65, 1852 (1941); (d) A. C. Cope, K. E. Hoyle, and D. Heyl, ibid., 63, 1843 (1941); (e) D. E. Whyte and A. C. Cope, ibid., 66, 1694 (1944).


An electron diffraction study by Wang and Bauer [J. Amer. Chem. Soc., 94, 5651 (1972)] suggests that the ground state of semibullvalene has only C₈ symmetry and that the double bonds are localized.


40. This procedure is based in part on the reports by Snyder that urazoles can be partially hydrolyzed to the ring-opened semicarbazine, an adaptation of the observations of Kelly who found that manganese dioxide oxidizes phenylhydrazides smoothly in aqueous acetic acid at room temperature, and of Pratt who uncovered the efficient oxidation of hydrazobenzenes to azobenzenes with this reagent.


44. The more vigorous alkaline hydrolysis reported by Paquette and Wingard did not afford the semibullvalene. Likewise, the oxidative hydrolysis (ethylene glycol-water, excess 30% aqueous \( \text{H}_2\text{O}_2 \), \( 120^\circ \)) followed by hexachlorodisilane treatment reported by Snyder was unsuccessful.


54. The ready formation of tetrahydrosemibullvalene under conditions of catalytic reduction has been recognized for some time and was actually employed in the initial structure proof of this ring system. 17b

55. Several grams of olefin 67 were kindly supplied by Robert E. Wingard, Jr.


57. The dimesylate used in the cyclization reaction was nearly analytical grade, the DMSO was distilled from calcium hydride, and the sodium sulfide nonahydrate was freshly recrystallized from ethanol.

58. Isopropyl alcohol is oxidized by silver nitrate under these conditions with formation of acetone and a silver minor.

59. Thanks are extended to H. C. Berk for a generous supply of keto alcohol 100.


63. J. D. Kramer, private communication.

64. Adapted from a procedure by Professor J. Berson, private communication.


69. When the solvents DMSO and HMPA were used, the dithiapropellene was obtained in very low yield.


72. The bridgehead proton assignments were confirmed by 100 MHz double-resonance decoupling studies.

73. Heating sulfone acacetate in acetonitrile-d3 at 80° (sealed nmr tube) for 2 hours did not affect a chemical change.


77. These values compare with those obtained by Anet for semibullvalene at slow exchange rate: H4, 5.6 (H4,H5), 5.0 (H3,H7), 3.2 (H5), 2.8 (H1), and 2.8 (cyclopropyl).


80. Solvent alterations are recognized to affect to a certain extent the chemical shift values of the time-averaged protons. The semibullvalenes 71 [CDCl3 (40°), 6 3.75; CS2 (45°), 3.68], 57 [CDCl3 (40°), 4.21; C6Cl4 (35°), 4.14; CS2 (45°), 4.08], and 97 [CDCl3 (40°), 5.58; CS2 (35°), 5.49] illustrate the point. That CDCl3 is a convenient, reliable solvent of choice for this purpose
is attested to by the pentamethylene derivative where the deviation between the experimentally derived $K_{eq}$ in deuteriochloroform at $40^\circ$ ($58/42$) deviates only slightly from the equilibrium constant computed on the basis of the thermodynamic quantities for the $\text{CF}_2\text{Cl}_2$ solvent system at the same temperature ($54/46$). Beyond this, internal consistency requires the comparison of the semibullvalenes under identical conditions to be entirely valid.

81. L. A. Paquette, J. R. Malpass, G. R. Krow, and T. J. Barton, 

82. The tetramethylene- and pentamethylenesemibullvalenes were reported earlier in ref. 77c.

83. The observation has been made with oxasemibullvalene 97 that a change from $\text{CS}_2$ to CDCl$_3$ solvent leads to a 0.09 Hz downfield shift in all absorptions. In the thiasemibullvalene case (same solvent change), a 0.09 Hz downfield shift is present in the $-\text{CH}_2S-$ and H$_2$ region.


87. See ref. 84, page 222, Table 7-13.

88. The change in the $36b + 36a$ equilibrium cannot be a function of strain changes. The relevant C-C bond lengths are: 1.539 Å in cyclopentane, 1.538 Å in tetrahydrofuran, and 1.536 Å in tetrahydrothiophene.


93. Evidence for the overwhelming preference by cycloheptatrienes, 1H-azepines, cyclooctatetraenes, and azocines to adopt their monocyclic valence isomeric forms is widely available from many sources.


96. Prepared from the corresponding 9,10-diazaazonane in the same fashion as 2,8-trimethylenesemibullvalene (57).


102. The author acknowledges with appreciation the invaluable advice and guidance of Professor R. J. Ouellette in the computer simulation work.

103. This shift must occur on the periphery of 163 rather than in the internal part of the structure, since migration in the latter sense gives 1 which cannot in turn provide 160.
A fourth possible isomer (ii) has been dismissed from the outset because it incorporates a highly strained trans-cycloheptene moiety.


114. Supportive data in the form of double resonance pmr studies were also compatible with this structural formulation.


119. For example, the uv spectrum of \( \text{III} \) \( \left[ \lambda_{\text{max}} \text{C}_6\text{H}_5\text{OH} \right] \) 247 nm (e 13,800)


124. The following parameters were employed: \( v_5 \), 292 Hz; \( v_4 \), 604 Hz; \( v_3 \), 569 Hz; \( v_7 \), 573 Hz; \( v_6 \), 608 Hz; \( J_{3,4} = 8.8 \) Hz; \( J_{3,5} = -0.5 \) Hz; \( J_{3,6} = 0.05 \) Hz; \( J_{3,7} = 0.05 \) Hz; \( J_{4,5} = 6.0 \) Hz; \( J_{4,6} = 0.5 \) Hz; \( J_{4,7} = 0.05 \) Hz; \( J_{5,6} = 2.4 \) Hz; \( J_{5,7} = -0.1 \) Hz; \( J_{6,7} = 5.2 \) Hz.


127. Thanks is given to Dr. Kurt L. Loening of Chemical Abstracts Service for help in naming several of the compounds described below.


129. All glassware was base washed and all solutions were degassed.


131. The dioxane was distilled from sodium-benzophenone.

132. The newly opened bomb evolves gases, which appear to be nitrogen oxides.

133. The DMF solution turns brilliant colors throughout the initial part of the reaction.

134. The \( m \)-chloroperbenzoic acid was washed with a phosphate buffer (pH 7) and then dried for 24 hr over \( \text{P}_2\text{O}_5 \) at 25°/0.02 mm before use.