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DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
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By

Judson Christopher Philips, B.S.

The Ohio State University
1969

Approved by

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Department of Chemistry
DEDICATION

To my parents
ACKNOWLEDGMENTS

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INTRODUCTION

The synthesis, structure and reactivity of unsaturated cyclic molecules represent an area of investigation which has fascinated organic chemists for over a century. The high degree of unsaturation in benzene (1) and its failure to undergo addition reactions proved difficult for chemists to rationalize. While Kekule's deduction of an oscillating structure for benzene \(^1\) satisfactorily explained the known chemistry of this hydrocarbon, it provided no rationale for the remarkable difference in the reactivity of benzene and ordinary olefins. This fluctuating cyclohexatriene theory is no longer tenable.

\[
\begin{array}{cc}
\text{1} & \text{2} \\
\end{array}
\]

The 6\(\pi\) electrons of benzene are evenly delocalized over the six carbon atoms resulting in a completely symmetrical \(\sigma\) and \(\pi\) framework.

The multistep synthesis of cyclooctatetraene (2) by Willstätter, and the discovery that this polyene possesses normal olefinic properties only served to emphasize further the unusual aromatic character of benzene.

With the development of Hückel molecular orbital theory in the 1930's, chemists began to gain an understanding of the relationship
between aromatic character and molecular structure. The scope and ramifications of the aromaticity concept have been the subject of a number of reviews. Although the Hückel method has been criticized in recent years, the Hückel \((4n + 2)\) rule has served well as a predictive tool in the development of aromatic theory. In essence, this rule states that "those monocyclic coplanar systems of trigonally hybridized atoms which contain \((4n + 2)\pi\) electrons will possess relative electronic stability." Some examples of systems adhering to this rule are depicted below.

In polycyclic cases, such as \textit{trans-15,16-dimethyldihydropyrene} (6) and \textit{acepleiadylene} (7), the periphery of the \(\pi\) system is considered in the application of the rule.
Unfortunately there is no satisfactory, concise definition of aromaticity. Chemists rely on a number of physical and chemical properties as criteria for aromatic character:

a) Possession of a large negative resonance energy as determined from heat of combustion or hydrogenation data.

b) The propensity to undergo electrophilic substitution rather than addition reactions.

c) Observation of a π electron induced ring current, most readily observable by nmr spectroscopy.

If "stabilization by delocalization" is designated as a working definition of aromaticity, what can be said of conjugated cyclic π systems which do not manifest this aromatic character, e.g., 4π-electron systems? While simple Hückel molecular orbital calculations predict a delocalization energy of zero for cyclobutadiene (square geometry 8), more sophisticated calculations predict resonance destabilization for such a cyclobutadiene structure. Dewar's calculations and the experimental results of the Pettit group indicate a rectangular structure (2) with alternating single and double bonds for cyclobutadiene. The cyclopropenyl anion (10) is a similar case. Breslow has designated these systems, which
are predicted to manifest destabilization by electron delocalization, as antiaromatic. The base-catalyzed deuterium exchange of 1,2-diphenyl-3-benzoylcyclopropene (11) is ~6000 times slower than that of the corresponding cyclopropane 12. This dramatic rate retardation is convincing evidence in support of the antiaromaticity hypothesis.

Cyclodecapentaene ([10]annulene) is an interesting \((4n + 2)\pi\)-electron system for which a number of geometries (e.g., 13-15) are possible. Cyclodecapentaene 13 contains two trans double bonds, and the steric interference of the internal 1,6-hydrogen atoms can be expected to produce significant distortion from planarity. The all cis structure 14 suffers from angle strain (bond angles of 114°), but the recent synthesis of the presumably planar cyclononatetrenyl
anion (16) with bond angles of $140^\circ$ would seem to deemphasize the importance of this type of strain. Attempts to produce a cyclo-

capentaene via thermal or photochemical valence isomerization of cis-9,10-dihydroannulene (17) have been unsuccessful. Low tempe-
tature photoisomerization of trans-9,10-dihydroannulene (18) gave an unstable product (perhaps the all cis cycloheptapentaene 14) which could be hydrogenated to cycloheptane with diimide. Mono-trans-
[10]annulene (15) has been postulated as an intermediate in the con-
version of bicyclo[6.2.0]deca-2,4,6,9-tetraene (19) to trans-9,10-
dihydroannulene (18), and the synthesis of a mono-trans-tribenz-
[10]annulene 20 has been reported.

\[
\begin{align*}
&\text{(16)} &\text{(17)} &\text{(18)} \\
\begin{array}{c}
\begin{array}{c}
\text{H} \\
\text{H}
\end{array}
\end{array} &\xrightarrow{\Delta} &\begin{array}{c}
\begin{array}{c}
\text{H} \\
\text{H}
\end{array}
\end{array} \\
\begin{array}{c}
\text{19} \\
\text{15} \\
\text{18}
\end{array}
\end{align*}
\]
In an interesting series of experiments designed to alleviate the internal 1,6-hydrogen eclipsing in [10]annulene, Vogel and co-workers have synthesized a number of bridged [10]annulene derivatives, e.g. 23, by a valence isomerization route. 1,6-Methano-cyclodecapentaene (23) is a stable crystalline solid. The distortion from planarity which accompanies introduction of the 1,6-methylene bridge is not sufficient to preclude delocalization in the 10π-electron system. Nuclear magnetic resonance studies indicate a significant ring current, and a number of electrophilic aromatic substitution reactions have been successfully performed on this hydrocarbon. Interest in the consequences of aromaticity and extended conjugation has stimulated the synthesis of larger 4n and (4n + 2)π-electron systems. For example, the Sondheimer group has synthesized a large number of annulenes and dehydroannulenes such as
24 and 25. Excellent reviews of this work are available. In recent years the investigation of formally non-conjugated \( \pi \)-electron interactions has also received considerable attention. Overlap of the double bond and cationic center in ion 26 involves electron delocalization across an intervening carbon atom. This type of electronic interaction has been termed 'homoconjugation' and involves a 1,3-overlap which is intermediate between \( \sigma \) and \( \pi \).

Protonation of cyclooctatetraene in concentrated sulfuric acid yields a cation (27), which may be considered a tropylion (28) in which the \( \sigma \) framework has been interrupted by the addition of a
methylene group - hence the name 'homotropylium ion.' The intervention of such cations has been postulated in the 1,4-addition of chlorosulfonyl isocyanate (CSI) to a variety of cyclooctatetraenes. Other homoaromatic species, such as \( \text{31-32} \), which contain 2-, 6-, and 10\( \pi \) electrons have been characterized.

A number of interesting hydrocarbons have been synthesized in attempts to observe homoaromaticity in neutral species. Hückel
molecular orbital calculations for trishomobenzene (cis,cis,cis-1,4,7-cyclononatriene, \(24\)) predict a ground state delocalization energy \(\varepsilon_D\) as large as benzene. The molecule has been synthesized, but careful scrutiny of its physical properties has failed to produce evidence in support of a homoconjugatively stabilized species. The same conclusions have been reached for triquinacene \(25\) \(30\) and hexahomobenzene \(26\). Barrelene \(27\), first recognized by Hine

![Diagram of trishomobenzene]

\(24\)

as a possible homoaromatic 6\(\pi\)-electron species, has been synthesized by Zimmerman and Paufler. The nmr spectrum shows no evidence of a ring current.

Anion \(32\) has been prepared by the Na-K alloy cleavage of 4-methoxybicyclo[3.2.2]nona-2,6,8-triene \(38\), and its nmr spectrum
is consistent with a completely delocalized homoaromatic structure. The anion is of special interest as an example of a species fitting Goldstein's criteria for "bicycloaromaticity." Simply stated, a bicyclic \( \text{C}_m\text{H}_m \) ion (\( m \) is odd) containing three \( \pi \) bridges should possess enhanced stability when compared to an appropriately chosen isoelectronic bicyclic ion with two \( \pi \) bridges. The definition stems from molecular orbital calculations which have been utilized in the division of bicyclic ions of the above type into four classes: stabilized, stabilized and bicycloaromatic, destabilized, destabilized and bicycloantiaromatic. Stabilization in the bicyclic ion results whenever the sum of the \( \pi \) electrons provided by the odd bridge and one even bridge equals \((4n + 2)\) while bicycloaromaticity requires a total of \(4n\pi\) electrons in the three bridges. Conversely, destabilization is predicted when an odd and even bridge provide \(4n\pi\) electrons while antibicycloaromaticity requires a total of \((4n + 2)\pi\) electrons from all three bridges. For example, the well known 7-bicyclo[2.2.1]heptyl cation \( (\text{I}0) \) is predicted to be stabilized and bicycloaromatic while the unknown \([2.2.1]\) anion \( (\text{I}1) \)
should be destabilized and antibicycloaromatic. The experimental
evidence in these cases agrees closely with the predictions, but
the general utility of the theory awaits elucidation of further
examples.

Spiroconjugation, the electronic interaction between two
perpendicular π systems which are joined by a tetrahedral atom, is
another special case of homoconjugation. Ultraviolet spectra of
ketals such as \( \text{42} \) have provided experimental observations of this
type of conjugation.

Although benzene does not possess the fluctuating cyclohexatriene
structure proposed by Kekule, interest in molecules which might
possess fluctuating or oscillating structures has led to the develop-
ment of a particularly intriguing area of investigation which in-
volves the reorganization of σ and π or π electrons within a mole-
cular framework.
Thus, valence bond isomerizations are unimolecular reactions which occur with changes in interatomic distances and bond angles, but without migrations of atoms or groups. The term "valence tautomerization" has been applied to reactions in which the species involved are interconvertible under normal working conditions while the term "valence isomerization" refers to a non-equilibrium process such as the conversion of 1,3,5-cyclononatriene (44) into trans-bicyclo[4.3.0]nona-2,4-diene (45). A typical example of valence bond tautomerization is the equilibrium of 1,3,5-cyclooctatriene (46) and bicyclo[4.2.0]octa-2,4-diene (47). The effect of substituents in the 7 and 8 positions has been investigated, and surprisingly, the nature and conformation of the substituents in-
fluence the position of the equilibrium to an amazing extent. To illustrate, the monocyclic form in equilibrium 48 predominates at 60°.

48

while the opposite is true in equilibrium 49. The factors which determine the position of these equilibria are not well understood at the present time. 42

Cycloheptatriene (tropolidene, 50) exists in the monocyclic form,

50

and all attempts to detect an equilibrium between cycloheptatriene (50) and norcaradiene (51) have been unsuccessful. 43 Although
cycloheptatriene reacts with maleic anhydride at elevated temperatures to yield a \((4 + 2)_\pi\) adduct \(^{52}\), this does not constitute proof of a valence tautomerism. However, introduction of substituents in the 7 position of cycloheptatriene exerts a surprising influence on the nature of the molecular structure. \(^{43,45}\)

The results of an elegant study by Ciganek \(^{45}\) indicate a monocyclic structure for 7,7-bis(trifluoromethyl)cycloheptatriene (56)
and a norcaradiene structure for the corresponding dicyano compound. The temperature-dependent nmr spectrum of 7-cyano-7-trifluoromethyl-cycloheptatriene \(^{58}\) is best interpreted in terms of an equilibrium with norcaradiene form \(^{57}\).

The use of 1,6-methylene bridges to 'freeze' cycloheptatrienes in the norcaradiene form has received the attention of two groups of workers. \(^{46,47}\) Anhydride \(^{59}\) and the corresponding hydrocarbon \(^{60}\) exist in the norcaradiene form. A four-carbon bridge, however, is not sufficient for this purpose, e.g. compounds such as \(^{61}\) are cycloheptatriene derivatives.

\[ \text{Diagram 59} \quad \text{Diagram 60} \quad \text{Diagram 61} \]

The synthesis and potential chemistry of unsaturated carbocyclic and heterocyclic derivatives of \(^{62}\) are of interest for a number of reasons.
Although a valence bond tautomerization involving cyclooctatetraene (2) and bicyclo[4.2.0]octa-2,4,7-triene (63) has been demonstrated, only about 0.01% of the bicyclic form is present at 100°C. Synthesis of a triene, such as 64, might present a chance to investigate and compare the chemistry of the bicyclic valence tautomer with that of cyclooctatetraene. For example, could a 10π-electron dianion (65) be prepared from a cyclooctatetraene valence isomer? Molecular models indicate that a three-carbon bridge should be sufficient to restrict valence tautomerism of triene 64 to a substituted cyclooctatetraene 66. It would be desirable to eluci-
date the appropriate chain length which would allow investigation of such a valence tautomerization.

Pentaene 67 and aza-derivative 68 offer a unique mode of $10\pi$-electron bishomoconjugation. The orthogonal overlap of p lobes of cyclobutene with the terminal p lobes of the cyclohexadiene moiety makes possible a delocalization of the $10\pi$ electrons across the top face of the molecule, as illustrated in structure 69. The molecular

distortion which accompanies valence tautomerization 67 to cyclo-
decapentaene derivative 70 may well be of such a magnitude as to preclude this process. However, the possibility is interesting and worthy of investigation for it might allow operation of normal olefin chemistry on the ethylene bridge without interruption of the $10\pi$-electron aromatic system.
Although the unusual and interesting chemistry of cycloocta-
tetraene has been widely investigated, there has been no report
of eight-membered heterocyclic analogs of this hydrocarbon. A
heterocyclic \( \pi \)-equivalent congener of cyclooctatetraene, such as
\( \text{71} \), could be expected to possess a tub-shaped geometry and could
conceivably be expected to exist in equilibrium with four distinct
valence bond tautomers (\( \text{72}-\text{75} \)). The steric and electronic inter-

\[ \text{72} \]
\[ \text{73} \]
\[ \text{71} \]
\[ \text{74} \]
\[ \text{75} \]

actions of substituents should have a significant influence on the
position of this equilibrium and, in some instances, could result in
enhanced stability of one isomer with respect to the rest. Interest
in the consequences of this type of valence tautomerization inspired
the development of workable syntheses for a number of annelated 7-
azabicyclo[4.2.0]octa-2,4,7-trienes such as 76.

The trivial name 'propellanes' has been suggested for this type
of tricyclic system in an attempted simplification of nomenclature.
Thus imino ether 76a would be named 11-ethoxy-10-aza[4.3.2]propella-
2,4,10-triene. The photochemistry of unsaturated carbocyclic and
heterocyclic propellanes and their valence isomers as well as the
chemistry of their Diels-Alder adducts and metal carbonyl complexes
should produce interesting and significant results. The initial
purpose of this study was to devise syntheses of these polyunsaturated
propellanes and undertake a study of their chemistry. The development
of viable syntheses of polyenic propellanes has required a considerable
time investment and will make up the bulk of this dissertation.
RESULTS AND DISCUSSION

PART I. AZOCINES AND UNSATURATED AZAPROPELLIANES

The synthesis of azaproppellatrienes was undertaken in the expectation that these compounds would represent suitable precursors to substituted azacyclooctatetraenes (azocines) via valence isomerization. The ready availability of azaproppellatrienes would permit initiation of a number of interesting chemical studies, as well as evaluation of the nearly orthogonal π-π interaction which is possible in such systems.

Inspection of molecular models indicated that bridging by a four- or five-membered methylene chain, as in 76b or 78, might be sufficiently large to allow valence isomerization to the corresponding substituted azacyclooctatetraenes. In contrast, a three-carbon bridge, as in 76a, was expected to restrict such a process and allow a comparison of the chemistry of the azaproppellatrienes with that of the azacyclooctatetraenes.
The synthesis of 1-azetines 76a and 76b is depicted in Scheme I.

**SCHEME I**

\[
\begin{align*}
80 & \xrightarrow{\text{CSI}} 81 \\
82 & \xrightarrow{\text{Et}_3\text{O}^+\text{BF}_4^-} 83 \\
84 & \xrightarrow{\text{NaOH}} 76
\end{align*}
\]

\[a \quad n = 1\]
\[b \quad n = 2\]
Indane was reduced to 4,7-dihydroindane (80a) by the action of sodium in liquid ammonia at -78°. The addition of chlorosulfonyl isocyanate (CSI) to 4,7-dihydroindane (80a) represents a crucial step, for the cycloaddition must occur at the tetrasubstituted double bond if the above synthesis is to be successful. The relative rate of addition of chlorosulfonyl isocyanate to substituted olefins is known to be $R_2C=CH_2 > R_2C=CHR > R_2C=CR_2 > RCH=CH_2 > RCH=CHR$. These rate differences can be sufficiently large to allow separation of olefin mixtures. In some cases, however, the cycloaddition is complicated by subsequent reactions of the initial cycloadduct. For example, the presence of protons $\beta$ to the nitrogen atom in the initially formed $N$-(chlorosulfonyl) $\beta$-lactams often results in the competitive formation of $\beta,\gamma$-unsaturated amides. The cyclo-

\[
\begin{align*}
\text{CSI} & \quad \text{85} \\
\text{R} & \quad \text{CHR}_2 \\
\text{R}_2\text{CH} & \quad \text{SO}_2\text{Cl} \\
\text{86} & \\
\text{87} & \\
\end{align*}
\]

addition of chlorosulfonyl isocyanate to 4,7-dihydroindane (80a) proceeded smoothly at room temperature. The unpurified $N$-(chlorosulfonyl) $\beta$-lactam 81a was hydrolyzed in 50% aqueous acetone with 4N sodium hydroxide solution. The resulting $\beta$-lactam 82a, mp 61-63°, was formed in 62% overall yield. The infrared and nmr spectra of 82a which exhibit a strong $5.72 \mu$ band and a two-proton multiplet in
the vinyl region, respectively, provide convincing evidence in support of the β-lactam structure. 

O-Ethylation of $\text{82a}$ with triethyl oxonium fluoroborate led to the isolation of imino ether $\text{83a}$ in 73% yield. The structure of this 1-azetine derivative was deduced from the following spectral parameters:

- $\lambda_{\text{max}}$ : 6.17 μ; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ : 5.72 (multiplet, 2H, vinyl protons), 4.17 (quartet, $J = 7$ Hz, 2H, $-\text{OCH}_2\text{CH}_3$), 0.90-2.84 [complex multiplet including triplet at 1.29 ($J = 7$ Hz), 13H, ring methylene protons and $-\text{OCH}_2\text{CH}_3$].
- The mass spectrum exhibited a low intensity molecular ion peak ($m/e$ 191) and a base peak ($m/e$ 120) which corresponds to the loss of ethyl cyanate ($m = 71$) from the molecular ion. This cleavage is probably a stepwise process for there is also a low intensity peak at $m/e$ 120 corresponding to loss of an ethyl radical. At the time that this work was performed, four-membered rings with an imino nitrogen were unknown. Since the completion of our synthesis, the preparation of several 1-azetines has been described.

Monobromination of $\text{83a}$ was effected through the agency of N-bromosuccinimide in refluxing carbon tetrachloride solution. The monobromide was not characterized, and the position of entry of the halogen was not determined. Dehydrobromination of $\text{84a}$ was achieved by the action of potassium $\text{t}$-butoxide in tetrahydrofuran at 0°. The stable azetine $\text{76a}$, which was isolated by direct distillation [bp 44° (0.07 mm)], exhibited an ultraviolet maximum in isooctane at 267 μ (ε 2200) and revealed in its nmr spectrum (Figure 1) a multiple-line pattern at $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.55-6.20 as would be expected for the four vinyl protons. The infrared spectrum of $\text{76a}$ shows a strong imino
Figure 1. The partial 60 MHz nmr spectra of some azocines and azocine valence isomers.
ether absorption at 6.24 μ. Thus the imino ether absorption in 76a appears at slightly longer wavelength than in its precursor 83a (6.17 μ). The mass spectrum shows a very weak molecular ion peak (< 1%, m/e 189) and a base peak (m/e 118) again corresponding to loss of a neutral ethyl cyanate fragment (m = 71). The above spectral properties are completely consistent with the closed azetine structure 76a. The azetine may be purified by vapor phase chromatography, and its nmr spectrum is temperature independent over the range 40-160°. The torsional strain which a three-carbon bridge imposes on the π system of the valence tautomeric azocine 88 is clearly too large to allow observation of such a species.

The available chemical evidence is also consistent with a tricyclic structure for 76a. Irradiation of an ethereal solution of 76a at 2537 Å resulted in the rapid production of indane. Ethyl cyanate was not isolated, but its formation was inferred from the strong infrared absorption at 4.46 μ.

\[
\begin{align*}
\text{76a} & \quad \xrightarrow{\text{hv}} \quad \text{88}
\end{align*}
\]
On being subjected to the same sequence of reactions, 5,8-dihydrotetralin (80b) was transformed into N-(chlorosulfonyl) β-lactam 81b and β-lactam 82b in 54% overall yield. The infrared spectrum (λ_{max} CHCl₃ 5.72 µ) of 82b and the vinyl region of its nmr spectrum (δ_{CDCl₃} 5.82, multiplet, 2H) again indicate that the chlorosulfonyl isocyanate cycloaddition had occurred at the tetrasubstituted double bond. The structure of 82b was further established by hydrogenation over platinum oxide to give 91 which was prepared independently from Δ⁹,¹⁰-octalin (93).
The commercially available mixture of 2-decalols (92) was dehydrated according to the procedure of Hussey to give a three-component mixture containing 67% of Δ⁹,¹⁰-octalin (93), 23% of Δ¹,⁹-octalin (94), and 10% of a third unidentified product. Hydroboration of the above mixture with diisoamylborane resulted in selective removal of the Δ¹,⁹-octalin (94) and gave ~90% pure Δ⁹,¹⁰-octalin (93) in 35% yield. The cycloaddition of Δ⁹,¹⁰-octalin and chlorosulfonyl isocyanate was carried out in the usual manner and resulted in the formation of β-lactam 91, mp 52-53.5°, in 30% yield.

Treatment of 82b with triethylxonium fluoroborate gave imino ether 83b, bp 62° (0.1 mm); λ<sub>max</sub> 6.16 μ. The nmr spectrum is completely consistent with the structural assignment. The mass spectrum shows a weak molecular ion (m/e 205) and a base peak (F-Tl) at m/e 134. Imino ether 83b was converted into the monobromide 84b by the action of N-bromosuccinimide. Dehydrobromination with potassium t-butoxide in tetrahydrofuran at 0° gave azapropellatriene 76b, bp 56-57° (0.04 mm), in 30% yield; λ<sub>max</sub> 272 μ (ε 2100). The strong imino ether infrared absorption appears at 6.24 μ, again at longer wavelength than the corresponding absorption in 83b. The nmr spectrum (Figure 1) shows a multiplet in the vinyl proton region attributable to a cyclohexadiene
moiety. The nmr spectrum of 76b is temperature independent from -70 to +170°. At the latter temperature, however, 76b undergoes a slow fragmentation to tetralin, which was identified by its characteristic nmr spectrum and vpc retention time. In contrast to azapropellatriene 76a, all attempts at purification of 76b by vapor phase chromatography have been unsuccessful.

The above synthesis (Scheme I) has proven to be extremely versatile and was employed in our laboratory to effect the synthesis of 2-methoxy-1-azocine (100a) and 3,7-dimethyl-2-methoxy-1-azocine (100b).

**SCHEME II**

```
95

R

R

\[ \rightarrow \]

96

R

\[
\begin{align*}
\text{N} & \quad R \\
\text{OCH}_3 & \quad R
\end{align*}
\]

\[ \rightarrow \]

97

R

\[
\begin{align*}
\text{N} & \quad R \\
\text{OCH}_3 & \quad R
\end{align*}
\]

\[ \rightarrow \]

98

R

\[
\begin{align*}
\text{Br} & \quad R \\
\text{OCH}_3 & \quad R
\end{align*}
\]

\[ \rightarrow \]

99

R

\[
\begin{align*}
\text{N} & \quad R \\
\text{OCH}_3 & \quad R
\end{align*}
\]

\[ \leftarrow \]

100

\[
\begin{align*}
\text{R} & \quad \text{N} \\
\text{OCH}_3 & \quad \text{R}
\end{align*}
\]

\[
\begin{align*}
a & \quad R = H \\
b & \quad R = \text{CH}_3
\end{align*}
\]
The structure of 100a was established unequivocally by hydrogenation over 10% palladium on carbon at atmospheric pressure to give 101 which was also prepared independently from the reaction of lactam 102 with trimethyloxonium fluoroborate. Azocine 100b was obtained as a stable yellow oil: \( \lambda_{max} \) isoctane 297 \( \mu \) (590); \( \delta_{\text{TMS}} \) 5.72 (singlet, 3H), 4.95 (broad singlet, 1H), and three three-proton singlets at 3.63, 1.92, and 1.82 (Figure 1). The surprisingly uncomplicated vinyl proton absorptions are in direct contrast with the complex multiplets observed for the vinyl protons of azapropellatrienes 76a and 76b.

The spectroscopic and chemical data concerning 100a and 100b clearly indicated that the likely initial products of dehydrohalogenation, e.g. 99a, are subject to valence bond isomerization via ready disrotatory ring opening to the favored azacyclooctatetraene tautomers. Azapropellatrienes 76a and 76b, however, exhibit no tendency to undergo this disrotatory ring opening. The strain introduced in the azacyclooctatetraene tautomers by three- or four-carbon bridges is evidently too great to allow the operation of such a process.
Azacyclooctatetraenes 100a and 100b as well as azapropellanes 76a and 76b readily undergo \((4 + 2)\pi\) cycloaddition with \(N\)-phenylmaleimide to form adducts which have been tentatively assigned the indicated structures.
The above adducts result from cycloaddition at the bottom side of the cyclohexadiene π systems in accordance with literature precedent, e.g. the cycloaddition of maleic anhydride to cyclo-octatetraene (2).
The endo stereochemistry of the N-phenylmaleimide moiety in such \((4 + 2)\pi\) adducts is a result of favorable secondary, non-bonding interactions between the appropriate molecular orbitals of the two reactants (the highest occupied MO of one reactant and the lowest unoccupied MO of the other reactant) throughout the bond forming process.

While the above synthetic sequence has successfully led to the isolation and characterization of azocines and derivatives of their valence tautomers (azapellatrienes), the length of the methylene bridge which would allow direct observation of valence tautomerization of azapellatrienes to azacyclooctatetraenes is still not evident. In order to clarify this problem, the synthesis of azapellatrienes with five- and six-carbon methylene bridges was undertaken (Scheme III).
SCHEME III

\[
\begin{align*}
  &\text{SCHEME III} \\
  &\text{1. } \text{SOCl}_2 \\
  &\text{2. } \text{AlCl}_3 \\
  &\text{Li} \\
  &\text{Et}_3\text{O}^+\text{BF}_4^- \\
  &\text{1. } \text{CSI} \\
  &\text{2. } \text{KOT-Bu} \\
  &\text{a n = 3} \\
  &\text{b n = 4}
\end{align*}
\]
5-Phenylvaleric acid was prepared in 56% yield by Friedel-Crafts acylation of benzene with glutaric anhydride and subsequent Clemmenson reduction of 109a. Acid 110a was converted to benzocycloheptene (112a) by standard procedures in 40% overall yield. The reduction of 112a with sodium in liquid ammonia at -78° was attempted in the usual manner. Surprisingly, the aromatic hydrocarbon was completely unreactive under these conditions and could be recovered in excellent yield. It was subsequently discovered that the desired reduction could be carried out with sodium metal in refluxing liquid ammonia. The resulting product, however, was a mixture of starting material, the desired 6,9-dihydrobenzocycloheptene and a third product. The third product was separated from the starting material and 113a by preparative vpc and tentatively assigned structure 117 on the basis of its elemental analysis and nmr spectrum: δ in CDCl₃ ~1.49 and 1.93 (overlapping multiplets in the ratio of 4 to 5).
Spinning band distillation of the crude reaction product effected separation of $117$ and gave $\sim90\%$ pure $113a$ in $52\%$ yield. This mixture was used without further purification. Cycloaddition of chlorosulfonyl isocyanate to $113a$ and subsequent sodium hydroxide hydrolysis of the N-(chlorosulfonyl) $\beta$-lactam gave the expected $\beta$-lactam $114a$, mp 67-70$^\circ$ in 29$\%$ yield. The elemental analysis, ir spectrum ($\lambda_{\text{max}}^{\text{CHCl}_3}$ 5.74 $\mu$), and nmr spectrum [$^6_{\text{TMS}}$ 5.62 (multiplet, 2H, vinyl protons)] are completely in accord with the assigned structure. $\beta$-Lactam $114a$ was converted to the corresponding imino ether $115a$, bp 84-86$^\circ$ (0.3 mm), $\lambda_{\text{max}}^{\text{neat}}$ 6.15 $\mu$, which was further characterized as its perchlorate salt, mp 108.5-110$^\circ$. Allylic bromination of the free base gave the corresponding monobromide which was not characterized but was immediately dehydrobrominated with potassium t-butoxide. The resulting oil, bp 92-94$^\circ$ (0.3 mm) exhibited an infrared absorption for the imino ether function at 6.24 $\mu$ which is indicative of an azapropellatriene structure. The azetine structure $116a$ was confirmed by the nmr spectrum which showed a 4-proton multiplet at $^6_{\text{TMS}}$ 5.22-6.22.

However, in contrast to $76a$ and $76b$, azapropellatriene $116a$ possesses a temperature-dependent nmr spectrum ($\text{Cl}_2\text{C}=\text{CCl}_2$ solution, Figure 2). As 100$^\circ$ is approached, the broad resonance line of the methylene proton signal and the vinyl proton absorptions begin to exhibit pronounced changes. Such changes, which are totally reversible, have been interpreted in terms of substantial displacement of the azapropellatriene-azocine equilibrium in the direction of the azacyclooctatetraene $116c$. Thus, in contrast to the bridged norcaradiene-cycloheptatriene and arene oxide-oxepin systems wherein
Figure 2. The partial 60 MHz nmr spectra of 13-ethoxy-12-aza-[5,4,2]propella-8,10,12-triene (116a).
the triene tautomers predominate when a chain length of five methylene
groups is reached, the strain imposed on the azacyclooctatetraene
form 116c remains sufficiently great that measurable concentrations
of this tetraene are attainable only in the vicinity of 100° and
above.

The conversion of 5-benzoylvaleric acid \(109b\) to benzocyclo-

cocene \(112b\) \(^{74}\) was carried out by standard procedures \(^{72-74}\) in 32%
overall yield. The reduction of \(112b\) was achieved with lithium metal
in refluxing liquid ammonia. Vapor phase chromatographic analysis of
the crude product indicated the presence of \(\sim 85\%\) of the desired 7,10-
dihydrobenzocyclooctene \(113b\) and \(\sim 15\%\) of three minor products (one
of which was identified as starting material).

Reaction of \(113b\) with chlorosulfonyl isocyanate followed by
sodium hydroxide hydrolysis resulted in the formation of \(\beta\)-lactam
\(114b\), mp 99-100°, in 51% yield. The ir spectrum showed an intense
carbonyl absorption at 5.74 \(\mu\). The nmr spectrum exhibited the ex-
pected 2-proton multiplet at \(\delta^{13} \text{CDCl}_3\) 5.76. Conversion of \(\beta\)-lactam
\(114b\) to the corresponding imino ether \(115b\) was achieved with tri-
ethylloxonium fluoroborate. \(57\) This azetine absorbs in the infrared
at 6.15 \mu, and its nmr spectrum is completely consistent with the assigned structure. The usual allylic bromination-dehydrobromination sequence resulted in the formation of a yellow oil (118) in 29\% yield which exhibited none of the characteristic spectral properties expected for an azapropellatriene, such as 116b. The infrared spectrum of 118 shows absorptions at 5.98 and 6.06 \mu. The uv spectrum [\lambda_{\text{max}} 292 (\epsilon 580), 278 (\epsilon 570), and 270 \mu (\epsilon 560)] and the vinyl region of the nmr spectrum [\delta_{\text{TMS}} CDCl_3 5.78 (broadened singlet, 3H), 5.03 (broadened singlet, 1H)] (Figure 1) are strikingly similar to those of azocine 100b. The calculated molecular weight (m/e 231.1623) agrees precisely with the observed value (m/e 231.1623). On the basis of the spectral properties of 118, it is apparent that the six-carbon methylene bridge allows complete displacement of the azapropellatriene equilibrium in favor of the azocine tautomer.

The effect of increasing the size of the methylene chain in azapropellatrienes has resolved our questions concerning the relative stabilities of azapropellatrienes and the valence tautomeric
azacyclooctatetraenes. The failure of azapropellatrienes 76a and 76b to exist in equilibrium with the corresponding azocines is apparently a manifestation of the torsional strain which three- and four-carbon bridges impose on the azacyclooctatetraene $\pi$ system. If the methylene chain is of sufficient length, a strain-free tub-shaped azacyclooctatetraene such as 118 is readily formed at the expense of the corresponding azapropellatriene.

The other question of interest in these systems concerns possible homoconjugation in the azapropellatriene series. Stabilization by such a process involves overlap of the appropriate $p$ lobes of the imino ether with the upper portion of the cyclohexadiene $\pi$ moiety, e.g. 76. As we have already observed, azabicyclooctatrienes and azapropellatrienes will prefer to exist as the tautomeric azocines whenever such an isomerization results in significant relief of strain. Hence, the above mechanism of homoconjugative delocalization does not result in stability sufficient to overcome the inherent strain in these tricyclic ring systems. However, there is some spectral evidence indicative of an interaction between the two orthogonal
The infrared absorption band of the imino ether linkage in 76a, 76b, and 116a appears at consistently longer wavelength (usually ~0.08 μ) than in the corresponding precursor azetines.

In order to obtain a better idea of the possible magnitude of such a mode of stabilization, the synthesis of azapellapentaene 119 was undertaken. Bishomoconjugation in 119 involves the upper face of the cyclohexadiene moieties and the entire imino ether π system. It was thought that this greater involvement of the imino ether π system would result in enhanced stability of this π system relative to the previously discussed azapellatrienes.

```
SCHEME IV

1. CSI
2. NaOH

Et₃O⁺BF₄⁻
```

The attempted synthesis of pentaene 119 is presented in Scheme IV.
1,4,5,8-Tetrahydronaphthalene (21), mp 57-58°, was prepared in 71% yield via sodium in liquid ammonia reduction of naphthalene. The condensation of 21 and chlorosulfonyl isocyanate was carried out in the usual manner and resulted in a 39% yield of β-lactam 120, mp 111-112°. The infrared carbonyl absorption (5.72 μ) and the four-proton multiplet in the vinyl region of the nmr spectrum of 120 are indicative of cycloaddition at the tetrasubstituted double bond. Further confirmatory evidence for structure 120 was obtained by hydrogenation to the previously prepared β-lactam 91.
O-Alkylation with triethyloxonium fluoroborate gave the expected imino ether 121, bp 65-66° (0.2 mm) in 53% yield. The structure of 121 was assigned on the basis of its ir spectrum (λ_max 6.14 μ), its nmr spectrum [δ CDCl₃ 5.72 (multiplet, 4H, vinyl protons), 4.13 (quartet, J = 7 Hz, 2H, -OCH₂CH₃), 1.67-2.67 (complex multiplet, 8H, allylic protons), and 1.27 (triplet, J = 7 Hz, 3H, -OCH₂CH₃)], and the elemental analysis of its perchlorate salt, mp 129-131°.

Allylic bromination of 121 was achieved with two equivalents of N-bromosuccinimide. No attempt was made at isolation or characterization of the resulting dibromide 122. The usual dehydrobromination was attempted with potassium tert-butoxide in tetrahydrofuran. The desired pentaene 119 was not observed. Nuclear magnetic resonance analysis of the crude dehydrobromination product indicated the presence of naphthalene. This was confirmed by vpc, and the hydrocarbon was isolated in 22% yield by column chromatography.

The observation of naphthalene from dehydrobromination of 122 implies the formation of pentaene 119 and also its relative insta-
bility compared to the previously characterized azapropellatrienes. The instability of 119 relative to the azapropellatriene series is most likely a manifestation of a lower transition state energy for fragmentation of the former molecule, for in both cases, the formation of ethyl cyanate and an aromatic nucleus is certainly an energetically favorable process.
PART II. UNSATURATED CARBOCYCLIC PROPELLANES

The possibility of valence bond tautomerization of cyclooctatetraenes to bicyclo[4.2.0]octatrienes has attracted the interest of chemists in recent years. Although it has not been possible to detect an equilibrium between cyclooctatetraene (2) and bicyclo[4.2.0]octatriene (63) by spectroscopic techniques, the reaction

\[ \text{2} \quad \rightarrow \quad \text{63} \]

of cyclooctatetraene with dienophiles is believed to occur via kinetically controlled \((4 + 2)_\pi\) cycloaddition to valence tautomer 63. Extrapolation from dilatometric rate data for such additions indicates that cyclooctatetraene exists in equilibrium with \(\sim 0.01\%\) of 63 at 100°C. Three groups have noted that unsensitized irradiation of 2 results in formation of an unstable photoproduct with ultraviolet absorption in the 281-283 μm region. The photoproduct was assumed to be the cyclooctatetraene valence tautomer 63, and hydrogenation of solutions of this photoproduct resulted in formation
of cyclooctane (125) and bicyclooctane 126. Further irradiation of 63 resulted in formation of benzene and acetylene.

Interestingly, low-temperature, acetone sensitized irradiation of 2 results in the reversible formation of semibullvalene (127). Triene 63 was not observed, but its existence as a short-lived intermediate has not been disproven.
Debromination of 7,8-dibromobicyclo[4.2.0]octa-2,4-diene with disodium phenanthrene at -78° resulted in the formation of bicyclo-[4.2.0]octatriene; however, only impure samples of 63 [uv maxima at 273 (ε 3100) and 277 μ (ε 3000)] were obtained because of the extreme thermal instability of the triene relative to cyclooctatetraene.

The question of the possible existence of a stable bicyclo[4.2.0]octatriene remained unanswered. The synthesis of annelated triene

![Diagram]

128 was undertaken with the intention of elucidating the thermal and photochemical stabilities of such tricyclic systems. A four-carbon methylene chain, as in 128, should preclude valence bond tautomerization to the corresponding cyclooctatetraene, and hence, make possible for the first time a direct comparison of the chemistry of the two interesting cyclic π systems.

The problems involved in a rational synthesis of 128 were not only the method of constructing the cyclobutene and cyclohexadiene moieties, but also the sequence in which these sites of unsaturation were to be introduced. The course of action decided upon involved the synthesis of diene 129 and subsequent allylic bromination-
dehydrobromination to yield the bicyclo[4.2.0]octatriene derivative 128

\[
\begin{align*}
129 & \rightarrow 128
\end{align*}
\]

This route was originally devised as a method of preparation of pentaene 67 and will be discussed in more detail in the latter portions of this section (see p. 55).

The successful synthesis of 128 is depicted in Scheme V.

4-Cyclohexene-cis-1,2-dicarboxylic anhydride (130) was isomerized to conjugated anhydride 131 by heating with a catalytic amount of phosphorous pentoxide for 48 hr. The cycloaddition of anhydride 131 and 1,3-butadiene (in excess) was carried out in an autoclave according to the procedure of Alder and Backendorf. Reduction of 132 with lithium aluminum hydride resulted in a 66% yield (after recrystallization from benzene) of diol 133, mp 145-147°. The diol was converted to the corresponding dimesylate, mp 124.5-125.5°, in 92% yield by means of methanesulfonyl chloride in pyridine. Cyclization of the dimesylate to the sulfide was effected with dehydrated sodium sulfide in hexamethylphosphoramide. The crystalline sulfide 135, mp 85-87°, was isolated in 77% yield by direct distillation of the crude product. The sulfide was further characterized as its sulfone (135a), mp 138-140°, obtained via oxidation of 135 with two equivalents of monoperphthalic acid. Confirmatory evidence of the
SCHEME V

130 \[ \xrightarrow{P_2O_5 \text{ } \Delta} \] 131

132 \[ \xrightarrow{\text{LiAlH}_4} \] 133

134 \[ \xrightarrow{\text{Na}_2\text{S \text{ } \text{HMP}}} \] 135

136 \[ \xrightarrow{\text{KOT-Bu}} \] 129

128
cis-9,10-disubstituted ring system for 133-135 is provided by their nmr spectra. In each case the methylene protons, due to the fact that the adjacent bridgehead carbon atom is asymmetrically substituted, appear as AB quartets.

Treatment of the sulfide with one equivalent of N-chlorosuccinimide resulted in the introduction of chlorine at the carbon atom adjacent to sulfur. The crude α-chloro sulfide was immediately oxidized with two equivalents of monoperphthalic acid to yield a mixture of the two possible epimeric α-chloro sulfones 136. An analytical sample (mp 127-134⁰), enriched in one epimer, was obtained after three recrystallizations from petroleum ether.

Potassium t-butoxide-induced Ramberg-Bäcklund rearrangement of 136 resulted in the formation of a liquid diolefin (129), bp 100-102⁰ (30 mm). The nmr spectrum of 129 was completely consistent with the assigned structure, and the mass spectrum exhibited the expected molecular ion peak (m/e 160). Hydrogenation of 129 at atmospheric pressure resulted in the absorption of two equivalents of hydrogen and formation of the known [4.4.2]propellane (137).
Treatment of olefin $\text{129}$ with slightly more than one equivalent of $N$-bromosuccinimide in refluxing carbon tetrachloride resulted in allylic bromination. The unpurified allylic bromide was dehydrobrominated with potassium $t$-butoxide in tetrahydrofuran. Vapor phase chromatography of the crude product indicated the presence of two difficultly separable hydrocarbons as well as some higher molecular weight material which was not identified. Preparative vpc separation of the hydrocarbon mixture gave recovered starting material $\text{129}$ (30%) and a new hydrocarbon $\text{128}$ (16%, based on unisolated starting material). The mass spectrum of $\text{128}$ exhibited an ion of the proper molecular weight ($m/e$ 158). The nmr spectrum (Figure 3) showed the expected $A_2B_2$ pattern for the cyclohexadiene protons with an overlapping singlet for the two cyclobutene protons. The ring methylene protons appear as a broadened singlet at higher field. Triene $\text{128}$ exhibits ultraviolet absorption (in isooctane) at 268 ($\epsilon$ 2400) and (slight inflection) 276 m$\mu$ ($\epsilon$ 2100). The assigned structure $\text{128}$ was confirmed by hydrogenation to [4,4,2]propellane (137). Irradiation of $\text{128}$

\[ \text{H}_2 \xrightarrow{\text{Pd/C}} \]

$\text{128}$

$\text{137}$

in ether with 2537 Å light results in facile formation of tetralin and acetylene. This observation gives support to the earlier con-
Figure 3. The partial 100 MHz nmr spectrum of [4,4,2]propella-2,4,11-triene (128).
tention that the low yield photolysis of 2 to benzene and acetylene proceeds via bicyclo[4.2.0]octa-2,4,7-triene (63). The nmr spectrum of the annellated bicyclooctatriene 128 is temperature independent from room temperature to +165°C. The triene was heated at 165°C for 30 min, and its nmr spectrum at this temperature exhibited no evidence of thermal decomposition or valence bond tautomerization to the disubstituted cyclooctatetraene derivative 139.

Triene 128 readily undergoes cycloaddition with N-phenyl-maleimide to yield a (4 + 2)π adduct whose structure has been tentatively assigned as 140.
[4,4.2]Propella-2,4,7,9,11-pentaene (67) is analogous to imino ether 119 in that the inherent geometry of these systems makes possible a novel type of nearly orthogonal π-π interaction involving the top lobes of the cyclohexadiene moieties and both lobes of the four-membered ring π system. Although 119 is unstable with respect to fragmentation to naphthalene and ethyl cyanate, the observed thermal stability of triene 128 indicates that pentaene 67 may well be a stable isolatable compound.

Interest in 67 also stems from possible valence bond tautomerization which would result in cyclodecapentaene system 70, and per-
bridge without destruction of the 10π-electron aromatic system. During the initial stages of the synthesis of 67 there appeared a description of a related molecule, [4.4.2]propella-2,4,7,9-tetraene (141), whose properties indicate that the above mentioned valence bond tautomeration will likely be unobservable. Tetraene 141 exhibits no tendency to undergo valence bond tautomeration to

![Diagram]

the corresponding cyclodecapentaene 142. This observation is in direct contrast to the methylene-bridged analog which exists completely in the open form 23. Apparently a two-carbon bridge con-necting the 1,6-positions of a cyclodecapentaene system results in torsional strain sufficient to preclude planarity and hence delocali-zation in the 10π-electron system.

Regardless of its structure, pentaene 67 remained a novel hydro-carbon with potentially interesting chemistry and was deemed worthy of attempts at its synthesis.
The initially chosen method of synthesis of 67 involved preparation of triene 143 and subsequent allylic bromination-dehydrobromination.

Scheme VI depicts one successful route utilized for the synthesis of triene 143.

The anhydride 144 (dehydrated bis adduct of acetylenedicarboxylic acid and 1,3-butadiene) was prepared according to the procedure of Scott. Lithium aluminum hydride reduction of the anhydride and subsequent mesylation gave the dimesylate 146. Cyclization of the dimesylate with dehydrated sodium sulfide in hexamethylphosphoramide gave the desired sulfide 147, mp 55.5-56.5°, in 88% yield.

In contrast to the previously mentioned octalin derivatives (see p. 47), the nmr spectra of 145-147 exhibit singlets for the methylene protons adjacent to the heteroatom. In these hexalin systems, the methylene protons in question are no longer adjacent to an asymmetric carbon atom, and hence, the observed change in the multiplicity of their nmr absorptions is completely in accord with the assigned structures. Sulfide 147 readily undergoes α-chlorination with N-chlorosuccinimide. The crude α-chloro sulfide was not isolated, but was oxidized directly to the corresponding α-chloro sulfone 148, mp 111-113°. The methylene protons α to the sulfone group in 148 are
SCHEME VI

144 \[\text{IAH} \rightarrow \text{IAH} \rightarrow \text{CH}_3\text{SO}_2\text{Cl}(\text{MsCl})\] pyridine

145

146 \[\text{Na}_2\text{S} \rightarrow \text{HMP} \rightarrow 1. \text{NCS} \rightarrow 2. [\text{O}]\]

147

148 \[\text{Kot-Bu} \rightarrow \]

143
non-equivalent, and accordingly, the nmr spectrum of 148 exhibits an AB quartet attributable to these protons. The methine proton appears as a sharp singlet at δ 5.05. Potassium t-butoxide-induced Ramberg-Bäcklund rearrangement of 148 results in formation of the desired triene 143 in 53% yield. The mass spectrum of 143 exhibits a molecular ion peak (m/e 158) and a base peak (m/e 104) corresponding to loss of a neutral butadiene fragment (m = 54). The nmr spectrum is completely consistent with the assigned structure, and hydrogenation of 143 at atmospheric pressure results in formation of the known tricyclic hydrocarbon 137.

At this point it becomes informative to pause and discuss in more detail the nature of the Ramberg-Bäcklund rearrangement. The generally accepted mechanism is depicted below.
Although the Ramberg-Bäcklund rearrangement has been utilized successfully in acyclic systems, considerably less work has been performed with cyclic systems. Attempted rearrangement of α-bromo sulfone 155 was reported to give a poor yield of cyclopentene (156), and an attempt to prepare a cyclobutene derivative from 157 was unsuccessful.
One of the initial objectives of this dissertation was concerned with the feasibility of the preparation of cyclobutenes, such as 1₄ᵢ₃, via Ramberg-Bäcklund rearrangement. The normal conditions of the rearrangement involve refluxing a mixture of the α-halo sulfone in 2N sodium hydroxide solution with an added co-solvent such as dioxane.

When α-chloro sulfone 1₄₈ was prepared and treated with refluxing, aqueous sodium hydroxide-dioxane, unchanged 1₄₈ was recovered in high yield. The formation of α-sulfonyl carbanions under these conditions was established unequivocally by employing deuterium oxide and isolating the trideuterated congener 1₅₉ in 78% yield.

\[
\begin{align*}
1₄₈ & \xrightarrow{\text{NaOH, H₂O \ Dioxane}} N.R. \\
1₄₈ & \xrightarrow{\text{NaOD \ D₂O}} \\
1₅₉
\end{align*}
\]

In contrast to these results, the treatment of 1₄₈ with potassium t-butoxide in tetrahydrofuran resulted in formation of the desired cyclobutene 1₄₃ as discussed previously. The failure of the
α-halo sulfone rearrangement under aqueous conditions may be attributed to the fact that strong solvation of the carbanionic centers prevents attainment of a geometry favorable to the requisite intramolecular $S_N2$ process. It is apparent that both base and solvent may play central positions in the practical applications of the Ramberg-Bäcklund rearrangement.

During the course of these investigations it was deemed desirable to develop an alternative synthesis of triene $143$ in case the above Ramberg-Bäcklund sequence proved unsuccessful.

The successful alternative synthetic route is described in Scheme VII.

**SCHEME VII**

160 → 161 → 162 → 163 → 143
The four-membered acyloin 161, mp 81.5-82°, was prepared by
cyclization of cis-9,10-bis(carbomethoxy)-Δ^2,6-hexalin according to
the procedure of Bloomfield and Irelan. Lithium aluminum hydride
reduction of 161 afforded a mixture of cis- and trans-1,2-diols 162
(86% yield) which was treated with N,N-thiocarbonyldiimidazole without
purification. The cis-diol was thereby readily transformed (48% yield) to the cis-thionocarbonate ester 163, mp 122.5-123°. When
a solution of 163 in trimethylphosphite was refluxed for 96 hr,
the desired triene 143, identical to material obtained by Ramberg-
Bäcklund rearrangement of 148, was obtained in 54% yield after dis­
tillation.

\[
\text{1. NBS} \quad \xrightarrow{2. \text{Kt-Bu}} \quad \text{Complex mixture}
\]

Treatment of triene 143 with slightly more than two equivalents
of N-bromosuccinimide followed by potassium t-butoxide dehydrobromi–
nation resulted in formation of complex mixtures. On the basis of
these results and the rather low yield observed in the transformation
of diene 129 to [4.4.2]propella-2,4,11-triene (128), the above route
was abandoned, and an alternate synthesis which involved introduction
of the cyclobutene π system via Ramberg-Bäcklund rearrangement in the
final step was attempted (Scheme VIII).
Sulfide 147 was oxidized with ethereal monoperphthalic acid to the corresponding sulfone, mp 115.5-116.5°, in 90% yield. The sulfone was treated with two moles of bromine, and the crude tetrabromide was directly dehydrobrominated with sodium methoxide in refluxing tetrahydrofuran to yield tetraene sulfone 165, mp 160-162°, in 45% yield (based on sulfone 164). The nmr spectrum of sulfone 165 exhibited a singlet at δ 3.36 for the protons α to the sulfone group and an A₂B₂ pattern centered at δ 5.82 for the vinyl protons.
Reduction of 165 with lithium aluminum hydride in ether gave the known sulfide 166. The sulfide was chlorinated with N-chlorosuccinimide and oxidized with monoperphthalic acid to give α-chloro sulfone 167, mp 151-153°, in 42% yield.

Treatment of α-chloro sulfone 167 with potassium t-butoxide in ether resulted in formation of a new hydrocarbon 67 which was purified by preparative vpc (110°) and isolated in 14% yield. The nmr spectrum (Figure 4) shows absorption only in the vinyl region and is completely consistent with the assigned structure. The mass spectrum exhibits a molecular ion peak (calcd m/e 154.0782, obs m/e 154.0776). Hydrogenation of 67 results in uptake of five equivalents of hydrogen and formation of the known tricyclic hydrocarbon 137.

\[
\text{H}_2, \text{Pd/C} \quad \xrightarrow{\text{CH}_3\text{OH}} \quad \begin{array}{c}
67 \\
\end{array} \quad \begin{array}{c}
137 \\
\end{array}
\]

Tables 1 and 2 present nmr and uv data for propellanes 128, 67, and some relevant cyclohexadiene systems. The spectral properties of 128 and 67 agree well with the indicated model compounds and support the conclusion that they are simply polyolefinic in nature. Thus, the normal olefin proton nmr absorption of 67 at 5.68 is not compatible with an aromatic cyclodecapentaene structure 70 which would
Figure 4: The 100 MHz nmr spectrum of [4.4.2]propella-2,4,7,9,11-pentaene (67).
### TABLE 1

**CHEMICAL SHIFT DATA FOR SOME 1,3-CYCLOHEXADIENES**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Diene olefinic protons (δ)</th>
<th>Splitting pattern</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Structure 1]</td>
<td>5.62</td>
<td>Multiplet</td>
<td>97</td>
</tr>
<tr>
<td>![Structure 2]</td>
<td>5.63</td>
<td>Multiplet</td>
<td>79</td>
</tr>
<tr>
<td>![Structure 3]</td>
<td>5.53</td>
<td>A&lt;sub&gt;2&lt;/sub&gt;B&lt;sub&gt;2&lt;/sub&gt;</td>
<td>This work</td>
</tr>
<tr>
<td>![Structure 4]</td>
<td>5.58</td>
<td>A&lt;sub&gt;2&lt;/sub&gt;B&lt;sub&gt;2&lt;/sub&gt;</td>
<td>98</td>
</tr>
<tr>
<td>![Structure 5]</td>
<td>5.50</td>
<td>A&lt;sub&gt;2&lt;/sub&gt;B&lt;sub&gt;2&lt;/sub&gt;</td>
<td>48,86</td>
</tr>
<tr>
<td>![Structure 6]</td>
<td>5.68</td>
<td>A&lt;sub&gt;2&lt;/sub&gt;B&lt;sub&gt;2&lt;/sub&gt;</td>
<td>This work</td>
</tr>
<tr>
<td>Compound</td>
<td>$\lambda_{\text{max}}$</td>
<td>Solvent</td>
<td>Reference</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------</td>
<td>---------</td>
<td>-----------</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>274 ($\epsilon$ 3340)</td>
<td>Cyclohexane</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>273 ($\epsilon$ 3100)</td>
<td></td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>277 ($\epsilon$ 3000)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isooctane</td>
<td>268 ($\epsilon$ 2400)</td>
<td>Isooctane</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>276 [slight inflection, ($\epsilon$ 2100)]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>242 ($\epsilon$ 3400)</td>
<td></td>
<td>98</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>245 ($\epsilon$ 4800)</td>
<td>Cyclohexane</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>233 ($\epsilon$ 4200)</td>
<td></td>
<td>95% Ethanol</td>
</tr>
<tr>
<td></td>
<td>284 ($\epsilon$ 2200)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>235 ($\epsilon$ 4700)</td>
<td>Cyclohexane</td>
<td>48, 86</td>
</tr>
<tr>
<td></td>
<td>285 ($\epsilon$ 2600)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isooctane</td>
<td>247 ($\epsilon$ 2500)</td>
<td>Isooctane</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>290 ($\epsilon$ 2100)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
be expected to exhibit a deshielded proton nmr absorption due to a ring current in the 10π-electron system. By comparison, 1,6-methano-
cyclodecapentaene (23) exhibits an A_2B_2 pattern at δ 7.1. Similarly, the uv data of 67 is quite similar to that of tetraene (141) and is indicative of little measurable interaction between the cyclohexa-
diene and cyclobutene π systems.

One of the interesting characteristics of 67 is its pronounced thermal stability (it can be purified by preparative vpc at 120°) with respect to aza-analog 119. The fragmentation of 67 to naphthalene and acetylene involves a retro (2 + 2)_π cycloaddition and on the basis of orbital symmetry properties cannot occur via a thermally concerted process. If the fragmentation of 119 involves formation
and subsequent decomposition of a diradical intermediate, stabilization by nitrogen and the ethoxyl oxygen atom should facilitate the stepwise process. In contrast, the diradical which would be generated from pentaene 67 does not have available such a mode of radical stabilization.

The synthetic methods developed in this dissertation have culminated in the synthesis of a number of novel and interesting carbo- cyclic and heterocyclic \( \pi \) systems. It is hoped that the ready availability of these compounds will stimulate interest in these systems and eventually lead to a better understanding of their chemistry.
EXPERIMENTAL

Melting points and boiling points are uncorrected. The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark; Galbraith Laboratories, Inc., Knoxville, Tennessee; and M-H-W Laboratories, Garden City, Michigan. Infrared spectra were determined with a Perkin-Elmer Model 237 spectrometer unless otherwise indicated. Ultraviolet spectra were recorded with a Cary Model 14 spectrometer. The nmr spectra were determined with Varian A-60, A-60A or HA-100 spectrometers. The mass spectra were measured with an AEI MS-9 mass spectrometer at an ionizing energy of 70 ev.

11-Oxo-10-aza[4.3.2]propell-3-ene (82a). Chlorosulfonyl isocyanate (71 g, 0.50 mole) was added dropwise to 60 g (0.50 mole) of 4,7-dihydroindan (80a), and the resulting reaction mixture was stirred magnetically for 1 hr under a nitrogen atmosphere. Scratching produced crude crystalline N-(chlorosulfonyl) \( \beta \)-lactam which was added in small portions to a 50% aqueous acetone solution maintained at neutrality by the dropwise addition of 4N sodium hydroxide solution. The neutralized reaction mixture was then extracted three times with ether. The combined extracts were washed three times with water and dried over magnesium sulfate. The solvent was removed and the resulting oily crystals were recrystallized from petroleum ether (bp 60-110°) to yield 50 g (0.31 mole, 62%) of white crystalline \( \beta \)-
lactam \(82a\). Two subsequent recrystallizations of this material from the same solvent gave an analytical sample, mp 61-63\(^\circ\); \(\lambda_{\text{max}}^\text{CHCl}_3\) 5.72 \(\mu\); \(\delta^\text{CDCl}_3\) TMS 6.50 (broad singlet, 1H, N-H), 5.80 (multiplet, 2H, vinyl protons), and 0.90-2.90 (complex multiplet, 10H, ring methylene protons).

Anal. Calcd for C\(\text{10H}_{13}\)NO: C, 75.59; H, 8.03; N, 8.58. Found: C, 75.76; H, 8.04; N, 8.44.

11-Ethoxy-10-aza[4.3.2]propella-3,10-diene (83a). A solution of 25.4 g (0.273 mole) of epichlorohydrin in 40 ml of ether was added dropwise to a mechanically stirred solution of 52.2 g (0.366 mole) of boron trifluoride etherate in 150 ml of ether under a nitrogen atmosphere. The reaction mixture was mechanically stirred for 2 hr. The ether was decanted under a rapid stream of nitrogen, and the white crystalline triethylxonium fluoroborate was thoroughly washed with additional ether. The salt was dissolved in 100 ml of methylene chloride, and the solution was cooled to 0\(^\circ\). A solution of 42.6 g (0.261 mole) of \(\beta\)-lactam \(82a\) in 50 ml of methylene chloride was added rapidly, and the reaction mixture was stirred for 6 hr at ambient temperature. The reaction mixture was cooled in ice, and 48 ml of 50% potassium carbonate solution was added dropwise. Stirring was continued for 12 hr, and the resulting mixture was filtered through magnesium sulfate. The solvent was removed, and the residual oil was vacuum distilled through a 6 in Vigreaux column to give 36 g (0.19 mole, 73%) of a colorless oil, bp 65\(^\circ\) (0.3 mm); \(\lambda_{\text{max}}^\text{neat}\) 6.17 \(\mu\); \(\delta^\text{CDCl}_3\) TMS 5.72 (multiplet, 2H, vinyl protons), 4.17 (quartet, 2H, \(J = 7\) Hz, \(-\text{OCH}_2\text{CH}_3\)), and 0.90-2.84 [complex multiplet including triplet at
1.29 (J = 7 Hz), 13H, ring methylene protons and -OCH₂CH₃].

Addition of an ethanolic solution of 60% aqueous perchloric acid to an ethereal solution of the imino ether gave an oil which crystallized upon scratching and cooling. The crystalline salt was washed with ether, collected, and air dried, mp 120-122°. The perchlorate salt was recrystallized from ethanol-ether, mp 120-122°.

**Anal. Calcd for C₁₂H₁₈ClNΟ₅:** C, 49.40; H, 6.22; N, 4.80. **Found:** C, 49.29; H, 6.17; N, 4.73.

**11-Ethoxy-10-aza[4.3.2]propella-2,4,10-triene (76a).** A mixture of imino ether 83a (30.6 g, 0.16 mole), N-bromosuccinimide (30 g, 0.17 mole), and a trace of benzoyl peroxide in 200 ml of carbon tetrachloride was refluxed for 1 hr under a nitrogen atmosphere. After filtration, the solvent was removed, and the residual oil was dissolved in 50 ml of dry tetrahydrofuran. This solution was added dropwise to an ice cold slurry of 29.0 g (0.258 mole) of potassium t-butoxide in 50 ml of anhydrous tetrahydrofuran. This reaction mixture was magnetically stirred at 0° under a nitrogen atmosphere for 2 hr. Ether and water were added, and the dark organic phase was separated, washed thoroughly with water, and filtered through magnesium sulfate. The solvent was removed, and the residual oil was distilled in a short-path distillation apparatus to yield 14.4 g (0.0754 mole, 47%) of a red-brown oil, bp 65-75° (0.1 mm). The imino ether was redistilled to give 12.2 g of pale yellow oil, bp 50-52° (0.1 mm), a portion of which was further purified by preparative vapor phase chromatography at 140°; \( \lambda_{\text{max}}^\text{neat} 6.24 \mu; \lambda_{\text{max}}^\text{isoctane} 267 \mu \)
$^1$H NMR (CDCl$_3$, 6 TMS) 5.52-6.19 (complex multiplet, 4H, vinyl protons), 4.14 (quartet, $J = 7$ Hz, 2H, $-\text{OCH}_2\text{CH}_3$), 0.92-2.25 [complex multiplet including triplet at 1.30 ($J = 7$ Hz), 9H, ring methylene protons and $-\text{OCH}_2\text{CH}_3$]; Calcd m/e 189.1154; Observed m/e 189.1154.

Anal. Calcd for C$_{12}$H$_{15}$NO: C, 76.15; H, 7.99; N, 7.40. Found: C, 75.74; H, 8.32; N, 7.02.

Irradiation of 11-Ethoxy-10-aza[4,3,2]propella-2,4,10-triene (76a).

A magnetically stirred solution of 300 mg (1.59 mmoles) of 76a and 100 ml of ether in a quartz cylinder was irradiated under nitrogen utilizing a bank of nine GE 615T8 (30 w germicidal, 2537 Å) lamps. After 60 min, the solvent was removed, and the residue was purified by preparative vapor phase chromatography ($5'/1/4'$, 5% SF 96 on Chrom. G). Indane (87 mg, 0.74 mmole, 46%) was collected and identified by infrared comparison with an authentic sample. The more volatile fraction contained ether and at least two other products. Infrared analysis of this fraction showed a strong absorption at 4.46 μ and a strong carbonyl band at 5.81 μ which was not present in the infrared spectrum of the crude photolysis product prior to preparative vapor phase chromatography.

Cycloaddition of 11-Ethoxy-10-aza[4,3,2]propella-2,4,10-triene (76a) and N-Phenylmaleimide. A magnetically stirred solution of 0.931 g (4.92 mmoles) of azetine 76a and 0.85 g (4.92 mmoles) of N-phenylmaleimide in 10 ml of toluene was refluxed under nitrogen for 7 hr. The solvent was removed, and the gum-like residue was triturated with petroleum
ether. The resulting crystals were collected and air dried. The yield was 1.54 g (4.25 mmole, 86%) of a cream colored solid. An analytical sample of 105, mp 172-174.5°, was obtained after three recrystallizations from benzene-hexane; $\lambda_{\text{max}}^\text{CHCl}_3$ 5.65, 5.86, 6.22 μ; $\delta_{\text{TMS}}^\text{CDCl}_3$ 7.0-7.56 (multiplet, 5H, aromatic protons), 6.19 (multiplet, 2H, vinyl protons), 4.16 (quartet, J = 7 Hz, 2H, -OCH$_2$CH$_3$), 3.08-3.58 (multiplet, 4H, bridgehead protons and protons α to carbonyl, and 1.08-2.37 [complex multiplet with triplet at 1.28 (J = 7 Hz), 9H, ring methylene protons and -OCH$_2$CH$_3$]).

Anal. Calcd for C$_{22}$H$_{22}$N$_2$O$_3$: C, 72.91; H, 6.12; N, 7.73. Found: C, 73.12; H, 6.25; N, 7.67.

12-Oxo-11-aza[4.4.2]propell-3-ene (82b). Chlorosulfonyl isocyanate (73 g, 0.52 mole) was added dropwise to 73 g (0.54 mole) of 5,8-dihydrotetralin (80b), and the resulting reaction mixture was magnetically stirred for 1 hr under a nitrogen atmosphere. Refrigeration produced crystalline N-(chlorosulfonyl) β-lactam which was added in small portions to a 50% aqueous acetone solution maintained at neutrality by the dropwise addition of 4N sodium hydroxide solution. The reaction mixture was extracted with three portions of ether. The combined extracts were washed with water and dried over magnesium sulfate. The solvent was removed and the crude β-lactam 82b was recrystallized from petroleum ether (bp 60-110°) to yield 51 g (0.29 mole, 54%) of colorless white crystals. Three more recrystallizations of this material from the same solvent gave an analytical sample, mp 90-91°; $\lambda_{\text{max}}^\text{CHCl}_3$ 5.72 μ; $\delta_{\text{TMS}}^\text{CDCl}_3$ 6.80 (broad
singlet, 1H, N-H), 5.82 (multiplet, 2H, vinyl protons), and 1.22-2.57 (complex multiplet, 12H, ring methylene protons).

**Anal.** Caled for C_{11}H_{15}NO: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.68; H, 8.68; N, 7.91.

**Hydrogenation of 12-Oxo-11-aza[4.4.2]propell-3-ene (82b).** A solution of 0.150 g (0.846 mmole) of β-lactam 82b in 15 ml of ethyl acetate was hydrogenated at atmospheric pressure. One equivalent of hydrogen was absorbed. After filtration, the solvent was removed leaving 0.145 g (0.809 mmole, 96%) of oily 12-oxo-11-aza[4.4.2]propellane whose ir and nmr spectra were identical with those of an authentic sample. One recrystallization of the crude β-lactam 91 gave white crystals, mp 51-53°.

**Octalin Isomer Mixture (93 and 94).** A mixture (100 g, 0.65 mole) of 2-decalol isomers (92) (Aldrich Chemical Co.) was added to 300 g of 100% phosphoric acid. The mixture was mechanically stirred, and the temperature was rapidly raised to 150° by means of a preheated oil bath. A vacuum (~60 mm) was applied to the system, and water was added dropwise maintaining the temperature of the reaction mixture between 135-150°. Steam distillation was continued for approximately 2 hr. The product was separated from the aqueous layer which was subsequently extracted with four 50-ml portions of ether. The combined extracts were washed with two 25-ml portions of 5% sodium carbonate solution and once with 25 ml of saturated sodium chloride solution. After filtration through magnesium sulfate, the
solvent was removed, and the olefin mixture was vacuum distilled to yield 71 g (81%) of a colorless oil, bp 105-115° (60 mm). Vapor phase chromatography indicated the presence of Δ^9,10^-octalin (67%), Δ^1,9^-octalin (23%), and an unidentified third product (10%).

Δ^9,10^-Octalin (93). In a three necked, round-bottom flask fitted with a magnetic stirrer, a dropping funnel, and a reflux condenser was placed 4.7 g (0.125 mole) of sodium borohydride, 23.1 g (0.33 mole) of 2-methyl-2-butene, and 100 ml of tetrahydrofuran. The mixture was stirred for 15 min, and 23.5 g (0.165 mole) of boron trifluoride etherate, dissolved in 22 ml of tetrahydrofuran, was added dropwise over a 45-min period. A sample of the octalin isomer mixture (93 and 94) (20 g, 0.147 mole) was added dropwise over a 10-min period. After the mixture had been stirred for 3.5 hr, 50 ml of water was added dropwise with slow stirring. Over a 10-min period, 35 ml of 3N sodium hydroxide solution was added. This was followed by the addition of 35 ml of 30% hydrogen peroxide solution over a 45-min period. After stirring for 5 hr at 44-45°, the mixture was cooled, and the layers were separated. The organic layer was washed with water, saturated sodium chloride solution, and filtered through magnesium sulfate. The solvent was removed, and the residual oil was fractionally distilled through a 6 in Vigreaux column to yield 7.0 g (0.051 mole, 35%) of a colorless liquid, bp 95-100° (40 mm) [lit bp 75-77° (14 mm)]. The nmr spectrum shows no vinyl protons although vpc indicated the presence of a minor impurity (~10%).
12-Oxo-11-aza[4.4.2]propellane (91). To an ice cold magnetically stirred solution of 5.2 g (0.038 mole) of \( \Delta^{9,10} \)-octalin (93) in 50 ml of methylene chloride was added dropwise under nitrogen 5.2 g (0.037 mole) of chlorosulfonyl isocyanate. The reaction mixture was allowed to warm to room temperature with continued stirring during a 1-hr period. The solvent was removed, and the crude N-(chlorosulfonyl) \( \beta \)-lactam was added in small portions to a 50% aqueous acetone solution maintained at neutrality by the dropwise addition of \( \text{CH}_3\text{OH} \) sodium hydroxide solution. The reaction mixture was extracted three times with ether, and the combined extracts were washed with water, dried over magnesium sulfate, and evaporated. The residual oil was triturated with hexane and refrigerated. The resulting crude \( \beta \)-lactam 91 was chromatographed on Woelm neutral alumina (activity I). Elution with ether gave an oil which crystallized upon trituration with cold hexane. The yield of 91 was 1.9 g (0.011 mole, 30%). Two subsequent recrystallizations from hexane at -20\(^\circ\) gave an analytical sample, mp 52-53.5\(^\circ\); \( \lambda_{\text{max}}^{\text{CHCl}_3} \) 5.75 \( \mu \); \( \delta_{\text{TMS}}^{\text{CDCl}_3} \) 7.17 (broad singlet, 1H, N-H) and 1.63 (broad singlet, 16H, methylene protons).

Anal. Calcd for C\(_{11}\)H\(_{17}\)NO: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.53; H, 9.56; N, 7.68.

12-Ethoxy-11-aza[4.4.2]propella-3,11-diene (93b). A solution of 30.6 g (0.33 mole) of epichlorohydrin in 40 ml of ether was added dropwise to a mechanically stirred solution of 62.5 g (0.44 mole) of boron trifluoride etherate in 150 ml of ether under a nitrogen atmosphere. The reaction mixture was mechanically stirred for 2 hr.
The ether was decanted under a rapid stream of nitrogen, and the white crystalline triethyloxonium fluoroborate was thoroughly washed with additional ether. The salt was dissolved in 125 ml of methylene chloride and cooled to \( \sim 10^\circ \). A solution of 55.0 g (0.310 mole) of \( \beta \)-lactam \( \text{82b} \) in 125 ml of methylene chloride was added rapidly, and the reaction mixture was stirred for 8 hr at ambient temperature. The reaction mixture was cooled in an ice bath, and a solution of 58 ml of 50% potassium carbonate was added dropwise. Stirring was continued for 12 hr, and the mixture was filtered through magnesium sulfate. The solvent was removed, and the residual oil was vacuum distilled through a Vigreaux column to give 52.0 g (0.255 mole, 82%) of a colorless oil, bp 62-64\(^\circ\) (0.25 mm). A redistilled sample gave an acceptable analysis. \( \lambda_{\text{max}} \) \( \text{neat} \) 6.16 \( \mu \); \( \delta_{\text{TMS}} ^{\text{CDCl}_3} \) 5.72 (multiplet, 2H, vinyl protons), 4.22 (quartet, \( J = 7 \) Hz, 2H, -OCH\(_2\)CH\(_3\)), and 1.12-2.57 \( \text{[complex multiplet including triplet at 1.33 (} J = 7 \text{ Hz), 15H, ring methylene protons and -OCH}_2\text{CH}_3\text{]} \)

**Anal. Calcd for C\(_{13}\)H\(_{15}\)NO: C, 76.05; H, 9.33; N, 6.82. Found: C, 76.23; H, 9.37; N, 6.87.**

\( \text{12-Ethoxy-11-aza[4.4.2]propella-2,4,11-triene (76b).} \) A slurry of 6.0 g (0.029 mole) of imino ether \( \text{83b} \), 5.3 g (0.03 mole) of N-bromosuccinimide, and a trace of benzoyl peroxide in 100 ml of carbon tetrachloride was refluxed for 1.5 hr under a nitrogen atmosphere. The resulting succinimide was removed by filtration, and the solvent was evaporated leaving a light yellow oil. The oil was dissolved in 50 ml of tetrahydrofuran, and this solution was added dropwise to an
ice cold suspension of 6.7 g (0.06 mole) of potassium t-butoxide in 100 ml of tetrahydrofuran. The reaction mixture was stirred magnetically at 0° for 1.5 hr. Ether and water were added, and the organic layer was separated and washed with three portions of water and one portion of saturated sodium chloride solution. The ethereal solution was dried over magnesium sulfate and the solvent was removed. The residual oil was vacuum distilled in a short-path distillation apparatus to yield 2.2 g (0.011 mole, 38%) of a yellow oil. An analytical sample of colorless 76b was obtained after three distillations in a short-path distillation apparatus equipped with a 3 in Vigreaux column, bp 56-57° (0.04 mm); λ\text{max} 6.24 μ; λ\text{isoctane} 272 μ (ε 2100); δ\text{DCl}_3 5.23-5.99 (complex multiplet, 4H, vinyl protons), 4.20 (quartet, J = 7.5 Hz, 2H, -OCH_2CH_3), 1.67 (broad absorption, 8H, ring methylene protons), and 1.31 (triplet, J = 7.5 Hz, 3H, -OCH_2CH_3).

Anal. Calcd for C_13H_17NO: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.35; H, 8.53; N, 6.68.

Irradiation of 12-Ethoxy-11-aza[4.4.2]propella-2,4,11-triene (76b). A magnetically stirred solution of 0.31 g (1.52 mmol) of 76b and 100 ml of ether in a quartz cylinder was irradiated under nitrogen utilizing a bank of nine GE 615T8 (30 w germicidal, 2537 Å) lamps for 60 min. The solvent was removed, and the residue was purified by preparative vapor phase chromatography (5'/1/4'' 10% SF 96 on Chrom. G). Tetralin (89 mg, 0.67 mmole, 44%) was collected and identified by infrared comparison with an authentic sample. The more volatile fraction contained at least two compounds and was not
investigated.

Cycloaddition of 12-Ethoxy-11-aza[4.4.2]propella-2,4,11-triene (76b) and N-Phenylmaleimide. A solution of 1.10 g (5.46 mmole) of 76b and 0.95 g (5.46 mmole) of N-phenylmaleimide in 10 ml of toluene was refluxed for 6 hr under nitrogen. The reaction mixture was cooled to room temperature, and the solvent was removed to yield 1.9 g (5.1 mmole, 93%) of a cream colored solid, mp 120-145°. An analytical sample of 106, mp 156-158°, was obtained after three recrystallizations from benzene-hexane; λCHCl₃ max 5.64, 5.85, and 6.18 µ; δCDCl₃ 6.92-7.43 (multiplet, 5H, aromatic protons), 6.08 (multiplet, 2H, vinyl protons), 4.10 (quartet, J = 7 Hz, 2H, -OCH₂CH₃), 2.83-3.29 (multiplet, 4H, bridgehead protons and protons α to carbonyl), and 1.08-2.07 [multiplet including triplet at 1.27 (J = 7 Hz), 11H, ring methylene protons and -OCH₂CH₃].

Anal. Calcd for C₂₃H₂₄N₂O₃: C, 73.38; H, 6.43; N, 7.44. Found: C, 73.53; H, 6.47; N, 7.39.

4-Benzoylbutyric Acid (109a) and 5-Phenylvaleric Acid (110a).

To a mechanically stirred mixture of 400 g of anhydrous aluminum chloride in 350 g of benzene, cooled in an ice bath, was added drop-wise a solution of 155 g (1.36 moles) of glutaric anhydride in 350 g of benzene over a period of 1 hr. After stirring an additional 30 min, 600 ml of water and 200 ml of concentrated hydrochloric acid were added cautiously. The benzene was removed by steam distillation, and the remaining hot mixture was poured into a 3-l beaker and cooled to 0°. The crude acid was collected and washed with 200 ml of 1:4
hydrochloric acid-water followed by 200 ml of water. The acid was dissolved in a boiling solution of 186 g of sodium carbonate monohydrate and 900 ml of water, and the remaining aluminum salts were removed by filtration. The filtrate was treated with charcoal and filtered again. After careful acidification with 260 ml of concentrated hydrochloric acid, the precipitated acid was collected, washed well with water, and dried in vacuo. The product was suitable for Clemmensen reduction without further purification. A small sample was recrystallized from benzene, mp 127-128° (lit mp 125-126°).

A mixture of 500 g of mossy zinc, 50 g of mercuric chloride, 25 ml of concentrated hydrochloric acid, and 750 ml of water was agitated by hand for five minutes. The solution was decanted, and the zinc metal was washed well with water. A mixture of 100 ml of water, 875 ml of concentrated hydrochloric acid, 500 ml of toluene, the amalgamated zinc, and the crude 4-benzoylbutyric acid (109a) prepared above was refluxed with stirring for 8 hr. The organic layer was separated, and the aqueous layer was extracted twice with 200 ml of 1:1 ether-benzene. The combined extracts were dried over magnesium sulfate, and the solvent was removed. The product was vacuum distilled to give 135 g (0.76 mole, 56% based on glutaric anhydride) of a colorless liquid, bp 125-130° (0.1 mm), which crystallized in the receiver, mp 53-56° (lit mp 60°).

1-Benzsuberone (111a). A solution of 30.0 g (0.168 mole) of 5-phenylvaleric acid in 25 ml of thionyl chloride was refluxed for 3 hr. The excess thionyl chloride was removed in vacuo, and the crude 5-
phenylvaleryl chloride in 300 ml of carbon disulfide was added drop-wise to a stirred slurry of 65 g of aluminum chloride in one liter of refluxing carbon disulfide. The addition was carried out over a 4-hr period. The reaction mixture was allowed to stir at reflux for 18 hr, and the solvent was subsequently removed by distillation. The residue was cooled in an ice bath. After cautious addition of 1 l of ice-water, the product was steam distilled. The distillate was extracted three times with chloroform, and the combined extracts were dried over magnesium sulfate. The solvent was removed and the residual oil was vacuum distilled to give 16.5 g (0.103 mole, 61% based on 5-phenylvaleric acid) of a colorless liquid, bp 80-85° (0.2 mm) [lit bp 128-130° (6-7 mm)].

Benzocycloheptene (112a). A magnetically stirred mixture of 52.0 g (0.325 mole) of 1-benzsuberone, 42 g of potassium hydroxide, 28.2 ml of hydrazine hydrate and 350 ml of triethylene glycol was refluxed for one hour. The water was removed by means of a Dean-Stark trap until the temperature of the reaction mixture reached 180°. The reaction mixture was stirred at this temperature for 3 hr and allowed to cool to room temperature. Water (500 ml) was added, and the reaction mixture was extracted three times with ether. The combined extracts were washed three times with water, once with saturated sodium chloride solution, and dried over magnesium sulfate. The solvent was removed, and the residual oil was vacuum distilled to give 31.3 g (0.214 mole, 66%) of a colorless oil, bp 118-120° (30 mm), nD 1.5381 [lit 70° bp 78-82° (3 mm), nD 1.5382].
6,9-Dihydrobenzocycloheptene (113a). To a mechanically stirred mixture of 14.7 g (0.092 mole) of benzocycloheptene and 27.6 g (0.60 mole) of ethanol in 150 ml of liquid ammonia was added 9.2 g (0.4 g-atom) of sodium metal in small pieces. Each successive piece of sodium was added upon the disappearance of the dark blue color, and the ammonia was allowed to reflux gently during the addition. The ammonia was allowed to evaporate, and 200 ml of water was added cautiously. The reaction mixture was extracted with two 200-ml portions of ether, and the combined extracts were washed with water, dried over magnesium sulfate, and evaporated. Vapor phase chromatography of the resulting oil indicated the presence of three products. Preparative vapor phase chromatography (10'/1/2'' 10% SF 96 on 60/80 Chrom. G) of a small sample allowed separation of the more volatile product. This product was tentatively assigned structure 117 on the basis of its nmr spectrum: $\delta_{\text{CDCl}_3}$ 1.49 and 1.93 (overlapping multiplets).

Anal. Calcd for C$_{11}$H$_{18}$: C, 87.92; H, 12.08. Found: C, 88.30; H, 11.84.

The remaining two products were inseparable under these conditions. The nmr spectrum of this mixture indicated the presence of the desired 6,9-dihydrobenzocycloheptene and starting material. The Birch reduction was repeated on the entire mixture to insure complete reduction of the benzocycloheptene. The mixture was then fractionally distilled utilizing a Nester-Faust spinning band column. The yield of 6,9-dihydrobenzocycloheptene was 7.1 g (0.048 mole, 52%), bp 78° (5 mm): $\delta_{\text{CDCl}_3}$ 5.62 (triplet, J = 1.2 Hz, 2H, vinyl protons), 2.64 (doublet,
\( J = 1.2 \text{ Hz, } ^4\text{H, doubly allylic protons}, \) ca. 2.03 (multiplet, \( ^4\text{H, allylic protons} \)), and ca. 1.55 (multiplet, \( 6\text{H, ring methylene protons} \)).

**Anal.** Calcd for \( \text{C}_{11}\text{H}_{16} \): C, 89.12; H, 10.88. Found: C, 89.42; H, 10.76.

**13-Oxo-12-aza[5.4.2]propell-9-ene (114a).** To an ice cold, magnetically stirred solution of 6.0 g (0.041 mole) of 6,9-dihydrobenzocycloheptene (113a) in 10 ml of methylene chloride was added under nitrogen 5.2 g (37 mmoles) of chlorosulfonyl isocyanate over a 10-min period. The reaction mixture was allowed to warm to room temperature during a 1-hr period with continued stirring. The solvent was removed and the crude N-(chlorosulfonyl) \( \beta \)-lactam was added in small portions to a 50% aqueous acetone solution maintained at neutrality by the dropwise addition of \( ^4\text{Na} \) sodium hydroxide solution. The reaction mixture was extracted with three portions of ether; the combined extracts were washed with water, dried over magnesium sulfate, and evaporated. The resulting oil was triturated with petroleum ether and refrigerated. After two days, the crystalline \( \beta \)-lactam 114a was filtered and air dried. The yield was 2.24 g (11.7 mmoles, 28.6%), mp 58-68°. An analytical sample, mp 67-70°, was obtained after chromatography on Woelm neutral alumina (activity III) followed by recrystallization from petroleum ether: \( \lambda_{\text{max}}^{\text{CHCl}_3} 5.74 \mu; \lambda_{\text{TMS}}^{\text{CDCl}_3} 6.60 \) (broad absorption, 1H, N-H), 5.62 (multiplet, 2H, vinyl protons), and 2.18, 1.64 (centers of broad absorptions, \( ^4\text{H, ring methylene protons} \)).
Anal. Calcd for C_{12}H_{17}NO: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.07; H, 9.19; N, 7.30.

13-Ethoxy-12-aza[5.4.2]propella-9,12-diene (115a). A solution of 1.19 g (0.013 mole) of epichlorohydrin in 15 ml of ether was added dropwise to a solution of 2.44 g (0.017 mole) of boron trifluoride etherate in 10 ml of ether under a nitrogen atmosphere. The reaction mixture was mechanically stirred for 2 hr. The ether was decanted under a rapid stream of nitrogen, and the white crystalline triethyl-oxonium fluoroborate was thoroughly washed with additional ether. The salt was dissolved in 10 ml of methylene chloride and cooled to ~10°C. A solution of 2.20 g (12 mmoles) of β-lactam 114a in 15 ml of methylene chloride was added rapidly, and the reaction mixture was allowed to stir for 4 hr at ambient temperature. The reaction mixture was cooled in an ice bath, and 1.83 ml (0.014 mole) of 50% potassium carbonate solution was added dropwise. Stirring was continued for another hour, and the methylene chloride solution was filtered through magnesium sulfate. The solvent was removed and the residual oil was vacuum distilled to give 1.10 g (5.0 mmoles, 42%) of a colorless oil, bp 84-88°C (0.3 mm): λ_{max} 6.15 μ; δ_{TMS} 5.70 (broadened singlet, 2H, vinyl protons), 4.19 (quartet, J = 7 Hz, 2H, -OCH₂CH₃), and 1.03-2.39 [complex multiplet with major absorptions at 1.58, 1.98, 2.13 and a triplet at 1.28 (J = 7 Hz, -OCH₂CH₃), a total of 17H].

Addition of an ethanolic solution of 60% aqueous perchloric acid to an ethereal solution of the imino ether gave a perchlorate salt which was recrystallized from ethanol-ether, mp 108.5-110°C.
Anal. Calcd for C₁₄H₂₂ClNOS: C, 52.58; H, 6.94; N, 4.38. Found: C, 52.32; H, 6.90; N, 4.22.

13-Ethoxy-12-aza[5.4.2]propella-8,10,12-triene (116a). To a solution of 1.50 g (6.85 mmol) of imino ether 115a in 40 ml of carbon tetrachloride was added 1.28 g (7.19 mmol) of N-bromosuccinimide and a trace of benzoyl peroxide. The reaction mixture was refluxed with magnetic stirring under a nitrogen atmosphere for 1.5 hr and allowed to cool to room temperature. The succinimide was removed by vacuum filtration. The solvent was removed, and the resulting oil was dissolved in 20 ml of anhydrous tetrahydrofuran. This solution was added dropwise to a magnetically stirred slurry of 1.53 g (14 mmol) of potassium t-butoxide in 20 ml of tetrahydrofuran at 0° under a nitrogen atmosphere. The reaction mixture was allowed to stir at this temperature, under a nitrogen atmosphere, for 2 hr. After the addition of 100 ml of ether and 20 ml of water, the aqueous layer was separated and extracted with ether. The combined extracts were washed three times with water, once with saturated sodium chloride solution, and dried over magnesium sulfate. The solvent was removed, and the residual oil was vacuum distilled to give 0.70 g (3.2 mmol, 47%) of a pale yellow liquid, bp 92-94° (0.3 mm). A small sample was molecularly distilled and submitted for analysis: λ<sub>max</sub> 6.24 μ; λ<sub>max</sub><sup>1</sup>isoctane 268 μ (ε 1900); δ<sup>1</sup>CDCl₃ 5.22-6.22 (complex multiplet, 4H, vinyl protons), 4.16 (quartet, J = 7 Hz, 2H, -OCH₂CH₃), and 0.95-2.05 [complex multiplet including triplet at 1.27 (J = 7 Hz, -OCH₂CH₃), total of 13H, ring methylene
protons and -OCH₂CH₂].

**Anal. Caled for C₁₄H₁₉NO:** C, 77.38; H, 8.81; N, 6.45. **Found:** C, 77.15; H, 8.66; N, 6.04.

5-Benzoylvaleric Acid (109b). A solution of 174 g (1.0 mole) of ethyl hydrogen adipate and 179 g (1.5 moles) of thionyl chloride was heated at 50-60° for 4 hr. The excess thionyl chloride was removed, and the crude acid chloride was added dropwise to a mechanically stirred slurry of 266 g (2.0 moles) of aluminum chloride in 400 ml of benzene. The reaction mixture was maintained at a temperature of 0-10° during the 1.5-hr addition period. After being heated on a steam bath for 3 hr, the mixture was poured over 2 kg of crushed ice. After the addition of 800 ml of 6N hydrochloric acid, the benzene was removed by steam distillation. The remaining aqueous mixture was extracted with ether and concentrated. The residue was stirred with 350 ml of 10% methanolic sodium hydroxide for 3 hr and warmed on a hot plate for an additional hour. After the addition of 500 ml of water, the methanol was removed, and the concentrated solution was filtered through Celite and acidified with concentrated hydrochloric acid. The acid was collected, dried, and recrystallized from benzene-hexane. The yield of the crude brown acid was 130 g (0.63 mole, 63%). A sample which was recrystallized from petroleum ether melted at 75-77° (lit mp 70-71°).

6-Phenylcaproic Acid (110b). A mixture of 35 g (0.17 mole) of 5-benzoylvaleric acid (109b), 33.7 g (0.6 mole) of potassium hydroxide,
21.3 g (0.425 mole) of hydrazine hydrate and 150 ml of diethylene glycol was refluxed for 2 hr with magnetic stirring. Water was removed by means of a Dean-Stark trap until the temperature of the reaction mixture reached 185°. The reaction mixture was refluxed at this temperature for 4 hr, cooled to room temperature, and poured into 1 l of water. The aqueous mixture was cooled to 0°, and 150 ml of concentrated hydrochloric acid was added. After extraction with four 200-ml portions of ether, the combined extracts were washed with saturated sodium chloride solution and dried over magnesium sulfate. The solvent was removed, and the dark residual oil was vacuum distilled through a 6 in Vigreaux column. The yield of 6-phenylcaproic acid (110b), a colorless oil, was 25.2 g (0.131 mole, 77%), bp 120-122° (0.05 mm) [lit72 bp 167-169° (1 mm)].

1,2-Benzocycloocten-3-one (105b). A solution of 86 g (0.45 mole) of 6-phenylcaproic acid (110b), 105 g (0.90 mole) of thionyl chloride and 400 ml of benzene was refluxed for 20 hr. The solvent was removed, and the residual oil was diluted with 450 ml of carbon disulfide and added dropwise to a refluxing, mechanically stirred slurry of 186 g (1.4 moles) of aluminum chloride in 2400 ml of carbon disulfide. The addition was carried out over a 3-day period, and the reaction mixture was refluxed for another two days. The carbon disulfide was removed by distillation, and the ice cold residue was carefully hydrolyzed with 1.5 l of ice water. The aqueous mixture was steam distilled. The distillate (8 l) was extracted three times with ether, and the combined extracts were dried over magnesium sul-
fate and concentrated. The yield of crude benzocyclooctenone was 39 g (0.22 mole, 50%). The ketone was homogeneous by vpc and was used without further purification.

Benzocyclooctene \((\text{112b})\). A solution of 39.0 g (0.224 mole) of 1,2-benzocycloocten-3-one \((\text{111b})\), 40.5 g (0.72 mole) of potassium hydroxide, 41 g (0.81 mole) of hydrazine hydrate, and 350 ml of diethylene glycol was refluxed for 1.5 hr. Water was removed through a Dean-Stark trap until the temperature of the reaction mixture reached 185°C. The reaction mixture was refluxed at this temperature for 4 hr. and cooled to room temperature. Water was added, and the aqueous mixture was extracted with four portions of ether. The combined extracts were washed three times with water, once with saturated sodium chloride solution, and filtered through magnesium sulfate. The solvent was removed, and the residual oil was vacuum distilled to give 30.1 g (0.188 mole, 84%) of a colorless oil, bp 55-57°C (0.3 mm), \(n_D^{27} 1.5369\) [lit. bp 115-125°C (8 mm), \(n_D^{21} 1.5392\)].

7,10-Dihydrobenzocyclooctene \((\text{113b})\). To a mechanically stirred solution of 20.0 g (0.125 mole) of benzocycloctene, 56.4 g (1.25 moles) of ethanol, and 25 ml of anhydrous ether in 1.0 l of liquid ammonia was added 7 g (1.0 g-atom) of lithium metal in small pieces over a 3-hr period. The ammonia was allowed to evaporate. The reaction vessel was then cooled in ice and 400 ml of ice water was added cautiously. The reaction mixture was extracted with three 150-ml portions of ether. The combined extracts were washed twice with
water and once with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and evaporated. The residual oil was vacuum distilled to give 18 g of a colorless liquid, bp 68-69° (0.5 mm), which consisted of one major (ca. 85%) and three minor components (ca. 15%). The major component was purified by preparative vapor phase chromatography and shown to be the desired 7,10-dihydrobenzocyclooctene; \( \delta_{\text{CDCl}_3} \) \( \delta_{\text{TMS}} \) 5.56 (triplet, \( J = 1 \) Hz, 2H, vinyl protons), 2.47 (doublet, \( J = 1 \) Hz, 4H, doubly allylic methylene protons), 2.10 (broad absorption, 4H, allylic methylene protons), and 1.15 (broadened singlet, 8H, remaining ring methylene protons).


One of the minor components was identified as benzocyclooctene by nmr and vpc retention time; the other two minor products were not identified.

14-Oxo-13-aza[6.4.2]propell-10-ene (114b). To an ice cold, magnetically stirred nitrogen-blanketed solution of 8.20 g (50.6 mmoles) of 7,10-dihydrobenzocyclooctene (113b) in 30 ml of methylene chloride was added dropwise 5.70 g (41 mmoles) of chlorosulfonyl isocyanate. The reaction mixture was allowed to warm to room temperature during 2 hr with continued stirring. The solvent was removed, and crude N-(chlorosulfonyl) \( \beta \)-lactam was added in small portions to a 50% aqueous acetone solution maintained at neutrality by the drop-wise addition of 4N sodium hydroxide solution. The reaction mixture was extracted with three portions of ether, and the combined extracts
were washed with water, dried over magnesium sulfate, and concentrated. The resulting oily crystals were triturated with ether, collected, and air dried. The yield of crude β-lactam 114b was 4.3 g (21 mmoles, 51%), mp 80-95 °. Five recrystallizations of this material from ether at -20 ° gave an analytical sample, mp 99-100 °; λ max CHCl₃ 5.74 μ; δCDC₃ TMS 7.45 (broad absorption, 1H, N-H), 5.76 (multiplet, 2H, vinyl protons), and 1.19-2.77 (multiplet, 16H, ring methylene protons).

Anal. Calcd for C₁₃H₁₉NO: C, 76.05; H, 9.33; N, 6.82. Found: C, 75.95; H, 9.37; N, 6.66.

14-Ethoxy-13-aza[6.4.2]propella-10,13-diene (115b). A solution of 1.55 g (16.8 mmoles) of epichlorohydrin in 10 ml of ether was added dropwise to a mechanically stirred solution of 3.18 g (22.4 mmoles) of boron trifluoride etherate under a nitrogen atmosphere. The reaction mixture was mechanically stirred for 2 hr. The ether was decanted under a rapid stream of nitrogen, and the white crystalline triethyloxonium fluoroborate was thoroughly washed with additional ether. The salt was dissolved in 20 ml of methylene chloride and cooled to 0 °. A solution of 3.13 g (15.3 mmoles) of β-lactam 115b in 10 ml of methylene chloride was added in one portion. The reaction mixture was allowed to warm to room temperature with continued stirring over a 3-hr period. The reaction mixture was cooled in ice, and 2.8 ml of 50% potassium carbonate solution was added dropwise. Stirring was continued for 3 hr, and the mixture was filtered through magnesium sulfate. The solvent was removed, and the residual oil was vacuum distilled in a short-path distillation apparatus to give
2.58 g (11.1 mmoles, 73%) of a colorless oil, bp 90-96° (0.1 mm):
\[ \lambda_{\text{max}}^{\text{neat}} \] 6.15 μ; \[ \delta_{\text{TMS}}^{\text{CDCl}_3} \] 5.72 (multiplet, 2H, vinyl protons), 4.16
(quartet, \( J = 7 \) Hz, 2H, \(-\text{OCH}_2\text{CH}_3\)), and 1.03-2.43 [complex multiplet
including triplet at 1.22 (\( J = 7 \) Hz), 19H, ring methylene protons
and \(-\text{OCH}_2\text{CH}_3\)].

A perchlorate salt was prepared by the addition of an ethanolic
solution of 60% aqueous perchloric acid to an ethereal solution of
the imino ether. The perchlorate was recrystallized three times from
ethanol-ether, mp 145-147°.

**Anal.** Calcd for \( \text{C}_{15}\text{H}_{24}\text{ClNO}_5 \): C, 53.97; H, 7.25; N, 4.20.

Found: C, 53.72; H, 7.40; N, 4.20.

14-Ethoxy-13-azabicyclo[6.4.2]tetradeca-8,10,12,13-tetraene (118).

A mixture of 1.73 g (7.43 mmoles) of azetine 115b, 1.46 g (8.2 mmoles)
of \( \text{N-bromosuccinimide} \), and a trace of benzoyl peroxide in 40 ml of
carbon tetrachloride was refluxed under a nitrogen atmosphere for
4 hr and allowed to cool to room temperature. The succinimide was
removed by filtration, and the residual oil was dissolved in 50 ml
of tetrahydrofuran. The solution was cooled to 0°, and 2.46 g (0.022
mole) of potassium \( t \)-butoxide was added in one portion. The reaction
mixture was stirred for 2 hr under nitrogen at 0°. Ether and water
were added, and the organic layer was separated, washed thoroughly
with water, and filtered through magnesium sulfate. The solvent was
removed, and the residual oil was vacuum distilled in a short-path
distillation apparatus to yield 0.50 g (2.16 mmoles, 29%) of a yellow
oil, bp 106-110° (0.2 mm). The distillate was eluted through a short column of Woelm basic alumina (activity I) with hexane. Redistillation of the eluent gave a pale yellow oil which was submitted for analysis: $\lambda_{max}^{neat}$ 5.98, 6.06 μ; $\lambda_{max}^{isooctane}$ 292 (e 580), 278 (e 570), 270 (e 560) μ; $\lambda_{max}^{95% \text{ EtOH}}$ 287 (e 540), 279 (e 550), 271 (e 560) μ; $\delta_{\text{TMS}}^{CDCl_3}$ 5.87 (broadened singlet with fine splitting, 3H, vinyl protons), 5.03 (broadened singlet with fine splitting, 1H, vinyl proton), 4.30 (quartet, J = 7 Hz, 2H, -OCH$_2$CH$_3$), and 1.05-2.94 [multiplet including triplet at 1.33 (J = 7 Hz), 15H, ring methylene protons and -OCH$_2$CH$_3$]; Calcd m/e 231.1623; Observed m/e 231.1623.

**Anal.** Calcd for C$_{15}$H$_{21}$NO: C, 77.88; H, 9.15; N, 6.05. Found: C, 77.24; H, 9.05; N, 5.06.

12-0xo-11-aza[4,4,2]propella-3,8-diene (120). To 35.0 g (0.264 mole) of 1,4,5,8-tetrahydronaphthalene (21) was added dropwise 36.5 g (0.258 mole) of chlorosulfonyl isocyanate under a nitrogen atmosphere. The resulting oil was stirred magnetically for 1 hr. Refrigeration produced crystalline N-(chlorosulfonyl) β-lactam which was added in small portions to a 50% aqueous acetone solution maintained at neutrality by the dropwise addition of 4N sodium hydroxide solution. The reaction mixture was extracted with three portions of ether, and the combined extracts were washed with water and dried over magnesium sulfate. The solvent was removed to give 17.8 g (0.102 mole, 39%) of crude β-lactam 120, mp 102-107°. An analytical sample, mp 111-112°, was obtained after three recrystallizations of the crude product from benzene-hexane; $\lambda_{max}^{CHCl_3}$ 5.72 μ; $\delta_{\text{TMS}}^{CDCl_3}$ 6.47 (broad singlet,
1H, N-H), 5.85 (multiplet, 4H, vinyl protons), and 1.62-2.68 (complex multiplet, 8H, allylic methylene protons).

Anal. Calcd for C_{11}H_{13}NO: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.39; H, 7.50; N, 7.98.

Hydrogenation of 12-Oxo-11-aza[4.4.2]propella-3,8-diene (91). A solution of 0.0458 g (0.261 mmole) of β-lactam 120 in 15 ml of ethyl acetate was hydrogenated at atmospheric pressure. Two equivalents of hydrogen were absorbed. After filtration of the catalyst, the solvent was removed leaving 0.045 g (0.251 mmole, 96%) of crude oily 12-oxo-11-aza[4.4.2]propellane whose ir and nmr spectra were identical with those of an authentic sample. One recrystallization of this material from hexane gave white crystalline β-lactam 91, mp 51-53°.

12-Ethoxy-11-aza[4.4.2]propella-3,8,11-triene (121). To a mechanically stirred solution of 15.6 g (0.109 mole) of boron trifluoride etherate in 50 ml of ether was added a solution of 7.65 g (0.083 mole) of epichlorohydrin in 20 ml of ether at such a rate as to maintain reflux of the ether. The reaction mixture was stirred for 2 hr. The solvent was decanted, and the triethyloxonium fluoroborate was washed thoroughly with ether and dissolved in 50 ml of methylene chloride. The triethyloxonium fluoroborate solution was cooled to ~10° and a solution of 13.8 g (0.079 mole) of β-lactam 120 in 30 ml of methylene chloride was added rapidly. The reaction mixture was allowed to stir at ambient temperature for 3 hr, and 19 ml of 50% potassium carbonate solution was added dropwise. Stirring was
continued for 4 hr, and the mixture was filtered through magnesium sulfate. The solvent was removed, and the residual oil was vacuum distilled in a short-path distillation apparatus. The yield of colorless oil, bp 65-66° (0.2 mm) was 8.5 g (0.042 mole, 53%); 
\[ \text{neat } \lambda_{\text{max}} 6.14 \mu \text{; } ^{1} \text{H} \text{NMR } \delta_{\text{TMS}} 5.72 \text{ (multiplet, } 4\text{H, vinyl protons)}, 4.13 \text{ (quartet, } J = 7 \text{ Hz, } 2\text{H, } -\text{OCH}_2\text{CH}_3)\text{, } 1.67-2.67 \text{ (complex multiplet, } 8\text{H, allylic methylene protons)}, \text{ and } 1.27 \text{ (triplet, } J = 7 \text{ Hz, } 3\text{H, } -\text{OCH}_2\text{CH}_3)\].

Addition of an ethanolic solution of 60% aqueous perchloric acid to an ethereal solution of imino ether 121 resulted in the formation of a viscous oil which crystallized upon scratching, mp 127-129°. An analytical sample, mp 129-131°, was obtained after two recrystallizations of this material from ethanol-ether.

Anal. Calcd for C_{13}H_{18}CINO_4; C, 51.41; H, 5.97; N, 4.61.
Found: C, 51.39; H, 6.08; N, 4.46.

Attempted Preparation of 12-Ethoxy-11-aza[4,4,2,4,7,9,11]-pentaene (119). A mixture of 2.89 g (14.3 mmoles) of imino ether 121, 5.35 g (30 mmoles) of N-bromosuccinimide, and a trace of benzoyl peroxide in 50 ml of carbon tetrachloride was refluxed for 1 hr under a nitrogen atmosphere. After removal of the succinimide by filtration, the solvent was evaporated, and the residual oil was dissolved in 50 ml of tetrahydrofuran. This solution was added dropwise, under a nitrogen atmosphere, to a magnetically stirred slurry of 4.82 g (42.9 mmoles) of potassium tert-butoxide in 50 ml of tetrahydrofuran at -50°. The reaction mixture was allowed to stir at -20° for 2 hr. Ether and ice cold water were added cautiously, not allowing the temperature of the reaction mixture to exceed 0°. The organic layer
was separated, washed with ice water and dried over magnesium sulfate at -20°. The solvent was removed. Vapor phase chromatography indicated the presence of naphthalene and a number of less volatile products. The nmr spectrum confirmed the presence of naphthalene. Column chromatography on Woelm basic alumina (activity 1) with petroleum ether gave 0.40 g (3.12 mmoles, 22%) of naphthalene. Continued elution with more polar solvents gave only dark viscous oils which were not further characterized.

Cyclohexene-cis-1,2-dicarboxylic Anhydride (131). The anhydride was prepared according to the procedure of Bailey and Amstutz.

$\Delta^2$-Octalin-9,10-dicarboxylic Anhydride (132). The anhydride was prepared according to the procedure of Alder and Backendorf.

cis-9,10-Bis(hydroxymethyl)-$\Delta^2$-octalin (133). To a mechanically stirred slurry of 19 g (0.50 mole) of lithium aluminum hydride in 250 ml of tetrahydrofuran was added dropwise a solution of 51.0 g (0.247 mole) of anhydride in 500 ml of tetrahydrofuran. The reaction mixture was refluxed for 12 hr, and a basic work-up was carried out. The aluminum salts were removed by filtration, and the filtrate was concentrated. Recrystallization of the crude diol from benzene gave 32.6 g (0.163 mole, 66%) of white crystalline diol, mp 145-147°: $\lambda^{\text{max}}_{\text{CHCl}_3}$ 2.80 and 3.01 μ; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.61 (multiplet, 2H, vinyl protons), 3.45, 3.64, 3.68 and 3.87 (maxima of AB quartet, $J = 12$ Hz, 4H, -CH$_2$OH), 2.91 (singlet, 2H, -CH$_2$OH), 2.08 (doublet, $J = 1$ Hz, 4H, allylic protons), and 1.53 (singlet, 8H, ring methylene protons).
cis-9,10-Bis(mesyloxymethyl)-Δ²-octalin (134). To an ice cold magnetically stirred solution of 27.7 g (0.14 mole) of diol 133 in 800 ml of pyridine was added dropwise 51.2 g (0.353 mole) of methane-sulfonyl chloride while keeping the temperature of the reaction mixture below 5°. The reaction mixture was magnetically stirred at 0-10° for 2 hr and poured into ice water. The yield of crude mesylate was 45.5 g (0.129 mole, 92%). An analytical sample, mp 124.5-125.5°, was obtained after three recrystallizations from methanol: \( \lambda_{\text{max}} \text{CHCl}_3 \) 7.40, 7.52, and 8.55 μ; \( \delta_{\text{TMS}} \text{CDCl}_3 \) 5.52 (broadened singlet, 2H, vinyl protons), 3.97, 4.12, 4.18, 4.33 (maxima of AB quartet, \( J = 9 \text{ Hz} \), 4H, -CH₂OSO₂⁻), 2.99 (singlet, 6H, -SO₂CH₃), 2.11 (broadened singlet, 4H, allylic protons), and 1.56 (singlet, 8H, ring methylene protons).

12-Thia[4.4.3]propell-3-ene (135). A mechanically stirred slurry of 41 g (0.17 mole) of sodium sulfide nonahydrate (recrystallized from ethanol) in 100 ml of hexamethylphosphoramide was heated under vacuum (~5 mm) until the temperature of the mixture reached 120°. Approximately 20 ml of distillate was collected and discarded. The sodium sulfide slurry was cooled to ~40°, and 20.0 g (0.057 mole) of dimesylate 134 was added in one portion. The reaction mixture was stirred under nitrogen at 120° for 24 hr. The reaction mixture was
cooled to room temperature, and 400 ml of water was added. The mixture was extracted with three 200-ml portions of ether, and the combined extracts were washed with water, dried over magnesium sulfate, and concentrated. The residual oil was vacuum distilled in a short-path distillation apparatus to give 8.5 g (0.044 mole, 77%) of a colorless oil which crystallized in the receiver, mp 78-85°. An analytical sample, mp 85-87°, was obtained after two recrystallizations from methanol and sublimation (80°, 15 mm): \( \lambda_{\text{max}} ^{\text{CHCl}_3} 3.46, 6.00, 6.89, \) and 7.02 \( \mu \); \( \delta_{\text{NMR}} ^{\text{CDCl}_3} 5.52 \) (multiplet, 2H, vinyl protons), 2.96, 2.78, 2.72 and 2.54 (maxima of AB quartet, \( J = 10 \) Hz, 4H, \(-\text{CH}_2\text{S}-\)), 2.05 (broadened singlet, 4H, allylic protons), and 1.52 (broadened singlet, 8H, ring methylene protons).

**Anal.** Calcd for C_{12}H_{16}S: C, 74.16; H, 9.33. Found: C, 74.12; H, 9.28.

**12-Thia[4.4.3]propell-3-ene 12,12-Dioxide (135a).** To an ice cold, magnetically stirred solution of 2.52 g (0.0119 mole) of sulfide 135 in 20 ml of ether was added dropwise a standardized ethereal solution containing 0.024 mole of monoperphthalic acid. The reaction mixture was magnetically stirred at ambient temperature for 2 hr. The phthalic acid was removed by filtration, and the ethereal filtrate was washed with 0.5N sodium hydroxide solution, water, and saturated sodium chloride solution. The ether was removed to give 2.6 g (0.0115 mole, 97%) of white, crystalline sulfone. An analytical sample, mp 138-140°, was obtained after two recrystallizations from hexane;
CHCl₃ 6.02, 7.69, and 8.96 μ; δ<sub>TMS</sub> 5.65 (triplet, J = ~1 Hz, 2H, vinyl protons), 3.41, 3.19, 3.10 and 2.88 (maxima of AB quartet, J = 13 Hz, 2H, -CH₂SO₂⁻), 2.24 (doublet, J = 1 Hz, 4H, allylic methylene protons), and 1.62 (singlet, 8H, ring methylene protons).

**Anal. Calcd for C₁₂H₁₈O₂S: C, 63.68; H, 8.01; S, 14.17. Found: C, 63.70; H, 8.03; S, 14.05.**

**11-Chloro-12-thia[4.4.3]propell-3-ene 12,12-Dioxide (136).** A mixture of 11.6 g (0.060 mole) of sulfide 135, 8.0 g (0.06 mole) of N-chlorosuccinimide and 150 ml of carbon tetrachloride was refluxed under N₂ for 1.5 hr. The reaction mixture was cooled, and the succinimide was removed by filtration. The carbon tetrachloride was evaporated, and the residual oil was dissolved in 50 ml of ether and cooled to 0°. To this magnetically stirred solution was added dropwise a standardized ethereal solution containing 0.12 mole of monoperphthalic acid. The reaction mixture was allowed to stir at ambient temperature for 6 hr. The phthalic acid was removed by filtration, and the filtrate was washed with two 100-ml portions of 1N sodium hydroxide solution, two 100-ml portions of water, and one 30-ml portion of saturated sodium chloride solution. The ethereal solution was dried over magnesium sulfate, and the solvent was removed to give 15 g (0.058 mole, 97%) of crude crystalline α-chloro sulfone mixture 136, mp 105-120°: λ<sub>max</sub> CHCl₃ 7.59 and 8.88 μ; δ<sub>TMS</sub> 5.61 (multiplet, 2H, vinyl protons), 4.95, 5.37 (singlets, total of 1H, >CHCl), and 1.15-3.78 (complex multiplet including broadened singlet at 1.58, 14H, methylene protons). Three recrystallizations from petroleum ether,
bp 60-110\(^\circ\), gave an analytical sample, mp 127-134\(^\circ\).

**Anal.** Calcd for C\(_{12}\)H\(_{17}\)ClO\(_2\)S: C, 55.26; H, 6.57; S, 12.30.

Found: C, 55.50; H, 6.60; S, 12.18.

[4.4.2]Propella-3,11-diene (129). To an ice cold, mechanically stirred solution of 7.0 g (0.027 mole) of \(\alpha\)-chloro sulfone \(\text{136}\) in 100 ml of tetrahydrofuran was added in one portion 12.1 g (0.108 mole) of potassium tert-butoxide. The reaction mixture was stirred at ambient temperature for 12 hr. Water was added, and most of the tetrahydrofuran was removed. Ether was added to the reaction mixture, and the organic layer was separated, washed with water, and dried over magnesium sulfate. The solvent was removed, and the crude product was passed through 200 g of Woelm neutral Alumina (activity I) with 500 ml of \(\%\) ether-hexane. Concentration and vacuum distillation gave 2.4 g (0.015 mole, 56\%) of a colorless oil, bp 100-102\(^\circ\) (30 mm):

\(\lambda_{\text{max}}\) 3.33, 3.46, 13.06, and 14.78 \(\mu\); \(\delta_{\text{TMS}}\) 5.90 (singlet, 2H, cyclobutene protons), 5.75 (multiplet, 2H, vinyl protons), 1.87 (multiplet, 4H, allylic protons), and 1.57 (broadened singlet, 8H, methylene ring protons).

**Anal.** Calcd for C\(_{12}\)H\(_{18}\): C, 89.94; H, 10.06. Found: C, 90.01; H, 10.07.

[4.4.2]Propellane (137). Hydrogenation of [4.4.2]Propella-3,11-diene (129). A magnetically stirred solution of 0.276 g (1.72 mmoles) of \(\text{129}\) in 15 ml of methanol was hydrogenated at atmospheric pressure until the uptake of hydrogen ceased. Two equivalents of hydrogen were absorbed. The catalyst was removed by filtration, and the solvent was
removed to give a homogeneous oil which was purified by preparative vpc (5'/1/4") 10% SF 96 on 60/80 Chrom. G. The yield of 137 was 0.180 g (1.10 mmoles, 64%): \( \frac{n}{D} \) 1.4930; \( \lambda_{\text{max}}^{\text{CHCl}_3} \) 2970, 2930, 2865 and 2845 cm\(^{-1}\) (Perkin Elmer Model 357 Spectrometer); \( \delta_{\text{TMS}}^{\text{CDCl}_3} \) 1.64 (singlet, 4H, cyclobutane methylene protons) and 1.39 (singlet, 16H, cyclohexane methylene protons); [lit \( \frac{n}{D} \) 1.4958; \( \lambda_{\text{max}}^{\text{CHCl}_3} \) 2980, 2950, 2880 and 2850 cm\(^{-1}\); \( \delta_{\text{TMS}}^{\text{CCl}_4} \) 1.63 (singlet, 4H) and 1.37 (singlet, 16H).

\[ \text{[4.4.2]} \text{Propella-2,4,11-triene (128).} \] A magnetically stirred mixture of 0.60 g (3.74 mmoles) of olefin 129, 0.8 g (4.50 mmoles) of N-bromosuccinimide, and a trace of benzoyl peroxide in 50 ml of carbon tetrachloride was refluxed under nitrogen for 3 hr. The reaction mixture was cooled to room temperature, and the succinimide was removed by filtration. The carbon tetrachloride was evaporated and the residual oil was dissolved in 50 ml of tetrahydrofuran and cooled to 0\(^0\). To the magnetically stirred reaction mixture was added in one portion 1.2 g (11.25 mmoles) of potassium \( \text{t-} \) butoxide. The reaction mixture was magnetically stirred under nitrogen at ambient temperature for 20 hr. Water and ether were added, and the organic layer was separated, washed with water, and dried by filtration through magnesium sulfate. Concentration of the filtrate resulted in an oil composed of two major products. Preparative vapor phase chromatography (10'/1/4", 10% Carbowax on 60/80 Chrom. W) at 100\(^0\) gave 180 mg (1.12 mmoles, 30%) of starting diene 129 and 68 mg (0.43 mmoles, 16%) of a new liquid hydrocarbon 128: \( \lambda_{\text{max}}^{\text{neat}} \) 3.34, 3.46, 3.54, 13.06, and 14.40 \( \mu \); \( \delta_{\text{TMS}}^{\text{CDCl}_3} \) 6.96 (singlet, 2H, cyclobutene protons), 5.64 (center of \( A_2B_2 \))
pattern, 4H, cyclohexadiene protons), and 1.54 (broadened singlet, 8H, ring methylene protons).

**Anal.** Calcd for C_{12}H_{14}: C, 91.08; H, 8.92. Found: C, 91.20; H, 8.85.

**Hydrogenation of [4.4.2]Propella-2,4,11-triene (128).** A solution of 37 mg (0.234 mmole) of triene 128 in 15 ml of ethyl acetate was hydrogenated at atmospheric pressure over 10% palladium on carbon. Three equivalents of hydrogen were absorbed. The catalyst was removed by filtration, and the solvent was evaporated to give 26 mg (0.158 mmole, 68%) of an oil, homogeneous by vpc, which exhibited the characteristic ir and nmr spectra of propellane 137.

**Irradiation of [4.4.4]propella-2,4,11-triene (128).** A solution of 70 mg (4.4 mmoles) of propellatriene 128 in 10 ml of ether was irradiated under nitrogen utilizing a bank of nine GE 615T8 (30 w Germicidal, 2537 Å) lamps. After 1.5 hr, vpc analysis of the reaction mixture indicated complete loss of starting material and formation of a photoproduct with the same retention time as tetralin. The solvent was removed and the residue was purified by preparative vpc (10°/1/4°, 10% Carbowax on 80/80 Chrom. W) at 110°. The yield of tetralin was 35 mg (2.7 mmoles, 61%).

**Cycloaddition of [4.4.2]Propella-2,4,11-triene (128) and N-Phenylmaleimide.** A magnetically stirred solution of 46 mg (0.29 mmole) of triene 128 and 41 mg (0.24 mmole) of N-phenylmaleimide in 10 ml of benzene was refluxed under nitrogen for six hr. The solvent
was removed to give 80 mg (0.24 mmole, 100%) of a pale yellow solid, mp 193-195°. Recrystallization from cyclohexane gave fluffy white crystals, mp 195-197°: \( \delta_{\text{max}}^{\text{CHCl}_3} \) 5.64 and 5.86 \( \mu \); \( \delta_{\text{TMS}}^{\text{CDCl}_3} \) 7.06-7.55 (multiplet, 5H, aromatic protons), 6.07 (triplet, J = 4 Hz, 2H, vinyl protons), 5.77 (singlet, 2H, cyclobutene vinyl protons), 3.20 (doublet, J = 2 Hz, 2H, vinyl protons), and 1.21-1.89 (multiplet, 8H, ring methylene protons).

**Anal.** Calcd for C_{22}H_{21}NO_2: C, 79.73; H, 6.39; N, 4.23. Found: C, 79.43, 79.25; H, 7.15, 6.47; N, 4.03.

\[ ^{2,6}\Delta \text{Hexalin-cis-9,10-dicarboxylic Anhydride (144)} \]

Anhydride \[ ^{2,6}\Delta \text{Hexalin-cis-9,10-dicarboxylic Anhydride (144)} \] was prepared according to the procedure of Scott.

\[ ^{2,6}\Delta \text{cis-9,10-Bis(hydroxymethyl)-Hexalin (145)} \] and \[ ^{2,6}\Delta \text{cis-9,10-Bis(mesyloxyxymethyl)-Hexalin (146)} \]

Diol \[ ^{2,6}\Delta \text{cis-9,10-Bis(hydroxymethyl)-Hexalin (145)} \] and dimesylate \[ ^{2,6}\Delta \text{cis-9,10-Bis(mesyloxyxymethyl)-Hexalin (146)} \] were prepared according to the procedure of Snatzke and Zanati.

\[ ^{2,6}\Delta \text{12-Thia[4,4,3]propella-3,8-diene (147)} \]

A slurry of 45 g (0.19 mole) of sodium sulfide nonahydrate in 130 ml of hexamethylphosphoramide was heated in vacuo (20 mm) until the temperature of the mixture reached 105° (20 ml of distillate were collected and discarded). The sodium sulfide solution was cooled to 50°, and 36 g (0.103 mole) of dimesylate \[ ^{2,6}\Delta \text{146} \] was added. The mechanically stirred reaction mixture was heated at \( \sim 115° \) for 24 hr. The reaction mixture was cooled to room temperature, and 500 ml of water was added in one portion. The resulting dark solution was extracted with three 200-ml portions of ether. The combined extracts were washed with cold water.
and dried over magnesium sulfate. The solvent was removed, and the residual oil was vacuum distilled to give 17.5 g (0.091 mole, 88%) of sulfide, bp 83-86° (0.15 mm), which crystallized in the receiver, mp 48-51°. After four recrystallizations from methanol, a pure sample was obtained, mp 55.5-56.5°: \( \lambda_{\text{max}}^{\text{CHCl}_3} 3.53 \) and 6.04 \( \mu \); \( \delta^{\text{CDCl}_3}_{\text{TMS}} 5.45 \) (multiplet, 4H, vinyl protons), 2.76 (singlet, 4H, \(-\text{CH}_2\text{S}^-\)) and 2.08 (AB portion of ABX system, 8H, allylic protons).

**12-Thia[4.4.3]propella-3,8-diene 12,12-Dioxide (164)**. A standardized ethereal solution of monoperphthalic acid (0.078 mole) was added dropwise to an ice cold magnetically stirred solution of 7.51 g (0.039 mole) of sulfide 147. The reaction mixture was allowed to warm to room temperature over a 2-hr period. After filtration of the phthalic acid, the ethereal filtrate was washed with 0.5N sodium hydroxide, water, and saturated sodium chloride solution. The extract was dried over magnesium sulfate, and the solvent was removed to give 7.5 g (0.331 mole, 85%) of crude sulfone 164. Three recrystallizations from hexane gave an analytical sample, mp 115.5-116.5°: \( \lambda_{\text{max}}^{\text{CHCl}_3} 7.70 \) and 8.92 \( \mu \); \( \delta^{\text{CDCl}_3}_{\text{TMS}} 5.60 \) (multiplet, 4H, vinyl protons), 3.15 (singlet, 4H, \(-\text{CH}_2\text{SO}_2^-\)), and 2.33 (AB portion of ABX system, 8H, allylic protons).

**Anal.** Calcd for C_{12}H_{16}O_8S: C, 64.25; H, 7.19; S, 14.29. Found: C, 64.49; H, 7.25; S, 14.20.

**11-Chloro-12-thia[4.4.3]propella-3,8-diene 12,12-Dioxide (148)** and Trideuterio Analog 159. A magnetically stirred mixture of 14.1 g
(0.0733 mole) of sulfide. 9.8 g (0.0733 mole) of N-chlorosuccinimide and 150 ml of carbon tetrachloride was refluxed under nitrogen for 1.5 hr. The reaction mixture was cooled to room temperature, and the succinimide was removed by filtration. The filtrate was concentrated and the residual oil was dissolved in 50 ml of ether and cooled to 0°. To this magnetically stirred solution was added dropwise a standardized ethereal solution of monoperphthalic acid (0.147 mole). The ice cold reaction mixture was allowed to warm and stir at ambient temperature for 6 hr. The phthalic acid was removed by filtration, and the filtrate was washed twice with 100-ml portions of 1N sodium hydroxide solution, twice with 50-ml portions of water and once with 30 ml of saturated sodium chloride solution. The ethereal solution was dried over magnesium sulfate and concentrated to give 15.0 g (0.058 mole, 79%) of crude α-chloro sulfone. An analytical sample was obtained after five recrystallizations from ether at -20°, mp 111-113°: CHCl₃, λₘₐₓ 7.60 and 8.90; δCDCl₃ 5.59 (multiplet, 4H, vinyl protons), 5.05 (singlet, 1H, -CHClSO₂⁻), 2.89, 3.11, 3.21 and 3.42 (maxima of AB quartet, J = 13 Hz, 2H, -CH₂SO₂⁻) and 1.59-2.82 (complex multiplet, 8H, allylic protons).

Anal. Calcd for C₁₂H₁₅CIO₂S: C, 33.70; H, 3.72; Cl, 13.70. Found: C, 35.70; H, 3.72; Cl, 13.90.

To a magnetically stirred solution of 1.0 g (3.86 mmoles) of α-chloro sulfone in 30 ml of dioxane was added 10 ml of 10% sodium deuteroxide. The reaction mixture was refluxed for 20 hr. The reaction mixture was cooled to room temperature, and 50 ml of benzene
was added. The organic layer was separated and washed with four 2-ml portions of deuterium oxide. The solvent was removed, and the crystalline residue was recycled utilizing 30 ml of dioxane and 6 ml of 10% sodium deuterioxide in deuterium oxide. After a work-up identical to that above, the resulting benzene solution was dried over magnesium sulfate and evaporated to give 0.79 g (3.02 mmoles, 78%) of trideuterio-\(\alpha\)-chloro sulfone 159. The nmr spectrum indicated complete exchange of protons \(\alpha\) to the sulfone. After three recrystallizations from benzene-hexane, an analytical sample was obtained, mp 106-108\(^\circ\).

**Anal.** Calcd for \(C_{12}H_{12}D_3ClO_2S\): D (atom % excess), 20.0; Found: D (atom % excess), 19.45.

[4,4,3]Propella-3,8,11-triene (143) from \(\alpha\)-Chloro sulfone 148.

To an ice cold, magnetically stirred solution of 4.64 g (0.0179 mole) of \(\alpha\)-chloro sulfone 148 in 50 ml of tetrahydrofuran was added in one portion 6.0 g (0.0537 mole) of potassium t-butoxide. The reaction mixture was magnetically stirred for 5 hr at 0\(^\circ\) under a nitrogen atmosphere. A mixture of 40 ml of water and 30 ml of ether was added to the reaction mixture. The organic layer was separated, washed with two 20-ml portions of water, and filtered through magnesium sulfate. Concentration of the filtrate and subsequent short-path distillation of the residue gave 1.51 g (0.0095 mole, 53%) of a colorless oil, bp 75\(^\circ\) (5 mm): \(\lambda_{\text{max}}\) neat 3.33, 3.48, 3.58, and 6.08 \(\mu\); \(\delta_{\text{TMS}}^{\text{CDCl}_3}\) ~5.75 (multiplet, 6H, vinyl protons) and 2.02 (multiplet, 8H, allylic protons).
Anal. Calcd for C_{12}H_{14}: C, 91.08; H, 8.92. Found: C, 90.76; H, 8.93.

cis-9,10-Bis(carbomethoxy)-Δ^{2,6}_6-hexalin (160). The diester 160 was prepared according to the procedure of Scott.

Tricyclo[4.4.2.0^{1,6}]-11-one-12-ol-dodeca-3,8-diene (161). The acyloin 161 was prepared according to the procedure of Bloomfield and Irelan.

[4.4.2]Propella-3,8-diene-10,11-diol (162) and Thionocarbonate Ester 163. To a stirred mixture of 0.76 g (0.02 mole) of lithium aluminum hydride in 50 ml of ether was added dropwise a solution of 2.13 g (0.011 mole) of acyloin 161 in 50 ml of ether. The reaction mixture was refluxed for 1 hr and allowed to stir overnight. After a basic work-up, the resulting ethereal solution was decanted from the magnesium salts and filtered through magnesium sulfate. Concentration of the filtrate gave 1.8 g (0.094 mole, 86%) of a white solid, mp 66-70°. The crude diol was not purified but was converted to thionocarbonate 163.

A magnetically stirred solution of 6.0 g (0.031 mole) of diol 162, 6.1 g (0.034 mole) of thionocarbonylbisimidazole and 150 ml of toluene was refluxed under a nitrogen atmosphere for 40 min. The solvent was removed, and the residue was triturated with methanol. Filtration gave 3.45 g (0.015 mole, 48%) of brown crystals. Three recrystallizations from methanol gave an analytical sample, mp 122.5-123.5°: \( \lambda_{max} \) CHCl_3 7.68, 7.76 and 9.99 μ; \( \delta_{CDCl_3}^{TMS} \) 5.97 (multiplet, 4H,
vinyl protons), 4.62 (singlet, 2H, >CH0-), and 1.38-2.65 (complex multiplet, 8H, allylic protons).

**Anal. Calcd for C13H14O2S: C, 66.64; H, 6.02; S, 13.69. Found:**
C, 66.24; H, 6.03; S, 13.53.

**[4.4.2]Propella-3,8,ll-triene (143) from Thionocarbonate Ester**

_163_. A magnetically stirred solution of 6.0 g (0.026 mole) of thionocarbonate _163_ and 45 ml of trimethylphosphite was refluxed for 96 hr under a nitrogen atmosphere. After cooling in an ice bath, the reaction mixture was diluted with 500 ml of ether, and 200 ml of 2N sodium hydroxide was added dropwise. The mixture was allowed to warm to room temperature with continued stirring over a 6-hr period. The organic layer was separated, and the aqueous layer was extracted twice with ether. The combined extracts were washed with water and dried over magnesium sulfate. The solvent was removed, and the residual oil was distilled in a short-path distillation apparatus. There was obtained 2.2 g (0.014 mole, 54%) of triene _143_ as a colorless oil, bp 70° (5 mm). The hydrocarbon was identical to the material obtained via base-induced rearrangement of α-chloro sulfone _148_.

**Hydrogenation of [4.4.2]Propella-3,8,ll-triene 143.** A magnetically stirred solution of 0.131 g (0.83 mmole) of _143_ in 15 ml of methanol was hydrogenated over 10% palladium on carbon at atmospheric pressure until the uptake of hydrogen ceased. Three equivalents of hydrogen were absorbed. The catalyst was removed by filtration and the solvent was evaporated. Purification of the crude hydrogenation product by
preparative vpc (5°/1°/4°' 10% SF 96 on 60/80 Chrom. G) gave 0.090 g (0.55 mmole, 66%) of propellane 137 which was identified by its characteristic ir and nmr spectra.

12-Thia[4,4,3]propella-2,4,7,9-tetraene (166). To a magnetically stirred slurry of 2.0 g (0.053 mole) of lithium aluminum hydride in 150 ml of ether was added in one portion 5.84 g (0.0265 mole) of sulfone 165. The reaction mixture was refluxed for 6 hr. After a basic work-up, the solvent was removed to give 5.0 g (0.0265 mole, 100%) of crude sulfide 166: $\delta^{\text{CDCl}_3}$ 5.31-6.14 (A$_2$B$_2$ pattern, 8H, vinyl protons), and 3.13 (singlet, 4H, -CH$_2$S-) [lit $\delta^{\text{CCL}_4}$ 5.40-6.04 (A$_2$B$_2$ pattern, 8H, vinyl protons), and 3.08 (singlet, 4H, -CH$_2$S-)]. The sulfide was not purified but was converted directly to $\alpha$-chloro sulfone 167.

12-Thia[4,4,3]propella-2,4,7,9-tetraene 12,12-Dioxide (165). A solution of 10.0 g (0.0624 mole) of bromine in 10 ml of methylene chloride was added dropwise to an ice cold magnetically stirred solution of 6.99 g (0.0312 mole) of sulfone 164 in 50 ml of methylene chloride. The reaction mixture was allowed to warm to room temperature with continued stirring over a 4-hr period. The solvent was removed, and the crude tetrabromo sulfone was added to a mixture of 13.5 g (0.25 mole) of sodium methoxide in 200 ml of tetrahydrofuran. The reaction mixture was refluxed for 6 hr under nitrogen and cooled to room temperature. Most of the tetrahydrofuran was evaporated, and 50 ml of ether was added. The ethereal mixture was washed with three
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100-ml portions of water, and the resulting ethereal solution was filtered through magnesium sulfate and concentrated. The resulting oily crystals were recrystallized from benzene to give 3.1 g (0.0141 mole, 45%) of colorless sulfone 165, mp 155-160°. Chromatography on silica gel followed by recrystallization from benzene gave an analytical sample, mp 160-162°: $\lambda_{max}^{CHCl_3}$ 7.67 and 8.95 μ; $\delta_{TMS}^{CDCl_3}$ 3.36 (singlet, 4H, -CH$_2$SO$_2$-), and 5.82 (center of A$_2$B$_2$ pattern, 8H, vinyl protons).

Anal. Calcd for C$_{12}$H$_{12}$O$_2$S: C, 65.42; H, 5.49; S, 14.56. Found: C, 65.53; H, 5.34; S, 14.27.

11-Chloro-12-thia[4.4.3]propella-2,4,7,9-tetraene 12,12-Dioxide (167). To a magnetically stirred solution of 5.0 g (0.0265 mole) of sulfide 166 in 50 ml of carbon tetrachloride was added in one portion 3.55 g (0.0265 mole) of N-chlorosuccinimide. The reaction mixture was refluxed for 1 hr under nitrogen and allowed to cool to room temperature. The succinimide was removed by filtration, and the solvent was evaporated. The residual oil was dissolved in 50 ml of ether, and the resulting solution was cooled to 0°. To this magnetically stirred solution was added dropwise an ethereal solution of monoperphthalic acid (0.053 mole). The reaction mixture was allowed to stir at ambient temperature for 4 hr, and the precipitated phthalic acid was removed by filtration. The filtrate was washed with two 50-ml portions of 0.5N sodium hydroxide, two 50-ml portions of water and one 30-ml portion of saturated sodium chloride solution. The ethereal solution was dried over magnesium sulfate, and the solvent was evaporated. Trituration of the oily crystals with cold
ether and subsequent filtration gave 2.9 g (0.011 mole, 42%) of crude α-chloro sulfone \( \text{167} \), mp 125-135°. Three recrystallizations from benzene gave an analytical sample, mp 151-153°: \( \lambda_{\text{max}}^{\text{CHCl}_3} 7.56 \text{ and } 8.93 \mu; \delta_{\text{TMS}}^{\text{CDCl}_3} 5.14-6.47 \) (complex multiplet including sharp singlet at 5.29, 9H, vinyl protons and -CHClSO\(_2\)-), and 3.67, 3.45, 3.42, 3.19 (maxima of AB quartet, \( J = 13 \text{ Hz}, 2H, -\text{CH}_2\text{SO}_2\)).

**Anal. Calcd for C\(_{12}\)H\(_{10}\)ClO\(_2\)S:** C, 56.58; H, 4.35; Cl, 13.92.

**Found:** C, 56.45; H, 4.35; Cl, 14.14.

\([4.4.2]\)Propella-2,4,7,9,11-pentaene (67). To a magnetically stirred ice cold solution of 1.09 g (4.30 mmoles) of α-chloro sulfone \( \text{167} \) in 125 ml of ether was added in one portion 2.5 g (22 mmoles) of potassium t-butoxide. The reaction mixture was stirred magnetically under nitrogen for 4 hr at ambient temperature. Water (40 ml) was added, and the organic layer was separated and washed with two more 40-ml portions of water and one 20-ml portion of saturated sodium chloride solution. The ethereal solution was dried over magnesium sulfate, and the solvent was evaporated to give a dark oil. Purification by preparative vpc (5'1/4/'10° SE 30 on 6°/8° Chrom. G) gave 0.091 g (0.59 mmoles, 14%) of a colorless oil: \( \lambda_{\text{max}}^{\text{neat}} 3.46, 8.22, 10.48, 13.12, 13.90 \mu; \delta_{\text{TMS}}^{\text{CDCl}_3} 5.68 \) (center of A\(_2\)B\(_2\) pattern) and 5.90 (singlet); Calcd m/e 154.0782, Observed m/e 154.0776.

**Anal. Calcd for C\(_{12}\)H\(_{10}\):** C, 93.46; H, 6.54. **Found:** C, 93.56; H, 6.71.

**Hydrogenation of \([4.4.2]\)Propella-2,4,7,9,11-pentaene (67).** A magnetically stirred solution of 23.8 mg (0.154 mmoles) of pentaene \( \text{67} \)
in 20 ml of methanol was hydrogenated over 10% palladium on carbon at atmospheric pressure until the uptake of hydrogen ceased. Five equivalents of hydrogen were absorbed. The catalyst was removed by filtration, and the filtrate was concentrated to give 18 mg (0.110 mmole, 71%) of [4.4.2]propellane (137) identified via its characteristic ir and nmr spectra.
TABLE 3

MASS SPECTRAL DATA OF SOME UNSATURATED HETEROCYCLIC AND CARBOCYCLIC PROPELLANES

<table>
<thead>
<tr>
<th>Compound</th>
<th>m/e (% relative abundance)</th>
</tr>
</thead>
<tbody>
<tr>
<td>83a</td>
<td>27(10), 29(10), 41(12), 79(14), 91(65), 92(53), 105(12), 117(10), 119(11), 120(100), 121(10).</td>
</tr>
<tr>
<td>76a</td>
<td>27(15), 29(14), 39(14), 91(21), 115(18), 117(84), 118(100), 119(10).</td>
</tr>
<tr>
<td>83b</td>
<td>27(23), 29(22), 39(26), 41(19), 51(10), 53(11), 54(11), 55(11), 65(10), 67(13), 77(20), 78(17), 79(24), 80(17), 91(100), 92(84), 93(17), 104(13), 105(25), 106(33), 119(32), 120(11), 132(10), 133(11), 134(100).</td>
</tr>
<tr>
<td>76b</td>
<td>26(12), 27(36), 29(39), 39(17), 41(16), 43(12), 51(15), 57(16), 77(17), 78(10), 79(12), 91(60), 92(10), 104(100), 105(14), 115(18), 117(18), 128(22), 129(15), 130(12), 131(38), 132(80), 133(11), 134(13), 136(27), 174(14), 178(10).</td>
</tr>
<tr>
<td>129</td>
<td>27(14), 39(25), 41(19), 51(15), 65(13), 77(21), 78(24), 79(18), 91(100), 92(26), 105(10), 104(46), 105(24), 115(14), 117(70), 118(32), 119(17), 131(32), 132(53), 145(15), 160(14).</td>
</tr>
<tr>
<td>128</td>
<td>39(17), 51(16), 65(12), 65(11), 77(15), 78(11), 91(35), 102(44), 115(60), 116(19), 117(25), 127(13), 128(35), 129(100), 130(65), 131(17), 143(22), 157(23), 158(48).</td>
</tr>
<tr>
<td>143</td>
<td>27(17), 39(31), 41(15), 43(12), 51(26), 54(11), 65(15), 67(17), 77(35), 78(48), 79(27), 80(22), 91(80), 92(17), 103(25), 104(100), 105(12), 115(55), 116(27), 117(62), 127(11), 128(47), 129(72), 130(65), 131(15), 143(34), 158(23).</td>
</tr>
<tr>
<td>67</td>
<td>51(22), 65(15), 64(11), 76(13), 102(12), 127(12), 128(85), 129(12), 151(11), 152(35), 153(100), 154(45).</td>
</tr>
</tbody>
</table>
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