HALUSKA, Robert James, 1943-
SYNTHESIS AND REACTIONS OF POLYUNSATURATED
AZACYCLES.

The Ohio State University, Ph.D., 1970
Chemistry, organic

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SYNTHESIS AND REACTIONS OF POLYUNSATURATED AZACYCLES

DISSERTATION

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

By

Robert James Haluska, B.S.

The Ohio State University

1970

Approved by

Adviser
Department of Chemistry
DEDICATION

This dissertation is dedicated to my wife, Madeleine, and daughter, Sharon, who patiently endured this effort and to my parents for their years of sacrifice on my behalf.
ACKNOWLEDGMENT

The author wishes to express his gratitude to his adviser, Professor Leo A. Paquette, for his encouragement and guidance while this research was in progress. He would also like to thank his many friends at The Ohio State University who have contributed, in one way or another, to the success of this work.
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A. 2, 4, and 6π-Electron Systems

The development of the theory of cyclic unsaturated systems reached a milestone in 1931 when Hückel introduced his \((4n + 2)\pi\)-rule. This criterion for aromaticity can be expressed as follows: planar, monocyclic systems composed of triagonally hybridized atoms containing \((4n + 2)\pi\)-electrons possess a characteristic electronic stability. Not only did this rule provide an explanation for the unique properties of benzene (1) but it also allowed the prediction of similar stabilization in molecules yet to be synthesized.

The validity of this rule in carbocyclic systems has since been confirmed and reconfirmed through the properties exhibited by other \((4n + 2)\pi\)-electron systems, the simplest of which \((n = 0)\) is the cyclopropenium ion (2). Several functionalized derivatives of 2...
have been isolated and characterized and in 1967 Breslow and co-
workers reported the isolation of the hexachloroantimonate salt
of the parent cation \(^2\) in quantitative yield. The stability of
this species when considered in relation to the strain energy of
approximately 74 kcal/mole calculated for \(^2\) \(^{2a}\) attests to the aro-
matic character of this ion. Ring current effects in cyclopropenium
ions verify electron delocalization.

Very recently the preparation of the tetramethyl and tetra-
phenyl derivatives of the cyclobutenium dication \(^3\) have been
reported. Comparison of spectral data of these ions with that of
the isoelectronic cyclopropenium ion \(^2\) provided strong evidence
of aromatic character.

Isoelectronic with benzene \(^1\) are the cyclopentadienide anion
\(^4\) and the tropylium cation \(^5\), each of which possess charac-
teristics indicative of stabilization by electron delocalization.
Though unsubstituted \(^4\) has yet not been isolated as a simple salt,
many substituted derivatives have. \(^7\) Its presence in solution, how-
ever, has long been recognized. Thus, when cyclopentadiene was
treated with sodium or potassium and the resultant solution ex-
posed to agents capable of undergoing nucleophilic attack (eg. CO\(_2\)),
substituted cyclopentadienes were produced. \(^10\) Furthermore, when the
nucleophilicity of \(^4\) was reduced by complexation as in ferrocene,
\((\text{C}_6\text{H}_5)_2\text{Fe}\), \(^11\) then electrophilic substitution could be achieved. \(^12\)

The validity of Hückel's rule for \(n = 1\) was further verified by
the isolation of stable tropylium \(^5\) salts, the properties of which
reflect aromaticity.\textsuperscript{13}

Of course, aromaticity is certainly not restricted to carbon cycles. The chemistry of pyridine (6), pyrrole (7), furan (8), and thiophene (9) has been extensively investigated\textsuperscript{14} and in each case aromatic delocalization was confirmed for these 6\(\pi\)-electron \((n = 1)\) heterocyclic analogs of benzene (1).

Although it has until recently received somewhat less attention, Hückel suggested a correlative to the \((4n + 2)\) rule, viz., \((4n)\pi\)-electron systems with the same geometrical characteristics as required for aromaticity would be subject to destabilization if delocalization occurred. The fact that this phenomenon, which has been termed antiaromaticity,\textsuperscript{15} has had less empirical validation is due at least in part to the propensity of \((4n)\sigma\) systems to undergo, when possible, geometrical distortion from planarity or molecular rearrangement. Such processes, however, may \textit{per se} support Hückel's contention in an indirect way.

The three carbocycles which contain \((4n)\pi\)-electrons where \(n = 1\) and thus might be expected to exhibit antiaromatic properties are the cyclopropenyl anion (10), cyclobutadiene (11), and
the cyclopentadienylium cation (12).

Quantum mechanical calculations employing Pariser-Parr parameters confirm simple Hückel calculations that both 10 and 12 in their singlet states are antiaromatic, i.e., destabilized relative to their open-chain analogs.

Experimental verification of the antiaromaticity of 10 is plentiful. Perhaps significant is the fact that derivatives of this ion have resisted attempts at isolation. It has also been shown that cyclopropene readily exchanged its vinylic, but not its allylic, hydrogens for deuterium in the presence of base. Further support for this concept is provided by recent reports in which cyclopropenes substituted in the 3-position by benzoyl, sulfonyl, and cyano functions were seen to exchange at a drastically reduced rate relative to their cyclopropyl counterparts.

The question of the electronic structure of cyclobutadiene (11) and its derivatives remains open. Though it has been reported that 11 was liberated from its iron tricarbonyl complex and trapped at low temperature, the extreme reactivity of this species precluded any spectroscopic analysis. In fact the only real evidence for the existence of this ring system is provided by the structure of products.
derived from its apparent generation as a reaction intermediate. To be sure, this body of experimental observations leaves little doubt that cyclobutadienes do exist and that they are not aromatic systems but the distinction between a simple lack of resonance stabilization and an actual resonance destabilization has not yet been made possible. Some evidence for the latter phenomenon has been presented however.

Several substituted derivatives of the cyclopentadienylium ion $^{23}$ (12) have been generated at low temperatures and examined spectroscopically. Except in those cases where the substituents contribute to the overall $\pi$-system of the ion (eg., pentaphenyl), the preferred ground state of the molecule was shown to be a triplet and thus aromaticity or antiaromaticity loose their significance. Perhaps, though, an antiaromatic singlet would cause the observed spin dissymmetry.

As aromaticity is not limited to carbocycles, so antiaromaticity has been invoked to explain the elusiveness of $4\pi$-electron heterocycles. Notable examples of this class of compounds are $1H$-azirine (13), oxirene (14) and thiirene (15).

\[
\begin{align*}
\text{N} & \quad \text{O} & \quad \text{S} \\
\text{R} & & \\
13 & & 14 & & 15
\end{align*}
\]

Rees $^{24a}$ has reported the first presumed addition of the nitrene derived from 16 to acetylenes (17: $R' = H$ or $C_2H_5$, $R^2 = alkyl$) to give
1H-azirines (18) and the spontaneous rearrangement of the latter to the 2H-isomers (19). This author contends that, 'the very rapid rearrangement of 18, which is presumably formed first, to 19 under such mild conditions strongly supports the high energy, antiaromatic nature of the former.' Like cyclobutadiene (11), however, the probability of antiaromaticity in 15 must await the direct examination of a member of this class for verification.

The possibility of labile oxirenes (14) as intermediates in the oxidation of acetylenes has recently been proposed by Ciabattoni and co-workers.

Utilizing flash photolysis in conjunction with mass spectrometry the reaction between sulfur atoms and acetylenes has been
Among the species produced was a \( \text{C}_2\text{H}_2\text{S} \) fragment with a half-life of approximately 2 sec. which the researchers conclued was thiirene (15). Conventional photolysis afforded thiophene (2) presumably arising from the reaction of 15 with another molecule of acetylene.

\[
\text{HC} = \text{CH} + \text{COS} \xrightarrow{\text{hv}} \text{HC} = \text{CH} \quad \xrightarrow{\text{HC} = \text{CH}} \quad \begin{array}{c}
\text{S} \\
15
\end{array}
\]

In retrospect, the energetic advantage associated with electron delocalization in the 2 and 6\( \pi \) systems discussed is made possible by the planarity of these molecules. In most cases (1 - 4, 6 - 9) simply the size of the molecule and the type of hybridization present determine a rigid planar or nearly planar geometry. Only in the case of the tropylium ion (5) is a distortion from the non-planar cycloheptatriene (28, see below) geometry necessary for maximum orbital overlap. The resultant slight increase in angle strain is, however, more than compensated for by aromatic stabilization.

The same rigid geometry as in the small ring aromatics is similarly demanded in the (4n)\( \pi \) systems (where \( n = 1 \) discussed above (10 - 15). With respect to the latter, however, this planarity optimizes the possibility of electronic destabilization. The over-all result of this energetically unfavorable situation is that, at
best, these systems have a very transitory lifetime or exhibit, in the case of derivatives of $12$ (and possibly $11^2$), a triplet ground state.

B. Heterotropolidines - $8\pi$-Electron Systems: Conformation and Synthesis.

Cyclooctatetraene (20), the $8\pi$-electron analog of benzene (1) is a $(4n)\pi$ system which, if planar, might be expected to be antiaromatic. Raman spectroscopy, electron diffraction data, and nmr spectroscopy, however, have conclusively shown that cyclooctatetraene is a localized polyene with rapidly inverting "tub" geometry (21). Thus, the unfavorable consequences of the planar array of $(4n)\pi$ electrons seen in smaller rings are avoided in this system as a result of geometrical distortions allowed by the more flexible structures of larger rings. The properties of the recently reported 2-methoxyazocine system (22) similarly reflect no antiaromatic destabilization. The isoelectronic tropenide anion (23), on the other hand, has been shown to require a highly symmetrical structure and may in fact be antiaromatic. The propensity of this ion to undergo further reduction to form the dianion
radical \( ^{24} \) would tend to support this possibility.

The heterotropolilidines, \( 1H \)-azepine \( ^{25} \), oxepin \( ^{26} \), and thiepin \( ^{27} \), the \( 8\pi \)-electron analogs of pyrrole \( ^{7} \), furan \( ^{8} \), and thiophene \( ^{9} \) are isoelectronic with the tropenide anion \( ^{23} \) and, if planar, may display antiaromatic characteristics. Although planarity is feasible in such molecules (with some small increase in strain energy), it would seem unlikely that maintenance of such a conformation would be energetically rewarding since the resultant overlap of two heteroatomic electrons with the triene unit is predicted to lead to a total increase in the energy of the system. \( ^{34} \)

In addition, Hückel molecular orbital calculations \( ^{35} \) for \( 1H \)-azepine \( ^{25} \) reveal that this system would possess marked polyene character accompanied by strong localization of the electrons on nitrogen and the double bonds and little, if any, propensity toward delocalization.
Although 1H-azepine (25) itself has not yet been isolated (see below), the conformation of derivatives of this system and of similar systems has been examined in detail. Variable temperature nuclear magnetic resonance studies on cycloheptatriene (28) clearly reveal that this molecule exists in a "boat" conformation and like cyclooctatetraene rapidly undergoes ring inversion at room temperature. The equilibrium between 28 and norcaradiene (29) was not detected by this method. Vapor phase electron diffraction diagrams confirm the non-planarity of tropilidine (28).

Detailed analysis of the data obtained from the temperature variant nmr spectra of oxepin (26) reveal that it too is subject to rapid "boat to boat" interconversion but unlike cycloheptatriene this molecule also exists in equilibrium with its valence tautomer, benzene oxide (30).
Conformational analysis of N-carbethoxy-1H-azepine (31) shows its closer similarity to tropilidine (28). Nmr data indicate that in solution, 31 exists in a non-planar boat form (32).

![Chemical structures](image)

and that the concentration of the azanorcaradiene tautomer (33), if present at all, is below the detection limits of the instrumentation. The only authentic azanorcaradiene known at this time is 34 in which the constraining effect of the trimethylene bridge prevents ring opening.

![Chemical structure](image)

Before summarizing the synthesis of 1H-azepine derivatives, a word on nomenclature is in order. The name azepine applies equally well to four isomeric parent ring systems (25, 34-36), the particular structure in question is denoted by indicating the position of the odd hydrogen atom with a locant followed by an italicized
capital H. Thus, \(34\) is properly termed 2H-azepine, \(35\) becomes 3H-azepine, and \(36\) is 4H-azepine.

Since \(34-36\) are not \(8\pi\)-electron systems, the synthesis of these systems will not be reviewed here except for the cases in which 3H-azepines arise from rearrangement of initially formed 1H-isomers. Suffice it to say that no report of a 2H-azepine has appeared in the literature and that the chemistry of 3H- and 4H-azepines has recently been reviewed.

In 1912, Wolff reported the isolation of a new type of material which he called 'dibenzamil' from the pyrolysis of phenyl azide in the presence of aniline. The structure which he assigned to this substance, \(37\), was later modified by Huisgen and co-workers to that of a 2H-azepine derivative (38). In 1966, however, Doering and Odum remodified the structure (39) and showed that the reaction also proceeds with other amines bearing an active hydrogen to form 2-amino-3H-azepines. The mechanism suggested for this process (outlined below)
involves the closure of the initially formed aryl nitrene to azirine (40) which reacts with the amine to form a 1H-azepine (41) which spontaneously rearranges to the more stable 3H-isomer (42).

An analogous mechanism is probably operational in the conversion of enthrenils (43) to 3H-azepine derivatives (44).

Only one report has appeared in the literature involving the synthesis of 1H-azepine (25). The author claimed that alkaline hydrolysis of 31 gave the potassium salt of carbamic acid 45 which
was decarboxylated in the presence of dilute acids to afford 25. This molecule was said to be spectroscopically similar to pyrrole (7) and thermally very unstable, rapidly rearranging to 35. No detailed information concerning 25 has appeared since the publication of the preliminary report.

The photolysis or pyrolysis of ethyl azidoformate in the presence of benzene have led to the synthesis of the first stable 1H-azepine derivative (31). Evidence has been presented which in-

dicates that the reaction proceeds by the addition of a singlet nitrene to 1 in a concerted manner to afford 33, which rapidly opens to the observed product.

The broad utility of this method for the synthesis of azepines derived from benzene itself, i.e., those with no ring substituents
other than on nitrogen, has been verified. Thus, varying the azide employed, the preparations of N-carbophenoxy-, N-cyano-, and N-azidocarbonyl-1H-azepine have been reported. When substituted aromatic substrates are used in place of benzene, however, the first limitation of this synthetic route becomes evident. The nitrene intermediate is so reactive that its addition is random and isomeric mixtures of 1H-azepines are produced which, in general, defy separation. Unless symmetry simplifies matters, as in the preparation of 45, the synthesis of 1H-azepines with specific substituents at one of the three different ring positions is not therefore feasible by this method. A second limitation of this nitrene insertion route is seen in the decomposition of sulfonyl azides under the reaction conditions; only low yields of products derived from the formal insertion of the nitrene into C-H bonds are isolated (see Results and Discussion for further mention of this topic).

Prinzbach and co-workers have developed a method for the preparation of 4,5-dicarbomethoxy-1-substituted-1H-azepines (46a). These workers found that pyrrole derivatives (47a), substituted on nitrogen with strong electron-withdrawing groups, underwent Diels-
Alder cycloaddition with dimethyl acetylenedicarboxylate (48) to give 7-azanorbornadiene derivatives (49a). These adducts were converted upon irradiation to the corresponding azaquadricyclanes (50a) which in turn were transformed at 20-40° to the azepines (46a).

The only other synthetic route, a very limited one, to derivatives of this ring system has been reported by Childs and Johnson.

These workers found that treatment of 51 with potassium t-butoxide resulted in the formation of azepine 52 and the bicyclic molecule 53. The latter was seen to isomerize to the former at room temperature. The mechanism for the conversion has not been firmly elucida-
If the methyl group on nitrogen in 51 was replaced by a hydrogen atom, only $3\text{H}^-$ and $4\text{H}^-$-azepines were isolated.

Synthetic entry to the oxepin ring system (26) has been accomplished in three essentially different ways. Analogous to their azepine synthesis, and actually predating it, Prinzbach and co-workers achieved the conversion of furan $4\text{Jb}$ into the 4,5-disubstituted oxepin $4\text{Ob}$. More recently, van Tamelen and Carty reported that pyrolysis of $5\text{k}$, obtained from the epoxidation of Dewar benzene (55), resulted in the formation of oxepin (26).

In 1964 Vogel and co-workers introduced the most versatile method of oxepin synthesis. Their scheme, as illustrated below, was based upon the concept that oxonorcaradiene (30) and oxepin (26) were simply valence-bond isomers and that synthesis of the former would lead to the latter. Thus they found that bromination
of 56 gave dibromide 57 which upon double dehydrohalogenation afforded the equilibrium mixture 30 = 26. By the epoxidation of appropriate dihydrobenzene systems, specifically substituted derivatives of 56 have been prepared and converted to the corresponding oexepins.

Thiepin (27) has not yet been synthesized. Instead benzene and sulfur are produced in experiments directed toward the preparation of this molecule. The fact that benzo-fused thiepins have been reported to undergo, upon heating, extrusion of sulfur to form the corresponding aromatic hydrocarbon suggests that thiepin may have been present as a transient intermediate.

In 1967 Mock reported the synthesis of thiepin-1,1-dioxide (58). The increased stability of this 6π-electron molecule has been interpreted in terms of delocalization made possible by vacant d orbitals on sulfur in a manner somewhat similar to the delocalization
allowed by the polarized carbonyl bond in tropone (52). Upon melting, 58 expels sulfur dioxide to form benzene (1), presumably via episulfone 60. Although this synthetic route is not completely appli-
cable to the preparation of certain substituted derivatives of 58 those which have been isolated exhibit properties supporting the possibility of cyclic conjugation.

In view of our interest in the chemistry of 1H-azepines our efforts were directed toward the development of a general synthetic approach to this novel ring system, an approach which would avoid all of the serious limitations noted above. In particular, the scheme should be such that it would allow for the positionally selective introduction of one or more substituents at the three different ring positions and the placement of a variety of func-
tional groups on nitrogen.
The effort was divided into two parts reflecting the above-mentioned requirements. The aspects of the endeavor concerned with ring substitution received the attention of Dr. Donald E. Kuhla (Ph.D., The Ohio State University, 1969) and are here briefly reviewed.

The synthetic scheme was based upon the concept of valence-bond isomerization similar to that employed by Vogel in his oxazepin synthesis and is illustrated below. The introduction of substituents on selected ring positions was achieved by the utilization of properly substituted derivatives of 1,4-dihydrobenzene (61). For example, 2,5-dihydrotoluene (62) was converted to a mixture of β-iodocarbamates 63 and 64 and the latter individually processed as outlined to give the azepines 65 and 66. In this way there was produced a number of specifically substituted and annelated azepines.
Part I of this dissertation deals with the development of a versatile synthesis of 1H-azepines which allows the placement of a variety of functional groups on the nitrogen atom and substituents on the ring carbon atoms.
Results and Discussion

As was discussed in the introduction, the 1H-azepine system (67) possesses a continuous cyclic array of $8\pi$-electrons and thus may exhibit antiaromaticity. Aside from stereochemical factors, the extent to which this energetically unfavorable phenomenon would be expected to operate would depend upon the ability of the lone pair of electrons on nitrogen to enter into conjugation with the remainder of the $\pi$-system. If such is the case, then the antiaromaticity of 1H-azepine would be sensitive to the electronic nature of the substituent, R. Thus, electron-donating functions, such as an alkyl group, in the 1-position would be expected to increase the possibility of antiaromatic destabilization. On the other hand, a strong electron-withdrawing group (e.g., sulfonyl) would have the opposite effect.

Even apart from the possible antiaromaticity of this unusual system, our interest in the effect of nitrogen substituents on the properties of 1H-azepines prompted this undertaking.
The synthetic scheme was modeled after Vogel's valence-bond isomerization approach to oxepins and as such required the preparation of aziridine 68 as the key intermediate.

\[
\text{Scheme I}
\]

The introduction of nitrogen functions by the electrophilic addition of the pseudohalogen iodine isocyanate (INCO) to olefins has been extensively studied. It has been demonstrated that the additions generally occur in a stereospecific manner and that the iodine and isocyanate functions are introduced trans to each other and diaxially in rigid, fused cyclohexanes. The isocyanate function can usually be converted to a carbamate and the resulting \( \beta \)-iodocarbamates serve as convenient precursors to aziridines (Scheme I).

Utilization of this reagent allowed the preparation of the requisite aziridine (68) in practical quantities (Scheme II). Thus, monoaddition of iodine isocyanate (generated in situ by the reaction of iodine and silver cyanate) to 1,4-dihydrobenzene (61; obtained
Scheme II

by Birch reduction of benzene) gave β-idoisocyanate 62 which upon methanolysis afforded β-iodocarbamate \( \text{sec} \) in 53% yield (based upon 61). Simultaneous cyclization, saponification, and decarboxylation of 70 in refluxing aqueous potassium hydroxide gave aziridine 68 in 88% yield. Alternatively, treatment of 70 with powdered sodium
methoxide in anhydrous tetrahydrofuran produced aziridine 71 (54\%) \(^{40}\) which was hydrolyzed as above to afford an 83\% yield of 68. As another alternative, 69 was itself exposed to aqueous potassium hydroxide and thereby converted to aziridine 68 (51\% based upon 61). The comparative synthetic utility of these three alternative methods for the conversion of 61 to 68 is judged by a consideration of both yield and the amount of experimental manipulation necessary to achieve the conversion. In this instance, both factors point to the same conclusion. The most direct method, i.e., 61-69-68 is judged the best with an overall yield of 51\%. Secondly, the route 61-69-70-68 provided a 47\% yield and lastly, 61-69-70-71-68 reflected its complexity by affording a 25\% overall yield.

With the availability of 68, a secondary amine, progress through the synthetic scheme had reached the point at which functionality was to be introduced. The treatment of this aziridine with the acid chloride (RC\(\text{Cl}\)) corresponding to the group desired as the nitrogen substituent in the azepine was found to be an excellent means to achieve this end (Scheme III). In this way, functionalized aziridines \(72\) were obtained by the addition of methane-sulfonyl chloride (a), benzenesulfonyl chloride (b), p-bromobenzenesulfonyl chloride (c) and diphenylphosphinic chloride (d) to a solution of 68 in benzene at 0\(°\) containing triethylamine as an acid scavenger (see Table I for yields).

Bromination of aziridines \(72\) (Scheme III) in methylene chloride at -78\(°\) proceeded smoothly to give dibromides \(73\) in excellent yields (Table I).
Scheme III

![Chemical structure diagram]

Table I

<table>
<thead>
<tr>
<th>R</th>
<th>72 Yield</th>
<th>73 Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>a: $\text{SO}_2\text{CH}_3$</td>
<td>91.7</td>
<td>82.8</td>
</tr>
<tr>
<td>b: $\text{SO}_2\text{C}_6\text{H}_5$</td>
<td>96.4</td>
<td>71.2</td>
</tr>
<tr>
<td>c: $\text{SO}_2\text{C}_6\text{H}_4\text{Br}_p$</td>
<td>73</td>
<td>100</td>
</tr>
<tr>
<td>d: $\text{PO}((\text{C}_6\text{H}_5))_2$</td>
<td>100</td>
<td>99.2</td>
</tr>
</tbody>
</table>

Double dehydrchalogenation of dibromides $73\text{a-c}$ was achieved by the action of potassium t-butoxide in tetrahydrofuran at 0° (Scheme IV). Azeptines $74\text{a-c}$ were thereby obtained as very stable, highly
crystalline yellow solids in 47%, 52%, and 68% yields, respectively.

Scheme IV

\[
\begin{align*}
&\text{Br} \quad \text{Br}^* \\
&\text{Br} \quad \text{Br}^* \\
&\text{Br} \quad \text{Br}^*
\end{align*}
\]

\[ \text{KOT-Bu} \]

\[
\begin{align*}
&\text{NR} \\
&\text{NR}
\end{align*}
\]

\[ \text{73a-c} \]

\[ \text{75a-c} \]

This reaction is viewed as proceeding through benzene imine intermediates \text{75a-c} which undergo spontaneous ring opening to the observed products. This hypothesis is supported by the isolation of azanorcaradiene \text{34} from a completely analogous dehydrohalogenation. \text{40}

Unlike \text{73a-c}, dibromide \text{73d} was not transformed into the azepine (\text{74d}) by potassium t-butoxide. Instead, aziridine cleavage products \text{76} and \text{77} were isolated (Scheme V). The reason why this system is diverted from a simple dehydrohalogenation pathway is probably not
because of strain release since such factors would not be expected to vary significantly among the dibromides. This behavior, however, may simply reflect the greater ability of a diphenylphosphinic amide anion to compete effectively with bromide ion as a leaving group in an $E_2$ process and as such is probably associated with electronic factors.

The flexibility of this approach to $1H$-azepine synthesis is demonstrated by the successful conversion of $73d$ to $74d$. Since the last step in the scheme is merely a dehydrohalogenation, the particular reagent employed to accomplish the conversion may be varied to fit the peculiarities of the particular system in question. With respect to the case at hand, the addition of 1,5-
diazabicyclo[4.3.0]non-5-ene (78, DBN) to 73d in refluxing tetrahydrofuran afforded 74d in 85% yield as a stable, yellow solid.

As stated in the introduction, our goal was to develop a general synthetic approach to the 1H-azepine system which would allow for both selective ring substitution and varied nitrogen functionalization. The preparation of 2-methyl-N-(p-bromobenzenesulfonyl)azepine (79) (Scheme VI) attests to the versatility of the scheme. Thus,

Scheme VI

\[
\begin{align*}
&\text{\(63\)} \quad \text{\(\rightarrow\)} \quad \text{\(80\)} \quad \text{\(\rightarrow\)} \quad \text{\(81\)} \quad \text{\(\rightarrow\)} \quad \text{\(79\)} \\
\end{align*}
\]

\(\beta\)-iodocarbamate 63, when processes as above, gave 80 (72%), 81 (97%) and 82 (94%).

The reaction of 82 with base was, like 73d, sensitive to the type of base employed. Use of potassium t-butoxide resulted in the
isolation of two products of which 79 was the minor (4%). The major product (26%) was found to be the aromatized material 83, the forma-

\[
\begin{align*}
\text{CH}_3 \\
\text{NHSO}_2\text{C}_6\text{H}_4\text{Br}_p
\end{align*}
\]

\[83\]

\[
\begin{align*}
\delta^+\text{CH}_3 \\
\delta^-\text{N}
\end{align*}
\]

\[84\]

tion of which is probably associated with the methyl group's ability to stabilize a more polarized aziridine C-N bond (84). DBN (78), on the other hand, gave 47% of white, crystalline 79.

Since the completion of the above work other researchers in this laboratory have employed this technique to prepare azepines 85 and 86.

\[
\begin{align*}
\text{COCH}_3
\end{align*}
\]

\[85\]

\[
\begin{align*}
\text{NSO}_2\text{C}_6\text{H}_5
\end{align*}
\]

\[86\]

With the successful preparation of all of these compounds, it becomes clear that ready access to a large number of nitrogen-

\[40\]

-substituted azepines is now available without concern for the re-

activity of the corresponding nitrene.
Molecular Geometry of 1H-Azepines. As discussed earlier, the extent to which antiaromaticity would be expected to operate in heterotropyldidines would be a function of molecular geometry. As the preferred conformation approached planarity, the impact of the destabilizing influence of the cyclic $8\pi$-electrons upon the molecule would advance toward a maximum. The probability that the 1H-azepine system is not planar was indicated by the nmr studies of Gunther and Hinrichs in 1966.\textsuperscript{38} Successful synthesis of highly crystalline 7bc provided an excellent opportunity to examine directly the molecular geometry of a 1H-azepine. In conjunction with Professor I. C. Paul the crystal structure of 74c has been determined by X-ray studies (heavy atom method).\textsuperscript{71}

The molecule was found to exist in a boat conformation (87), the double bonds are localized at C$_2$-C$_3$, C$_4$-C$_5$, and C$_6$-C$_7$ and the two atoms which comprise each double bond and their four immediate neighbors are coplanar. Additional molecular dimensions denote
substantial $sp^2$ character for the nitrogen atom. This indicates that
74o (and presumably all closely related $1H$-azepines) is a true poly-
ene which exhibits little propensity to exist in the tautomeric az-
norcaradiene form (88) or as an azahomoaromatic entity such as 89.
In summary, it follows from these data that $1H$-azepines are non-
planar in the crystalline state and very likely also when in solu-
tion. As such, antiaromaticity would not be expected to be sig-
nificant in this system and no effects unequivocally attributable
to this phenomenon have been observed.

**Interaction of Nitrogen's Non-bonded Electrons with the Triene
$\pi$-Systems.** Although antiaromatic effects would be at a minimum in
the $1H$-azepine system for stereochemical reasons, the interaction
of the lone pair of electrons on nitrogen with the triene $\pi$-system
is evident from nmr data. In principle, as the availability of these
non-bonded electrons increases, the charge density in the ring would
be expected to increase and as a result the ring protons would ex-
perience greater shielding; and vice-versa.72 The variation of the
positions of vinyl proton resonance signals in a series of $1H$-azepines
in relation to the electronic nature of the nitrogen function re-
veals the existence of electron delocalization.

Nuclear magnetic resonance data for N-methylazepine (90),73
N-carbomethoxyazepine (91),40 N-methanesulfonylazepine (74a), and
N-($p$-bromobenzensulfonyl)azepine (74c) (Table II) illustrate this
point. The effect of an electron-donating substituent in the 1-
position as in 90 is to increase the availability of the lone pair
Table II
Vinyl Proton Resonances of Selected 1H-Azepines

<table>
<thead>
<tr>
<th>Compound</th>
<th>Vinyl Resonances&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Cycloheptatetraene" /></td>
<td>4.5 - 5.0</td>
</tr>
<tr>
<td><img src="image" alt="Cycloheptenone" /></td>
<td>6.0 (H₄), 5.83 (H₂), 5.3-5.55 (H₃)</td>
</tr>
<tr>
<td><img src="image" alt="Cycloheptenone" /></td>
<td>6.20 (2H), 5.76 (4H)</td>
</tr>
<tr>
<td><img src="image" alt="Cycloheptenone" /></td>
<td>5.74 - 5.87</td>
</tr>
</tbody>
</table>

<sup>a</sup>δ-values vs. internal TMS.  <sup>b</sup>Ref. 73.  <sup>c</sup>Ref. 40.
and as a result the vinyl proton absorptions in this molecule appear at the highest field. Replacement of the methyl with a withdrawing substituent such as carbomethoxy (91) produces a marked downfield shift indicating less overall contribution from the nitrogen electrons. A further increase in the electron-attracting power of the N-substituent as in 74a is seen to cause a corresponding decrease in ring charge density as reflected in the greatest downfield movement of the vinyl proton patterns. Similarly, the olefinic proton resonances in 91 extend 0.57 ppm further upfield than those of 74c.

That these effects are in fact due to interaction of the nitrogen electrons with the \( \pi \)-system and not simply inductive influences operating along the \( \sigma \)-bonding framework has been demonstrated by other researchers in our laboratories. Their experiments on derivatives of 91 have verified implications from molecular orbital calculations, that the proton at the 3-position is the most shielded of the ring protons. If inductive effects were responsible for differences in the chemical shifts of the ring protons, then proximity to the nitrogen would govern the ordering of the absorption sequence and the protons in the 4-position would be expected to resonate at highest field. In actuality these protons appear at the lowest field of the three.

**Mass Spectra.** The overwhelmingly favored electron impact fragmentation of 1H-azepines 74a-c and 72 occurs between the ring nitrogen atom and the 1-substituent to give the corresponding azatropylium cation 92 (illustrated in Scheme VII for 74a) as the base peak
Although the azepinium molecular ion is always seen, its intensity is variable within the series (see Table III). Another feature of the spectra is the loss of HCN from 92 (possibly via 94) to give the cyclopentadienylium ion 95 (m/e 65) which decomposes further by the loss of acetylene to yield the cyclopropenium ion 96 (m/e 39). This fragmentation pattern parallels the behavior of aniline under such conditions since the latter compound decomposes by way of intermediate azepinium ions. N-carbalkoxyazepines with no ring substituents follow this same pattern.
Table III
Prominent Mass Spectral Fragments of 74a-d and 79

<table>
<thead>
<tr>
<th>Compound</th>
<th>m/e (% relative abundance)</th>
</tr>
</thead>
<tbody>
<tr>
<td>74a</td>
<td>39 (20), 65 (70), 92 (100), 171 (15)</td>
</tr>
<tr>
<td>74b</td>
<td>39 (15), 65 (38), 92 (100), 233 (15)</td>
</tr>
<tr>
<td>74c</td>
<td>39 (18), 65 (45), 92 (100), 311 (2), 313 (5)</td>
</tr>
<tr>
<td>74d</td>
<td>39 (9), 51 (13), 65 (17), 77 (26), 92 (25), 201 (100), 293 (48)</td>
</tr>
<tr>
<td>79</td>
<td>39 (25), 53 (13), 65 (37), 77 (35), 79 (19), 106 (100), 325 (4), 327 (5)</td>
</tr>
</tbody>
</table>

Azepine 74a is also seen to follow this fragmentation pathway but the base peak is associated with scission of the P-N bond to give (C₆H₅)₂PO⁺.

Selected Reactions of N-Methanesulfonylazepine. The effect of increasing the electron-withdrawing power of the N-substituent of 1H-azepines is reflected in another property of this system, i.e., overall stability. While N-alkyl azepines (eg. 90)⁷³ are extremely labile materials prone to rapid decomposition, ⁴⁰b the N-carbonyl azepines ⁴⁰b,⁴⁹,⁵⁰ are considerably more stable. For example, N-carbalkoxyazepines can readily be handled in the atmosphere at room temperature. Longer exposure to these conditions is, however,
frequently found to lead to loss of azepine structure. The stability of N-sulfonyl (74a-c, 79) and N-diphenylphosphinoxyazepines (74d), on the other hand, is seen to be remarkable. Samples of these materials have been stored at ambient temperature with no special treatment for 3 years with no observable change. The increase in stability within the series parallels the increase in effective electronegativity of the N-substituent and therefore may be due to the resultant decrease in delocalization of the non-bonded nitrogen electrons.

In view of the similarities and differences discussed above and because of the ready availability of the N-substituted azepines allowed by our synthetic approach, selected chemical transformations of N-methanesulfonylazepine (74a), as a representative example of the series 74a-c and 79, were examined. The purpose of this study was to compare the behavior of 74a with the chemical reactivity of other azepines in an effort to more completely characterize the nature of this novel heterocycle.

Thermal dimerization of 1H-azepine derivatives has received much attention in recent years. It has been shown, for example, that N-carbomethoxyazepine (91) at 120-130° undergoes dimerization to form the (6+4) adduct (97a) (Scheme VIII) and that thermolysis of this material (or 91) at 200° caused its transformation into 98. In similar fashion, we have found that pyrolysis (122°, 2 hr.) of N-methanesulfonylazepine (74a) in a sealed thick-walled ampule gave, after chromatography, dimer 97b (51%) whose nmr spectrum is
remarkably similar to that of 97a and is clearly indicative of eight vinyl protons, three protons on allylic carbon bearing nitrogen, and two nonequivalent methanesulfonyl groups. A 6% yield of methanesulfonylanilide was also obtained. As expected, partial hydrogenation of 97b gave enamide 99b; again, nmr spectral correlation confirmed its structural similarity to 99a. Compound 99b resisted all attempts at further catalytic reduction.

A symmetrical dimer of the type 98 was not obtainable from 74a since the higher temperatures required for this conversion caused
total decomposition.

Another cycloadditive transformation of the 1H-azepine ring system which has received attention in recent years is the Diels-Alder addition of tetracyanoethylene (100, TCNE). For example, 91, when heated with TCNE, was shown to give rise to the (4+2) adduct 101a (Scheme IX). Analogously, we have found that in refluxing toluene

\[ \text{Scheme IX} \]

\[
\begin{align*}
R & = -\text{CO}_2\text{CH}_3 & 100 & \quad \text{R} & = -\text{CO}_2\text{CH}_3 \\
74a & : R = -\text{SO}_2\text{CH}_3 & 101a & : R = -\text{CO}_2\text{CH}_3 \\
74b & : R = -\text{SO}_2\text{CH}_3 & b: R = -\text{SO}_2\text{CH}_3
\end{align*}
\]

74a reacted with TCNE to form 101b.

As was stated in the introduction, decomposition of sulfonyl azides in the presence of aromatic substrates results only in the isolation of anilides, i.e., formal C-H insertion products. A recent report, while confirming this observation, suggests the possibility of the corresponding azepine as a transient intermediate. These authors report that they were able to trap N-methanesulfonyl-azepine (74a) as its tetracyanoethylene adduct (101b) by the pyrolysis of the corresponding azide in benzene at 120\(^\circ\) in the presence of excess TCNE. The data which they present for the adduct are identical
to that which we have observed for 101b. Their attempts to isolate
the azepine by pyrolysis at a lower temperature were unsuccessful.

N-Methanesulfonylazepineiron Tricarbonyl. A number of \( \pi \)-bonded
olefin complexes of transition metals are known in which the free
ligand has \( \pi \)-electrons to offer in excess of the electronic require-
ments of the metal. Several of these \( \pi \)-complexes are now recognized
to be subject to degenerate tautomerism by virtue of the capability
of the metal atom to move from one conjugated diene unit to the
next. The best known species of this type is the cyclooctatetraene-
iron tricarbonyl complex. \(^{79}\) Iron tricarbonyl complexes of \( 1H \)-
azepines were considered by us to be possible new examples of such
fluxional molecules.

The reaction of N-methanesulfonylazepine (7\( \alpha \)) with iron
enneacarbonyl at ambient temperature in tetrahydrofuran solution
produced in 69\% yield the air stable, highly crystalline iron tri-
carbonyl complex 102. In our laboratories, several other azepines

\[
\begin{align*}
\text{Fe(CO)}_3 \quad (\text{CO})_3\text{Fe} \\
\text{N} \quad \text{SO}_2\text{CH}_3 \\
\text{N} \quad \text{SO}_2\text{CH}_3
\end{align*}
\]

have also been found to react analogously. The proton nmr spectra
of the various complexes, 102 included, are dramatically temperature
dependent. At room temperature, the equilibrium process as shown for 102, is occurring at such a rate that broad coalesced peaks are observed. In the vicinity of 65-85°, the movement of the iron tricarbonyl residue between the two possible positions becomes sufficiently rapid that a symmetrical spectrum of the AA'XX'YY' type results. At 0°, however, a spectrum indicative of a fixed structure is recorded. Thus, 1H-azepineiron tricarbonyls represent new examples of fluxional π-bonded organometallic molecules.
PART II
SYNTHESIS AND PHOTOISOMERIZATION OF HOMO-1H- AZEPINE DERIVATIVES

Introduction

A. Valence-Bond Isomerizations in Cyclic Systems

The facility with which the Cope rearrangement of cis-divinyl substituted three-membered rings (103 $\rightarrow$ 104) occurs is now recognized to depend upon the group X. This differing thermal stability is revealed in the findings that cis-2,3-divinylcyclopropane (103a) and aziridine (103b) rearrange as rapidly as they are formed, even at low temperatures, whereas the oxirane (103c) and thirane (103d) rearrange at 60 and 100°, respectively. In none of these systems was the reverse process, i.e., 104 $\rightarrow$ 103 observed.
The situation is somewhat different when the termini of the vinyl groups are bonded together as in 105. The norcaradiene (105a) -

\[ \begin{array}{c}
\text{105} \\
a: \quad X = \text{CR}_2 \\
b: \quad X = \text{O} \\
c: \quad X = \text{NR} \\
d: \quad X = \text{CO (106d = 59)}
\end{array} \]

cycloheptatriene (106a) system has received considerable attention and it is now known that a mobile equilibrium exists in this system and that the equilibrium constant varies with the substituents R. Similarly, most oxepins equilibrate with their arene oxide forms (105b-106b). On the other hand, the only authentic azanorcaradiene (105c) known at this time is \(34\), the \(1\H\)-azepine tautomers (106c) being greatly preferred in the absence of steric inhibition to ring opening. Analogously, tropone (59) shows no tendency to exist as 105d, undoubtedly because of aromatic delocalization in 59 and ring strain in 105d. Thus, the intrinsic reversibility of the Cope rearrangement seen in the carbon and oxygen systems (105a and b, respectively) is often masked by an excessive thermodynamic bias in favor of one or the other of the members of a conjugate pair, such as with azepines (106c) and tropones (59).

The first detailed examination of a completely reversible Cope rearrangement was reported in 1963 by Doering and Roth. These
authors found that cuprous chloride catalyzed decomposition of diazomethane in the presence of tropilidine (28) afforded 2,3- (107) and 4,5-homotropilidine (108). Variable temperature nmr spectral characteristics of the latter clearly revealed the propensity of this molecule to undergo rapid, degenerate Cope rearrangement (108a =108b).

\[
\begin{align*}
\text{28} & \quad + \quad \text{CH}_2\text{N}_2 & \quad \text{CuCl} & \quad \rightarrow \\
& & & \\
\text{107} & \quad + & \quad \text{108}
\end{align*}
\]

The unchanging nature of the nmr of 107 between -50° and +180° indicated to these workers that this molecule does not undergo a rapid tautomeric reorganization.

Like tropone (59), neither 2,3- (109) nor 4,5-homotropone (110) show any tendency to exist in equilibrium with 111 and 112, respectively. This thermal stability may reflect either the inability of 111 and 112 to allow cyclic delocalization of electrons or the greater
strain energy of cyclopropanones relative to cyclopropanes, or both.

B. Homoconjugation.

Considerable recent attention has been paid to 6π-electron homoaromatic systems, principally the homotropylium cation (113), wherein

the cationic charge is stabilized by a homoaromatic sextet of electrons, two of which in the more classical structure 114 form part of
a cyclopropyl ring. The aromaticity of this system is attested to by two significant features. Firstly, the ion is stable enough to allow isolation of its salts and secondly, the large difference in chemical shift (5.9 ppm) displayed by the two methylene protons reflects the presence of a ring current.

The possible antiaromaticity of heterotropilidines (discussed in Part I) suggested that 'homo' derivatives of these systems should constitute suitable substrates for study of homocantiaromaticity, should such a phenomenon exist.

C. Photochemistry of Hetero- and Homoconjugated Systems.

Irradiation of a number of conjugated medium-sized ring dienes and trienes in solution has been shown to give bicyclic structures which incorporate a cyclobutene ring. Several recent photochemical studies have established that the course of such entirely general electrocyclic reactions remains unaltered upon the introduction of hetero atoms into the ring system. Thus, just as tropilidines (106a) give rise to bicyclic systems (115a), so do oxepins (106b) a: X = CR₂
b: X = O
c: X = NR
and azepines (106c). Woodward and Hoffmann have analyzed these and related transformations in terms of orbital symmetry conservation and have advanced the theory that cyclobutene formation is a concerted process resulting from allowed, disrotatory cyclization from the first excited state of the olefin.

Incorporation of a cyclopropyl group into the unsaturated system has been found to present alternative reaction pathways but not to the exclusion of cyclobutene formation. For instance, Roth and Feltzer have reported that irradiation of 2,3-homotropilidine (107) results in the generation of three products (116-118), 116 being analogous to the product formed from the triene. Similarly, the photochemistry of 2,3-homotropone (109) reveals an increased complexity associated with
a less simple structure. Nevertheless, the cyclobutene-containing isomer \( \text{119} \) remained the major product.

The photochemistry of homoheterotropolidines, systems which would incorporate both of the above features into the same molecule, promised to be an interesting subject for study if such systems could be synthesized.

Part II of this dissertation deals with the preparation of homazepines \( \text{120} \) and \( \text{121} \) and the photoisomérisation of the former.
Results and Discussion

From the facts that nitrenes add to benzene to give azepines and that carbenes add to cycloheptatriene to afford homotropolidines it was reasoned that the addition of a nitrene to tropilidine should give rise to homoazepines. We have found this to be the case. Thus, when a 7% solution of methyl azidoformate in cycloheptatriene was heated in a sealed tube at 127-128° for 4 hr., there was obtained after recovery of excess hydrocarbon, a mixture of nitrene addition and insertion products. Careful distillation of this mixture afforded homoazepines 120 and 121 in a combined yield of 35% and in a ratio of 2.2:1, respectively (vpc analysis). Final separation was achieved by preparative-scale gas chromatography.

Homoazepine 120 was obtained as a pale yellow liquid exhibiting infrared bands (film) at 1730, 1655 and 1635 cm⁻¹ and ultraviolet absorption (ethanol) at 262 nm (ε 8430). The nmr spectrum of this
substance (CDCl$_3$) shows a doublet ($J = 9.5$ Hz) at $\delta 6.65$ attributable to H-3 and three doublets of doublets centered at $\delta 6.12$ (H-6, $J = 11.1$ and 3.1 Hz), 5.66 (H-5, $J = 11.1$ and 6.6 Hz), and 5.10 (H-4, $J = 9.5$ and 6.6 Hz). In addition, a methoxyl singlet is displayed at $\delta 3.90$ and three multiplets assignable to H-1 ($\delta 3.15$), H-7 and the anti C-8 proton ($\delta 1.1$-1.6), and the syn proton at C-8 ($\delta 0.1$-0.4) are also seen.

Homoazepine 121 was isolated as a colorless oil, with infrared bands at 1725 and 1670 cm$^{-1}$ and ultraviolet absorption (ethanol) at 231 nm ($\epsilon 11,430$). The nmr spectrum of 121 reveals the symmetrical nature of the structure; thus H-3 and H-5 appear together as a doublet ($J = 9.8$ Hz) at $\delta 6.65$ and H-2 and H-6 are seen as a broad doublet ($J = 9.8$ Hz) at $\delta 5.15$. The remainder of the spectrum consists of a singlet at $\delta 3.86$ due to the methoxyl group, and multiplets centered at $\delta 1.0$-1.6 (3H) and 0-0.3 (1H) attributable to H-1, H-7, and the anti proton at C-8 on the one hand, and the syn proton at C-8, respectively.

The temperature-invariant nmr spectra of 120 and 121 (40-170$^\circ$) attest to the fact that the internal cyclopropyl bond in these structures is not prone to delocalization or to valence-bond isomerization. If equilibria of the type 120 $\rightleftharpoons$ 122 and 121 $\rightleftharpoons$ 123 are operative, the concentrations of 122 and 123 do not rise above the detection limits of the spectrometer. In view of the logical mechanistic conclusion that 120 and 121 result from valence-bond rearrangement of initially formed methoxycarbonylaziridines 122 and 123, respectively, it is
clear that 122 and 123 exhibit a marked tendency for symmetry-allowed [1,5] and [3,3] sigmatropic rearrangements, respectively. The apparent irreversibility of the $\text{123} \rightarrow \text{121}$ rearrangement is in marked contrast to the ease with which 108 undergoes rapidly reversible degenerate [3,3] sigmatropic change, i.e., Cope rearrangement. This observation clearly reveals the pronounced influence of the nitrogen function even when the molecules are so constructed that strain factors are closely balanced, as in 121 and 123. The strong bias toward structures 120 and 121 may be the result of delocalization of the nitrogen electron pair which can only be made manifest in the homoaepines. In this respect it is significant that the ordering of the sequence of vinyl proton nmr absorptions in 120 is not that which would be expected by the influence of nitrogen on local magnetic fields if this
influence was transmitted through the $\sigma$-framework.

The minor products from the nitrene reaction appear to be a mixture of air-sensitive cycloheptatrienylurethans on the basis of infrared and nmr spectra. These substances have not been investigated further.

Irradiation of an ether solution containing a mixture of 120 and 121 through Vycor optics with a 200 W Hanovia mercury arc for 2.5 hr. (followed by vpc) resulted in the complete disappearance of 120 and the simultaneous formation of two new products in the ratio of 3:2. The 4,5-isomer (121) was unaffected under these conditions and was recovered. Separation of the various components of the photolysate was achieved by means of preparative thick layer chromatography on alumina.

The major component is an isomeric, colorless liquid, the spectral properties of which strongly suggest the 5-carbomethoxy-5-azatricyclo-$[4.2.0.0^{2,4}]$oct-7-ene structure (124). Thus, the material displays a strong infrared band (film) at 1710 cm$^{-1}$ and only end absorption in the ultraviolet region. In the nmr (CDCl$_3$), 124 exhibits a narrow multiplet centered at $\delta$ 6.23 (H-7 and 8), a broadened doublet
centered at δ 4.47 (H-6), a methoxyl singlet at δ 3.63, a broad multiplet at δ 3.15-3.48 (H-1 and 4), and three well-resolved multiplets at δ 1.49, 0.77 and 0.29 (H-2 and syn and anti protons on C-3).

Although the stereochemistry of 124 was not clearly revealed by the nmr data, the 1α,2α,4α,6α configuration was assigned by analogy to the high degree of stereospecificity observed in the photoinduced electrocyclizations of 2,3-homotropone (109) and 2,3-homotropilidine (107). Thus, while this particular cyclization very likely follows a concerted, disrotatory pathway there are, however, two disrotatory modes of cyclization possible, as depicted in 126 and 127. That only one of the pathways is followed is probably due to secondary steric forces operative during the bond reorganization. For example, as bond rotation in 127 commences (to give the 1β,2α,4α,6β isomer), the two vinyl protons at the terminus of the diene system and the endo-cyclopropyl hydrogen atom are forced into close proximity. Such repulsive forces, which are absent when the same process is effected with 126, in all likelihood result in a
relative decrease in the activation energy of the process involved in the formation of $^{124}$ via $^{126}$.

The less abundant CsH$_{11}$NO$_2$ photoproduct is a colorless liquid which spectrally is indicated to possess structure $^{125}$. The compound displays intense infrared absorptions (film) at 1720, 1630, and 1610 cm$^{-1}$ and an ultraviolet maximum (ethanol) at 233 nm ($\varepsilon$ 11,500). In the nmr (CDCl$_3$), this material exhibits a broad doublet ($J = 4.5$ Hz) centered at $\delta$ 6.54 (H-3), a two proton singlet at $\delta$ 5.68 (H-6 and 7), a doublet of doublets ($J = 4.5$ and 2.5 Hz) centered at $\delta$ 5.09 (H-4), three broad multiplets at $\delta$ 4.45-4.9 (H-1), 3.9-4.2 (H-5), and 2.25-3.2 (2H, H-8), and a sharp methoxyl singlet at $\delta$ 3.74. The structural assignment of this substance as $^{125}$ is further verified when direct comparison is made with the nmr spectrum of 2-carbethoxy-2-azabicyclo[3.3.0]octa-3,6-diene ($^{128}$) (Table IV).

Chemical conformation of this assignment was derived from catalytic hydrogenation of $^{125}$, which proceeded with the uptake of two molar equivalents of hydrogen to give cis-2-carbethoxy-2-azabicyclo[3.3.0]octane ($^{129}$). The unequivocal independent synthesis of $^{128}$ is shown in Scheme X.

Cyclopentylidinecyanoacetic acid ($^{130}$) was prepared according to an established procedure.

Provita and co-workers have found that simultaneous decarboxylation of $^{130}$ and distillation gives cyclopentylidineacetonitrile ($^{131}$) in 58% yield. We have found, however, that such a procedure results in the codistillation of $^{130}$ and $^{131}$ and that refractionation
Table IV

Nmr Chemical Shift Data for \( \text{125} \) and 2-Carbethoxy-2-azabicyclo[3.2.0]hepta-3,6-diene (\( \text{128} \))

<table>
<thead>
<tr>
<th>Proton</th>
<th>( \text{125} )</th>
<th>( \text{128} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-1</td>
<td>4.45-4.49</td>
<td>4.88</td>
</tr>
<tr>
<td>H-3</td>
<td>6.54</td>
<td>6.56</td>
</tr>
<tr>
<td>H-4</td>
<td>5.09</td>
<td>5.18</td>
</tr>
<tr>
<td>H-5</td>
<td>3.9-4.2</td>
<td>3.88</td>
</tr>
</tbody>
</table>

\( a \) - Values vs internal TMS.  
\( b \) - Values for \( \text{128} \) are taken from Ref. 92a.

Scheme X

\[ \text{129} \xrightarrow{\text{ClCO}_2\text{CH}_3, \text{Et}_3\text{N}} \text{134} \]

\[ \text{130} \xrightarrow{\Delta} \text{131} \xrightarrow{\text{Pd-C}} \text{132} \]

\[ \text{133} \xrightarrow{\text{LiAlH}_4} \]
of the distillate is required to isolate pure 131 (67%). Alternatively, we have found that prior decarboxylation of 130 at 180° followed by distillation affords a 78% yield of pure 131. Hydrogenation of this material at atmospheric pressure over palladium on charcoal gave cyclopentylacetonitrile (132) in 83% yield.

A 95% yield of 2-cyclopentylethylamine (133) was obtained from the reduction of 132 with lithium aluminum hydride when the quantity of reducing agent employed was equimolar with the amount of nitrile to be reduced. Only small quantities of product were obtained when the customary 0.5 molar ratio of lithium aluminum hydride to nitrile was used. Protiva and coworkers have reported the preparation of this amine directly from 131 via a sodium/butanol reduction but careful examination of their experimental procedure revealed that the quantities of alkali metal and alcohol which they reported using were not sufficient to effect the reported transformation. In addition, we have found that employment of the proper stoichiometric quantities of reagents in a manner analogous to the reported procedure failed to convert 131 to 133.

Cyclization of 133 to cis-2-azabicyclo[3.3.0]nonane (134) was effected by means of the Hofmann-Löffler-Freytag reaction. In 1966, Schmitz and Murawaski reported the first successful cyclization of a primary amine by this method. These workers contended that the undesirable disproportionation of primary chloramines which occurs in weakly acidic solution is the result of a reaction between
a protonated and unprotonated species. The recommendation was made that concentrated sulfuric acid rather than the usual 80-85% variety be employed to prevent this side reaction. In the case of \( \text{I} \), however, the use of concentrated sulfuric acid and ferrous ammonium sulfate resulted only in tar formation, whereas the employment of milder conditions resulted in the desired transformation. Thus, \( \text{I} \) was converted to the chloramine with sodium hypochlorite and the product dissolved in 80% sulfuric acid and irradiated. The resultant \( \delta \)-chloroamine was then cyclized by the action of potassium hydroxide to give \( \text{II} \) in 30% yield (based upon \( \text{I} \)).

Functionalization of \( \text{II} \) with methylchloroformate in the usual manner gave \( \text{III} \) (73%), identical in all respects to the hydrogenated photoprodut.

Because photochemically induced vinylcyclopropane rearrangements of the type involved in the conversion of \( \text{I} \) to \( \text{II} \) were not encountered with 2,3-homotropone \( \text{IV} \) or 2,3-homotropilidin \( \text{V} \), but only with their dihydro counterparts, \( \text{VI} \), it was considered imperative to demonstrate that \( \text{II} \) did not arise by an extraneous thermal process. This is seen from the following facts: (a) \( \text{I}, \text{II}, \text{III} \) are entirely stable to the vpc conditions used during the purification procedures; (b) both \( \text{II} \) and \( \text{III} \) are seen to be present (nmr and tlc analysis) in the crude photolysate prior to any exposure to elevated temperatures.

With regard to the multiplicity of the photorearrangement of \( \text{I} \), the inability of acetone to sensitize the reaction denotes that, under the conditions of direct irradiation, \( \pi \rightarrow \pi^* \) singlet states are
probably involved and as such analysis of the two photoisomerization pathways with respect to orbital symmetry conservation is possible. As was discussed earlier, the conversion of $120$ to $124$ very likely follows the concerted, disrotatory mode of cyclization allowed in photochemical butadiene-cyclobutene transformations. The effectiveness with which the vinylcyclopropane rearrangement leading to $125$ competes with cyclobutene formation suggests that the reaction profile of the former process involved an equally low energy of activation. The fact that a vinylcyclopropane rearrangement is a sigmatropic shift of the order $[1,3]$ and that such a process is photochemically allowed if a $(\sigma^2s + \pi^2s)$ mode is followed may be significant especially since the stereochemistry expected from this type of bond reorganization is that which is observed. In the case of $120$, however, the situation is complicated by the fact that this molecule is not a simple vinylcyclopropane but one in which the migration terminus of the internal cyclopropyl bond is in the middle of a conjugated diene unit. As such the possible concertedness of this type of isomerization is uncertain and, therefore, the possibility of a stepwise radical mechanism is not ruled out.

We have found homoazepines to be singularly unreactive in cycloaddition reactions. For example, no cycloadducts were obtained when benzyne was generated in the presence of either homoazepine, nor when solutions of $120$ containing diphenylisobenzofuran or N-phenylmaleimide were refluxed for varying periods of time.
Mass Spectra. The prominent electron impact fragments of 120, 121, 124, and 125 are listed in Table V. It is clear that the fragmentation pattern followed by all four compounds is identical and that the parent ion (m/e 165) is seen in each case. It is possible
that prior to decomposition the photoproduct ions revert to a homo-
azepinium ion structure but these observations have not been studied
to an extent sufficient to warrant mechanistic speculation. Of
particular interest, however, is the structure of the ion at m/e
106. This fragment may in fact be the aromatic azahomotropilium
ion (135).
PART III
STUDIES DIRECTED TOWARD THE SYNTHESIS OF cis-9-BENZENESULFONYL-9-AZABICYCLO[6.1.0]NONA-2,4,6-TRIENE

Introduction

The impressive verification which the Hückel rule has received in the past several years suggested that a cyclic conjugated system of 10π-electrons would be endowed with aromatic character, provided that it were incorporated into a planar molecular structure. Interest in such systems has been intense in recent years; this has been prompted by a desire to demonstrate the factors that control the balance between aromatic delocalization and destabilization associated with planarity, especially in larger molecules.

Cyclodecapentaene, i.e., [10]annulene, is the simplest \((4n + 2)\pi\)-electron homolog of benzene. That this substance in its all-cis configuration (136) has been indicated only as a transient reaction

![Diagram](image)
intermediate \textsuperscript{109,110} suggests that the delocalization energy of this form is not sufficient to overcome the angle strain associated with C-C-C bond angles of 144°.

Vogel \textsuperscript{108} has suggested that cyclodecapentaene in the configuration having two trans double bonds, i.e. 137, also would not possess aromatic character because the two internal 1,6-hydrogens interfere sterically with each other, thus imposing a non-planar geometry on the carbon skeleton. This worker realized, however, that by replacing the internal 1,6-hydrogens in 137 with a monoatomic bridge considerable flattening of the C\textsubscript{10} framework was possible. He further reasoned that such a structure (138) was a valence isomer

![Diagram](image)

\begin{align*}
139 & \quad \rightarrow \quad 138 \\
\text{a)} & \quad X = \text{CH}_2 \\
\text{b)} & \quad X = \text{NH} \\
\text{c)} & \quad X = \text{O}
\end{align*}

of the cis-9,10-dihydronaphthalene derivative 139 and that as a "double norcaradiene" the latter would be expected to spontaneously rearrange to the former. Thus, synthesis of 139 would be tantamount to the preparation of 138. Such reasoning has proven correct for not only has the 1,6-methylene compound 138a been prepared by this method.
but the analogous nitrogen (136b)\textsuperscript{112} and oxygen-bridged (136c)\textsuperscript{113} systems have also. Spectroscopic characteristics and chemical properties attest to the aromaticity of these substances.

Aromatic delocalization in 10\(\pi\)-electron systems is certainly not limited to neutral molecules. In 1960, Katz reported that reduction of cyclooctatetraene, a non-planar molecule, with alkali metals proceeded with the transfer of two electrons to form the cyclooctatetraenyl dianion (140).\textsuperscript{114} Detailed nmr analysis of this material\textsuperscript{115} led to the conclusion that 140 is in actuality a planar molecule possessing a diamagnetic ring current, i.e., it is aromatic.\textsuperscript{116} Electrochemical studies confirmed this conclusion. Very recently, chemical and electrochemical studies revealed that the 2-methoxyazo-cinyl dianion (141) and several methylated derivatives display characteristics indicative of aromatic delocalization.\textsuperscript{117}

Thus, unlike all-cis cyclodecapentaene (136), eight-membered rings with 10\(\pi\)-electrons are capable of assuming a planar geometry and thereby take full advantage of the stabilizing influences associated with maximum orbital overlap. Of course, the angle strain to be overcome in the latter systems would be less since the internal
angles of a regular octagon are 135° compared to the 144° angles in 136.

If angle strain were the sole destabilizing influence to be overcome by resonance, then the balance point might be expected to lie somewhere between the strain imposed by eight- and ten-membered rings. In 1963, two independent research groups showed further that the angle strain associated with all-cis nine-membered rings is also more than compensated for by aromatic stabilization. It was found that treatment of anti-9-chloro-cis-bicyclo[6.1.0]nona-2,4,6-triene (142a)\textsuperscript{118a,b} or the anti-9-methoxy compound (142b)\textsuperscript{118a,b} with alkali metals (M) in tetrahydrofuran afforded (at room temperature) the salt of the all-cis cyclononatetraenide anion (143c). The nmr spectrum of this material consisted of a single sharp peak (δ 7.04, potassium salt; δ 6.85, lithium salt). On the basis of the known relationship\textsuperscript{119} between the charge at a particular carbon atom and the chemical shift of a proton attached to it, conversion of 142 to 143c would be anticipated to result in a shielding of the vinyl protons by

\[ \begin{align*}
R & \quad \text{M} \quad \text{RT} \\
\text{142a, } R = \text{Cl} & \quad \text{M}^+ \\
\text{b, } R = \text{OCH}_3 & \quad \text{RT} \\
\text{143c} & \quad \text{M}^+ \\
\text{143t} & \quad \text{M, RT}
\end{align*} \]
ca. 1.1 ppm from their location at ca. δ 6.0 in 142. That a rather sizeable downfield shift is in fact observed attests to the existence of a substantial aromatic ring current in the anion. The tetraethylammonium salt (M = (C₆H₅)₄N⁺) of 143 was isolated as a white solid which was stable in an inert atmosphere.  

Very recently, Boche and associates have reexamined the course of the reaction of 142b with potassium. These workers reasoned that thermal ring opening of the initially formed cyclopropyl anion would be expected to proceed in a conrotatory fashion and as such would give potassium trans,cis,cis,cis-cyclononatetraenide (143t, M⁺ = K⁺) as a primary product. In complete accord with their expectations, they found that at -40° in tetrahydrofuran-d₈ complete consumption of 142b by reaction with one equivalent of potassium afforded a solution consisting of 96 ± 2% of 143t (M⁺ = K⁺) (nmr analysis), the remainder being 143c (M⁺ = K⁺). Very significantly, the chemical shifts of the protons in 143t clearly revealed the aromaticity of this substance: the external protons resonated in the range δ 6.4-7.27 while the chemical shift of the internal proton was found to be δ 3.52. Upon warming to room temperature 143t was seen to cleanly isomerize to 143c.

In 1964, Masamune and Castellucci reported the preparation of iminocyclooctatriene 144 by the addition of the corresponding nitrene to cyclooctatetraene (20). Along with 34, this molecule is the only other example of a cis-divinylaziridine known at this time to be stable at ambient temperature (see Part II for a discussion of this subject). Upon heating at 80°, however, this substance was
found to isomerize rapidly to \( \text{145} \). That this process presents a striking contrast to the thermal conversion of the all-carbon analog \( \text{146} \) to the dihydroindene structure \( \text{147} \) has given rise to mechanistic speculation. Anastassiou has analyzed the symmetry allowed thermal processes available to \( \text{144} \) and has concluded that \( \text{145} \) is not a primary product. The possible intermediacy of N-carbethoxyazonin (\( \text{148} \)) (and a mono-trans isomer) was suggested, these being unstable
under the thermolysis conditions. It is of interest that 148 is a potentially aromatic molecule in that it does contain a continuous cyclic array of 10π-electrons in a nine-membered ring; a ring size which has been shown to be capable of assuming a planar geometry.

Part III of this dissertation deals with our efforts directed toward the synthesis of N-benzenesulfonyliminocyclooctatriene (149) for the purpose of examining its possible isomerization to the corresponding azonin (150) (and/or a mono-trans isomer).
Results and Discussion

For some time our interests have resided in the study of valence-bond isomerization routes to unsaturated nitrogen heterocycles. Thus, we have shown (Part I) that spontaneous isomerization of azanor-caradienes (75) gives rise to a variety of 1H-azepine derivatives (67)

\[
\begin{align*}
\text{N-R} & \quad \rightarrow \quad \text{N} \\
75 & \quad \rightarrow \quad 67
\end{align*}
\]

and that homo-1H-azepines 120 and 121 are available from their aziridine valence isomers 122 and 123, respectively (Part II). As a logical extension of these results our attention was focused on the next higher vinyllog of 75, specifically the N-benzenesulfonyl derivative 149 viewed as a possible precursor to azonin (150) (and/}

\[
\begin{align*}
\text{NSO}_2\text{C}_6\text{H}_5 & \quad \rightarrow \quad \text{NSO}_2\text{C}_6\text{H}_5 \\
149 & \quad \rightarrow \quad 150
\end{align*}
\]
or a mono-trans isomer).

The reasoning behind the selection of the sulfonyl group as the nitrogen function was based upon two factors. First, the N-carbethoxy derivative of 150, i.e. \( \text{148} \), was suggested to be a very unstable molecule (see Introduction). The second influence was the finding in our work with azepines that replacement of carbethoxy with benzenesulfonfyl in these systems was accompanied by a change in physical state from oils to highly crystalline solids with a concomitant large increase in overall stability. It was theorized, then, that similar desirable effects may operate in the azonin series and that 150 for that reason may be more amenable to isolation and characterization than would 148.

The first and most obvious route to 149 which was examined was the decomposition of benzenesulfonyl azide (151) in the presence of cyclooctatetraene (20). Irradiation through quartz or pyrex of a solution of 151 in 20 and of a similar solution diluted with carbon tetrachloride caused no azide decomposition to occur. In none of the photolysis experiments was nitrogen evolved nor did the intensity of the infrared absorption of the azide linkage decrease.

Thermal decomposition of the azide was then investigated. Kwart and Kahn have shown that the presence of elemental copper lowers the decomposition temperature of benzenesulfonyl azide, presumably by the formation of a more thermally labile complex. The more desirable reduced temperature afforded by this method prompted its use in this study. Thus, when benzenesulfonyl azide was heated at 85° in the presence of excess cyclooctatetraene and metallic copper
powder, loss of nitrogen was observed accompanied by the formation of, not 149, but imine 152 in 49% yield. The structure assigned to the product was deduced from infrared absorptions (film) at 1550 cm\(^{-1}\) (C=N) and 1300 and 1150 cm\(^{-1}\) (SO\(_2\)N) and the close correspondence of the nmr spectrum with that of the N-cyano derivative. Since all attempts at chromatographic purification were thwarted by partial hydrolysis, the imine was eluted through deactivated alumina and thereby cleanly converted to the corresponding ketone (153)\(^{124}\) which was spectrally identical to authentic 153.\(^{125}\)

The failure of these experiments to generate 149 led us to undertake a less direct but more general approach, one employing the bromination-dehydrobromination method of increasing unsaturation that was found to be eminently successful in our azepine synthesis. The fundamental synthetic sequence which was adopted is outlined
in Scheme XI.

**Scheme XI**

\[
\begin{align*}
\text{154} & \rightarrow \text{156} \\
\text{157} & \\
\text{156} & \leftarrow \text{156} \\
\text{160} & \\
\text{162} & \\
\end{align*}
\]

Analogous to our findings with 1,4-dihydrobenzene (61), 1,5-cyclooctadiene (154) underwent electrophilic addition of iodine isocyanate (generated in situ) to give β-iodoisocyanate 155 (Scheme XII), which without purification was converted to aziridine 156 in 48% yield (based upon 154) by the action of refluxing aqueous potassium hydroxide. A significant difference between the conversions of 69 and 155 to the corresponding aziridines 68 and 156,
respectively, is that in the latter case the reaction is much slower (27 hr. at 100° vs 9 hr. at room temperature for 69). A possible explanation for this is that in the cyclooctyl system the steric relation of the nitrogen atom to the carbon bearing iodine is not as favorable with regard to backside attack as in that conformation of
the cyclohexyl system in which these substituents are trans
diaxially disposed.

Aziridine 156 was smoothly transformed into the N-benzenesul-
fonyle derivative 157 in 77% yield by treatment with benzenesulfonyle
chloride in ether solution at 0°.

Two alternate routes to 157 were investigated. In 1969, Hassner
and coworkers reported that iodine azide, IN₃, like iodine iso-
cyanate, was a versatile pseudohalogen which was found to add to
olefinic linkages. The β-iodoazides thereby produced were shown to
be capable of undergoing reductive cyclization to aziridines. We
have applied this method to the preparation of 156 in an effort to
compare its synthetic utility in this system with that of the iodine
isocyanate method. Thus, a solution of iodine azide was prepared
by the dropwise addition of iodine monochloride to a cold (-10°)
suspension of sodium azide in acetonitrile. This mixture was then
cautiously added to a similarly cooled solution of 154 in the same
solvent. Usual work-up gave β-iodoazide 158 which without purifi-
cation was reduced and cyclized with lithium aluminum hydride to
afford aziridine 156. Sulfonylation of 156 in the predescribed
manner gave 157 in an overall yield of 50%.

Both methods, iodine isocyanate and iodine azide, were therefore
found to give rise to acceptable quantities of 157 with the
latter being slightly the better of the two. The iodine isocyanate sequence, however, was found to require less experimental manipulation than the iodine azide route and thus both methods were judged about of equal synthetic merit.

The copper-catalyzed thermal decomposition of benzenesulfonyl azide in the presence of 1,5-cyclooctadiene was also studied as a possible route to 157. Analogous to the reaction with cyclooctatetraene, however, warming of a suspension of copper powder in a solution of the azide in 1,5-cyclooctadiene (154) gave imine 159 in 48%

\[
\begin{align*}
\text{C}_6\text{H}_5\text{SO}_2\text{N}_3, \text{Cu} & \quad \text{C}_6\text{H}_{10} \rightarrow \text{NSO}_2\text{C}_6\text{H}_5 \\
70^\circ & \rightarrow \\
\end{align*}
\]

yield. This material was identified by infrared absorptions (film) at 1610 cm\(^{-1}\) (C=N) and 1310 and 1160 cm\(^{-1}\) (SO\(_2\)N) and by its clean conversion to 4-cyclooctenone.

Treatment of 157 in methylene chloride solution at -78\(^\circ\) with one equivalent of bromine gave dibromide 160 (Scheme XI) in quantitative yield.

Dehydrohalogenation of 160 proved to be a much more complex and inefficient process than would be expected. In all fourteen different sets of reaction conditions (see Experimental section for details)
were examined in which the reaction solvent (tetrahydrofuran, hexamethyolphosphoramide, 1,2-dimethoxyethane, dimethyl sulfoxide, pyridine, ethanol, and benzene), dehydrohalogenation agent (potassium t-butoxide, trityl lithium, DEN (78), sodium methoxide, potassium hydroxide, silver oxide, and silver nitrate), reaction temperature and time were varied. In summary, it was generally found that (if reaction occurred at all) work-up afforded, after chromatography, four components, the first of which was unchanged 160.

The next fraction to elute from either alumina or Florisil was an incompletely separated mixture of the monoelimination product 161 and the desired diene 162, both in poor yield. Final separation was achieved by means of fractional recrystallization. The fourth component was benzenesulfonamide.

Spectral characteristics of the monoelimination product, especially nmr, revealed that its gross structure was that of the allylic bromide as opposed to an isomeric vinyl bromide. This was made evident by the fact that the molecule contained, inter alia, two vinyl protons and one proton on carbon bearing bromine. The
remainder of the spectrum was also consistent with the assigned structure.

Our assignment of the cis stereochemical relationship of the bromine and the aziridine ring in the monoe limination product follows from the fact that this substance is not an intermediate in the conversion of 160 to 162. Thus, under conditions in which diene 162 is produced from dibromide 160, the monobromide was found not to undergo dehydrohalogenation. Instead, prolonged treatment of 161 with base resulted only in aziridine cleavage to give benzene-sulfonamide. Since it is reasonable to assume, however, that the conversion of 160 to 162 is a stepwise process, it was concluded that in the presence of an effective dehydrohalogenation agent 160 must be partitioned between cis and trans stereoisomeric monoe limination products, 161 and 163, respectively; one of which rapidly under-

\[
\text{Br} \quad \text{NSO}_2\text{C}_6\text{H}_5
\]

163

goes further dehydrohalogenation while the other does not.

Examination of molecular models of 161 and 163 led to the conclusion that the former is the correct formulation of the monobromide which was isolated. Thus it was indicated that in each isomer nonbonded interactions would be at a minimum in only one of
the many conformations in which the molecule may exist. A striking
difference between this most stable conformation of each is that
only in the trans isomer (163) does the bromine assume a position
in which it is trans-coplanar with one of the hydrogens on the
adjacent carbon atom, i.e. in a position where the energetics of a
concerted E2 process to form 162 would be expected to be at a mini-
mum. The probable preferred conformation of the cis isomer (161),
on the other hand, was found to be one in which the bromine is
staggered with respect to the vicinal hydrogens. Though bimo-

cular cis-1,2-eliminations are documented, the greater energy of ac-
tivation of this process relative to the trans type in a cyclooctyl
system might be expected to divert the reactivity of the cis
compound away from dehydrohalogenation especially since it has
another mode of reaction available to it, i.e. strain-relieving
aziridine cleavage. Hence, we conclude that the trans isomer once
formed rapidly undergoes further reaction with base to form 162
while the less reactive cis isomer 161 is that which is isolated.

Further support for this contention is derived from the fact
that molecular models of 160 indicated that this molecule may exist
in either of two stable conformations in which the trans-coplanar
elimination of hydrogen bromide from one would produce 161 while
the same process involving the other would generate 163.

As was stated before, conversion of 160 to 162 was poor under
the best of conditions and was always accompanied by the formation
of dark, intractable tar. Additionally, it was often found that re-
sults were not reproducible, especially in scale-up experiments, the yield of 162 in which was always seen to decrease. Frequently no diene was isolated at all. As a result, modifications of the synthetic scheme were investigated.

It was reasoned that treatment of 157 with one or two equivalents of N-bromosuccinimide (NBS) would give rise to 164 or 165, respectively. Further, 164 would be expected, upon treatment with base, to undergo either 1,4-dehydrohalogenation to afford 162 or 1,2-elimination generating an isomeric diene. In either event, treatment of the product with NBS would produce the same radical intermediate and thus give rise to 166 or a useful isomer thereof. On the other hand, 165

would be expected to undergo 1,4-debromination to 162 or, better yet, double dehydrohalogenation to give 142.
In actuality, upon reaction with two equivalents of NBS in refluxing carbon tetrachloride, 157 was converted in poor yield to a mixture of 160 (18%) and 164 (3%, stereochemistry unknown). No 165 was isolated. Unlike most NBS brominations which, once initiated, are sufficiently exothermic as to be self-sustaining, the above reaction required constant application of external heat to maintain solvent reflux. Similar treatment of 157 with one equivalent of NBS resulted only in the partial recovery of starting material.

It is known that in some systems reaction of olefins with NBS results in the formation of allylic bromides in which positional isomerization of the unsaturated linkage has occurred. That unrearranged structure 164 correctly represents the product formed in the reaction of 157 with NBS is clearly indicated by nmr spectral data. As can be seen in Table VI resonance positions of the aziridines of

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift, δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>157</td>
<td>2.85</td>
</tr>
<tr>
<td>161</td>
<td>4.0-4.5</td>
</tr>
<tr>
<td>162</td>
<td>4.4-4.7</td>
</tr>
</tbody>
</table>
dine ring protons in 157, 161 and 162 are sensitive to the location of transannular double bonds in these molecules. These effects are reasonable since the magnetic anisotropic influence of an olefinic linkage on a given proton is very dependent upon the spatial relationship that exists between the two. Not by coincidence then the decreased shielding of the aziridine protons upon going from 157 to 162 is directly related to the geometrical changes which occur as indicated by molecular models. Thus 157 was shown to exist in a highly puckered tub form with the aziridine protons located in the shielding cone of the double bond, whereas 162 was found to be a considerably flatter molecule in which the aziridine protons would be expected to be much less shielded. The geometry of 161 revealed that, as observed, the effect of a 4,5-positioned double bond would be similar to that seen in diene 162. In view of this, the chemical shift of these resonances in the bromination product in question (ca. 8 2.6-3.0) clearly indicates the presence in this molecule of 5,6-unsaturation (as in 157), hence, structure 164.

Structure 164 is also favored from a slightly more direct argument. It can be seen that the rearranged structures which could reasonably be arrived at in the NBS reaction are in fact 161 and 163. The compound certainly isn't 161 since this substance had already been prepared and found not to be the same as the bromination product. Further, 163 would not be expected to exhibit nmr characteristics more similar to 157 than to 161 whereas the product actually does.

In any event the synthetic merit of this approach was considered to be minimal.
The second modification of Scheme XI was designed to increase
the yields of 162 by making aziridine cleavage a less favorable alternate reaction mode. It was reasoned that the presence of the
electron-withdrawing benzenesulfonyl group lowered the energy of
activation of this undesirable process by stabilizing intermediates
in which the nitrogen atom bears a negative charge. Apparently, then,
the change of reaction sequence illustrated in Scheme XIII would be

**Scheme XIII**

\[
\begin{align*}
\text{156} & \xrightarrow{1. \text{Br}_2} \text{167} & \xrightarrow{2. \text{KOT-Bu}} \text{162}
\end{align*}
\]

expected to be of greater synthetic utility since the sulfonyl group
would not be introduced until after dehydrohalogenation.

In view of this, 156 was brominated in methylene chloride solu-
tion at -78°C and the product was treated with two equivalents of
potassium t-butoxide in tetrahydrofuran at room temperature. Since
it was found in a preliminary experiment that the material obtained
in this manner polymerized upon mild warming, the crude product was
immediately reacted with benzenesulfonyl chloride at 0°C. Chromato-
graphy of the resulting mixture afforded no diene 162 but only small
quantities of dibromide 160 (11%) and monoelimination product 161
(11%). The dehydrohalogenation process was obviously inefficient and either produced no 167 or this material decomposed prior to functionalization. With regard to the latter, a considerable quantity of dark, tarry material was formed during the reaction with alkoxide.

Another alternative route to 162 (or an isomer differing in location of double bonds) was briefly examined. 1,3,6-Cyclooctatriene (168) is readily available from reduction of cyclooctatetraene with

\[
\text{168} \xrightarrow{\text{Zn} + \text{NaOH}} \text{168}
\]

zinc and sodium hydroxide. Subjection of this material to the iodine isocyanate-potassium hydroxide and iodine azide-lithium aluminum hydride sequences gave only unusable, possibly polymeric, products.

It was concluded, then, that the original approach to 162 (Scheme XI) was, while very inefficient (<1% overall yield, at best), the method of choice.

The conversion of 162 to 166 was achieved once by the action of NBS in refluxing carbon tetrachloride with benzoyl peroxide present as a radical initiator. Similar to the transformation of 157 to 164, this reaction was not self-sustaining, i.e. reflux stopped upon re-
moval of the external heat source. Despite attempts to duplicate the reaction it was completely non reproducible. As a result of these difficulties and due to recent developments from other laboratories, work on this project was discontinued.
Recent Developments

During the course of the above work several reports had appeared in the literature concerning the synthesis and properties of heteronins.

Anastassiou and Cellura\(^{131}\) have shown that oxonin (169) can be produced by low temperature sensitized photoisomerization of cyclo-

\[ \text{hv} \quad \text{sens.} \quad \rightarrow \quad \text{oxonin} \quad \rightarrow \quad \text{structure} \]

octatetraene oxide (170) and that at room temperature this monocycle rapidly isomerizes to cis-dihydrobenzofuran structure 171. Both the nmr spectrum\(^ {131,132}\) and thermal lability of 169 suggest classical polyenic rather than aromatic character. Two other research groups have arrived at the same conclusion.

Thionin, the sulfur analog of 169, is not known at this time but highly substituted derivatives of this molecule have been reported.\(^ {134}\) The molecules show no evidence of aromatic delocalization.
N-Carbethoxyazonin (148) like 169 was found to arise from sensitized photoisomerization of its corresponding cyclooctatrienyl bicyclic form (144) and also was seen to isomerize to 172 in a manner analogous to 169. No aromatic character was seen to be associated with 148. Brief low-temperature contact of 148 with potassium t-butoxide in tetrahydrofuran, however, has been reported to give rise to the parent compound, 1H-azonin (173), which has been classified as being aromatic. The first piece of evidence suggesting aromaticity is that the substance is much more thermally stable than 148 or 169, undergoing no change on
heating for 2 hr. at 34° followed by 1 hr. at 5°. Secondly, the presence of a fairly sizeable diamagnetic ring current is indicated by the fact that all of the resonances in the nmr spectrum of $^{173}$ appeared at considerably lower field than their counterparts in either $^{148}$ or $^{169}$.

It appears clear then that heteronins, being isoelectronic with the cyclononatetraenide anion ($^{143}$), may exhibit aromaticity but their tendency to do so is dependent upon the effective electronegativity of the heteroatomic function.
PART IV

THE BEHAVIOR OF 1,2,3,4,5,6-HEXAMETHYL-7-PHENYL-7,8,9-
TRIAZATRICYCLO[4.3.0.0\(^2\),5\]NONA-3,8-DIENE TOWARD
PHOTOLYSIS, THERMOLYSIS, AND AQUEOUS ACID

Introduction

A. \( \Delta^2 \)-1,2,3-Triazolines: Mechanism of Formation

The addition of organic azides (174) to olefinic linkages has long
been known to give rise to \( \Delta^2 \)-1,2,3-triazolines (175).\(^{137}\) Mechanistic

\[ \begin{align*}
\text{C} & \quad + \quad \text{N}^* \\
\text{N} & \quad \rightarrow \\
\text{N} & \\
\text{R} & \\
\end{align*} \]

\(174\quad 175\)

studies\(^{138}\) have clearly shown that this reaction represents an example
of a concerted 1,3-dipolar cycloaddition, a reaction type which has
been described in detail by Huisgen.\(^{139}\) Thus, Scheiner and co-workers
have found that the reaction of norbornene (176) with various meta-
and para-substituted phenyl azides (177) to give exo-triazolines 178
proceeded at a rate that was relatively independent of solvent polarity.
This finding, along with the high entropy of activation ($\Delta S^\neq = -29$ to $-36$ e.u.) of such a process, indicating a highly ordered transition state, led to the conclusion that the reaction followed a concerted pathway. In apparent contradiction to this conclusion, however, the reaction was shown to be subject to a sizeable substituent effect ($\rho = +0.84$ at $25^\circ$) which is most readily explicable in terms of stabilization of a negative charge. It was therefore suggested that the reaction proceeds by a one-step addition process that involves a transition state best represented by 179 in which bond formation at

a has progressed to a greater extent than at b. The observed rate enhancement by electron-withdrawing substituents on the phenyl group is
then attributable to stabilization of the partial negative charge which develops on the 1-nitrogen atom.

This mechanistic interpretation is further substantiated by two additional observations. In the first place, the addition occurs in a stereospecific manner: a cis olefin affords a triazoline in which the cis relationship of functional groups is maintained and vice-versa. For example, cis-(180) and trans-β-methyl styrene (181) upon reaction with phenyl azide (182) have been found to give rise exclusively to 183 and 184, respectively. Secondly, the orientation of addition of azides to unsymmetrical olefins is seen to take place in such a way as to suggest that a partial positive charge is developed on C-5. For instance, in the above reaction no 4-phenyl-5-methyl compounds were isolated; rather, the addition took place in such a way that the α-carbon atom of the styrene molecule becomes C-5
in the product. Only in this mode of addition is it possible for the aryl group to contribute to a lowering of transition state energy by delocalization of the partial charge as it develops on C-5. Similarly, 1-alkenes react with aryl azides to afford 5-alkyltriazolines and enamines have been shown to give rise to analogous 5-amino compounds. Shechter and Bleiholder have observed similar directive effects in the addition of azides to allenes.

Two additional factors which characterize this type of 1,3-dipolar addition are that, in general, strained double bonds are more reactive toward azides than unstrained linkages and, secondly, the ease with which a particular olefin undergoes triazoline formation is, to a degree, dependent upon steric considerations. With respect to the former, Huisgen and co-workers have shown that the rate of phenyl azide addition to a series of olefins parallels the heat of hydrogenation. This thermodynamic parameter is considered to be a measure of the degree of strain associated with these molecules. A striking example of the increased dipolarophilic activity of strained double bonds is seen in the fact that the addition of phenyl azide to dicyclopentadiene (185) occurs exclusively on the double bond of
That steric factors influence triazoline formation is evident from the finding that, while norbornene (176) smoothly affords 178 (X = -H) upon reaction with phenyl azide, analogous cycloaddition fails in 186 where exo attack is hindered by the methyl group on C-7.

B. Decomposition of Triazolines Derived from Norbornene and Norbornadiene

In general, exposure of Δ²-1,2,3-triazolines (175) to elevated temperatures or to electromagnetic radiation of the proper wavelength has been found to result in loss of molecular nitrogen accompanied by the formation, in varying amounts, of aziridines (187) and imines (188).

\[
\begin{align*}
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{R} \\
\text{R} & \quad \text{hν or } \Delta \\
\end{align*}
\]

175

\[
\begin{align*}
\text{N} & \quad \text{R} \\
\text{N} & \quad + \\
\end{align*}
\]

187

188

The two modes of decomposition, however, have been shown to differ considerably in the proportions of the two products which they generate.

The photolytic decomposition pathway is frequently found to afford exclusively the aziridine (187), or at least a far greater preponderance of this heterocycle over the amount of the imine (188) formed. Thus irradiation of the triazolines derived from the reaction of norbornene (176) with phenyl azide or methyl azidoformate,
i.e., 189a and b, respectively, has been found to cleanly give rise

![Diagram]

\[ R = -C_6H_5 \]
\[ R = -CO_2CH_3 \]

to the corresponding exo-aziridines (190). Scheiner has recently examined the mechanism of this photoinduced process, specifically as it is applied to the decomposition of 183 and 184. In these systems direct photolysis was characterized by high photoefficiency, insensitivity to solvent, and predominant retention of initial geometry. It was, therefore, concluded that the reaction proceeded through the singlet state of a short-lived 1,3-diradical intermediate.

The thermal decomposition of 189a and b, on the other hand, proved to be a much more complex process. The former upon pyrolysis in decalin (160°C), gave, in addition to 190a (49%), 191a (18%), 192a (11%), 193a (10%) and 194a (9%), while 189b afforded 190b (40%), 191b (55%) and 192b (9%). In addition an increase in solvent polarity was found to cause significant rate enhancement of the decomposition reaction. To account for this and for the presence of apparent Wagner-Meerwein rearrangement products (192 and 193) the
reaction is viewed as proceeding through a diazonium-betaine intermediate (195).

As the electron-withdrawing power of the N-1 substituent in 189 is increased the triazoline becomes far more thermally labile, decomposing rapidly to the corresponding aziridine (190). Thus, the 1-benzoyl compound (189, R = \(-\text{COC}_{6}\text{H}_{5}\)) expels nitrogen at 40° to give 190 (R = \(-\text{COC}_{6}\text{H}_{5}\))\(^{138b}\). Further, the intermediacy of the triazoline has only been inferred from thermodynamic data in the reaction of norbornene (176) with benzenesulfonyl (174, R = \(-\text{SO}_{2}\text{C}_{6}\text{H}_{5}\))\(^{148}\) and cyanogen azides (174, R = \(-\text{CN}\))\(^{148}\). In both cases the reaction proceeds to afford the aziridine (190) without any directly observable

\[ \text{191} \]
\[ \text{192} \]
\[ \text{193} \]
\[ \text{194} \]

\[ a: R = -\text{C}_{6}\text{H}_{5} \]
\[ b: R = -\text{CO}_{2}\text{CH}_{3} \]
triazoline formation. It would appear reasonable then that while strong electron-withdrawing azide substituents tend to facilitate 1,3-dipolar additions to form triazolines these same groupings enhance the rate of nitrogen loss from these molecules by stabilizing the negative charge in the polar decomposition intermediate (195).

The course of the reactions of norbornene with organic azides is to a degree paralleled by the processes observed when norbornadiene (196) is analogously treated. Thus, exo-triazoline 197a was reported to result from the reaction of 196 with phenyl azide (182). Unlike the analogous norbornene adduct (189a), this material upon pyrolysis
underwent a retro-Diels-Alder fragmentation to afford cyclopentadiene (198) and 1-phenyltriazole (199). Photolysis of the adduct was described as producing uncharacterizable tar.\textsuperscript{150}

Not surprisingly, benzenesulfonfyl azide\textsuperscript{151} and cyanogen azide\textsuperscript{152} upon reaction with 196 afforded exo-aziridines 200a and b, respectively, with no directly observable triazoline formation. The intermediary of latter (197b and c) were, however suggested. It was further observed that the aziridines themselves were thermally labile, rapidly giving rise to 201a and b. This rearrangement was visualized as occurring via Cope rearrangement of intermediate 202 in a manner analogous to bond relocations seen in similar systems. For example, Meinwald and co-workers\textsuperscript{153} have reported the formation of exo-epoxide 200c and its rapid rearrangement at room temperature to 202c. The latter was found by Rey and Dreiding\textsuperscript{154} to exist in mobile equilibrium with 201c. In addition, Brown\textsuperscript{155} has shown that the all-carbon analog of 202 (X = CH\textsubscript{2}) spontaneously rearranges to 201 (X = CH\textsubscript{2}).
Significantly, the **endo**-aziridine \((203a)\)\(^{156}\) and epoxide \((203b)\)\(^{157}\) were found to be thermally stable and not prone to isomerize to \(202a\) or \(c\). Thus, such rearrangement would appear to be facilitated by back-side participation of the transannular double bond.

Part IV of this dissertation describes the synthesis of triazolines derived from the reaction of hexamethyl(Dewar benzene) with methyl azidoformate and phenyl azide and the decomposition (thermal, photochemical and acid-catalyzed) of the latter.
Results and Discussion

An interesting aspect of the chemistry of hexamethyl(Dewar benzene) (204, HMDB) is that the cation produced by the addition of electrophilic reagents (E⁺) to this molecule shows a marked tendency to undergo skeletal rearrangement. Thus, from such reactions, products have been isolated derived from cations 205-209.
The question therefore arises: What would be the course of reaction if HMDB was exposed to organic azides? It will be recalled from the Introduction that the apparent intermediate (179) for such additions is one in which a degree of cationic character is developed within the olefinic reactant. This type of mechanism as it would be expected to apply to addition to HMDB would generate an intermediate somewhat akin to 205 in which at least a partial positive charge exists. Would any structural reorganization occur in such a situation to give products from intermediates similar to 206-209 and, if so, would the extent to which this rearrangement occurs depend upon the nature of the azide employed?

Additional questions arise. What would be the decomposition pathway(s) followed by the adduct(s)? Considering unrearranged structure 210, loss of nitrogen might afford aziridine 211. This

structure would represent the first example of a tricyclic azepine (67) valence-bond isomer. Further, would 211 in an exo-configuration exhibit the thermal lability associated with the influence of a transannular double bond in a manner analogous to norbornadiene derivatives 200a and b?
Alternatively, would cycloaddition occur in such a way as to give an adduct similar to that obtained from the reaction of HMDB with tetracyanoethylene (100), i.e. 212?

\[
\begin{align*}
\text{212}
\end{align*}
\]

In an effort to answer some of these questions, the following research endeavor was undertaken.

The reaction of phenyl azide (182) with excess HMDB (204) afforded after 142 hr. in refluxing hexane a single 1:1-adduct. The

\[
\begin{align*}
\text{204} & \quad + \quad \text{C}_6\text{H}_5\text{N}_3 & \quad \rightarrow & \quad \text{213}
\end{align*}
\]

structure of this cycloaddition product was found to be 213 as opposed to the mechanistically reasonable possibilities 214-216, by analysis of the nmr (100 MHz) spectral characteristics of this material and by its photodecomposition behavior.
On the basis of nmr alone 214 was removed from consideration since the adduct exhibits a singlet (δ 1.713, 6H) in the region which in this type of system is characteristic of vinyl methyl absorption, i.e., allylic hydrogens. The remainder of the simple spectrum consists of (apart from the normal downfield phenyl multiplet) two pairs of slightly separated singlets (δ 1.237, 1.257 and 0.941, 0.959; 6H total for each pair).

The most symmetrical structure with respect to nmr of those considered is 215. This molecule would be expected to give rise to two singlets (6H each) and one pair of slightly separated singlets (6H total). The experimental observations described above, however, reveal one singlet and two pairs of slightly separated singlets. These data rule out structure 215.

At this point, then, only 215 and 216 remained to be considered, both of which could give rise to the observed proton resonances.

The structure of the product derived from photoinduced nitrogen expulsion from the adduct made possible the rejection of formula 216. Thus, irradiation of an acetone solution of the adduct through Vycor optics with a 200 W Hanovia lamp resulted in the rapid evolu-
tion of one equivalent of nitrogen (measured volumetrically) and the formation of essentially (> 9%) a single product. Significantly, the nmr spectrum of the photoproduct consisted of (apart from phenyl proton absorptions) three sharp singlets (δ 1.66, 1.27, and 1.03; 6H each). Obviously, the structural feature in the starting material which gave rise to the slight dissimilarity between the members of each pair of upfield methyl groups had been removed and, therefore, the photoproduct was symmetrical with three pairs of equivalent methyl groups. In addition, the close proximity of the various absorptions in the photoproduct to the chemical shifts observed for the adduct indicated that no skeletal rearrangement accompanied the loss of nitrogen. Hence, the photolysis involved the conversion of 213 into aziridine 217 and not the generation of azetidine 218 from 216.

Although at this point, structure 213 is somewhat favored by default, i.e., the other reasonable alternatives have been ruled out, the nmr data support in a positive manner this exo unrearranged structure (see Table VII).
Table VII
Methyl Chemical Shift Data for HMDB, 213 and 217

<table>
<thead>
<tr>
<th>Compound</th>
<th>Vinyl methyl</th>
<th>N-C-CH₃</th>
<th>C-CH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMDBᵃ</td>
<td>1.6</td>
<td>----</td>
<td>1.1</td>
</tr>
<tr>
<td>213ᵇ</td>
<td>1.713</td>
<td>1.237, 1.257</td>
<td>0.941, 0.959</td>
</tr>
<tr>
<td>217</td>
<td>1.66</td>
<td>1.27</td>
<td>1.03</td>
</tr>
</tbody>
</table>

ᵇ100 MHz spectrum.

Due to the inductive electron-withdrawing effect associated with nitrogen atoms it is reasonable that the δ 1.2 absorptions in 213 and 217 be assigned to the methyl groups bonded to the ring carbon bearing this heteroatom. In 213 the slight difference in the chemical shifts of these methyls is undoubtedly associated with differences in the magnetic anisotropy of the two ends of the triazolo linkage. The removal of this dissymmetry upon the formation of 217 causes this absorption to collapse to a singlet.

The farthest upfield absorptions in 213 and 217 are then assigned to the methyl groups corresponding to the original bridgehead methyls in HMDB. Again, the slight chemical shift dissimilarity of these substituents in 213 must be due to the dissymmetry of the triazolo bridge since it too is removed upon conversion to 217.
Two characteristics of this upfield pair of singlets in $\text{213}$ are, however, seen to be inconsistent with the influence at these methyl groups of inductive electron-withdrawal by nitrogen operating through the bonding framework of the molecule. First, the chemical shift difference between the two bridgehead methyls ($C_2-\text{CH}_3$ and $C_5-\text{CH}_3$) is slightly larger than the difference observed between the pair of methyls ($C_1-\text{CH}_3$ and $C_6-\text{CH}_3$) and one carbon closer to the nitrogen function. If the effect of the nitrogen was being transmitted through the $\sigma$-framework to this more remote site this would not be expected since inductive effects are diminished with distance. Secondly, the bridgehead absorptions are shifted upfield from their position in HMDB. This is the opposite of the effect expected by inductive electron drain toward nitrogen. It is concluded, therefore, that the effect of the $-\text{N}^1\text{N}-\text{C}_6\text{H}_5$ grouping upon the $C$-2 and $C$-5 methyl groups is not transmitted through the bonding framework of the system but rather through space. The stereochemical implication of this conclusion is that the nitrogen bridge must lie in a position with respect to these bridgehead methyl groups where this "through space" interaction may realistically be expected to occur.

It is clear from examination of molecular models of $\text{213}$ and its endo-isomer that only $\text{213}$ possesses the required structural features which allow the methyl groups in question to lie above the $\pi$-system of the triazo bridge where shielding may be expected to take place and, therefore, we have assigned structure $\text{213}$ to the 1:1-adduct of HMDB ($\text{204}$) and phenyl azide ($\text{182}$).
With regard to the stereochemistry of the amines iridine photoproduct this type of nmr analysis is not possible. It is significant, however, that photolytic expulsion of nitrogen from other rigid exo-phenyl triazolines proceeds to form aziridines with retained stereochemistry.\textsuperscript{147,150,153} The generation of an endo aziridine from an exo triazoline has been observed to occur to a limited extent (1-9\%) in the thermal decomposition of \textsuperscript{178} (X = H).\textsuperscript{147} This phenomenon, however, required the rupture of the triazoline's C-C bond and consequently resulted in the formation of non-aziridine products totalling 36-58\% of the reaction mixture. Since in our experiment the aziridine comprised > 9\% of the photolysis mixture it would not seem reasonable that C-C bond cleavage, and therefore inversion, occurred. Thus the photoproduct was assigned \textsuperscript{exo} structure 217.

The reaction of HMDB (204) with methyl azidoformate at room temperature in pentane was found to give rise to an analogous triazoline, 219.

The results described above and those contained in a very recent report by Anastassiou and Eachus\textsuperscript{160} allow some of the questions raised
earlier to be answered. These workers found that reaction of HMDB with cyanogen azide \((17^4, R = \text{CN})\) at or below ambient temperature resulted in the formation of products having structures analogous to 215 and 216 but in which the remaining double bond had undergone further reaction with azide. No unrearranged material was isolated. It is evident then that HMDB can undergo skeletal reorganization upon reaction with organic azides but that its propensity to do so is sensitive to the nature of the particular azide. Thus as the electron-withdrawing power of the azide substituent increases there would be a corresponding increase in the amount of cationic charge developed in the olefin as interaction between the two occurs. In such instances, there would be a greater tendency toward rearrangement. The reactions of HMDB with phenyl azide and methyl azidoformate in all probability follow the concerted addition pathway via a transition state of the type depicted in structure 179 while cyanogen azide may in fact add to this olefin in a stepwise fashion via a zwitterionic intermediate. In support of the latter contention, Anastassiou observed a rate enhancement when the dielectric constant of the reaction solvent was increased.

Aziridine 217, a tricyclic azepine valence-bond isomer, was found to be a very stable molecule. Unlike norbornadiene derivatives 200a and b, this substance showed no tendency to undergo bond relocation below 150° (in tetrachloroethylene). At or above this temperature, however, 217 was seen to give rise to a complex mixture (nmr analysis) of products possibly structurally analogous to those derived from the
pyrolysis of hexamethyl(Dewarbenzene) oxide. Separation of the product mixture was thwarted by decomposition on chromatographic adsorbents.

Not surprisingly, the pyrolysis of 213 proved to be a much more complex process than the photolytic decomposition of this material. Heating of a solution of 213 in decalin at reflux (195°) for 25 min. resulted in the complete disappearance of the triazoline (tlc). After cooling, the golden yellow pyrolysate was chromatographed on alumina allowing the separation of three components, each of which required a considerable amount of further processing before a pure sample could be obtained (see Experimental).
The major product (42%), a yellow-orange solid, exhibited a moderately intense infrared band (KBr) at 1640 cm⁻¹, suggestive of an enamine double bond. In addition, extended π-electron conjugation was indicated by absorption maxima observed in the ultraviolet and visible regions [ethanol: 222 nm (ε 28,000), 353 (5,780); isooctane: 224 (28,600), 358 (4,390)]. The nmr spectrum (60 MHz, CDCl₃) of the material displayed sharp singlets at δ 2.17 and 2.20 (6H total) and a broadened singlet (12H) at δ 1.99 (partially resolved into a multiplet at 100 MHz) along with the usual downfield phenyl absorptions (δ 6.6-7.4, 5H); the implication from such chemical shift data is that the product contains six vinyl methyl groups, two of which are bonded to carbon bearing a nitrogen atom. Further, elemental analysis and high-resolution mass spectral molecular weight determination showed conclusively that the substance was isomeric with 213 (C₁₈H₂₃N₃)!

Two mechanically reasonable structural formulations which would tend to be compatible with these observations and were therefore considered are triazonin 220 and azepine 223. In order for the latter
to give rise to the observed nmr spectrum, however, either the
two α-methyl groups would have to be magnetically non-equivalent by
reason of restricted rotation about the triazene N2-N3 single bond
or the lower field pair of singlets are in fact an unresolved mul-
tiple arising from homoallylic coupling of equivalent α-methyl
groups with the β methyl substituents, the corresponding multiplet
of the latter being buried under the broadened singlet at δ 1.99.

In regard to the first possibility, i.e. of magnetically non-
equivalent α-methyl groups, it has recently been shown that such
a phenomenon has been observed in the nmr spectra of 3,3-dimethyl
triazenes below (and in one instance at) room temperature. In all
instances mild warming was found to cause coalescence. That the
proton resonance spectrum of the pyrolysis product was unchanged up
to 118° made it unreasonable then to conclude that this type of
phenomenon would cause 223 to give rise to the observed spectrum.

On the other hand, careful examination of the nmr spectra of the
product at both 60 and 100 MHz clearly showed that the two lower
field singlets are not due to spin-spin coupling but in fact are
attributable to two distinct methyl groups. Thus, at 60 MHz (CCl4)
the difference in chemical shift between these peaks was found to be
3.55 Hz while at 100 MHz it was seen to be 5.9 Hz. Since coupling
constants do not vary with the strength of the external magnetic
field, it is evident that the second alternative favoring 223 is not
tenable.

As a result of these experiments it was concluded that structure
220, a structure which would certainly be expected to display the ob-
served spectral characteristics, was a much more reasonable alternative.

The second component to be eluted from alumina (14%) displayed infrared absorptions at 1650 and 1625 cm\(^{-1}\) and ultraviolet maxima in ethanol at 218 nm (ε 19,700) and 330 (2,180) and in isoctane at 222 (20,500) and 333 (2,520). In the nmr (CDCl\(_3\)) the substance exhibited, aside from phenyl absorptions, a singlet at δ 2.51 (3H), a pair of singlets at δ 2.06 and 1.97 (6H each) and another singlet (3H) at δ 1.29. These data, along with an empirical formula of C\(_{18}H_{23}N_3\) (mass spectrally determined) and clean thermal conversion of this material into 220 (see below) suggested a structure as depicted in 221.

The spectral data obtained from the third component (12%) revealed that it was azanorbornadiene derivative 222. Thus the nmr spectrum consisted of (apart from phenyl absorptions) two sharp singlets at δ 1.70 (12H) and 1.39 (6H) while the ultraviolet spectrum was a composite of that expected from a norbornadiene and an aniline derivative.

Compound 221 was found to be very thermally labile. A sample of this material was smoothly transformed into 220 at 80°.
during 100 min. in tetrachloroethylene solution. This type of
cyclobutene ring opening is well documented and as such tended
to support the structural assignments, but at the same time made it
apparent that 221 could not have been a direct thermal product of
213. It was concluded that 221 must have been formed by rearrange-
ment of an unknown intermediate during the chromatographic procedure.
This contention was experimentally verified in the following way.
A sample of 213 was heated as above in decalin and, after sol-
vent removal, the nmr spectrum of the mixture was recorded. Clearly
present were, inter alia, 220 and 222, but no 221. Treatment of this
mixture in pentane with alumina resulted in the appearance of 221
with no change in the proportions of 220 and 222. The structure of
the precursor to 221 remains unknown, but it is certain that neither
213 nor 220 gives rise to 221 in this way. The former was recovered
completely unchanged after standing in contact with this adsorbent
for several hours while the latter was seen to darken and decompose
under similar conditions.

Pyrolysis of 213 in tetrachloroethylene (121°) during a period of
65 min. resulted in the complete consumption of starting material
(tlc, nmr) and the formation of a reaction mixture approximately 80%
of which was 220. The presence of neither 221 nor 222 was indicated,
but the former was generated by elution of the material through Florisil.
The absence of 222 was considered to be a function of the lower pyroly-
sis temperature but attempted verification of this by analogous ther-
molysis in a sealed tube at 195° caused complete decomposition to
black tarry materials with no recognizable products being present (nmr).
Cycloaddition of both 220 and 221 with 4-phenyl-1,2,4-triazoline-3,5-dione was attempted in an effort to obtain additional structural information. Compound 220 was completely unreactive toward this strong dienophile, while 221 in the presence of this material in CDCl₃ was cleanly and quantitatively converted to 220 during 20 min. at ca. 40°.

Further, 220 was found to resist catalytic hydrogenation and photoinduced rearrangement or nitrogen expulsion.

Recently Sanders and Williams have reported that addition of tris(dipivalomethyl)euroinium to organic molecules having non-bonded electrons (eg. alcohols and amines) caused remarkable changes in the nmr spectra of the latter, presumably by the formation of euroinium complexes. Thus, it was observed that a marked "spreading-out" of the various proton resonances occurred to the point where complete spectral analysis of these compounds was possible. We have found, however, that treatment of 220 in this manner caused absolutely no change in the spectrum.

Although rearrangement of triazolines at elevated temperatures without nitrogen liberation lacks precedent, the individual steps of the possible mechanistic interpretation outlined in Scheme XIV for such a process are in fact analogous to those proposed to account for previously discussed transformations. The origin of 220 is most readily visualized (path a) as resulting from thermal cyclobutene ring opening of 213 to give cyclohexadiene derivative 224 followed by disrotatory [3,3]sigmatropic rearrangement of the latter.
Alternatively (path b), backside participation of the transannular double bond in the triazoline in a way similar to that suggested in the rearrangement of 200 would be expected to afford 225. In order for this substance to be the unidentified precursor to 221 its thermal stability would have to be assumed. It is perhaps significant in
this respect that the ketone corresponding to 225 is generated at
$210^\circ$ and is unchanged (n.m.r.) upon heating at $120^\circ$. The con-
version of 225 to 221 on alumina is viewed as being homologous to
the transformation of 202 to 201.

The formation of 222 from 213 (Scheme XV) is considered to occur
via azaquadricyclane 226. Intermediates 227 and 228 are completely

Scheme XV

\[ \text{213} \xrightarrow{\Delta} \text{227} \]

\[ \text{226} \xrightarrow{} \text{228} \]

\[ \text{222} \]
analogous to those suggested to account for the thermal behavior of norbornene derivatives while a conversion of the type to was proposed by Hale and Zalkow for a similar norbornadiene reaction. Quadricyclanes are well known to give rise thermally to norbornadienes.

The most striking feature of triazonin is that it possesses a continuous cyclic array of 10π-electrons and as such has the potential for being an aromatic molecule (see Part III for a discussion of this subject). The permethylated nature of the compound, however, makes it impossible to detect a ring current by nmr methods since the chemical shifts of such groupings would not be as sensitive to deshielding as would protons bonded directly to the ring. On the other hand, none of the observed spectral properties are inconsistent with the operation of aromatic delocalization. In addition, the substance has been shown to be quite thermodynamically stable as evidenced by its resistance to chemical transformations.

A third method by which triazolines are decomposed is by reaction with aqueous acids. The interesting cations derived from protonation of HMDB, i.e. 205-209, suggested that a study of the behavior of in an acid medium would be of value. Very surprisingly, it was found that treatment of in acetone at room temperature with one equivalent of aqueous hydrochloric acid gave rise to diol . No rearrangement products were isolated. In addition, aziridine was seen to undergo the same transformation with either hydrochloric or perchloric acid. These results
are in striking contrast to the general observation that Wagner-Meerwein rearrangements follow from such protonations.

Not noted in the literature was the fact that 229, upon melting, clearly undergoes thermolysis accompanied by gas evolution. We have found that under such conditions dehydration of 229 occurs to give a quantitative yield of diene 230.

The isolation of unrearranged diol 229 from 213 and 217 is most readily explicable if it is concluded that during the course of reaction little or no cationic character was developed in the HMDB portion of the molecule. This would be the case if the bond forming and bond breaking processes were synchronous or nearly so and is therefore suggestive of backside attack by a water molecule resulting in displacement of a protonated nitrogen moiety or, in the case
of 213, possibly a molecule of nitrogen from a diazonium salt. The overall result of such a process then would be a stereochemical inversion at both sites of displacement and, thus, the formation of a bis-endo diol. (No reference is made in the literature as to the stereochemistry of the product.) That the hydroxyl groups are at least cis to one another is indicated by the nmr spectrum of the material, which reveals the presence of three pairs of identical methyl groups.

In addition, bis-endo stereochemistry of 229 would appear to be much more compatible with the observed smooth conversion to 230 than would a bis-exo configuration. It will be recalled that thermolysis of similar compounds which involve displacement of exo-substituents has been found to afford products attributable to a backside displacement by the transannular double bond. On the other hand, the departure of endo HMDB substituents are considered to be assisted by migration of the internal single bond (see below). A mechanistic scheme based upon the latter principle (Scheme XVI) is found to account well for the clean transformation of 229 into 230.

Scheme XVI

\[
\begin{align*}
\text{229} & \xrightarrow{\Delta, \text{H}_2\text{O}} \text{230}
\end{align*}
\]
EXPERIMENTAL

Melting points are corrected and boiling points are uncorrected. The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark; Galbraith Laboratories, Inc., Knoxville, Tennessee; M-H-W Laboratories, Garden City, Michigan; and George I. Robertson, Jr., Florham Park, New Jersey. Infrared spectra were determined with a Perkin-Elmer Model 237 spectrometer. Ultraviolet and visible spectra were recorded with a Cary Model 14 spectrometer. The nmr spectra were determined with Varian A-60, A-60A, and HA-100 spectrometers. The mass spectra were measured with an AEI MS-9 instrument. Vapor phase chromatography was carried out with Varian-Aerograph Models A-90-P3 and 600-D.

Silver Cyanate. To a solution of 81.12 g (1.0 mole) of potassium cyanate in 1 l. of distilled water was added with stirring a solution of 180 g. (1.06 moles) of silver nitrate in 600 ml. of the same solvent. The resulting silver cyanate precipitate was filtered with suction, slurried with distilled water and filtered again. The slurrying and filtration procedures were repeated with methanol and ether, respectively. The solid was then dried under vacuum at 50° to give 147.0 g. (0.98 mole, 98%) of product as an off-white powder which was used without further purification. Silver cyanate stored
in a well stoppered container in the dark showed no loss of activity after several months.

1,4-Dihydrobenzene (61). Into a 5-l. three-necked flask fitted with a Dry Ice condenser and mechanical stirrer and cooled in a Dry Ice-isopropyl alcohol bath was distilled ca. 2 l. of ammonia. The stirrer was started and 156.2 g. (2.0 moles) of benzene added. To this mixture was added over a period of 2.5 hr. 150 g. (6.5 moles) of sodium chips and the whole stirred for an additional 2.5 hr. A solution of 320 g. (10 moles) of methanol and 200 ml. of ether was then introduced dropwise, again over 2.5 hr. After an additional hour stirring was stopped and the ammonia allowed to evaporate overnight.

The flask was cooled in an ice bath and the contents decomposed by the slow addition of 1 l. of ice water under a nitrogen atmosphere. The cooling bath was removed and after 1 hr. the organic layer was separated and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the filtrate fractionated through a 50-cm. column packed with glass beads and helices to give 98 g. (1.2 moles, 61%) of product as a clear, colorless liquid, b.p. 85-87\(^\circ\) (lit. 84-89\(^\circ\)).

Methyl N-(trans-2-Iodo-4-cyclohexene)carbamate (70). To a stirred slurry of 16.02 g. (0.2 mole) of 1,4-dihydrobenzene (61) and 39.0 g. (0.26 mole) of silver cyanate in 300 ml. of anhydrous tetrahydrofuran cooled in an ice bath was added in one portion 50.8 g. (0.2 mole) of iodine. The reaction mixture became dark brown but
after stirring for 3 hr. at 5° the color faded to the canary-yellow characteristic of silver iodide. The inorganic salts were removed by filtration through Celite and the filtrate concentrated in vacuo to ca. 100 ml. Anhydrous methanol (400 ml.) was added and the resulting solution allowed to stand at room temperature for 26.5 hr. The solution was concentrated under reduced pressure to ca. 50 ml., this residue taken up in 400 ml. of ether and the ether solution washed with dilute aqueous sodium bisulfite. The layers were separated and the aqueous phase extracted with three 100-ml. portions of ether. The combined organic layers were dried over anhydrous magnesium sulfate. Removal of the drying agent by filtration and evaporation of the filtrate in vacuo afforded a slightly orange solid which was recrystallized from methanol. There was obtained 29.9 g. (0.106 mole, 53.2%) of \( \text{70} \) as white needles, m.p. 99-100° \( \text{sec} \) m.p. 93-95°).

1,2-Iminocyclohex-4-ene (68). A. From \( \beta \)-Iodocarbamate \( \text{70} \). To a stirred refluxing solution of 40 g. of 85% potassium hydroxide pellets in 200 ml. of water was added 20.0 g. (0.071 mole) of \( \text{70} \). Reflux was maintained for 1 hr., during which time the insoluble iodocarbamate dissolved. After cooling, the reaction mixture was extracted with four 200-ml. portions of ether, the combined ether layers dried over anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure. The residue was subjected to bulb-to-bulb distillation at 0.3 mm. \( \text{171} \) with the collector cooled in a Dry Ice-isopropyl alcohol bath to give after warming to room temperature,
5.91 g. (0.062 mole, 87.5%) of 68 as a clear, colorless liquid; 

\[ \nu_{\text{film}}^\text{max} 3230 (\text{NH}) \text{ and } 1650 \text{ cm}^{-1} (\text{C} = \text{C}); \delta_{\text{CCl}_4}^\text{NMR} 5.37 \] (unresolved multiplet, 2H, vinyl protons), 2.38 (unresolved multiplet, 4H, allylic protons), 2.04 (unresolved multiplet, 2H, aziridine protons), and 1.55 (broad signal, 1H, NH).

This amine formed a picrate, m.p. 146-147° dec. (from 95% ethanol).

**Anal.** Calcd for C$_{18}$H$_{16}$N$_4$O$_7$: C, 44.45; H, 3.73; N, 17.28.

**Found:** C, 44.32; H, 3.84; N, 17.38.

**B.** From N-Carbomethoxyaziridine 71. Treatment of 71 in an analogous manner afforded 68 in 83% yield.

**C.** Direct from β-Iodoisocyanate 69. A mixture of 4.64 g. (0.058 mole) of 1,4-dihydrobenzene (61), 17.2 g. (0.115 mole) of silver cyanate, and 14.5 g. (0.057 mole) of iodine in 200 ml. of tetrahydrofuran was stirred at 0° for 1 hr. The precipitated silver salts were removed by filtration and the filtrate concentrated to ca. 50 ml. in vacuo. The resultant β-Iodoisocyanate solution was cooled in an ice bath and with stirring a solution of 20 g. of 85% potassium hydroxide pellets in 100 ml. of water was added dropwise. After addition was complete the ice bath was removed and the reaction mixture allowed to rise to ambient temperature where it was stirred for 9 hr. The same work-up as above afforded 2.76 g. (0.029 mole, 51% overall) of aziridine 68.
N-Functionalization of $68$. General Procedure. A solution of $68$ (0.026-0.059 mole) and triethylamine (slightly over one equivalent) in benzene (50-100 ml.) was cooled in an ice bath and with stirring an equivalent of the appropriate acid chloride in the same solvent (50-100 ml.) was added dropwise. After addition was complete the cooling bath was removed and the reaction mixture stirred for 1-5 hr. The precipitated triethylamine hydrochloride was removed by filtration, the solvent evaporated from the filtrate under reduced pressure and the product residue purified by distillation or recrystallization.

N-Methanesulfonyl-1,2-iminocyclohex-4-ene ($72a$). Distillation of the residue from the above generalized procedure afforded $72a$ in 91.7% yield as a clear, colorless, viscous liquid, b.p. 107-113° (0.3 mm.); $\nu_{\text{max}}^\text{film}$ 1660 (C=C), 1310 and 1150 cm$^{-1}$ (SO$_2$N); $\delta^\text{CDCl}_3$ 5.47 (broad singlet, 2H, vinyl protons), 2.97 (singlet, 5H, overlapping methyl and aziridine protons), and 2.42 (broad singlet, 4H, allylic protons).

Anal. Calcd for C$_7$H$_{11}$NO$_2$S: C, 48.53; H, 6.40; S, 18.51. Found: C, 48.34; H, 6.63; S, 18.57.

N-Benzenesulfonyl-1,2-iminocyclohex-4-ene ($72b$). The benzene-sulfonyl derivative ($72b$) was obtained in 96.4% yield as lustrous, white plates, m.p. 86-87° (tetrahydrofuran/pentane); $\nu_{\text{max}}^\text{CHCl}_3$ 1670 (C=C), 1590 (aromatic nucleus), 1325 and 1165 cm$^{-1}$ (SO$_2$N); $\delta^\text{CDCl}_3$ 7.92 (complex multiplet, 2H, aromatic protons), 7.55 (complex multiplet, 3H, aromatic protons), 5.41 (unresolved multiplet, 2H,
vinyl protons), 3.13 (unresolved multiplet, 2H, aziridine protons), and 2.37 (broad singlet, 4H, allylic protons).

**Anal.** Calcd for C₁₃H₁₃NO₂S: C, 61.25; H, 5.57; S, 13.63.
Found: C, 60.98; H, 5.80; S, 13.51.

N-(p-Bromobenzensulfonyl)-1,2-iminocyclohex-4-ene (72c). Triple recrystallization (tetrahydrofuran/hexane) of 72c obtained as above afforded lustrous, white plates (73%), m.p. 106.5-107.5°; \( \nu_{\text{max}}^{\text{CHCl}_3} \)
1660 (C=C), 1580 (aromatic nucleus), 1330 and 1165 cm⁻¹ (SO₂N); \( \delta^{\text{CDCl}_3} \) 7.73 (quartet, 4H, aromatic protons), 5.42 (broad singlet, 2H, vinyl protons), 3.14 (broad singlet, 2H, aziridine protons) and 2.35 (broad singlet, 4H, allylic protons).

**Anal.** Calcd for C₁₃H₁₂BrNO₂S: C, 45.85; H, 3.81; S, 10.21.
Found: C, 45.99; H, 3.81; S, 10.24.

**Diphenylphosphinic Chloride.** Into a vigorously stirred solution of 13.27 g. (0.061 mole) of diphenylphosphinous chloride in methylene chloride (150 ml.) at room temperature under nitrogen was dripped 4.60 g. (0.0589 mole) of dimethylsulfoxide in 100 ml. of the same solvent. After addition was complete stirring was continued for 6 hr. and the solvent removed in vacuo. Distillation of the residue gave 12.38 g. (0.0524 mole, 89%) of acid chloride as a clear, colorless oil, b.p. 130-134⁰/0.2 mm. (lit. b.p. 132-135⁰/0.3 mm.).

N-Diphenylphosphinoxy-1,2-iminocyclohex-4-ene (72d). The employment of diphenylphosphinic chloride in the generalized procedure gave 72d in quantitative yield, m.p. 119-120.5⁰ (ether); \( \nu_{\text{max}}^{\text{CHCl}_3} \)
1655 (C=C) and 1590 cm$^{-1}$ (aromatic nucleus); $\nu_{\text{max}}$ 1205 cm$^{-1}$ (P=0); CDCl$_3$ 7.7-8.1 (multiplet, 4H, aromatic protons), 7.42 (multiplet, 6H, aromatic protons), 5.52 (broad signal, 2H, vinyl protons), 3.13 and 2.87 (broad signals, 1H each, aziridine protons), and 2.33 (broad singlet, 4H, allylic protons).

Anal. Calcd for C$_{18}$H$_{18}$NOP: C, 73.21; H, 6.14; N, 4.74.
Found: C, 73.20; H, 6.37; N, 4.64.

Bromination of 72. General Procedure. A solution of 72 in methylene chloride (approx. 0.05 mole in 100 ml.) was cooled in a Dry-Ice-isopropanol bath and, with stirring, a solution of bromine in the same solvent added dropwise until slight permanent coloration set in. The solution was allowed to warm to room temperature, the solvent removed in vacuo and the residue recrystallized.

4,5-Dibromo-1,2-(N-methanesulfonylaziridino)cyclohexane (73a).

Recrystallization of the solid obtained from the generalized procedure from tetrahydrofuran-pentane afforded 73a as white needles (82.8%), m.p. 126.5-127.5$^\circ$; $\nu_{\text{max}}$ 1330 and 1155 cm$^{-1}$ (SO$_2$N); CDCl$_3$ 4.24 (unresolved complex, 2H, CHBr), 3.07 (singlet, 3H, methyl protons), and an unresolved pattern centered at approx. 2.9 (6H, allylic and aziridine protons).

Found: C, 25.59; H, 3.55; S, 9.85.

4,5-Dibromo-1,2-(N-benzenesulfonylaziridino)cyclohexane (73b).

Dibromide 73b was obtained in 71.2% yield after triple recrystallizza-


tion from tetrahydrofuran-pentane as white needles, m.p. 123-124°; 
\( \nu_{\text{max}} \) \( \text{CHCl}_3 \) 1325 and 1170 cm\(^{-1}\) (SO\(_2\)N); \( \delta_{\text{TMS}} \) \( \text{CDCl}_3 \) 7.92 (complex multiplet, 
2H, aromatic protons), 7.51 (complex multiplet, 3H, aromatic pro-
tons), 4.13 (unresolved, 2H, CHBr), 2.1-3.2 (complex absorptions, 
6H, allylic and aziridine protons).

**Anal.** Calcd for C\(_{12}\)H\(_{13}\)Br\(_2\)NO\(_2\)S: C, 36.47; H, 3.32; S, 8.12.
Found: C, 36.62; H, 3.35; S, 8.16.

\( \text{4,5-Dibromo-1,2-[N-(p-bromobenzensulfonyl)aziridino]cyclo-} \)
hexane (73c). The above procedure afforded 73c in quantitative yield 
as white crystals, m.p. 165-167° (tetrahydrofuran-hexane); \( \nu_{\text{max}} \) \( \text{CHCl}_3 \) 1330 and 1165 cm\(^{-1}\) (SO\(_2\)N); \( \delta_{\text{TMS}} \) \( \text{CDCl}_3 \) 7.74 (quartet, 4H, aromatic 
protons), 4.20 (broad absorption, 2H, CHBr), and 2.1-3.2 (complex 
absorptions, 6H, allylic and aziridine protons).

**Anal.** Calcd for C\(_{12}\)H\(_{16}\)Br\(_2\)NO\(_2\)S: C, 30.40; H, 2.55; S, 6.76.
Found: C, 30.67; H, 2.64; S, 6.90.

\( \text{4,5-Dibromo-1,2-(N-diphenylphosphinoxyaziridino)cyclohexane} \)
(73d). Dibromide 73d was obtained in 99.2% yield, m.p. 192-192.5° 
(tetrahydrofuran); \( \nu_{\text{max}}^{\text{CS}2} \) 1205 cm\(^{-1}\) (P=0); \( \delta_{\text{TMS}} \) \( \text{CDCl}_3 \) 7.7-8.1 (multiplet 
4H, aromatic protons), 7.42 (multiplet, 6H, aromatic protons), 
4.3 (broad quartet, 2H, CHBr), and 2.1-3.2 (complex absorptions, 
6H, allylic and aziridine protons).

**Anal.** Calcd for C\(_{18}\)H\(_{18}\)Br\(_2\)NOP: C, 47.50; H, 3.99; N, 3.08.
Found: C, 47.62; H, 4.13; N, 3.11.
N-Methanesulfonylazepine (74a). To a stirred, ice-cooled suspension of potassium t-butoxide (12.0 g., 0.107 mole) in 75 ml. of tetrahydrofuran was added dropwise a solution of 12.7 g. (0.0382 mole) of dibromide 73a in 100 ml. of the same solvent. After stirring for 2 hr. at 0° the reaction mixture was filtered with suction through Celite and the gelatinous residue thus removed washed with tetrahydrofuran until the washings were colorless. The filtrate was concentrated in vacuo and the oily residue added to 100 ml. of water. The aqueous mixture was extracted with ether until the ether extract was colorless (5 x 100 ml.). The combined organic phases were dried over anhydrous magnesium sulfate and the solvent removed under reduced pressure. The yellow crystalline residue was recrystallized from ether-pentane to afford 3.1 g. (0.0181 mole, 47.4%) of 74a as lustrous, yellow needles, m.p. 91.5-92.5°; \( \nu_{\text{max}}^{\text{CHCl}_3} 1640, 1620 \text{ (C=C)}, 1350 \text{ and } 1165 \text{ cm}^{-1} \text{ (SO}_2\text{N)}; \delta_{\text{CDCl}_3}^{\text{HMS}} 6.20 \) (multiplet, 2H, vinyl protons), 5.76 (multiplet, \( ^4\text{H}, \text{vinyl protons} \)), and 2.89 (singlet, 3H, methyl protons); \( \lambda_{\text{max}} \) 205 (e 17,200) and 307 nm (e 760); m/e 171 (M+).

Anal. Calcd for C\(_7\)H\(_8\)NO\(_2\)S: C, 49.10; H, 5.30; N, 8.18.
Found: C, 49.06; H, 5.50; N, 8.08.

N-Benzensulfonylazepine (74b). Treatment of 6.8 g. (17.2 mmoles) of dibromide 73b with 5.6 g. (50 mmoles) of potassium t-butoxide in a manner analogous to that employed with the methanesulfonyl derivative (74a) afforded, after triple recrystallization from tetrahydrofuran-pentane, 2.1 g. (9.02 mmoles, 52.4%) of azepine
74\textsubscript{b} as yellow plates, m.p. 132-133\degree C; CHCl\textsubscript{3} \( \nu_{\text{max}} \) 1645, 1625 (C=C), 1360 and 1175 cm\textsuperscript{-1} (SO\textsubscript{2}N); CDCl\textsubscript{3} \( \delta_{\text{TMS}} \) 7.62 (multiplet, 5H, aromatic protons), 5.56-6.0 (multiplet, 6H, vinyl protons); EtOH \( \lambda_{\text{max}} \) 205 (e 22,200) and 266 nm (e 3,000); m/e 233 (M\textsuperscript{+}).

Anal. Calcd for C\textsubscript{12}H\textsubscript{11}NO\textsubscript{2}S: C, 61.78; H, 4.75; N, 6.00.
Found: C, 61.82; H, 4.65; N, 6.08.

N-(p-Bromobenzensulfonyl)azepine (74c). Dehydrobromination of 20.0 g. (0.042 mole) of 73\textsubscript{c} in the usual manner with 11.2 g. (0.1 mole) of potassium t-butoxide yielded 8.93 g. (0.0286 mole, 68\%) of yellow, crystalline 74c, m.p. 132.5-134\degree C (tetrahydrofuran); CHCl\textsubscript{3} \( \nu_{\text{max}} \) 1645, 1625 (C=C), 1365 and 1170 cm\textsuperscript{-1} (SO\textsubscript{2}N); CDCl\textsubscript{3} \( \delta_{\text{TMS}} \) 7.59 (broad doublet, 4H, aromatic protons), 5.87 (multiplet, 2H, vinyl protons) and 5.74 (broad doublet, 4H, vinyl protons); EtOH \( \lambda_{\text{max}} \) 233 (e 13,200) and 268 sh nm (e 3,800); m/e 311 and 313 (M\textsuperscript{+}).

Anal. Calcd for C\textsubscript{13}H\textsubscript{10}BrNO\textsubscript{2}S: C, 46.16; H, 3.23; N, 4.49.
Found: C, 46.30; H, 3.33; N, 4.55.

Reaction of 73\textsubscript{d} with Potassium t-Butoxide. Potassium t-butoxide (10 g., 89.2 mmoles) was added to an ice cold solution of 15.1 g. (33.2 mmoles) of dibromide 73\textsubscript{d} in 150 ml of anhydrous tetrahydrofuran. After stirring for 1.5 hr., the usual work-up afforded 7.98 g. of viscous orange brown residue which solidified upon refrigeration. Chromatography of 1.13 g. of this material on Florisil gave 591 mg. of P,P-diphenylphosphinic amide 76\textsubscript{173} and 214 mg. of N,P,P-triphenylphosphinic amide 77\textsubscript{174}. Extrapolation suggests that the former was isolated in 58\% yield with
the latter in 15.3%.

N-Diphenylphosphinoxyazepine (74d). To a stirred refluxing solution of 3.49 g. (8.66 mmoles) of dibromide 73a in 150 ml. of anhydrous tetrahydrofuran was added dropwise a solution of 3.26 g. (26.3 mmoles) of 1,5-diazabicyclo[4.3.0]non-5-ene (78) in 10 ml. of the same solvent. The reaction mixture was refluxed for 4 hr., cooled in ice and the precipitated amine hydrobromide dissolved by the addition of 150 ml. of water. After stirring for 30 min. the product was extracted into ether and the ether extracts washed with water. Subsequent processing of the organic layer in the usual fashion gave 2.16 g. (7.37 mmoles, 87%) of 74d as large yellow crystals, m.p. 151.5-155° (tetrahydrofuran-ether, 1:4); \( \nu_{\text{CS}_2}^{\text{max}} \) 1640, 1610 (C=C), and 1220 cm\(^{-1}\) (P=O); \( \delta_{\text{CDCl}_3}^{\text{TMS}} \) 7.64-8.13 (multiplet, 4H, aromatic protons), 7.37 (multiplet, 6H, aromatic protons), 6.20 (multiplet, 2H, vinyl protons), and 5.48 (multiplet, 4H, vinyl protons); \( \lambda_{\text{EtOH}}^{\text{max}} \) 238 sh (\( \epsilon \) 9,860), 261 (\( \epsilon \) 2,130), 267 (\( \epsilon \) 2,220), 273 (\( \epsilon \) 1,750) add 310 sh nm (\( \epsilon \) 590); m/e 293 (M\(^+\)).

Anal. Calcd for C\(_{18}\)H\(_{16}\)NOP: C, 73.71; H, 5.50; N, 4.78. Found: C, 73.64; H, 5.46; N, 4.82.

1-Methyl-1,2-[N-(p-bromobenzenesulfonyl)aziridino]cyclohex-4-ene (81). To a refluxing solution of 40 g. of potassium hydroxide in 200 ml. of water was added 20.0 g. (0.068 mole) of iodocarbamate 63. Heating was continued for 30 min., during which time the solid dissolved. After cooling, the organic product was
extracted with ether and the oil thus obtained was transferred under high vacuum to give 5.32 g. (72%) of colorless 1-methyl-1,2-iminocyclohex-4-ene (80); \( \nu_{\text{film}}^{\text{max}} \) 330 cm\(^{-1}\) (N-H).

The N-(p-bromobenzenesulfonyl) derivative 81 was obtained by the previously described procedure as colorless crystals (96.8%), m.p. 128-129.5\(^\circ\) (tetrahydrofuran); \( \nu_{\text{max}}^{\text{CHCl}_3} \) 1675 cm\(^{-1}\) (C=C), 1320 and 1165 cm\(^{-1}\) (SO\(_2\)N); \( \delta_{\text{TMS}}^{\text{CDCl}_3} \) 7.68 (quartet, 4H, aromatic protons), 5.37 (broad doublet, 2H, vinyl protons), 3.91 (broad signal, 2H, aziridine proton), 2.2-2.5 (multiplet, 4H, allylic protons), and 1.79 (singlet, 3H, methyl protons).

**Anal. Calcd for C\(_{13}\)H\(_{14}\)BrNO\(_2\)S: C, 47.57; H, 4.30; N, 4.27; S, 9.77. Found: C, 47.81; H, 4.38; N, 4.26; S, 9.75.**

4,5-Dibromo-1-methyl-1,2-[N-(p-bromobenzenesulfonyl)aziridino]cyclohexane (82). Bromination of 81 under the usual conditions gave, after triple recrystallization from ether, 82 as white fibers (93.5%), m.p. 132.5-133.5\(^\circ\) (tetrahydrofuran); \( \nu_{\text{max}}^{\text{CHCl}_3} \) 1325 and 1165 cm\(^{-1}\) (SO\(_2\)N); \( \delta_{\text{TMS}}^{\text{CDCl}_3} \) 7.67 (quartet, 4H, aromatic protons), 4.16 (broad, 2H, CHBr), 1.9-3.2 (multiplets, 5H, allylic and aziridine protons), and 1.77 (singlet, 3H, methyl protons).

**Anal. Calcd for C\(_{15}\)H\(_{14}\)Br\(_3\)NO\(_2\)S: C, 31.99; H, 2.89; S, 6.57. Found: C, 32.86; H, 3.13; S, 6.65.**

2-Methyl-N-(p-bromobenzenesulfonyl)azepine (79). A. By the action of Potassium t-Butoxide on 82. Treatment of dibromide 82 in the usual fashion with potassium t-butoxide gave, after chroma-
tography on basic alumina (activity III), two characterizable fractions. The first (eluted in 10% ether/hexane) was doubly recrystallized from ether-hexane to afford the desired azepine (79) in 4.34% yield as white powder, m.p. 94.5-95.5°, \( \nu_{\text{max}}^{\text{CHCl}_3} 1645, 1625 \text{ cm}^{-1} (\text{SO}_2\text{N}) \); \( \delta_{\text{TMS}} \) 7.80 (quartet, 4H, aromatic protons), 5.75-6.35 (multiplets, 5H, vinyl protons), and 2.29 (singlet, 3H, methyl protons); \( \lambda_{\text{EtOH}} \) max 254 (ε 13,000) and 269 sh nm (ε 3,580); m/e 325 and 327 (M+).

Anal. Calcd for C_{13}H_{12}BrNO_{2}S: C, 47.86; H, 3.71; N, 4.29.

Found: C, 48.00; H, 3.83; N, 4.18.

The second product, obtained in 26% yield, was p-bromobenzene-sulfonyl-o-toluidide (83), identical in all respects to an authentic sample prepared by the reaction of p-bromobenzensulfonyl chloride with o-toluidine.

B. Using 1,5-Diazabicyclo[4.3.0]non-5-ene (78). Dehydrobromination of the dibromide (82) (5.46 g., 11.2 mmoles) was achieved by the use of 78 (4.18 g., 33.7 mmoles) in 150 ml. of tetrahydrofuran as described above. There was produced 1.73 g. (5.3 mmoles, 47.4%) of azepine 79.

Dimerization of N-methanesulfonylazepine. A 1.76 g. (10.3 mmoles) sample of 74a was sealed in a thick wall glass tube and heated at 122° for 2 hr. Chromatography of the crude product on Florisil gave 952 mg. (54%) of 77b as a waxy solid which resisted a number of attempts at recrystallization; \( \nu_{\text{max}}^{\text{CHCl}_3} \) 1670 (C=C), 1350, 1345, 1170,
and 1165 cm\(^{-1}\) (SO\(_2\)N), \(\delta^{CDCl_3}_{\text{TMS}}\) 4.2-6.4 (multiplets, 11H, vinyl and CHN protons), 3.1-3.55 (multiplet, 1H, H-1), 2.81 and 2.93 (singlets, 3H each, methyl protons); m/e 342 (M\(^+\)).

Also obtained was 104 mg. (5.9\%) of methanesulfonaniline.

Hydrogenation of 586 mg. of 97b over 10\% palladium on carbon in ethyl acetate at 50 psig for 24 hr. afforded, after chromatography on Florisil, 367 mg. (62\%) of 99b as large white needles, m.p. 139.5-141\° (ether); \(\nu_{\text{max}}^{\text{CHCl}_3}\) 1675 (C=C), 1345, 1330, 1165, and 1150 cm\(^{-1}\) (SO\(_2\)N); \(\delta^{CDCl_3}_{\text{TMS}}\) 6.59 (doublet, J\(_{10,11}\) = 10 Hz, 1H, H-10), 4.38-5.16 (multiplets, 4H, H-2,7,8,11), 3.00 and 3.06 (singlets, 3H each, methyl protons), 2.3-2.8 (multiplet, 1H, H-1), and 1.5-2.2 (broad signals, 4H and 8H); m/e 348 (M\(^+\))


Tetracyanoethylene Adduct 101b. A solution of 1.0029 g. (5.86 mmole) of N-methanesulfonylazepine (74a) and 0.7433 g. (5.80 mmoles) of TCNE (100) in 200 ml. of toluene was refluxed with vigorous stirring for 5 hr. during which time the deep orange color of the initial reaction mixture faded noticeably. Solvent removal and recrystallization of the residue from methanol gave 0.661 g. (2.21 mmoles, 38.1\%) of adduct 101b as a white powder identical to that reported in the literature.

Iron Enneacarbonyl. A solution of 25.0 g. (0.128 mole) of iron pentacarbonyl in 450 ml. of glacial acetic acid was irradiated
with a 450 W Hanovia lamp through Pyrex optics for 4 hr. The precipitated product was isolated by filtration, the filtrate then irradiated for an additional eight hours and the solid was collected in the same manner. The product was washed with ethanol followed by diethyl ether and was allowed to air dry to give 14.7 g. (63.2%) of iron enneacarbonyl as orange flakes.

It is important that all operations were carried out in a fume hood since Fe₂(CO)₉ is very toxic.

N-Methanesulfonyleazepineiron Tricarbonyl (102). To a stirred solution of 967 mg. (5.65 mmoles) of 74a in 40 ml. of tetrahydrofuran at ambient temperature was added 2.04 g. (5.61 mmoles) of iron enneacarbonyl. After stirring for 75 min., all of the metal carbonyl had dissolved and the dark reaction mixture was filtered through Celite. The filtrate was evaporated and the residue was crystallized from hexane to give 1.20 g. (69%) of complex 102 as lustrous orange-yellow prisms, m.p. 94.5-96°, \( \nu_{\text{max}}^{\text{CHCl}_3} 2070, 1990 \) (Fe-CO), 1635 (C=C), 1350, and 1170 cm⁻¹ (SO₂N); \( \delta_{\text{CDCl}_3}^{\text{TMS}} 3.5-6.5 \) (broad humps, temperature dependent, 6H, vinyl protons) and 2.92 (singlet, 3H, methyl protons); \( \lambda_{\text{EtOH}}^{\text{max}} 232 \text{ sh nm} \) (e 14,600).


Methyl Azidoformate. This material was prepared by the reaction of sodium azide with methyl chloroformate using the procedure employed by Cotter and Beach to generate the ethyl derivative.
Reaction of Cycloheptatriene with Methyl Azidoformate. A 7% solution of methyl azidoformate in cycloheptatriene in a sealed thick-walled tube was immersed in an oil bath preheated to 127-128°C, where it was maintained for 4 hr. Removal of excess hydrocarbon in vacuo followed by preparative scale gas chromatography (5 ft. x 0.25 in. Al column packed with 20% SE-30 on 60-80 mesh Chromosorb W) and molecular distillation permitted separation of three fractions.

The first fraction to be eluted was 2,3-homo-lH-azepine (2-carbomethoxy-2-azabicyclo[5.1.0]octa-3,5-diene), a pale yellow oil; $v_{max}^{film}$ 1730 (C=O), 1655 and 1635 cm$^{-1}$ (C=C); $^1H_{TMS}$ 6.65 (doublet, 1H, H-3, $J_{3,4} = 9.5$ Hz), 6.12 (doublet of doublets, 1H, H-6, $J_{6,5} = 11.1$ Hz and $J_{6,7} = 3.1$ Hz), 5.66 (doublet of doublets, 1H, H-5, $J_{5,6} = 11.1$ Hz and $J_{5,4} = 6.6$ Hz), 5.10 (doublet of doublets, 1H, H-4, $J_{4,3} = 9.5$ Hz and $J_{4,5} = 6.1$ Hz), 3.80 (singlet, 3H, methyl protons), 3.15 (multiplet, 1H, H-1), 1.1-1.6 (multiplet, 2H, H-7 and anti C-8 proton), and 0.1-0.4 (multiplet, 1H, syn proton on C-3); $\lambda_{max}$ 262 nm ($\varepsilon$ 8,430); m/e 165 ($M^+$).

Anal. Calcd for C$_9$H$_{11}$NO$_2$: C, 65.43; H, 6.71; N, 8.48. Found: C, 65.16; H, 6.74; N, 8.36.

The second component to elute, a colorless oil, was 4,5-homo-lH-azepine (4-carbomethoxy-4-azabicyclo[5.1.0]octa-2,5-diene); $v_{max}^{film}$ 1725 (C=O) and 1670 cm$^{-1}$ (C=C); $^1H_{TMS}$ 6.65 (doublet, 2H, H-3 and H-5, $J_{3,2} = 9.8$ Hz), 5.15 (broadened doublet, 2H, H-2 and H-6, $J_{2,3} = 9.8$ Hz), 3.86 (singlet, 3H, methyl protons), 1.0-1.6 (mul-
triplet, 3H, H-1, H-7, and the anti proton on C-8), and 0-0.3
(multiplet, 1H, syn proton on C-8); \( \lambda_{\text{max}} = 231 \text{ nm} \) (e 11,430).
m/e 165 (M\(^+\)).

Anal. Calcd for CeH\(_{11}\)NO\(_2\): C, 65.43; H, 6.71; N, 8.48.
Found: C, 65.60; H, 7.11; N, 8.26.

On the basis of infrared and nmr spectra, the third fraction
was seen to contain a mixture of cycloheptatrienyl urethanes, which
were not further characterized.

In another experiment the crude reaction mixture was fractionated through a 55 cm. stainless steel spinning band column. Although
clean separation of \(120\) and \(121\) was not achieved, the procedure did
effect the separation of this homoaepine mixture (b.p. 60-80°/
0.4 mm.) from the nitrone insertion products. A combined yield
of 35% was obtained. The ratio of \(120\) to \(121\) was 2.2:1 (vpc anal-
ysis) both before and after distillation.

**Photoisomerization of 120.** A solution of 2.33 g. of a mixture
of \(120\) and \(121\) in a ratio of ca. 3:1 in 450 ml. of anhydrous ether
was irradiated under nitrogen through Vycor optics with a 200-W
Hanovia lamp in a standard immersion vessel. The progress of the
reaction was monitored at 30 min. intervals by vpc (160°, 12 ft. x
0.25 in. Al column packed with 10% SE-30 on 60-80 mesh Chromosorb
G). After 2.5 hr. the reaction was complete and solvent removal
afforded 2.25 g. of orange oil. Preparative scale vpc, utilizing
the above column, allowed the separation and collection of the two
observed fractions. The first consisted of a mixture of photopro-
ducts 124 and 125, while the second was unchanged 121. Preparative scale thick layer chromatography (alumina, developed in 7% ether in hexane) resulted in the separation and isolation of 124 and 125 in an approximate ratio of 3:2. Final purification was achieved by preparative vpc on the above column followed by molecular distillation.

The major photoisomer was identified as 5-carbomethoxy-5-aza-1α,2α,4α,6α-tricyclo[4.2.0.02,4]oct-7-ene (124), a colorless oil; $\nu_{max}^{film}$ 1710 cm$^{-1}$ (C=O); $\delta_{TMS}^{CDCl_3}$ 6.23 (narrow multiplet, 2H, vinyl protons), 4.47 (broadened doublet, 1H, H-6), 3.63 (singlet, 3H, methyl protons), 3.15-3.48 (broad multiplet, 2H, H-1 and H-4), and well resolved multiplets at 1.49, 0.77 and 0.29 (1H each, H-2 and H-3 syn and anti); $\delta_{EtOH}$ end absorption only; m/e 165 (M$^+$$^\ast$).

Anal. Calcd for C$_9$H$_{11}$NO$_2$: C, 65.43; H, 6.71; N, 8.48.

Found: C, 65.34; H, 6.71; N, 8.30.

cis-2-Carbomethoxy-2-azabicyclo[3.3.0]octa-3,6-diene (125), a colorless oil, was found to be the minor photoisomer; $\nu_{max}^{film}$ 1720 (C=O), 1630 and 1610 cm$^{-1}$ (C=C); $\delta_{TMS}^{CDCl_3}$ 6.54 (broad doublet, 1H, H-3, $J_{3,4}$ = 4.5 Hz), 5.68 (singlet, 2H, H-6 and H-7), 5.09 (doublet of doublets, 1H, H-4, $J_{4,3}$ = 4.5 Hz, $J_{4,5}$ = 2.5 Hz), 4.45-4.9 (multiplet, 1H, H-1), 3.9-4.2 (broad signal, 1H, H-5), 3.74 (singlet, 3H, methyl protons), and 2.25-3.2 (broad signal, 2H, H-8); $\lambda_{max}$ 233 nm ($e$ 11,500); m/e 165 (M$^+$$^\ast$).

Anal. Calcd for C$_9$H$_{11}$NO$_2$: C, 65.43; H, 6.71; N, 8.48.

Found: C, 65.07; H, 6.66; N, 8.30.
Irradiation of $^{120}$ in Acetone. An acetone solution of $^{120}$ was irradiated through pyrex in a manner identical to the photoisomerization in ether. As a result of these modifications the rate of reaction was decreased to the extent that it had proceeded to only $\frac{2}{3}$ completion after 14.5 hr.

Cyclopentylidinecyanoacetic Acid ($^{130}$). A solution of 50 g. (0.59 mole) of cyclopentanone, 50 g. (0.59 mole) of cyanoacetic acid and 2 g. of ammonium acetate in 50 ml. of benzene was heated for 7 hr. at a bath temperature of 155° with continuous removal of water. Upon cooling to room temperature the product crystallized and was dried in vacuo to give 84 g. (94%) of $^{130}$. Recrystallization from water afforded small white crystals, m.p. 129-133° (dec.) [lit.101 m.p. 125-128°]; $\nu_{\text{max}}^{\text{KBr}}$ 2230 (C=N), 1710 (C=O), and 1600 cm$^{-1}$ (C=C).

Cyclopentylidineacetonitrile ($^{131}$). A Decarboxylation Prior to Distillation. To a 250-ml. one-neck flask equipped with a magnetic stirrer and reflux condenser was added 40 g. (0.265 mole) of unrecrystallized $^{130}$. Heat was applied to melt the reactant, the stirrer started, and the temperature gradually raised to 180° during which time decarboxylation commenced. When carbon dioxide evolution subsided, as evidenced by means of a gas bubbler, the reaction mixture was allowed to cool and the condenser replaced by a 7 cm. Vigreaux distillation head. Distillation afforded 21.8 g. (0.204 mole, 79%) of pure $^{131}$ as a clear, colorless liquid, b.p. 82-85°/
136

14 mm. (lit. b.p. 85-88°/20 mm.); \( \nu_{\text{film}} \) 2250, 2220 (C=N), 1660 and 1640 cm\(^{-1} \) (C=C); \( \delta_{\text{CDCl}_3} \) 5.79 (multiplet, 1H, vinyl proton), 3.17 (unresolved signal, 2H, allylic ring methylene protons cis to -C=N), and 1.6-2.7 (complex patterns, 6H).

B. Simultaneous Decarboxylation and Distillation. The procedure was that employed by Protiva, et al. This technique resulted in the collection of a mixture of 131 and unreacted 130. Redistillation of the mixture gave pure 131 in 67% yield.

Cyclopentylacetonitrile (132). A solution of 21.8 g. (0.203 mole) of 131 in 150 ml. of methanol was hydrogenated over 5% palladium on charcoal at ambient temperature in a Brown apparatus equipped for external generation. Reaction stopped after the uptake of one molar equivalent of hydrogen. Careful solvent removal in vacuo followed by distillation of the residue afforded 18.3 g. (0.168 mole, 83%) of clear, colorless 132, b.p. 91-92.5°/26 mm. (lit. b.p. 88°/27 mm.); \( \nu_{\text{film}} \) 2250 cm\(^{-1} \) (C=N); \( \delta_{\text{CDCl}_3} \) 2.35 (broad signal, 2H, -CH\(_2\)CN) and 1.1-2.2 (complex, 9H, ring protons).

2-Cyclopentylethylamine (133). To a stirred suspension of 4.42 g. (0.116 mole) of lithium aluminum hydride in 200 ml. of anhydrous ether was added dropwise 10.93 g. (0.10 mole) of 132 in 50 ml. of the same solvent. The reaction mixture was refluxed for 24 hr., cooled in an ice bath and the salts decomposed by the careful addition of 4.4 g. of water, 4.4 g. of 30% aqueous potassium hydroxide and 13.2 g. of
water, in that order. The reaction mixture was filtered with suction and the filtrate carefully concentrated under reduced pressure. Distillation of the residue afforded 10.75 g. (0.095 mole, 95%) of 133 as a clear colorless liquid, b.p. 83-84°/45 mm. (lit. \textsuperscript{101} b.p. 55-70°/25 mm); HCl salt, m.p. 192-195° (lit. \textsuperscript{101} m.p. 197°); \( \nu_{\text{film}} \) 3300, 3240 (assym. and sym. \( \text{NH}_2 \) stretch), 1610 (\( \text{NH}_2 \) scissoring), 1065 (C-N), and 820-830 cm\(^{-1}\) (out-of-plane \( \text{NH}_2 \) bending); \( \delta_{\text{NMR}} \) 2.68 (broad triplet, 2H, \(-\text{CH}_2\text{N}\)) and 0.8-2.0 (complex, 13H).

\textit{cis-2-Azabicyclo[3.3.0]nonane (134)}. A 3.77 g. sample (33.3 mmoles) of 133 was added to 40 ml. of a stirred, ice-cold, 0.82 M sodium hypochlorite solution (32.8 meq.) and the mixture immediately became cloudy. After an additional 15 min., the stirring was stopped causing the separation of two layers. A drop of the upper layer gave a positive test for \( N \)-chloramine with sodium iodide. This mixture was extracted with pentane (4 x 25 ml.), the pentane extract was added dropwise during 15 min. with stirring to 40 ml. of cold 80% sulfuric acid, and the whole was stirred vigorously for an additional 15 min. The opalescent acid layer was separated and irradiated in a quartz tube with a bank of nine 15-W germicidal lamps for 10 min. The resulting dark, slightly warm solution was poured onto 200 g. of ice and, with ice cooling, the solution was rendered highly alkaline by the addition of potassium hydroxide pellets at such a rate that the temperature never rose above 20°.

The alkaline solution was decanted from the precipitated salts
and extracted with ether (6 x 100 ml.). The combined organic layers were dried and evaporated and the residue was distilled to give 1.26 g. (29.4%) of 134 as a clear, colorless liquid, b.p. 82-85° (44 mm.); \( \text{film }^{180} \nu_{\text{max}} \) 3240 (singlet, \( R_2NH \)), 1610 (\( R_2NH \) scissoring), 1080 (C-N), and 840 cm\(^{-1} \) (broad, out-of-plane NH bending).

**cis-2-Carbomethoxy-2-azabicyclo[3.3.0]octane (129).** A Hydrogenation of 125. A solution of 80 mg. of 125 in 15 ml. of anhydrous tetrahydrofuran was hydrogenated over Adams catalyst at 50 psig. Filtration followed by solvent removal gave 84 mg. of pale yellow oil. Isolation of purified product (82%) by preparative vpc (137°, 12 ft. x 0.25 in. Al column packed with 10% SE-30 on 60-80 mesh Chromosorb G) gave colorless liquid 129; \( \text{film }^{1700} \nu_{\text{max}} \) 1700 cm\(^{-1} \) (C=O); \( ^{6}_{\text{TMS}} \) 3.9-4.3 (broad signal, 1H, H-1), 3.71 (singlet, 3H, methyl protons), 3.1-3.65 (multiplet, 2H, H-3), 2.4-2.9 (broad signal, 1H, H-5), and 1.2-2.2 (complex, 8H).

**Anal.** Calcd for C\(_9\)H\(_{15}\)N\(_2\): C, 63.88; H, 8.94; N, 8.28. Found: C, 63.71; H, 9.14; N, 8.21.

**E. Carbomethoxylation of 134.** A solution of 933 mg. (9.88 mmoles) of methyl chloroformate in 10 ml. of dry ether was added dropwise to a stirred, ice-cold solution of 1.095 g. (9.85 mmoles) of 134 and 1.196 g. (11.82 mmoles) of triethylamine in 25 ml. of the same solvent. After completion of addition, the stirred reaction mixture was allowed to warm to ambient temperature during 1 hr. Water (10 ml.) was added and the ether layer was separated, dried and evaporated. Preparative vpc on the above column afforded 129
in 73% yield, identical in all respects with the sample prepared above.

**Benzenesulfonyl Azide.** Prepared by the method of Zalkow and Cehlschlager.\(^\text{182}\)

1-Benzenesulfonylimino-2,4,6-cyclooctatriene (152). A suspension of 20 mg. of copper powder in a solution of 300 mg. (1.64 mmoles) of benzenesulfonyl azide in 4 ml. of freshly distilled cyclooctatetraene was heated with stirring for 18 hr. at 85°. The copper and a dark tarry substance were removed by filtration and washed well with ether. The combined filtrate and ether washings were concentrated in vacuo and the dark oily residue chromatographed on Florisil.

Aside from recovered COT there was obtained 75 mg. (0.48 mmole, 29%) of benzenesulfonamide and 210 mg. (0.81 mmole, 49%) of 152 as a somewhat immobile yellowish oil; \(v_{\text{film}}\) max 1550 (C=N), 1300 and 1150 cm\(^{-1}\) (SO\(_2\)N); \[^{1}D\text{Cl}_{3}\,\text{TMS}\] 7.96 and 7.57 (multiplets, 2H and 3H, aromatic protons), 6.1-6.8 (multiplet, 5H, vinyl protons), 5.3-6.1 (broad multiplet, 1H, vinyl proton), 3.2-3.7 (broad signal, 1H, proton \(\alpha\) to C=N), and 2.9 (broadened triplet, 1H, proton \(\alpha\) to C=N).

Attempted purification of 152 by rechromatography resulted in the recovery of only 75 mg. (29 mmole) of this imine the remainder having been hydrolyzed to give 32 mg. (16 mmole) of 2,4,6-cyclooctatrien-1-one (153), identical to an authentic sample.\(^\text{125}\) No attempt was made to elute the benzenesulfonamide.
Chromatography of the remainder of 152 on deactivated alumina led to its quantitative conversion to 153 and benzenesulfonamide.

cis-1,2-Iminocyclooct-5-ene (156). To a vigorously stirred, ice-cold suspension of 51.0 g. (0.340 mole) of silver cyanate in a solution of 30.00 g. (0.277 mole) of 1,5-cyclooctadiene in 400 ml. of anhydrous tetrahydrofuran was added 70.2 g. (0.277 mole) of iodine. After 3 hr. the silver salts were removed by filtration and the filtrate stripped of solvent in vacuo. The resultant β-iodoisocyanate was added to a solution of 60 g. of potassium hydroxide pellets in 250 ml. of water and the mixture refluxed for 27 hr. After cooling the reaction mixture was extracted with three 200-ml. portions of ether, the combined ether layers dried over anhydrous magnesium sulfate, filtered and evaporated under reduced pressure. The residue was distilled into a receiver cooled in Dry Ice-isopropyl alcohol to afford 16.33 g. (0.133 mole, 48%) of 156, a clear, colorless liquid, b.p. 40.5-41.5° (0.3 mm.); $^{133}$νfilm $^{\text{max}}$ 3210 (NH) and 1660 cm$^{-1}$ (C=C); $\delta$TMS 5.58 (multiplet, 2H, vinyl protons), 1.2-2.7 (complex, 10H) and 0.88 (singlet, 1H, NH).

This amine formed a picrate, m.p. 162-162.5° (95% ethanol).

Anal. Calcd for C$_{14}$H$_{12}$N$_4$O$_7$: C, 47.73; H, 4.58; N, 15.90.
Found: C, 47.80; H, 4.85; N, 15.70.

cis-N-Benzensulfonyl-1,2-iminocyclooct-5-ene (157). To a stirred solution of 3.97 g. (0.0322 mole) of 156 and 3.29 g. (0.0325 mole) of triethylamine in 30 ml. of anhydrous ether cooled in ice was added dropwise 5.67 g. (0.0321 mole) of benzenesulfonyl chloride
in 10 ml. of the same solvent. The reaction mixture was stirred for 1 hr., water (100 ml.) added and the layers separated. Ether extraction followed by drying and solvent removal afforded 8.22 g. of slightly moist white solid. Triple recrystallization from ether gave 6.48 g. (0.0246 mole, 76.6%) of 157 as large, colorless crystals, m.p. 77-79° (lit. m.p. 79-80.5°).

The oily moisture adhering to the product prior to recrystallization could conveniently be removed by washing with hexane. The material obtained in this way was completely suitable for bromination.

Preparation of 157 by the Iodine Azide-Lithium Aluminum Hydride Sequence. To a stirred slurry of 15 g. (0.23 mole) of sodium azide in 100 ml. of acetonitrile was added dropwise 18.3 g. (0.113 mole) of iodine monochloride. The internal temperature was maintained at -10° by the periodic addition of Dry Ice to an isopropyl alcohol bath surrounding the reaction flask. The addition required 20 min. and the yellow-orange reaction mixture was stirred for an additional 20 min.

The resulting iodine azide solution was then added in 5-10 ml. portions at 5 min. intervals to a similarly cooled solution of 40 g. (0.37 mole) of 1,5-cyclooctadiene in 200 ml. of the same solvent. When addition was complete the cooling bath was removed and the mixture stirred for 12 hr. The resulting solution was poured into 1 l. of water, extracted with ether (4 x 250 ml.) and the combined organic phases washed with % aqueous sodium thiosulfate and then
water. Drying followed by solvent removal at room temperature gave
36 g. of crude \( \text{158} \) as an orange-brown liquid which was not further
purified; \( \nu_{\text{max}}^{\text{film}} \) 2080 cm\(^{-1}\) (\( \text{N}_3 \)).

This material was added dropwise with caution over 2 hr. to
an ice-cold slurry of 8.0 g. (0.21 mole) of lithium aluminum hydride
in 300 ml. of anhydrous ether. Gas evolution was monitored by
means of a bubbler and the rate of addition adjusted accordingly.
After addition was complete the mixture was allowed to warm to am-
bient temperature, stirred for 19 hr. and hydrolyzed by the careful
dropwise addition of 32 ml. of 20% sodium hydroxide solution. The
resulting white slurry was vigorously stirred for 45 min., dried
by the addition of anhydrous magnesium sulfate and filtered. Sol-
vent removal from the filtrate gave a clear, slightly yellow mix-
ture of \( \text{156} \) and excess diene (by \( \text{vpc, SE-30} \)). The latter was re-
moved by distillation and the aziridine sulfonylated in the usual
manner without further purification. There was obtained 15.11 g.
(0.057 mole, 50.3% based upon iodine monochloride) of \( \text{157} \).

1-Benznesulfonylimino-5-cyclooctene (159). A mixture of 10 g.
of 1,5-cyclooctadiene, 1.0 g. (5.46 mmoles) of benzenesulfonyl azide
and 50 mg. of copper powder was heated with stirring at 70° for 27
hr. Filtration followed by solvent removal and chromatography on
Florisil gave 644 mg. (2.44 mmoles, 44.7%) of imine \( \text{159} \) as a slightly
yellow oil; \( \nu_{\text{max}}^{\text{film}} \) 1610 (C=N), 1310 and 1160 cm\(^{-1}\) (SO\(_2\)N).

Elution of this material through deactivated alumina gave 280
mg. (2.26 mmoles, 97% based upon \( \text{159} \) used) of 4-cycloocten-1-
trans-5,6-Dibromo-cis-1,2-(N-benzenesulfonylaziridino)cyclooctane (160). Fornination of 157 utilizing the procedure described above afforded a quantitative yield of 160 as small, white crystals, m.p. 153-154°; $\nu_{\text{max}}$ CHCl$_3$ 1330 and 1160 cm$^{-1}$ (SO$_2$N); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.7-8.0 (multiplet, 2H, aromatic protons), 7.3-7.7 (multiplet, 3H, aromatic protons), 4.0-4.5 (unresolved, 4H, aziridine protons and CHBr), and 1.6-2.7 (complex, 8H).

Anal. Calcld for C$_{14}$H$_{17}$Br$_2$NO$_2$S: C, 39.73; H, 4.05; S, 7.58. Found: C, 39.73; H, 4.08; S, 7.48.

Treatment of 160 with Dehydrohalogenation Agents. A. A solution of 3.00 g. (7.1 mmole) of 160 in 50 ml. of anhydrous tetrahydrofuran containing 1.58 g. (14.1 mmole) of suspended potassium t-butoxide was refluxed for 6 hr., cooled and 100 ml. of water added. Extraction with ether (5 x 50 ml) followed by drying and solvent removal in vacuo gave 2.22 g. of orange-red oily residue. Chromatography on Florisil allowed the separation of three sulfonamide-containing fractions.

The first (5% ether in hexane) contained 327 mg. (11%) of unreacted 160.

The second (10-20% ether in hexane) consisted of 1.09 g. of an approx. 1:1 incompletely separated mixture of 161 (first to begin eluting) and 162. Fractional recrystallization gave 161 as colorless
crystals, m.p. 109-110° (ether); $\nu_{\max}^{\text{CDCl}_3}$ 1330 and 1160 cm$^{-1}$ (SO$_2$N); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.6-7.9 (complex, 2H, aromatic protons), 7.2-7.6 (complex, 3H, aromatic protons), 5.8 (multiplet, 1H, vinyl proton), 5.6 (multiplet, 1H, vinyl proton), 4.0-4.5 (broad signal, 3H, aziridine protons and CHBr), and 1.5-2.6 (unresolved pattern, 6H).

Anal. Calcd for C$_{14}$H$_{15}$BrNO$_2$S: C, 49.13; H, 4.71; S, 9.37.
Found: C, 49.20; H, 4.74; S, 9.49.

Diene 162 was obtained as colorless crystals, m.p. 154.5-156.5°; $\nu_{\max}^{\text{CDCl}_3}$ 1330, 1320 and 1160 cm$^{-1}$ (SO$_2$N); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.7-8.0 (complex, 2H, aromatic protons), 7.3-7.6 (complex, 3H, aromatic protons), 5.65 (unresolved, 4H, vinyl protons), 4.4-4.7 (broad signal, 2H, aziridine protons), and 1.5-2.6 (complex, 4H); $\lambda_{\max}^{\text{EtOH}}$ 230 nm ($\epsilon$ 5,350).

Anal. Calcd for C$_{14}$H$_{15}$NO$_2$S: C, 64.34; H, 5.79; N, 5.36.
Found: C, 64.06; H, 6.06; N, 5.28.

The third chromatography fraction contained 141 mg. (8%) of benzenesulfonamide, identical in all respects with an authentic sample.

B. To a solution of 5.00 g. (11.8 mmoles) of dibromide 160 in 40 ml. of hexamethylphosphoramide (distilled from calcium hydride) was added 2.66 g. (23.7 mmoles) of potassium t-butoxide. The reaction mixture was heated at 70° for 20 hr., cooled and poured into 250 ml. of water. The aqueous solution was extracted with ether (5 x 200 ml.), the combined ether layers washed with water (5 x 200 ml.), dried and evaporated. The residue was processed as above to give 807 mg. (16.2%) of unreacted 160, 58 mg. (0.7%) of mono-
elimination product 161, and 694 mg. (22.5%) of diene 162.

C. Treatment of 160 as in method A with reflux continued for 24 hr. and chromatography on alumina produced 162 in 9.4% and 161 in 1.6% yield.

D. Potassium t-butoxide (3.00 g., 26.7 mmoles) was added to 5.00 g. (11.8 mmoles) of 160 in 100 ml. of 1,2-dimethoxyethane (distilled from sodium). After stirring for 2.5 hr. at room temperature and 45 min. at reflux the reaction mixture was cooled, filtered through Celite and evaporated under reduced pressure. The residue was fractionally recrystallized from ether to afford 620 mg. (8%) of unchanged 160 and 1.10 g. (36.8%) of 161.

E. The action of -2 molar equivalents of trityl lithium on 213 mg. (0.5 m mole) of dibromide 160 in tetrahydrofuran solution (6 ml.) produced, after solvent removal, a moist solid residue. This material, after washing with 30 ml. of pentane in two portions, was taken up in ether, washed with water, dried, and evaporated. The resulting solid consisted of a mixture of 160 and benzenesulfonamide (ir and nmr). The pentane washings, upon solvent removal, afforded a semi-solid residue in which the presence of triphenyl-methane was detected (ir).

The following experiments resulted only in the recovery of un-reacted 160 in the amounts indicated.

F. Method A., ice bath temperature, 82%.
G. Potassium t-butoxide in dimethyl sulfoxide at 0°. Worked-up as in method B. Recovered 63%.

H. Same as method G., but at room temperature, 70%.

I. Experimental procedure utilizing 1,5-diazabicyclo[4.3.0]non-5-ene was analogous to that employed in the preparation of 79, refluxed 19 hr., 93%.

J. Pyridine reflux, 2½ hr., 81%.

K. Method A. employing freshly prepared sodium methoxide instead of potassium t-butoxide, 88%.

L. Refluxed 160 with potassium hydroxide in 95% ethanol, 80%.

M. Refluxed 7.1 mmoles of 160 with 14.5 mmoles of freshly prepared silver oxide in 50 ml. of anhydrous benzene for 5 days. The mixture was filtered through Celite and the filtrate evaporated with recovery of 78% of 160.

N. A solution of 160 (2.16 g., 5.1 mmoles) in tetrahydrofuran (50 ml.) was stirred at room temperature for 4 hr. with two molar equivalents of both silver nitrate and pyridine. The solvent was removed and 100 ml. of water containing 10 ml. of concentrated ammonium hydroxide added to the residue. Extraction with ether followed by drying and solvent removal returned 2.02 g. (4.8 mmoles, 94%) of 160.
Silver Oxide. To a solution of 17 g. (0.1 mole) of silver nitrate in 100 ml. of distilled water in a 250-ml. Erlenmeyer flask was added a solution of 4 g. (0.1 mole) of sodium hydroxide in 50 ml. of the same solvent and the tightly stoppered flask was shaken vigorously for about 15 sec. The water was then decanted and the precipitate washed twice (shook and decanted) with fresh distilled water, twice with ethanol, once with acetone and twice with anhydrous ether. The residual ether was removed in vacuo and the product dried for 15 hr. at 0.01 mm. to give 10.8 g. (0.48 mole, 93%) of silver oxide as a brown powder.

Reaction of 161 with Potassium t-Butoxide. To a stirred solution of 3.15 g. (9.2 mmoles) of 161 in 40 ml. of refluxing tetrahydrofuran was added 1.04 g. (9.3 mmoles) of potassium t-butoxide. After 3.5 hr. at reflux, thin layer chromatography (alumina, ether development) revealed that unreacted 161 was the only mobile component present. An additional 2 g. of base was added and reflux was continued for 20.5 hr. At the end of that time tlc showed the presence of some still unreacted 161 and dark immobile materials, but no 162. Usual work-up (see method A above) gave 163 mg. (5.2%) of unchanged 161 and 740 mg. (4.7 mmoles, 51%) of benzene sulfonamide. The dark tars failed to elute from the column.

Reaction of 157 with NBS. A mixture of 5.00 g. (19 mmoles) of 157, 6.76 g. (38 mmoles) of recrystallized NBS and approx. 50 mg. of benzoyl peroxide was refluxed as above for 12 hr. in 100 ml. of car-
bon tetrachloride. Processing analogous to that employed in the preparation of 166 allowed the separation of three components.

The first material eluted (5% ether in hexane) was 1.45 g. (3.43 mmoles, 18%) of dibromide 169, identical to that prepared above.

The next fraction (10% ether in hexane) consisted of 470 mg. (1.8 mmoles, 9.5%) of unreacted 157.

The third component (210 mg., 3.2%), eluted with 20-22% ether in hexane was 164, m.p. 116-118.5\(^\circ\) (1:10 ether:pentane); \(\nu_{\text{max}}^{\text{CHCl}_3}\) 1310 and 1160 cm\(^{-1}\) (SO\(_2\)N); \(\delta_{\text{DMSO}}^{\text{CDCl}_3}\) 7.7-8.0 (complex, 2H, aromatic protons), 7.4-7.7 (complex, 3H, aromatic protons), 5.3-6.0 (multiplets, 2H, vinyl protons), 4.5-5.1 (multiplet, 1H, CHBBr), and 1.7-3.2 (unresolved, 8H).

**Anal. Calcd for C\(_{14}\)H\(_{10}\)BrNO\(_2\)S:** C, 49.13; H, 4.71; N, 4.09.

**Found:** C, 49.47; H, 4.77; N, 3.86.

The major portion of the reaction mixture consisted of brown tarry substances which were removed during the filtration and chromatography.

**Delayed Introduction of the Sulfonyl Group.** A solution of aziridine 156 (3.022 g., 24.5 mmoles) in methylene chloride at -78\(^\circ\) was brominated in the usual manner. Solvent removal in vacuo gave an oil to which a small amount of ether was added. Scratching induced crystallization and the resulting tan solid was isolated by filtration. There was obtained 6.88 g. (24.3 mmoles, 99%) of moist
powder which was not further purified.

The product was dissolved in 100 ml. of tetrahydrofuran, cooled in ice and 6.0 g. (53.4 mmoles) of potassium tert-butoxide added. The reaction mixture rapidly became very dark and was allowed to warm to room temperature and stirred for 20 hr. Filtration through Celite allowed the removal of a mass of dark, tarry (polymeric?) material. The filtrate was concentrated under reduced pressure and the dark oily residue partitioned between ether and water. The organic phase was dried and the solvent removed to give 3.44 g. of orange-brown oil. (A preliminary experiment showed this material to polymerize upon slight warming).

This material was dissolved in 100 ml. of ether and treated with 4.35 g. of benzenesulfonyl chloride in the usual manner (a two-fold excess of triethylamine was used). Chromatography of the semi-solid residue produced gave 1.13 g. (2.67 mmoles) of dibromide \(160\) and 912 mg. (2.66 mmoles) of monooelimination product \(161\), each identical to authentic material.

No diene \(162\) was isolated. Small amounts of unidentified materials were formed but were not further investigated.

\[\text{3-Bromo-cis-1,2-(N-benzenesulfonylaziridino)cycloocta-4,6-diene (166)}\]. A mixture of 990 mg. (3.8 mmoles) of diene \(162\) and 658 mg. (3.7 mmoles) of \(N\)-bromosuccinimide (recrystallized from water) in 50 ml. of carbon tetrachloride containing approx. 100 mg. of benzoyl peroxide was refluxed by means of a sunlamp (General Electric 250 W
Reflecto r Lamp) under a flow of nitrogen for 6 hr. Upon cooling
the orange reaction mixture was filtered and the residue obtained
by solvent removal from the filtrate was chromatographed on Flor-
sil. The allylic bromination product, 166, was obtained as 415 mg.
(1.22 mmoles, 33%) of white crystals, m.p. 121.5-122° (from ether);
\[ \text{max} \nu_{\text{CHCl}_3} 1330 \text{ and } 1165 \text{ cm}^{-1} \text{ (S}0_2N) ; \text{max} \delta_{\text{TMS}} 7.7-8.0 \text{ (complex, } 2H, \text{ aromatic protons)} , 7.3-7.5 \text{ (complex, } 3H, \text{ aromatic protons)} , \text{ doublet of triplets centered at } 5.7 \text{ (} 4H, \text{ vinyl protons)} , 4.75 \text{ and } 4.35 \text{ (unresolved, } 1H \text{ and } 2H, \text{ resp.}, \text{ CHBr and aziridine protons)} ; \text{ Et}_{\text{CH}} 2.6 \text{ (multiplets, } 2H) ; \lambda 226 \text{ sh nm } (e 8,200).

Anal. Calcd for C_{14}H_{14}BrNO_{2}S: C, 49.92; H, 4.15; N, 4.12.
Found: C, 49.59; H, 4.31; N, 4.22.

Phenyl Azide. Prepared by the method of von Doering and
Odum.

1,2,3,4,5,6-Hexamethyl-7-phenyl-7,8,9-triazatricyclo[4.3.0.
0^2,5]nona-3,8-diene (213). A solution of 30 g. (0.185 mole) of
hexamethyl(Dewarbenzene) (HMDB) and 10 g. (0.084 mole) of phenyl
azide in 60 ml. of hexane was heated at reflux with stirring in a
flask wrapped with aluminum foil to protect the contents from
light. After 142 hr. all of the phenyl azide had been consumed, as
indicated by the absence of the azide infrared absorption, and the
solvent was removed in vacuo. The product was filtered from excess
HMDB, washed with cold pentane and sublimed (75°/0.02 mm.) to give
15.47 g. (65.5%) of 213 as white crystals, m.p. 115-116.5° (hexane);
\( \delta_{\text{TMS}}^{\text{CDCl}_3} \) (100 MHz spectrum) 7.30 (doublet, 4H, aromatic protons), 7.05 (multiplet, 1H, aromatic proton), 1.713 (singlet, 6H, allylic protons), 1.237 and 1.257 (singlets, 6H total, C\textsubscript{1}-CH\textsubscript{3} and C\textsubscript{6}-CH\textsubscript{3}), and 0.941 and 0.959 (singlets, 6H total, C\textsubscript{2}-CH\textsubscript{3} and C\textsubscript{5}-CH\textsubscript{3}); \( \lambda_{\max}^{\text{EtOH}} \) 288 (\( \varepsilon 7,900 \)) and 302 nm (\( \varepsilon 8,090 \)).

**Anal.** Calcd for C\textsubscript{14}H\textsubscript{23}N\textsubscript{3}: C, 76.83; H, 8.24. Found: C, 77.11; H, 8.31.

1,2,3,4,5,6-Hexamethyl-7-carboxemethoxy-7,8,9-triazatricyclo[4.3.0.0\textsubscript{2,5}]nona-3,8-diene (219). A solution of 20.0 g. (0.123 mole) of HMDB and 12.4 g. (0.123 mole) of methyl azidoformate in 50 ml. of pentane was allowed to stand for 10 days in a stoppered flask in the dark. The precipitated crystals were removed by filtration and sublimed (85°/0.02 mm.) to give 17.8 g. (0.0675 mole, 57%) of 219 as a white powder. Recrystallization of a portion of this material from ether-pentane afforded small colorless crystals, m.p. 126-128° (dec. with gas evolution); \( \nu_{\max}^{\text{KBr}} \) 1720 cm\textsuperscript{-1} (C=O); \( \nu_{\max}^{\text{CHCl}_3} \) 1725 cm\textsuperscript{-1} (C=O); \( \delta_{\text{TMS}}^{\text{CDCl}_3} \) 3.90 (singlet, 3H, -OCH\textsubscript{3}), 1.69 (broadened singlet, 6H, allylic protons), 1.30 and 1.36 (broadened singlets, 6H total, C\textsubscript{1}-CH\textsubscript{3} and C\textsubscript{6}-CH\textsubscript{3}), and 0.88 (unresolved multiplet, 6H, C\textsubscript{2}-CH\textsubscript{3} and C\textsubscript{5}-CH\textsubscript{3}); \( \lambda_{\max}^{\text{EtOH}} \) 241 nm (\( \varepsilon 3,920 \)).

1,2,4,5,6,7-Hexamethyl-3-phenyl-3-azatricyclo[3.2.0.0\textsubscript{2,4}]hept-6-ene (217). Irradiation of a solution of 3.05 g. (10.85 mmoles) of 213 in 400 ml. of acetone through Vycor optics with a 200 W Hanovia lamp resulted in the evolution of one equivalent of nitrogen (244 ml.) over a period of 25 min. Solvent removal afforded 2.87 g. of a mix-
ture of 217, a white solid, and a small amount of orange oil.
Neither sublimation nor chromatography on silica gel or alumina
affected the removal of the oily contaminant (< 5% by nmr analysis).
Upon exposure to air, however, the impurity soon decomposed to a non-
volatile orange-brown residue from which pure 217 was separated by
elution through charcoal with hexane. Sublimation (70°/20 mm.)
gave 217 as a white solid, m.p. 105-106.5°; $^{1}$H NMR $^6$CDCl$_3$ 6.65-6.95 (mul-
tiplets, 5H, aromatic protons), 1.66 (singlet, 6H, allylic protons),
1.27 (singlet, 6H, C$_2$-CH$_3$ and C$_4$-CH$_3$) and 1.03 (singlet, 6H, C$_1$-CH$_3$
and C$_5$-CH$_3$); $\lambda_{max}$ 252 (ε 14,800) and 287 sh nm (ε 1,630).
m/e Calcd. for C$_{18}$H$_{23}$N: 253.18303960
Found: 253.18241441
0.00062519
Anal. Calcd for C$_{18}$H$_{23}$N: C, 85.32; H, 9.15. Found: C, 85.18;

Preparative Scale Pyrolysis of 213 in Decalin. A solution of
2.90 g. (10.3 mmoles) of 213 in 60 ml. of decalin was immersed in an
oil bath preheated to 200° where it was maintained for 25 min. Elu-
tion of the cooled reaction mixture through alumina (activity III),
without prior solvent removal, afforded three major fractions (after
decalin elution).

The first fraction (1.21 g.) was processed as follows to give
pure 220.
The golden oil obtained from chromatography was subjected to molecular distillation (pot temp. 50°C/0.02 mm.). After 121 mg. of an oily forerun had distilled the bath temperature was raised to 75°C whereupon the remainder of the material sublimed to a slightly moist crystalline mass. Resublimation (75°C/0.02 mm.) after a minute oily forerun afforded pure 220 as a yellow-orange powder which resisted all attempts at recrystallization, m.p. 78.5-79.5°C (softening at 74°C); \( \nu_{\text{KBr}}^{\text{max}} \) 1640 (C=C), 1590 (aromatic ring), 1490, 1365, 1350 and 1130 cm\(^{-1}\); \( \delta_{\text{CDCl}_3}^{\text{TMS}} \) (60 MHz) 6.6-7.4 (complex, 5H, aromatic protons), 2.20 and 2.17 (sharp singlets, 6H total) and 1.99 (broadened singlet, 12H); \( \delta_{\text{C}^6\text{Cl}_4}^{\text{TMS}} \) (60 MHz) 6.6-7.5 (complex, 5H, aromatic protons), 2.20 and 2.13 (sharp singlets, 6H total) and 1.97 (broadened singlet, 12H); \( \delta_{\text{EtOH}}^{\text{TMS}} \) (100 MHz) 6.5-7.4 (complex, 5H, aromatic protons), 2.17 and 2.11 (sharp singlets, 6H total), 1.87-1.97 (multiplet, EtOH, 12H), \( \lambda_{\text{max}} \) 222 (e 8,000) and 353 nm (e 3,780); \( \lambda_{\text{max}} \) isooctane 224 (e 28,600) and 358 nm (e 4,390).

m/e Calcd. for C\(_{18}\)H\(_{23}\)N\(_3\): 281,1891872

Found: 281.1891893

0.000632


Pure 220 (nmr, ir) was also obtained by preparative thick layer chromatography on silica gel (2:3 ether in hexane) of the crude first sublimate. It was necessary to quickly extract the material from the adsorbent with ether to minimize decomposition. Material isolated
in this manner, however, did not crystallize even after sublimation.

The second fraction obtained from the column (412 mg.) was shown by analytical tlc (alumina; 1:3 ether:hexane) to be composed mainly of \(^{221}\) contaminated with small amounts of both \(^{220}\) and \(^{222}\). Molecular distillation (80°/0.02 mm.) served only to increase the proportion of \(^{220}\) in the sample (see text for further examination of this phenomenon). Isolation of pure \(^{221}\) was achieved by two successive preparative thick layer chromatographies (see above for conditions and precautions) followed by subjecting the golden oily \(^{221}\) at room temperature to high vacuum (0.01 mm.). The resistance of \(^{221}\) to recrystallization and its thermal instability precluded any further attempts at purification; \(\nu_{\text{max}}^{\text{film}}\) 1650 and 1625 (C=O), 1590 (aromatic ring), 1490, 1430, 1365, 1345 and 1130 cm\(^{-1}\); \(\delta^{\text{CDCl}_3}\) 7.1-7.5 (multiplet, 3H, aromatic protons), 6.5-6.8 (multiplet, 2H, aromatic protons), 2.51 (singlet, 3H), 2.06 and 1.97 (singlets, 12H total), and 1.29 (singlet, 3H); in \(\text{C}_2\text{Cl}_4\) these signals appeared at 7.0-7.4, 6.5-6.7, 2.48, 2.02, 1.93 and 1.24 with the same multiplicity and relative areas as in \(\text{CDCl}_3\); \(\lambda_{\text{max}}^{\text{EtOH}}\) 218 (\(\epsilon 19,700\)) and 330 nm (\(\epsilon 2,180\)); \(\lambda_{\text{max}}^{\text{isoctane}}\) 222 (\(\epsilon 20,500\)) and 333 nm (\(\epsilon 2,520\)).

\[\text{m/e Calculated for } \text{C}_{18}\text{N}_{23}\text{N}_3: } 281.1891872 \]
\[\text{Found: } 281.1895554 \]
\[0.0003682 \]

The material isolated in the third fraction (319 mg.) after molecular distillation (60°/0.02 mm.) gave 259 mg. of \(^{222}\) contaminated with small amounts of \(^{220}\) and \(^{221}\) (from tlc). These latter
substances were removed by elution of the mixture through charcoal with pentane. Solvent removal and sublimation (50°/0.05 mm.) afforded 222 as a white solid, m.p. 76.5-78°, which resisted all attempts at recrystallization; \( \nu_{\text{KBr}}^{\text{max}} = 1590 \text{ cm}^{-1} \) (C=C); \( \delta_{\text{TMS}}^{\text{CDCl}} = 6.6-7.2 \) (multiplets, 5H, aromatic protons), 1.70 (sharp singlet, 12H, allylic protons), and 1.39 (sharp singlet, 6H, bridgehead methyl groups); \( \lambda_{\text{EtOH}} \) 220 sh (\( \epsilon \) 8,580), 241 sh (\( \epsilon \) 4,390), and 276 sh nm (\( \epsilon \) 1,210).

\[ m/e \text{ Calcd for } C_{18}H_{23}N: \quad 253.18303960 \]
\[ 253.18285239 \]
\[ 0.00018721 \]

**Thermal Conversion of 221 to 220.** A solution of 221 in tetra-chloroethylene sealed under vacuum in a thick-walled nmr tube was suspended in an oven at 80° with periodic removal for nmr analysis of the contents. During 100 min. 221 was cleanly and quantitatively converted to 220.

**Treatment of Crude 213 Pyrolysate with Alumina: The Origin of 221.** A solution of 200 mg. of triazoline 213 in 5 ml. of decalin was refluxed (195°) for 15 min. After cooling the solvent was removed in vacuo (bath temp. < 50°). The nmr spectrum of the residual orange-brown oil revealed the presence of 220 and 222 (approx. 5:1) inter alia, but no 221. The CDCl\textsubscript{3} was removed under reduced pressure and the pyrolysate mixture was dissolved in 10 ml. of pentane to which 500 mg. of alumina was then added. The result-
ing slurry was stirred for 20 min. at room temperature, filtered and evaporated. Nmr of this golden residue indicated the unquestionable presence of 221. The relative amounts of 220 and 222 were not noticeably changed but the intensity of some of the unidentified absorptions decreased. Repetition of the alumina treatment further increased the amount of 221 present without effecting the 220:222 ratio.

Pyrolysis of 213 in Tetrachloroethylene Monitored by NMR. A solution of 213 in C2Cl4 was sealed under vacuum in a thick-walled nmr tube and the tube suspended in an oven at 118° from which it was periodically removed for nmr analysis of the contents. Over a period of 65 min. at the above temperature 213 was converted smoothly into a pyrolysis mixture approximately 80% of which was 220. The presence of neither 221 nor 222 was detected. An additional 15 min. at elevated temperature caused no further change. Analytical tlc of the contents of the tube confirmed the presence of 220 and the absence of 221. At least five other very minor components were observed.

A similar solution heated at 195° for 10 min. gave rise to black, tarry decomposition products.

Preparative Scale Pyrolysis of 213 in Tetrachloroethylene. A solution of 1.89 g. of 213 in 15 ml. of C2Cl4 was refluxed until nmr analysis of an aliquot indicated that all of the starting material had been consumed (approx. 2 hr.). Solvent removal in vacuo gave
1.91 g. of brown oil the nmr of which indicated > 80% 220, no 221 nor 222. Preparative tlc (see above for conditions and precautions) was effective in separating pure 220 from the crude mixture.

Chromatography of a portion of the crude mixture of Florisil led to the generation of 221.

4-Phenyl-1,2,4-triazoline-3,5-dione. Prepared by the method of Stickler and Finkle.182

Conversion of 221 to 220 by the Action of 4-Phenyl-1,2,4-triazoline-3,5-dione. To a solution of 221 in CDCl₃ in an nmr tube was added a slight excess of 4-phenyl-1,2,4-triazoline-3,5-dione. The tube was shaken to ensure mixing and inserted into the probe of the nmr instrument (40°). Periodic scans revealed that 221 was being cleanly transformed into 220. Reaction was complete in 20 min.

endo-1,2,3,4,5,6-Hexamethylbicyclo[2.2.0]hex-5-ene-2,3-diol (229). A. From Triazoline 213. 2N Hydrochloric acid (3.6 ml., 7.2 meqs.) was added dropwise to a stirred solution of 2.063 g. (7.3 mmoles) of 213 in 50 ml. of acetone at ambient temperature. Gas evolution was observed during the course of addition. After 30 min. the reaction mixture was neutralized with saturated aqueous sodium bicarbonate, the solvent evaporated and the residue was partitioned between ether and water. The organic layer was dried and the ether removed in vacuo to give an orange mixture (1.58 g.) of oil and solid (229). Nmr. examination of this residue revealed the presence of aniline and 229 with the signals from the latter con-
tributing approx. 70% to the total peak area between 0.8 and 2.2 s.
A sample of pure $^{229}$ was obtained in the following way.

The residue was washed with two 5-ml. portions of pentane to
give 345 mg. of $^{229}$ as a tan solid. This material was taken up in
30 ml. of ether, treated with charcoal, filtered and the ether
evaporated. The white solid residue was recrystallized from hexane
to afford 306 mg. (1.56 mmoles, 21.4%) of $^{229}$ as fine white fibers,
m.p. 153-155° (with gas evolution; softening at 145°) [lit. 169
m.p. 155-157°]. Infrared and nmr spectra were identical to those
reported for $^{229}$. 169

B. From Aziridine $^{217}$. To a stirred acetone (30 ml.) solution
of $^{217}$ (637 mg., 2.51 mmoles) at room temperature was added dropwise
1.3 ml. (2.6 meqs.) of 2N hydrochloric acid. Processing as above
gave 371 mg. (1.89 mmoles, 75.2%) of the diol.

In another experiment a drop of 60% perchloric acid was added to
a solution of $^{217}$ in acetone-d$_6$ in an nmr tube and the tube shaken to
ensure mixing. Repeated nmr scans at brief intervals showed the
183 clean conversion of $^{217}$ to $^{229}$. The reaction was complete after
5 min. No further change was observed when the spectrum was recorded
after an additional 30 min. at probe temperature.

5-Acetyl-1,2,3,4,5-pentamethylcyclopenta-1,3-diene (230) from
Pyrolysis of $^{229}$. A sample of $^{229}$ (27.5 mg., 0.14 mmole) was placed
in an nmr tube and the tube was partially immersed in an oil bath
preheated to 155°. Upon melting evolution of water vapor began and
continued for 2 min. after which time the tube was cooled and the product dissolved in an appropriate amount of carbon tetrachloride (insoluble water droplets were clearly visible). The nmr spectrum of the sole product was identical to that reported for ketone 230. The contents of the tube were diluted with ether and dried over anhydrous magnesium sulfate. Filtration followed by solvent removal afforded 24.7 mg. (0.139 mmole, 39%) of 230 as a colorless oil which solidified upon refrigeration. The infrared spectrum of the product was, like the nmr, identical to that reported for 230.
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\[
\text{\includegraphics[width=0.2\textwidth]{image.png}}
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171. Distillation at higher pressures (b.p. 60.5-61°/14 mm.) was
accompanied by considerable loss of product due to polymeriza-
tion. The distillate from either technique was of excellent
purity.

172. In all cases the uptake of bromine was very rapid and the amount
of this halogen consumed was always within a few percent of the
calculated amount.


175. The addition of water also serves to convert excess 78 into water-soluble hydrolysis products.


178. In compounds having structure II, calculations and experiments

\[ \text{II} \]

\[ \text{X = NR or CR}_2 \]

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179. Amine 133 rapidly forms a carbonate upon exposure to moist air. Consequently, the material was always kept in a dry nitrogen atmosphere.


of their scheme which involves the reductive cyclization of ethyl 2-hydroxyiminocyclopentyl acetate was not successful.


183. Extensive polymerization accompanied distillation, even with pot temperature below 70°.

184. N. Horton, private communication.

185. Vigorous frothing occurs if addition is too rapid.

186. In most cases the treatment of 160 with bases resulted in the formation, in varying amounts, of dark, tarry, intractable substances and, therefore, loss of material balance.


190. The nmr spectrum of this material indicated the presence of an ethyl group but no aromatic ring. It was not further investigated.

191. The relative intensities of other absorptions suggests that 220 and 222 comprise approximately 80% of the reaction mixture.


193. Proton-deuteron exchange with the solvent was also observed (multiplet, δ 2.1).