THE CYCLOHEPTATRIENE-NORCARADIENE EQUILIBRIUM
THE CYCLOHEPTATRIENE-NORCARADIENE EQUILIBRIUM

By

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ABSTRACT

The effect of a C-7 substituent on the position of the cycloheptatriene/norcaradiene equilibrium has been investigated. For this purpose a series of monosubstituted cycloheptatrienes was prepared in which the C-7 substituent was a carbonium ion grouping. From the spectral properties of these systems, it has been concluded that proportion of the norcaradiene valence tautomer present increases as the electron withdrawing ability of the carbonium ion substituent is enhanced.

From a comparison of the pmr spectra of 7-norcaradienylmethyl cations with suitable model systems it is suggested that these norcaradienes are aromatic and that they support an induced diamagnetic ring current when in a magnetic field. It would appear that this type of cyclic delocalization is enhanced by the presence of an electron deficient substituent at C-7 of a norcaradiene and possible reasons for this are discussed.

The 7-norcaradienylmethyl cations underwent a thermal isomerization to give benzenoid materials at relatively low temperatures. A mechanism for this rearrangement has been proposed and the implication of these results to the general pathways involved in the rearrangements of the C$_8$H$_9^+$ family of cations discussed.

Several synthetic routes to 9-substituted-3,4-homotropylidenes were investigated. A number of new compounds were isolated and a new synthetic approach to this class of compounds is suggested.
Diamagnetic susceptibility exaltations of a series of substituted cycloheptatrienes were determined and used as a criterion of aromaticity. It was concluded that cycloheptatrienes are best regarded as homoaromatic molecules. Moreover it would appear that the substantial diamagnetic susceptibility exaltations observed with these compounds are related to the bulk of a C-7 substituent. One neutral norcaradiene was examined by this technique and was found to be nonaromatic.
A M\^{e}me et M. Paul André
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CHAPTER I

INTRODUCTION

Cycloheptatriene is perhaps the most intensively studied member of the odd-numbered cyclic polyenes. Yet despite this, the structure of cycloheptatriene which was variously reported as 1 or 2, was not definitely established until fairly recently.\(^1\)

\[
\begin{align*}
\text{1} & \quad \text{2} \\
\end{align*}
\]

In 1885 Büchner and Curtius reported that the thermal decomposition of methyl diazoacetate in benzene led to a series of isomeric esters, consequently to become known as the "Büchner esters". They concluded that the mixture consisted of the methoxycarbonylcycloheptatrienes 2, 4, 5, and 7-methoxycarbonylbicyclo[4.1.0]hepta-2,4-diene, 6.\(^2\)

\[
\begin{align*}
\text{3} & \quad \text{4} & \quad \text{5} \\
\end{align*}
\]

\[
\begin{align*}
\text{6} & \quad \text{7} \\
\end{align*}
\]
While the evidence presented by Büchner and Curtius was not unambiguous, for a long time the structure of 6 was generally accepted. Indeed compounds of this type were called norcaradienes on the basis of the similarity of the basic ring system to that of the natural product carone, 7.

In 1957 Meerwein claimed to have prepared norcaradiene itself by the photolysis of diazomethane in benzene. 3 In contradiction to this report, Doering insisted that apart from a small amount of toluene, cycloheptatriene was the only product formed in this reaction. 4 On repeating Büchner's original experiments, Doering also suggested that the Büchner esters were all positionally isomeric cycloheptatrienes and that in particular, 6 was not a norcaradiene derivative but had the structure 8. 5

\[ \text{Chemical evidence was of little help in distinguishing between structures such as 1 and 2. For example, while oxidation of the carboxylic acid derived from 8 with potassium permanganate gave a cyclopropane-1,2,3-tricarboxylic acid, 2 8 was readily converted on heating to the three isomeric cycloheptatriene esters, 2, 4 and 5. 2 Similarly, while the addition of a dienophile to cycloheptatriene usually gives products derived from norcaradiene, 6 } \text{ eq.1, cycloheptatriene can be hydrogenated to give cycloheptane, eq. 2. Under conditions where} \]
hydrogenolysis of the cyclopropane ring should be minimized (Rh catalyst),
cy cloheptatriene has been shown to give less than 0.005% of norcarane.\textsuperscript{7}

\[
\begin{align*}
\text{R} & + \text{Ph} \\
\rightarrow & \\
\text{R} & + \text{Ph} \\
\end{align*}
\]

This duality of the chemical reactions of these systems has been rationalized by two hypotheses:

a. Cycloheptatriene can be regarded as a pseudo-aromatic compound\textsuperscript{5} in which the C-1, C-6 σ bond is fully uncoupled but with overlap of the C-1 and C-6 π-orbitals.

In this view the structures 1 and 2 represent just two resonance forms of the resonance hybrid 2 and the molecule can be regarded as "homobenzene".\textsuperscript{8}

b. Norcaradiene and cycloheptatriene (NCD and CHT) are rapidly equilibrating valence tautomers.

In suggesting the homoaromatic structure of cycloheptatriene,
Doering assumed that the molecule had a planar structure, it being thought that this was a necessary condition for effective cyclic delocalization.\textsuperscript{5}

**The Geometry of the Cycloheptatriene Molecule**

While the room temperature proton magnetic resonance (pmr) spectrum of cycloheptatriene is consistent with a planar structure in that only a single resonance is observed for the two C-7 hydrogens, at very low temperatures two signals are found for these protons. This would imply that the seven-membered ring of 1 is not planar and is consistent with a boat conformation as illustrated in 1\textsuperscript{a}.

The two C-7 protons in a conformation such as 1\textsuperscript{a} are non-equivalent and at low temperatures when ring inversion is slow, two separate resonances would be expected for these protons in the pmr spectra.\textsuperscript{9,10} As the temperature of the sample is raised, ring inversion would become more rapid and these signals would be expected to coalesce and average. The barrier to inversion of the two boat conformations was found to be 6 kcal/mol.\textsuperscript{9}

![Diagram](image)

The structure of cycloheptatriene has also been examined by microwave spectroscopy\textsuperscript{11} and electron diffraction measurements\textsuperscript{12} and the boat shape has been confirmed. Such a conformation is also consistent with the ease of the transannular 1,5-hydride shifts that cyclo-
heptatriene and many of its derivatives undergo. In the solid phase, the structure of 7,7-dimethylcycloheptatriene-3-carboxylic acid has been determined by X-ray crystallography and again a boat shape was found for the seven-membered ring.

While the structural analyses performed by either of the afore-mentioned methods invariably indicated that cycloheptatriene exists in a boat conformation as shown in Figure 1, the detailed shape of the ring seems to be dependent upon the presence and nature of any substituents as well as the experimental method used.

Figure 1: The geometry of cycloheptatriene and some of its derivatives.

\[
\begin{align*}
R = H & \quad \beta = 40.5 \pm 2^\circ \quad \alpha = 36.5 \pm 2^\circ & \text{ref.} \ 12 \\
R = H & \quad \beta = 29.5 \pm 4^\circ \quad \alpha = 50 \pm 5^\circ & \text{15} \\
R = CH_3 & \quad \beta = 24.4^\circ \quad \alpha = 47.9 & \text{14} \\
R = CF_3 & \quad \beta = 25^\circ & \text{11,16}
\end{align*}
\]

From the position of pmr absorption of the C-7 protons and the coupling constants between protons at C-1 and C-7 in monosubstituted cycloheptatrienes, Müller and Günther have concluded that a substituent preferentially adopts the pseudo equatorial position.

Seemingly, after the establishment of the non-planar structure
of 1, the Doering homoaromatic model of cycloheptatriene has largely fallen into disfavour. However, although the C-1, C-6 separation in 7, 7-dimethylcycloheptatriene-3-carboxylic acid, as determined by X-ray crystallography, 13 is much greater than that expected for a bicyclic structure, it does not exclude the possibility of some overlap of the C-1, C-6 \( \pi \)-electrons.

**The Cycloheptatriene - Norcaradiene Equilibrium**

It is currently accepted that the cycloheptatriene and norcaradiene are valence tautomers and that they are in rapid equilibrium, 19 eq. 3. This equilibrium is similar to that known for some time for bicyclo 4.2.0 octa-2,4-diene/cyclooctatriene, 20 eq. 4.

\[ \text{Cycloheptatriene} \rightleftharpoons \text{Norcaradiene} \]  \hspace{1cm} (3)

\[ \text{Bicyclo 4.2.0 octa-2,4-diene} \rightleftharpoons \text{Cyclooctatriene} \]  \hspace{1cm} (4)

The existence of such a tautomerism was definitely established only with the advent of nuclear magnetic resonance spectroscopy. 1 Whereas the chemical evidence is ambiguous, nmr spectroscopy can clearly distinguish between the two tautomers. For example, the protons on
carbons C-1 and C-6 of cycloheptatriene resonate in a typical olefinic region (above $\delta 5.0$), while the corresponding cyclopropyl-proton signals of a norcaradiene appear around $\delta 3.5$. In rapidly equilibrating mixtures of certain substituted cycloheptatrienes and norcaradienes, these proton resonances often occur in some intermediate position between these two values, the exact position being dependent on the equilibrium concentration of the respective isomers.$^{19}$ Examples of systems have been found in which the cycloheptatriene form predominates, the norcaradiene form predominates, and in which both isomers are present in about equal amounts.

The existence of unsubstituted norcaradiene remains as yet to be demonstrated. Both kinetic$^{21}$ and spectroscopic$^{22}$ methods have failed to detect 2 in cycloheptatriene and only an upper limit to the concentration of norcaradiene can be set.

The magnitude of the energy difference between the isomers 1 and 2 remains obscure. The value of $11 \pm 4$ kcal/mole suggested$^{23}$ on the basis of bond energy calculations$^{24}$, is frequently cited in the literature.$^{1a,21,25}$ This number would correspond to an equilibrium norcaradiene concentration of some $8.3 \times 10^{-4}$ to $1.3 \times 10^{-9}$% at room temperature. Kinetic norcaradiene trapping experiments could be taken to suggest a much smaller energy difference, $4.0-4.5$ kcal/mole, and a norcaradiene equilibrium concentration of 0.1%. However this latter value is open to criticism.$^{21}$

With some substituted cycloheptatrienes, when both valence tautomers are present in more or less equal amounts, low temperature nmr can be used to obtain the equilibrium ratio directly.$^{26}$ Other spectroscopic techniques have been of limited (Raman$^{26}$) or little use (ir, uv$^{27}$)
in determining the ratio of the two forms present.

Just as with the parent compound, the majority of simply substituted cycloheptatrienes also exist very largely in the monocyclic form. It is worth noting at this point however that the position of the equilibrium between the cycloheptatriene and norcaradiene forms of these substituted systems could be considerably different from that encountered with the parent compound and yet still be beyond the range of detection by nmr (usually 5-10%).

To state the obvious, two general methods can be employed to make the norcaradiene form predominate in these equilibria. These are -

a) to stabilize the norcaradiene form in some way

b) to destabilize the cycloheptatriene form

Either or both of these two methods have been used to prepare stable norcaradienes.

Stable Norcaradienes

One method of stabilizing the bicyclic form is to incorporate one or both double bonds of a norcaradiene into an aromatic system. For example the rearrangement of benzonorcaradiene 10, into its seven-membered ring valence tautomer 11, eq. 5 would involve the loss of considerable resonance energy. It is thus not unexpected that 10 is the predominant valence tautomer present.26

\[ \text{10} \quad \xrightarrow{} \quad \text{11} \]

(5)
The norcaradiene structure can also be stabilized by placing a three carbon bridge between the C-1 and C-6 of these systems. An example of this type of compound is 12. The cycloheptatriene derivative derived from this compound would have two bridgehead double bonds and therefore would not be expected to be stable. In fact, 12 is the only isomer observed. The extension of the C-1, C-6 bridge by a fourth methylene group eliminates some of the strain in the cycloheptatriene form and this later valence tautomer, 13, now predominates.

\[ \text{12} \quad \text{13} \]

Compound 14 presents another type of "sterically stabilized" norcaradiene. The cycloheptatriene isomer derived from this compound would be expected to experience a severe steric interaction between the methyl groups and the benzene rings. The bicyclic form 14 has been found to predominate.
The hydrocarbon 15 had also been found to exist very largely in the norcaradiene form. It has been suggested that the wide external angle at C-7, necessitated by the attached five-membered ring, causes the C-1, C-7, C-6 angle to be small and to thus stabilize the bicyclic form of this compound. 30 If this is indeed so, then an opposite effect may be expected in 16 and indeed this compound was found to exist almost completely in the monocyclic form. 31

The norcaradiene structure also can be stabilized by the incorporation of heteroatoms into the ring system, e.g. 17, 18 and 19, 20. It can be readily calculated from tables of average bond energies, that 3,4-diazanorcaradiene, 17, is expected to be thermodynamically more stable than the monocyclic isomer 18. Experimentally 17 was found to be
the more stable tautomer.\textsuperscript{32}

\begin{center}
\begin{tabular}{c}
\textbf{17} \hspace{2cm} \textbf{18}
\end{tabular}
\end{center}

The reasons for the increased stability of the bicyclic form of oxepine are much less obvious, however the bicyclic compound \textbf{19} was found to exist in a 1/10 ratio with \textbf{20}.\textsuperscript{33}

\begin{center}
\begin{tabular}{c}
\textbf{19} \hspace{2cm} \textbf{20}
\end{tabular}
\end{center}

Compounds \textbf{14} and \textbf{15} are examples of norcaradiene systems stabilized by substitution at carbon 7. The preference for the bicyclic form in these compounds is very likely due to steric reasons. Of greater interest is a series of C-7 substituted CHT/NCD systems in which the bicyclic form seems to be stabilized by an electronic rather than a steric effect.
7-Substituted Cycloheptatriene/norcaradiene Systems

Cycloheptatrienes substituted at C-7 can be prepared by the addition of a suitably substituted carbene to benzene. Therefore when Ciganek attempted the photolytic decomposition of dicyanodiazomethane in benzene, he had every reason to believe that the product of the reaction would be 7,7-dicyanocycloheptatriene. The uv and pmr spectra of the major product, however did not resemble the spectra of 7-cyanocycloheptatriene but rather those of a norcaradiene such as 12. Comparison of the spectral data of this new compound with those of 22, confirmed the norcaradiene structure of 21.

A series of related disubstituted cycloheptatrienes was consequently prepared and many of these systems were shown to exist as rapidly equilibrating mixtures of 23 and 24. At the start of this work however, 21 was the only known compound of this type which had the equilibrium position located almost completely on the norcaradiene side. Thermodynamic data for several systems of this type, 23 ⇌ 24, are compiled in Table 1.
Table 1: Ground state enthalpy and entropy differences, $H^0 (24) - H^0 (23)$ and $S^0 (24) - S^0 (23)$.

<table>
<thead>
<tr>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$\Delta H^0$</th>
<th>$\Delta S^0$</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td>CN</td>
<td>6$^a$</td>
<td></td>
<td>38</td>
</tr>
<tr>
<td>CN</td>
<td>COOME</td>
<td>4$^a$</td>
<td></td>
<td>26</td>
</tr>
<tr>
<td>CN</td>
<td>Ph</td>
<td>3-5$^a$</td>
<td></td>
<td>26</td>
</tr>
<tr>
<td>COOME</td>
<td>Ph</td>
<td>5.4</td>
<td>16.8</td>
<td>19</td>
</tr>
<tr>
<td>COOME</td>
<td>p-MeOPh</td>
<td>2.3</td>
<td>7.4</td>
<td>19</td>
</tr>
<tr>
<td>COOME</td>
<td>p-O$_2$NPh</td>
<td>3.5</td>
<td>11.0</td>
<td>19</td>
</tr>
<tr>
<td>CN</td>
<td>CF$_2$</td>
<td>0.4</td>
<td>5</td>
<td>26</td>
</tr>
<tr>
<td>COOME</td>
<td>COOME</td>
<td>0.2</td>
<td>3</td>
<td>39</td>
</tr>
<tr>
<td>GF$_3$</td>
<td>CF$_3$</td>
<td>b</td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>CN</td>
<td>H</td>
<td>b</td>
<td></td>
<td>41</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>b</td>
<td></td>
<td>42</td>
</tr>
</tbody>
</table>

a. estimated values
b. only the tautomer 23 is observed

Examination of these results indicate that $\pi$-electron deficient substituents are essential for norcaradiene stabilization. As all electroneutral monosubstituted cycloheptatrienes, with the possible exception of 7-cycloheptatrienyl carboxylic acid, are reported to exist
in the monocyclic form, it would seem that two substituents are normally necessary to measurably shift the position of equilibrium between $23/24$ towards the norcaradiene side.

Recent reports seem to indicate that the carboxyl group ($-\text{COOH}$) has a greater NCD stabilizing ability than the cyano group. However no data about $24, R_1=R_2=\text{COOH}$ are available, even though the corresponding diester is known.

Although these NCD stabilizing substituents can be classified as electron-withdrawing, there appears to be no simple correlation between $\Delta H^0$ and any parameter that measures the electron-withdrawing ability of these substituents. For example, although the cyano and the trifluoromethyl group have similar $\delta$ constants (+0.66 and +0.54), compound 21 is a stable norcaradiene while $7,7$-bis(trifluoromethyl)cycloheptatriene exists almost exclusively in the triene form.

**Origin of the C-7 Substituent Effect**

Several explanations have been put forward to account for the effect of a C-7 substituent on the position of the CHT/NCD equilibrium. Ciganek suggested that a dipole-dipole interaction between two cyano substituents could possibly increase the bond angle between the two groups and consequently decrease the internal bond angle at C-7 so as to favour the norcaradiene structure. This proposal is in accord with the X-ray structures of $7,7$-dicyano-2,5-dimethyl/norcaradiene and malononitrile, for both of these molecules the NC-C-CN angle (115° and 114° respectively) is distorted from the normal sp$^3$ value of 109°. The stability of norcaradiene 15, with a wide external angle at
C-7, as opposed to the stability of cycloheptatriene 16, also seems to support Ciganek's argument.

A second explanation that has been suggested is based on the difference in bond energies between carbon atoms of different hybridization. The C-7 carbon of norcaradiene, which as a cyclopropyl carbon is approximately sp\(^2\) hybridized, should form stronger bond with a sp or sp\(^2\) hybridized substituent than would the sp\(^3\) hybridized carbon of cycloheptatriene. This difference in bond energies would favour the bicyclic isomer when unsaturated substituents are bound to C-7.

Other factors mentioned in this connection include a possible intramolecular charge transfer complex of the norcaradiene double bonds with one of the C-7 groups or the attenuation of the homoaromaticity of cycloheptatriene by the C-7 substituents. However these rationalizations are difficult to accommodate with the experimental evidence.

A widely accepted explanation of the effect of a C-7 substituent on the CHT/NCD equilibrium was advanced independently by Hoffmann and Gunther. They both suggested that there is a donor acceptor interaction between the π-molecular orbitals of a C-7 substituent and the Walsh orbitals of the cyclopropyl ring of a norcaradiene (Figure 1). When the ligand π-system possesses low lying electron deficient molecular orbitals, then the electrons of the antisymmetric Walsh orbital, \(\psi_3\), of the cyclopropane will delocalize over the adjacent π-system. As a consequence of this net electron transfer from cyclopropane to the substituent, the antibonding contribution to the C-1, C-6 bond is weakened. The net result of this would be to strengthen the C-1, C-6 bond.
If on the other hand, the C-7 substituent possesses an occupied, high energy molecular orbital of suitable symmetry, this could interact with the unoccupied antibonding orbital, $W_4$, of the cyclopropane ring. This additional antibonding interaction will weaken the C-1, C-6 bond. Thus, according to this suggestion, electron-donating substituents on C-7 should cause the CHT form to be preferred.

It is interesting to note that, according to this suggestion the thermodynamic stability of the cycloheptatriene tautomer is little affected by substitution at C-7 but rather it is the energy of the norcaradiene form that is dependent on the nature of the C-7 substituent.

This explanation of the effect of a C-7 substituent is consistent with the results of an X-ray determination of the structure of 2,5-dimethyl-7,7-dicyanonorcaradiene. The C-1, C-6 bond was found to be considerably shorter (1.501 Å) than the remaining two cyclopropyl bonds (1.554 Å and 1.559 Å). It should be pointed out however, that this pattern of bond distortion is not found in all norcaradienes. For
example all three cyclopropane bonds of 7-dimethoxyphosphoryl-7-phenyl-norcaradiene were found to be equal.\textsuperscript{52}  

On the basis of these considerations, a carbonium ion, which of course is a strongly electronwithdrawing $\pi$-substituent, was suggested to be perhaps the most effective norcaradiene stabilizing substituent.\textsuperscript{49}  

Some confirmation of this prediction was derived from the results of solvolytic studies of some 7-cycloheptatrienylcarbinyl esters. Sargent\textsuperscript{53} and other workers\textsuperscript{54,55} have suggested on the basis of rate and product studies that norcaradienylcarbinyl cations are involved in these reactions, eq.6.

\[
\begin{align*}
\text{products} & \quad (6)
\end{align*}
\]

Some recent studies of 7-cyclohepta-1,3,5-trienylcarbinyl cations\textsuperscript{56,57} will be discussed in the next chapter.

**Theoretical Calculations of Substituent Effects on Related Systems**

Semibulvalene, 25 $R=H$, is one of several compounds with a $\pi$-molecular orbital system analogous to that of 2. The energy barrier to the interconversion of 25a and 25b and the effect of a substituent $R$ on the position of this equilibrium have been calculated using MINDO/2\textsuperscript{58} and extended Hückel treatments.\textsuperscript{44} Both of these approximate methods led
to predictions which were qualitatively the same. Some conclusions from the calculations of Hoffmann and Stöhrer are presented in Table 2.

\[
\begin{array}{ccc}
R & \Delta n & \Delta E \\
\hline
+ & 0.058 & 16.6 \\
CHO & 0.030 & 10.0 \\
COOH & 0.024 & 9.2 \\
CN & 0.020 & 8.5 \\
OH & -0.016 & -11.5 \\
F & -0.016 & -11.5 \\
NR_2 & -0.021 & -2.8 \\
\end{array}
\]

- results of extended Hückel calculations reported by Hoffmann and Stöhrer

\[\Delta n - \text{C-2, C-8 bond order change compared to 25a } R=H\]

\[\Delta E - \text{difference in energy between 25a and 25b.}\]

A positive number indicates that 25a is more stable than 25b.

Two limitations should be kept in mind in considering the data in Table 2. Firstly, the energies resulting from the extended Hückel calculations should be regarded as indicators of relative trends and not as
a quantitative guide to stability. Secondly, these calculations can not account for the effect of a 6 electron accepting group, such as \( \text{CF}_3 \).

From the results in Table 2, the authors have concluded that \( \pi \)-electron donors shift the equilibrium between 25a and 25b markedly towards 25b, while \( \pi \)-electron accepting groups shift the equilibrium in the opposite direction. Recently the equilibrium position between 25a and 25b has been studied experimentally. Although only a limited range of substituents \( \text{R} \) was examined, the results were consistent with the trends indicated in Table 2.\(^{59}\)

**Criticism of Prevailing Ideas on the Origin of the C-7 Substituent Effect**

While the donor acceptor molecular orbital arguments presented by Hoffmann and Günther have received wide acceptance, there appears to be an increasing number of systems found that contradict their model. For example, the observed decrease in \( \Delta H^0 \) caused by both p-nitro and p-methoxy substituents on the phenyl ring of 7-methoxycarbonyl-7-phenylcycloheptatriene/norcaradiene (Table 1) cannot be accounted for on this basis. Moreover, the intriguing recent report by Klärner that the replacement of the methine hydrogen in 7-methoxycarbonylcycloheptatriene by a methyl group, an ostensibly electron donating substituent, destabilizes the CHT form and shifts the equilibrium towards the NCD side, would also seem to contradict this approach.\(^{60}\)

The following order of magnitude of NCD stabilizing substituent effect was recently observed on a 7-substituted-7-methylcycloheptatriene/norcaradiene: \( \text{CN} > \text{COOMe} > \text{COOH} \).\(^{60}\) This sequence does not correspond to
the order of energies calculated by MINDO/2 method (Table 2) nor to the order of their size (COOEt > COOH > CN). Therefore this observation can not be explained by Hoffmann's concept of a donor acceptor interaction nor by the Ciganek's suggestion concerned with C-7 bond angles.26

\[ \text{Me} \quad \text{R} \]

\[ \text{Me} \quad \text{R} \]

It is obvious from these examples that the effect of substituents on the position of the cycloheptatriene - norcaradiene equilibrium is by no means fully understood.

**Objective of this Work**

As has been pointed out, the equilibrium positions of the CHT/NCD system do not seem to follow any simple trend. One possible reason for this could be that two substituent effects are operative. Not only perhaps is the electronwithdrawing ability of each individual substituent important but the mutual interaction of these could also be a contributing factor.

In order to overcome this problem it would be of value to prepare some mono-C-7 substituted systems in which there was sufficient norcaradiene form present to enable the equilibrium positions to be determined. As it has been suggested that a carbonium ion attached to C-7 should be one of the most powerful norcaradiene stabilizing substituents, attempts
have been made to prepare and study such systems. Chapter II discusses the results that have been obtained in this area.

A further factor impeding the investigation of the CHT/NCD valence tautomerism is the great difference in thermodynamic stability of the parent monocyclic, 1, and bicyclic, 2, forms. As a result, only the effect of a limited number of electron-withdrawing substituents can be studied.

To overcome the problems associated with this large energy gap between 1 and 2, the preparation of some substituted 3,4-homotropolidenes, 28/29, has been attempted. This system can also undergo a facile tautomeric rearrangement, however an important feature of this degenerate Cope rearrangement²⁰ is that the basic carbon skeleton is regenerated in the reaction. The tautomers 28 and 29 differ only in the position of the substituent and thus there is no difference in energy of the two forms attributable to a change in the basic carbon framework. The synthesis

![Diagram](image)

of such systems should enable a much more systematic study of the substituent effects to be made. The results of this study are presented in Chapter III.
CHAPTER II

PREPARATION OF SOME 7-NORCARADIENYLCARBINYL CATIONS

As has been discussed earlier in this thesis, it has been suggested that a carbonium ion substituent attached to C-7 of a cycloheptatriene should be one of the most effective groups with which to stabilize the norcaradiene valence tautomer.$^{44,48}$ However, in addition to this valence tautomerism, a 7-cycloheptatrienylcarbinyl cation could undergo several other types of reaction. As are depicted below, these include ring expansion to a homotropilium cation,$^{49}$ elimination of a carbene to give the tropilium cation$^{57}$ or loss of a proton and formation of a heptafulvene.$^{57}$

![Scheme 1](image)
To examine these possibilities and to evaluate the effect of the electron-withdrawing ability of a C-7 substituent on the position of the CHT/NCD equilibrium, the preparation of some carbonium ion substituted cycloheptatrienes was attempted.

The 7-cycloheptatrienyl methyl cation was first invoked by Cope as a possible intermediate in the oxidation of cyclooctatetraene to phenylacetaldehyde, eq. 8. Although this report appeared before the existence of the CHT/NCD tautomerism was recognized, the possibility of a norcaradiene intermediate in this reaction was considered. 61

$$\text{Cyclooctatetraene} \xrightarrow{\text{H}^+} \text{7-cycloheptatrienyl cation} \xrightarrow{\text{Hg(OAc)}_2} \text{7-cycloheptatrienyl methyl cation} \xrightarrow{\text{H}^+} \text{7-cycloheptatrienyl formaldehyde}$$

A similar intermediate was postulated by Pettit in the acid catalyzed rearrangement of 7,8-epoxy-1,3,5-cyclooctatriene, eq. 9. 62

$$\text{7,8-epoxy-cyclooctatriene} \xrightarrow{\text{H}^+} \text{7,8-epoxy-1,3,5-cyclooctatriene} \xrightarrow{\text{H}^+} \text{7,8-epoxy-1,3,5-cyclooctatriene} \xrightarrow{\text{H}^+} \text{7,8-epoxy-1,3,5-cyclooctatriene} \xrightarrow{\text{H}^+} \text{7,8-epoxy-1,3,5-cyclooctatriene}$$

This reaction has been reinvestigated by Huisgen and co-workers, who reported that reaction of cyclooctatetraene epoxide with HFSO₃ gave
the 8-hydroxyhomotropolium cation. However they proposed that there was some contribution from a 7-cycloheptatrienyl cation to the overall structure, eq.10.

\[
\begin{array}{c}
\text{H} \\
\text{OH}
\end{array}
\xrightarrow{\text{eq.10}}
\begin{array}{c}
\text{C} \\
\text{O} \\
\text{H}
\end{array}
\]

Diazotation of 2(7-cycloheptatrienyl)2-aminodiethylmalonate has been reported to give a substituted heptafulvene as the major product, eq.11. It seems very likely that a cycloheptatrienylmethyl cation is involved in this reaction, however in this case no ring contraction was observed.

\[
\begin{array}{c}
\text{EtOOC} - \text{C} - \text{COOEt} \\
\text{NH}_2
\end{array}
\xrightarrow{\text{NOBF}_4}
\begin{array}{c}
\text{EtOOC} - \text{C}^+ - \text{COOEt} \\
\text{EtOOC} - \text{C} - \text{COOEt}
\end{array}
\xrightarrow{\text{NOBF}_4}
\begin{array}{c}
\text{C} - \text{COOEt}
\end{array}
\]

As was mentioned earlier the 7-norcaradienylcarbinyl cation has been suggested to be an intermediate in the sovolysis and rearrangement of several cycloheptatrienylcarbinyl esters.

Although cycloheptatrienyl- and/or norcaradienylmethyl cations have been invoked as reactive intermediates, no stable carbonium ion of this type had been reported at the start of this project. Simultaneously
with our work, several such systems were investigated by Betz and Daub and their reported results are in some respects similar to those found in this work.

A direct route for the production of stable 7-cycloheptatrieny1-methyl cations appeared to be the elimination of a leaving group $X$ from the compound $\text{30}$. However previously attempted preparations of $\text{31}$ or $\text{32}$ using the reactions indicated in eq.12, were unsuccessful. Polymerization was reported to occur when $R=H$ and aromatic rearrangement products were observed with $R=\text{Ph}$ or $p-\text{MeO}-\text{C}_6\text{H}_4$. Thus the stabilization of the positive charge by two anisyl groups did not prevent a rapid collapse of the seven-membered ring, eq.12.

\[
\begin{align*}
\text{30} & \quad \xrightarrow{Y} \quad \text{21} \\
\text{30} & \quad \xrightarrow{Y} \quad \text{22}
\end{align*}
\]

\[
\begin{array}{llll}
\text{a)} & R = H & X = \text{Cl} & Y = \text{SbCl}_5, \text{SbF}_5, \text{AgBF}_4 \\
\text{b)} & R = H & X = \text{OH} & Y = \text{HFSO}_3 \\
& R = \text{Ph} & \\
& R = p\text{MeO}-\text{Ph}
\end{array}
\]
Further stabilization of the positive charge in $\text{21/22}$ could possibly be achieved by employing hetercatom groups as the substituents $R$. For example the oxygen substituted carbonium ion system $\text{33/34}$ would be expected to be more stable than $\text{21/22}$.

$$\begin{align*}
\text{22} & \rightleftharpoons \text{33} \\
\text{32} & \rightleftharpoons \text{34}
\end{align*}$$

One possible approach to this system appeared to be the protonation of the ester $\text{25}$ with a strong acid, eq.$\text{14}$. The attempts to protonate $\text{25}$ with $\text{HFSO}_3$ led only to the formation of black polymeric material.

$$\begin{align*}
\text{23} & \rightleftharpoons \text{24} \\
\text{25} & \rightarrow \text{26}
\end{align*}$$

A similar protonation reaction of a 5-acetylcyclopentadiene has been studied and it was found that a strong Brönsted acid protonated not only the oxygen of the carbonyl group but also the carbon of the diene system to give a dication, eq.$\text{15}$. Lewis acids, on the other hand, were found to react only with carbonyl oxygen and no electrophilic attack on the diene moiety was observed. It is known that strong Lewis acids, (L.A.) form stable complexes with a carbonyl group eq.$\text{16}$, and the
extension of this technique to the preparation of cycloheptatrienyl and norcaradienyl carbonium ions has been attempted.

\[ R - \text{GOOR} \xrightarrow{\text{L.A.}} R^+\text{L.A.} \]

**Lewis Acid Complexes of Methyl Cycloheptatrienyl-7-carboxylate**

The addition of a slight excess of BCl$_3$ at $-78^\circ$ to a solution of 35 in CD$_2$Cl$_2$, resulted in formation of a 1:1 complex between the ester and the Lewis acid. The low temperature pmr spectrum of this complex was found to be independent of the ratio of the Lewis acid to the ester used provided there was at least one equivalent of the acid present. The complex was stable at $-78^\circ$ and could be reacted with dimethylamine to regenerate 35 in high yield, eq.17.

The pmr spectrum of the complex (Figure 3) was fully consistent with the formation of a zwitterion in which the Lewis acid was complexed to the carbonyl oxygen of the ester. For example, the resonance of the methyl group is deshielded by 0.44 ppm on reaction with BCl$_3$. Formation
Figure 3: Fmr spectrum of 35 and 37.
of a similar complex from methylacetate is reported to cause a 
downfield shift of the methoxy resonance. Moreover, only one pmr signal was observed for the C-1 and C-6 protons, indicating that the complexed molecule at least retained its plane of symmetry on a time averaged basis. The recovery of ester 35 in the reaction of the complex with a stronger Lewis base showed that no extensive and irreversible reorganization of the carbon framework had occurred.

The resonance positions of the ring protons however, had drastically changed on complexation. Thus the signals of the olefinic hydrogens on C-2, C-3, C-4 and C-5 appeared as multiplet centred at δ 6.39. The absorption of the C-7 hydrogen, which in 26 is in a geminal position to the strongly electron withdrawing trivalent carbon substituent, might well have been expected to resonate downfield from the corresponding hydrogen in 35. In fact the resonance of this hydrogen is shifted 0.88 ppm upfield on complexation! An even greater upfield shift, 1.93 ppm, was observed for the C-1, C-6 resonances on complexation of 35. These protons, which in a structure such as 36 are vicinal to
to the carbonium ion group, might also be expected to resonate at a lower field than the related protons of \( 35 \). Clearly, structure \( 36 \) is not compatible with the pmr spectrum of the complex.

The pmr data however, are compatible with the formation of the norcaradiene complex \( 37 \). The upfield shift of C-1, C-6 resonances is then understandable as these protons are attached to cyclopropyl carbons in \( 37 \), rather than to olefinic carbons. The resonance of the C-7 hydrogen however seemed to appear at somewhat too high a field even for a structure such as \( 37 \) and this factor will be discussed in more detail later. It would appear therefore that the position of the CHT/NCD equilibrium between \( 36 \) and \( 37 \) must reside very largely on the norcaradiene side, eq.18. Daub and Betz have also prepared a dimethoxycarbonium

\[
\begin{align*}
36 & \quad \stackrel{+}{C} \quad ^{\cdot}O\text{-BCl}_3 \\
\text{C} & \quad ^{\cdot}O\text{-Me} \\
37 & \quad \stackrel{+}{C} \quad ^{\cdot}O\text{-BCl}_3 \\
\text{C} & \quad ^{\cdot}O\text{-Me}
\end{align*}
\]

substituted norcaradiene (see p. 44) and from the pmr evidence have concluded, that this compound existed fully in the bicyclic form.

Some additional information about the structure of the complex was derived from its uv spectrum. A methylene chloride solution of the complex at \(-50^\circ\) exhibited an absorption band with a \( \lambda_{\text{max}} = 284 \text{ nm} \) (log \( \varepsilon = 4.3 \)). This absorption cannot simply be due to the complex of the ester group, as the \( \text{BCl}_3 \) complex of methylacetate, prepared under the same conditions, had no absorption with an extinction coefficient greater than 100 above 235 nm. Since the uv spectra of cycloheptatrienes
typically exhibit maxima between 257 and 268 nm\(^1\), the longer wavelength absorption of the complex would seem to indicate that its structure is different from \(36\). Stable norcaradienes have been reported to have the absorption maxima in the region of 268-279 nm.\(^{67,38}\)

In order to determine how much monocyclic isomer was present in equilibrium with \(37\), the low temperature pmr spectrum of the complex was examined. It has been reported that the CHT-NCD rearrangement is sufficiently slow at -112\(^\circ\) that signals attributable to the separate isomers can be observed.\(^35\) No additional signals were found in the pmr spectrum of a CHCl\(_2\) solution of \(37\) recorded at -135\(^\circ\). Although the resolution of this low temperature was not that good, it is estimated that 5-10\% at \(36\) could have been observed if it were present.

Formally two different stereoisomers of \(37\) are possible in which the C-7 substituent can be either in the exo or endo position, \(37a\) and \(37b\) respectively.

![Diagram of 37a and 37b]

From the nmr spectrum obtained, it is clear that only one of these isomers is present. Comparison of the magnitude of the coupling constant between the proton at C-7 and protons at C-1 and C-6 (3.1 Hz) with that reported for other cyclopropanes, would indicate that the
isomer formed is 37a. Typical values for cyclopropyl coupling constants are $J_{\text{trans}} = 3.0-6.5$ Hz and $J_{\text{cis}} = 6.0-9.5$ Hz. A similar preference for the formation of the exo isomer was reported by Betz and Daub. This behaviour has been attributed to unfavourable secondary orbital interactions in the endo isomer.

It is concluded therefore that C-7 substitution of cycloheptatriene with a carbonium ion resulted in reversal of the normal position of the CHT/NCD equilibrium and converted at least 90% of 26/37 into the bicyclic form. In accord with Hoffmann's and Günther's model and from semiempirical calculations, it can be expected that by modification of the electron deficiency of the C-7 carbonium ion substituent, it would be possible to regulate the amount of the bicyclic tautomer in the CHT/NCD mixture.

Modification of the Electronwithdrawing ability of C-7 Substituent

The electronwithdrawing ability of the substituent 38 can be amended by an exchange of one or both groups attached to the trivalent carbon. Three types of such group alterations were examined:

a) exchange of the Lewis acid
b) exchange of one or both oxygen groups for another heteroatom group
c) exchange of one or both oxygen groups for hydrogen atoms or carbon groups.

The results of these experiments are described in the next three sections.
Complexation of 35 with Different Lewis Acids

The reaction of a CD$_2$Cl$_2$ solution of 35 with BBr$_3$, eq.19, resulted in the formation of complex 39. This complex was stable at -78°C and could be reacted with dimethylamine to give back 35. The pmr spectrum of zwitterion 39 was almost identical with that of 37, Table 3, suggesting that both these complexes exist predominantly in the norcaradiene form.

Borontribromide is reported to be the strongest of the common Lewis acids. Complexation of the oxygen atom of a carbonyl group with BBr$_3$ results in the accumulation of a larger fraction of a positive charge on the carbon atom of the group than is found with similar BCl$_3$ complexes. Hoffmann and Stöhrer have suggested that the amount of the norcaradiene tautomer in a CHT/NCD equilibrium mixture should increase as the electronwithdrawing power of C-7 substituent is increased. If this were so then the BBr$_3$ complex of 35 would be expected...
to contain a greater percentage of the bicyclic tautomer than the corresponding \( \text{BCl}_3 \) complex. As the equilibrium composition of the \( \text{BCl}_3 \) and \( \text{BBr}_3 \) complexes of \( 35 \) would appear to be the same this could either mean that both complexes exist almost completely in the NCD form or that the position of the CHT/NCD equilibrium is independent of the electron-withdrawing power of a C-7 substituent. As it will be shown later the first possibility is correct.

Table 3: Proton chemical shifts of \( 35 \) and its complexes

<table>
<thead>
<tr>
<th>Lewis acid</th>
<th>Lewis acid to ester ratio</th>
<th>Temp °C</th>
<th>Proton chemical shifts, ( \delta ) a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>H-7</td>
</tr>
<tr>
<td>none b</td>
<td>0.0</td>
<td>-40</td>
<td>2.48</td>
</tr>
<tr>
<td>( \text{BCl}_3 ) b</td>
<td>1.3</td>
<td>-40</td>
<td>1.60</td>
</tr>
<tr>
<td>( \text{BBr}_3 ) b</td>
<td>1.2</td>
<td>-40</td>
<td>1.65</td>
</tr>
<tr>
<td>( \text{AlCl}_3 ) b</td>
<td>1.3</td>
<td>37</td>
<td>2.26</td>
</tr>
<tr>
<td>( \text{AlCl}_3 )</td>
<td>10.0</td>
<td>37</td>
<td>1.92</td>
</tr>
<tr>
<td>( \text{SnCl}_4 ) c</td>
<td>1.2</td>
<td>37</td>
<td>2.53</td>
</tr>
<tr>
<td>( \text{SnCl}_4 ) c</td>
<td>1.2</td>
<td>-20</td>
<td>2.21</td>
</tr>
<tr>
<td>( \text{SnCl}_4 ) d</td>
<td>1.3</td>
<td>-75</td>
<td>1.71</td>
</tr>
</tbody>
</table>

a \( \text{CHCl}_3 \) used as internal standard (\( \delta \ 7.3 \))

b \( \text{CD}_2\text{Cl}_2 \) used as the solvent

c \( \text{CDCl}_3 \) used as the solvent

d \( \text{CHClF}_2 \) used as the solvent
The reaction of 35 with other Lewis acids was also examined however, the low solubility of the so formed complexes generally hindered their study. The products formed on reaction of 35 with SbCl₅, SbF₅, TiCl₄ and BF₃ were insufficiently soluble in such solvents as CDCl₃, CD₂Cl₂ and SO₂, or mixtures of these solvents, to obtain satisfactory pmr spectra. The results obtained with 35 and Al₂Cl₆ were not very reproducible and seemed to depend on an L.A./ester ratio. This again probably stems from the very low solubility of Al₂Cl₆ in the solvents listed above and resulting incomplete reaction with the ester.

The complex of 35 with SnCl₄, 40, had a low temperature pmr spectrum which was very similar to that of 37. However, at room temperature the spectrum resembled that of 35, Table 3. It would appear that dissociation of a complex such as 40 is occurring at higher temperatures. 72

\[
\begin{align*}
\text{\large 40} \\
\text{Replacement of the Methoxy Group with a Nitrogen Function} \\
\text{N,N-Dimethyl(7-cycloheptatrienyl)carboxamide, \textit{41}, was reacted with BCl₃ in CD₂Cl₂ solution. The pmr spectrum of the product was consistent with complexation of the carbonyl oxygen with the Lewis acid,\textsuperscript{70} Figure 4.}
\end{align*}
\]
However, the positions of the ring proton resonances were now intermediate between those observed for 35 and complexes 37 and 39. Thus it appeared that this product was a mixture containing a considerable amount of both 42 and 43, interconverting sufficiently rapidly at -40° for their pmr spectra to be averaged. Reaction of the complex with dimethylamine or water regenerated 41 in high yield, eq.21.

\[
\begin{align*}
\text{Me}_2\text{NH} & \quad \text{BCl}_3 \\
\text{O} & \text{C} \quad \text{NMe}_2 \\
\text{41} & \quad \text{42} & \quad \text{43}
\end{align*}
\]

As the dimethylamino group is known to be more effective at stabilizing a positive charge than is a methoxy group,\textsuperscript{73} it appears that the position of the CHT/NCD equilibrium of these zwitterion is dependent on the electron-deficiency of the C-7 substituent. The more electron-withdrawing is the substituent, the greater is the amount of norcaradiene in the mixture of tautomers. The observation that the BCl\textsubscript{3} complex 37 and its BBr\textsubscript{3} analogue 39 have the same tautomeric composition despite the different withdrawing powers of their respective C-7 substituents implies that they both exist almost entirely in the norcaradiene form.

In order to evaluate the position of a CHT/NCD equilibrium such as 42/43 it is necessary to know the resonance positions of some of the
protons in the pmr spectra of the individual isomers. One way this can be achieved is to record the pmr spectra at a sufficiently low temperature where the interconversion becomes slow in the pmr time scale.\textsuperscript{38} In the case at hand, the poor solubility of the BCl\textsubscript{3} complex of \textsuperscript{41}, prevented measurement of pmr data at sufficiently low temperatures to stop interconversion of \textsuperscript{42} and \textsuperscript{43}. It was therefore necessary to estimate the expected chemical shifts of various protons in \textsuperscript{42} and \textsuperscript{43} using suitable model compounds.

The BCl\textsubscript{3} complex of 3-methoxycarbonyl-1,4-cycloheptadiene, \textsuperscript{45}, was chosen as a model for \textsuperscript{42}. As the synthesis of the neutral precursor of this complex, \textsuperscript{44}, has not been reported previously, a new procedure for preparation of 3-substituted-1,4-cycloheptadienes was developed and is described at the end of this chapter.

\[
\begin{align*}
\text{COOMe} & \xrightarrow{\text{BCl}_3} \text{Me}_2\text{NH} \\
\begin{array}{c}
\text{44} \\
\text{45}
\end{array}
\end{align*}
\]

The complex \textsuperscript{45} was prepared by reaction of \textsuperscript{44} with a slight excess of BCl\textsubscript{3}, eq.22, in a CD\textsubscript{2}Cl\textsubscript{2} solution. The complex was stable at -78°.
and its pmr parameters, recorded at this temperature, are presented in Table 4. From the pmr data it is clear that 45 has the structure indicated. For example, the low field absorptions of the α and β protons are an unambiguous evidence that the rearrangement of 45 to 1,2-divinyl-cyclopropane, which would parallel the isomerization of 36 to 37, did not occur. The reaction of 45 with dimethylamine at low temperature produced a high yield of 2-methoxycarbonyl-1,3-cycloheptadiene, rather than the starting ester, 44. However, as 44 was found to undergo a facile rearrangement to give the conjugated diene, this result is not surprising and does not cast any doubt on the structure of 45. Heated to 0°, 45 rearranged to an unidentified product.
Table 4: Proton chemical shifts of some BCl$_3$ complexes and their neutral precursors.$^a$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Proton chemical shifts$^{b,c}$ (δ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H_α$</td>
</tr>
<tr>
<td>35</td>
<td>2.48</td>
</tr>
<tr>
<td>27</td>
<td>1.60</td>
</tr>
<tr>
<td>41</td>
<td>2.40</td>
</tr>
<tr>
<td>42+43</td>
<td>3.20</td>
</tr>
<tr>
<td>44</td>
<td>4.23</td>
</tr>
<tr>
<td>45</td>
<td>5.31</td>
</tr>
</tbody>
</table>

$^a$ in CD$_2$Cl$_2$ at -40°C
$^b$ the subscript indicates the position of the proton with regard to the ester group
$^c$ CHCl$_3$ (δ7.30) used as an internal standard

A striking feature of the pmr spectrum of 35 is the unexpectedly high field position of the C-7 proton ($H_α$) resonance. This resonance appears at δ 2.48, while that of $H_α$ of the model compound 44 occurs at δ 4.23 (Table 4). The reasons for this behaviour will be discussed in more detail in Chapter IV. At this point however, it can be concluded that since 44 does not appear to be a good model for 35, probably the complex 45 cannot be considered to be a good model for the cycloheptatriene complexes.
It was therefore necessary to estimate what the proton resonance positions of the fully cycloheptatriene complex 42 and norcaradiene complex 43 would be. To this end it was assumed that the deshielding of the C-1, C-6 and C-7 proton resonances, accompanying the transformation of 41 to 42, would be the same as those observed for the corresponding protons of 44 as it was transformed into 45. This of course assumes that the deshielding expected in the amide and ester cases would be much the same, and based on the similarity of the downfield shifts of the appropriate methyl resonances of protonated methylacetate and N,N-dimethylacetamide this would appear to be a reasonable assumption.75,76 As a model for the chemical shifts of the norcaradiene complex, 43, the chemical shifts of 37 were used and it was again assumed that the cyclopropyl protons of 43 would resonate at nearly the same position as those of 37.

The amount of the norcaradiene form present can then be calculated using the following formula:19

\[ p_N = \frac{(\delta_C - \delta)}{(\delta_C - \delta_N)} \times 100\%
\]

where \( \delta \) is the observed chemical shift of a proton, \( \delta_N \) and \( \delta_C \) are the chemical shifts of the same proton in the individual cycloheptatriene and norcaradiene isomers. As the \( \beta \)-proton resonances appear at considerably different positions in cycloheptatriene and norcaradiene, these resonances appear to be especially suitable for this type of calculation. Using \( H_\beta \): \( p_N = \frac{(5.26 - 4.81)}{(5.26 - 3.45)} \times 100 = 25\% \). That is, the equilibrium concentration of norcaradiene tautomer 43 is 25\%.
Replacement of One Oxygen Group with a Hydrogen Atom

Huisgen\textsuperscript{77} has reported that cyclooctatetraene epoxide, $46$, can be protonated with FSO$_3$H to give the 8-hydroxyhomotropylium cation. The epoxide, $46$, was reacted with various Lewis acids, in order to see if a comparable homotropylium cation or a 7-norcaradienylmethyl cation, $47$, could be prepared.

\[
\text{AlCl}_3 \\
\text{TlCl}_4 \\
\text{SnCl}_4
\]

\[
\text{CH}_2\text{-}C=\text{H} \\
\text{CH}_2\text{-CH(OMe)}_2
\]

\[
\text{H}_2\text{O/MeOH}
\]

Treatment of CDCl$_3$ solution of $46$ at -78$^\circ$ with a series of Lewis acids gave in each case only benzenoid products. No indication of the presence of a homotropylium cation, norcaradiene $47$, or its cycloheptatriene tautomer was found when the pmr spectra were recorded at -75$^\circ$, shortly after mixing $46$ with the Lewis acids. The spectra obtained under these conditions resembled the spectrum of the complex $48$ prepared by reacting the Lewis acids with phenylacetaldehyde.
Reaction of an Al₂Cl₆ complex of 46 with a mixture of water, methanol and sodium bicarbonate, resulted in recovery of phenylacetaldehyde, the dimethylacetal of this aldehyde and some apparently polymeric material. The latter material was involatile and exhibited a broad resonance in the aromatic region of its pmr spectrum. The volatile products were separated and identified by comparing their pmr and ir spectra and gc retention times with those of authentic materials. The reasons for the difference in behaviour of 46 on protonation and on complexation with Lewis acids are not clear at this time.

7-Formylcycloheptatriene, 49, became available in 1971 when Grigg reported that it could be prepared by a rhodium catalyzed rearrangement of 46. All attempts to prepare 47 by reaction of 49 with a series of Lewis acids were unsuccessful. Once again, the Lewis acid complex of phenylacetaldehyde was the only product detected by pmr, even when the aldehyde and the Lewis acid were reacted and the pmr spectrum recorded at -100°C.

\[
\begin{align*}
\text{CHO} & \quad \xrightarrow{\text{L.A.}} \quad \text{CHO} \\
\text{CHO} & \quad \xrightarrow{\text{SO₂ClF or CH₂Cl₂}} \quad \text{CHO}
\end{align*}
\]

\[49\]

L.A. = BCl₃, TiCl₄, SnCl₄
Conclusions from the Experiments in which the Electronwithdrawing Power of the C-7 Substituent was Modified

In this work it has been shown that the position of the CHT/NCD equilibrium in 7-cycloheptatrienylmethylcations which have two C-8 oxygen substituents, resides almost entirely on the NCD side. Another compound of this type, 50, was reported by Betz and Daub. Based on the pmr spectrum of this system, which incidentally is very similar to that of 37 and 39, the authors have also concluded that this cation exists completely in the norcaradiene form.

Zwitterions 37, 39 and the cation 50 are the first examples of monosubstituted norcaradienes and their existence demonstrates that norcaradiene can be made stable by attachment of a single substituent at C-7.

When the positive centre at C-7 of these systems is stabilized with both an oxygen and a nitrogen substituent, both tautomers, cycloheptatriene and norcaradiene, are present in substantial amounts. Thus in this work 42 and 43 were shown to exist in a ratio 3:1. A series of
similar cations has been prepared by Betz and Daub and with all these systems the tautomeric composition was found to be close to that of \( 42/43 \). The same authors have also reported the preparation of one 7-cycloheptatrienylcarbonium ion, which had two nitrogen containing substituents at C-8, 51. From the pmr data of this cation they concluded that it existed completely in the monocyclic form 51.

\[ \text{FSO}_3^- \]

The electronwithdrawing ability of these cationic substituents would be expected to diminish in the following order:

\[ -\text{Me}^+ < -\text{Me}^+ < -\text{N}^+ < -\text{N}^+ \]

This same order was observed for the norcaradiene stabilizing ability of these substituents. It would thus seem that the amount of norcaradiene tautomer present in equilibrium with the norcaradiene increases with the rising electronwithdrawing ability of the C-8 carbon.
Although the attempted complexation of 46 with Lewis acids resulted only in formation of benzenoid materials, the neutral aldehyde itself, was found to be of interest. In the original paper, this compound was assumed to have the monocyclic structure. However the pmr spectrum of 46, Fig. 3, would seem to indicate that it exists as a rapidly equilibrating mixture containing a detectable amount of the bicyclic tautomer. For example, the overlap of the pmr resonances of the C-2/C-5 and C-3/C-4 protons is a common feature of norcaradienes or tautomeric mixtures of norcaradienes and cycloheptatrienes. The higher field position of the resonance of the C-1/C-6 protons of 49, as compared with that of corresponding 7-methoxycarbonylcycloheptatriene protons, also indicates the presence of some of the norcaradiene tautomer. Taking the C-1/C-6 proton chemical shifts of 35 as a model for those of 49, and if the corresponding resonances of 52 are used as model for those of 7-formynorcaradiene, the amount of the NCD isomer in the equilibrating mixture could be estimated to be 7%.

\[ \eta_N = \frac{(5.43 - 5.25)}{(5.43 - 2.63)} \times 100 = 7\% \]

According to the calculations of Stöhrer (Table 2) the formyl group should be the best uncharged norcaradiene stabilizing substituent and a carboxylic acid function the next best norcaradiene stabilizing group. It is interesting that, as has been shown very recently, some 3% of the norcaradiene form, 52, exists in an equilibrium with 7-cycloheptatrienylcarboxylic acid.
The Structure of Norcaradienes 37 and 39

Examination of the pmr spectra of the complexes 37 and 39 revealed that the positions of the resonances attributable to the three cyclopropyl protons were seemingly anomalous. For example, the C-7 proton signal of both 37 and 39 occurred at about δ 1.6. This resonance is found at much higher field than would be expected for the resonance of an α proton of a cyclopropylcarbinyl cation (typically δ 2.8 - 3.8). Moreover resonances of β protons of cyclopropylmethyl cations either occur at higher field than that of the α proton (δ 1.8 - 3.0), or the resonances of both the α and β protons overlap and appear as one multiplet. In the norcaradiene complexes 37 and 39 however, this order is reversed and the α proton signals appear as much as 1.8 ppm upfield from those of β protons.
The unusual chemical shifts found in the complexes 27 and 29 could either be due to the norcaradiene structure of these compounds or be a common feature of cyclopropylcarbinyl cations substituted with -OMe and -OB₃ groups. In order to distinguish between these two possibilities, the pmr spectra of some BCl₃ complexes of some cyclopropylcarboxylic esters were investigated.

The model cyclopropyl zwitterions were prepared from methyl cyclopropylcarboxylate, 52, and 9-methoxycarbonylbicyclo[6.10]nonatriene, 54. Ester 52 was prepared from the commercially available acid and the bicyclic compound 54 was obtained by transesterification of the known corresponding ethyl ester. 82

Reaction of the cyclopropyl compound 52 in CD₂Cl₂ with BCl₃ resulted in the formation of the zwitterion 55, eq. 23. The pmr spectrum of 55 (Table 5) consisted of a singlet at δ 4.10, multiplet at δ 1.65 and a further multiplet at δ 2.76 in a ratio 3 : 4 : 1. This
spectrum is comparable to that of similar cations in which the positive charge was induced by protonation of the carbonyl oxygen.81

While the chemical shifts of cyclopropyl protons of 55 are quite different from those of 37, it could be argued that 55 is not a good model for one of these norcaradiene complexes. For example the cyclopropyl ring in 55 does not have any vinyl substituents and these would be
expected to deshield the β protons. However the cyclopropyl group of the zwitterion 56 bears two such vinyl substituents and this complex could therefore be considered to be a fairly good model for the norcaradienes 27 and 29. Complex 56 was prepared by reaction of 24 in CD₂Cl₂ with BCl₃ at low temperatures eq.24. The complex was found to be stable below 0°, and could be reacted with dimethylamine to recover 24 in a high yield.

\[
\begin{align*}
\text{COOMe} & \quad \text{Me₂NH} & \quad \text{BCl₃} \\
\text{54} & \quad & \quad \text{56}
\end{align*}
\]

In the pmr spectra of 56, recorded at -40° (Table 5), the resonances of the cyclopropyl protons appeared as one overlapping multiplet between δ 2.56 and 2.83 and the individual α and β proton resonances could not be assigned. Although it is apparent that the resonances of the β protons of 56 are deshielded as compared to that of 55, they are still within the range of values expected for a cyclopropylcarbinylication. 81

Thus in both model compounds 55 and 56, the chemical shifts of the cyclopropyl protons do not seem to be different from that which would be expected if the positive charge had been induced by protonation. In
other words, the seemingly anomalous resonance position of the cyclo-
propyl protons of 37 and 39 must be a function of the norcaradiene
structure itself and not of the Lewis acid moiety.

Table 5: Proton chemical shifts of cyclopropyl zwitterions

<table>
<thead>
<tr>
<th>Compound</th>
<th>Proton chemical shift (δ)ᵃ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hᵣ</td>
</tr>
<tr>
<td>37</td>
<td>1.60</td>
</tr>
<tr>
<td>55</td>
<td>2.76</td>
</tr>
<tr>
<td>56</td>
<td>2.56</td>
</tr>
</tbody>
</table>

ᵃ. in CDCl₃ at -40°C, CHCl₃ used as internal standard

It could be suggested, that the unexpected resonance positions of the
cyclopropyl protons of 37 could be accounted for on the basis of the
diamagnetic anisotropy of the double bonds in the six-membered ring. Since
the norcaradiene ring system is rigid and its geometry is fairly well
established,⁵¹,⁵² the magnitude of such an effect can be calculated.

However the shielding effect of the double bonds of norcaradienes on the
cyclopropyl protons, estimated using the tabulated results of Pople,⁸³
was found to be very small. Thus the endo C-7 proton would be expected
to experience a shielding of 0.1 ppm while the C-1 and C-6 protons were
predicted to be deshielded by the same amount, Table 6. Tillieu⁸⁴ has
reported a different calculation of the diamagnetic anisotropy of a
double bond and using his results the effect on the cyclopropyl atoms
was again found to be very small.
An alternative possibility is that norcaradienes 37 and 39 are aromatic. If this were the case then in a magnetic field, a ring current would be induced in the six-membered ring. This situation would result in a shielding of the protons above and below the centre of the ring and deshielding of the protons residing in the periphery of the ring, Figure 6.

Figure 6: Ring current in norcaradiene

The effect of the induced diamagnetic ring current of a benzene on protons located in its vicinity has been estimated using theoretical and semiempirical calculations. The latter methods appear to give
better results for the protons located in close proximity to a benzene ring and the tabulated results obtained by this method have been used in this work. Table 6 presents the experimentally measured shielding of the cyclopropyl protons of 37 obtained using 56 as a model, the shielding calculated for the structure 37 with localized double bonds and the shielding calculated for norcaradiene in which the six-membered ring is assumed to have the same degree of aromaticity as benzene.

Table 6: Shielding of norcaradiene cyclopropyl protons

<table>
<thead>
<tr>
<th>Protons</th>
<th>$H_\alpha$</th>
<th>$H_\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured shielding b</td>
<td>1.0</td>
<td>-0.6</td>
</tr>
<tr>
<td>Calculated for localized double bonds c</td>
<td>0.1</td>
<td>-0.05</td>
</tr>
<tr>
<td>Calculated for aromatic norcaradiene d</td>
<td>1.0</td>
<td>-0.4</td>
</tr>
</tbody>
</table>

a) in ppm, the negative values refer to deshielding;
b) obtained as a difference in chemical shifts of the corresponding protons in 37 and 56;
c) obtained using data in ref. 83;
d) obtained using data in ref. 85b.

The results in Table 6 seem to indicate that a model for norcaradiene with an aromatic structure fits the experimental data better than a structure with isolated double bonds.

Molecular orbital methods have been frequently used to describe the interaction of the cyclopropyl ring with the diene moiety in norcaradiene and analogous molecules. According to this
view point the highest occupied molecular orbitals (HOMO) of norcaradiene arise from a mixing of the two cyclopropyl Walsh orbitals \( \psi_{2a} \) and \( \psi_{1s} \) with the butadiene molecular orbitals (MO) \( \psi_{2a} \) and \( \psi_{1s} \). The symmetry element used for qualification of the MO's of norcaradiene is the plane intersecting C-7 and the centre of C-1, C-6 and C-3, C-4 bonds. The subscript "a" denotes antisymmetric and "s" symmetric with regard to this symmetry element, Figure 7.56a

Figure 7: Highest occupied molecular orbitals of norcaradiene
While this method can account for the effect of a C-7 substituent on the stability of a norcaradiene, it reveals little about the possible aromatic character of such a system. In Winstein's original formulation of the concept of homoaromaticity, it was suggested that when a suitable geometrical arrangement is maintained, an interruption of a cyclic polyene array (for example by a CH$_2$ group) does not completely prevent the cyclic delocalization. In this sense homoaromaticity is an extension of Hückel aromaticity to cyclic systems with an interrupted polyene chain.

Previously, the concept of homoaromaticity has been applied mainly to the charged species, cations and anions. Perhaps the best known representative of such compounds is the homotropylium cation. It is interesting to note that this system is isoelectronic with norcaradiene.

An insight into the mechanism of homoconjugation can be derived from consideration of the interaction between cyclopropane and the residual $\pi$-system. One factor which affects such an interaction is the difference between the energies of the donor and the acceptor orbitals. Haddon$^{89}$ has considered the union of a butadiene with a cyclopropane to form a homobenzene. He assumes that there is some homoconjugative interaction in the norcaradiene molecule. Nevertheless he has concluded that the large energy gap between the molecular orbitals involved ($\psi_{3s} + W_{1s}$ and $\psi_{2a} + W_{3a}$) and the lack of drive for a charge delocalization in this neutral system reduces the interaction and the homoaromaticity.$^{89}$

This situation may well be changed when an electron withdrawing substituent is placed on C-7. Withdrawal of the electron density from $W_{2a}$
to the substituent would induce donation from $\psi_{2a}$ of the diene to the electron deficient $W_{2a}$. In this situation the back donation from $W_{1s}$ into $\psi_{3s}$ may be of increased importance. The net result of such an interaction should be a stabilization of the norcaradienylcarbinyl cation. Thus an electron deficient C-7 substituent could facilitate the homoconjugative overlap of the formally neutral ring system and enhance the homoaromaticity of norcaradiene.
A slightly different formulation of homoaromaticity was put forward by W. J. Hehre. He visualized homoaromatic compounds as derivatives of aromatic polyenes formed by replacement of one double bond by a cyclopropyl ring. The logic behind such a move is suggested by the resemblance of the symmetric Walsh orbital to the $\pi$ orbital of the double bond. According to this view the two electrons occupying $W_{1s}$ should be able to delocalize over the ring. The resulting homoaromatic polyene would have a similar structure as the aromatic parent compound and would contain an identical number of electrons in cyclic conjugation.

In this view, 6-electrons of norcaradiene would delocalize over the six carbons in a Hückel ring. The relationship between norcaradiene and benzene would be analogous to that of the tropylium and homotropylium cation.
One consequence of this would be that in the presence of an external magnetic field a ring current should be induced in the six-membered ring.\textsuperscript{91} Shielding of the C-7 proton and deshielding of the C-1, C-6 protons, compatible with the presence of a ring current was in fact observed in both 37 and 39. It can be concluded that the 7-norcara-dienylcarbinyl cations are homoaromatic compounds. In this connection it is interesting to note that when Sargent initially considered the 7-norcara-dienylmethyl cation he remarked that formulation of the cyclopropylmethyl cation in a conventional way imparts some benzenoid character to norcaradiene.\textsuperscript{53}

A controversy has developed recently about the length of the homoconjugated linkage (a-b) in systems such as the homotropylium cation. Using a perturbational approach based on frontier orbitals, Haddon\textsuperscript{89a,c} has arrived at the conclusion that homotropylium has an "open" cyclopropane unit, and using a MINDO/3 method he has calculated the length of a-b bond to be 1.621 Å.\textsuperscript{89b} On the other hand, based on ab initio
calculations at the STO-3G level, Mehre has formulated homotropylium as the bicyclo[5.1.0]octadienyl cation, with an a-b bond length of 1.512 Å. No experimental data are presently available to corroborate either of these calculations.

This work presents some evidence that homoaromatic compounds and are norcaradienes rather than compounds with an "open" cyclopropyl ring (cycloheptatrienes). An experimentally determined value of the C-1, C-6 distance in these compounds would be of a great interest.

**Thermal Rearrangement of Zwitterions**

The norcaradiene complexes were found to be stable when kept at low temperatures however, on heating they underwent a ring contraction to give benzenoid products. Thus at temperatures above 0°, 27 rearranged to give three products, one of which was identified as the BCl₃ complex of methyl phenylacetate. The pmr spectrum of this product (resonances δ 4.19, 4.62 and 7.4 ) was consistent with the structure 57. Methyl phenylacetate, 58, was recovered when the solution containing the rearranged product was reacted with dimethylamine. The reaction of 58 with
BCl₃ in a CD₂Cl₂ solution gave the complex 57, which had an identical pmr spectrum to that described above.

In addition to the signals attributable to 57, the pmr spectrum of the rearrangement products of 37 contained some other resonances. In particular, signals at 3.87, 4.16 and part of signal at 7.4 δ remained to be accounted for, Table 7.

Table 7: Proton chemical shifts of rearranged products of 37 and 39

<table>
<thead>
<tr>
<th>Product</th>
<th>Proton chemical shift a, δ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ArH</td>
</tr>
<tr>
<td>57</td>
<td>7.2 - 7.6</td>
</tr>
<tr>
<td>62</td>
<td>7.2 - 7.6</td>
</tr>
<tr>
<td>60 + 61</td>
<td>7.2 - 7.6</td>
</tr>
<tr>
<td>60 + 63</td>
<td>7.2 - 7.6</td>
</tr>
<tr>
<td>64</td>
<td>7.1 - 7.5</td>
</tr>
</tbody>
</table>

a) CHCl₃ (δ 7.30) used as an internal standard

When the solution of the rearrangement products of 37 was reacted with ethanol, two compounds were formed. These products were isolated and identified as 58 and 59. A similar reaction of 57, prepared from phenylacetaldehyde and BCl₃ gave 58 as the sole product. On this basis and by comparison with the results obtained with rearrangement of 39 (vide infra) it would seem that the additional products formed on thermal rearrangement of 37 were the acylium cation 60, BCl₄, and 61, Scheme 2. Some evidence for the presence of 61 has been obtained from the pmr
study of the reaction product of BCl₃ and MeOH. This reaction has been reported to give methoxyboronhalides such as 61 in the following manner:

\[ \text{BCl}_3 + \text{MeOH} \xrightarrow{-80^\circ} (\text{MeO})_{n} \text{BX}_{3-n} + nX^- \]

The methyl resonance ascribed here to 61 occurred in the same region of the pmr spectrum as that of an equimolar solution of BCl₃ and methanol in CDCl₃.

Scheme 2: Thermal rearrangement of 37
The BBr₃ complex 39 rearranged in a comparable manner to that of 37, to give the BBr₃ complex of methyl phenylacetate, 62, the acylium cation 60, the counterion BBr₄, and 63, Table 7. The rearrangement of 39 however, occurred at much lower temperatures than those required for 37. Thus with a two-fold excess of BBr₃, 39 rearranged at -43° with a half life of 40 min, Table 8.

Table 8: Rate constants for rearrangement of norcaradiene complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>ester to Lewis acid ratio</th>
<th>k_{obs} (sec⁻¹)</th>
<th>temp °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>37</td>
<td>1 : 1.1</td>
<td>4.6 x 10⁻⁵</td>
<td>0</td>
</tr>
<tr>
<td>37</td>
<td>1 : 10</td>
<td>2.8 x 10⁻⁴</td>
<td>0</td>
</tr>
<tr>
<td>39</td>
<td>1 : 2</td>
<td>2.7 x 10⁻⁴</td>
<td>-43</td>
</tr>
<tr>
<td>42 + 43</td>
<td>1 : 1.1</td>
<td>5.2 x 10⁻⁶</td>
<td>0</td>
</tr>
</tbody>
</table>

a) obtained by following the reaction by pmr.

The complex 62, formed on thermal rearrangement of 39 or by reacting 58 with BBr₃, was at -43° slowly converted to 60 and 63. The ir spectrum of the rearranged product was obtained and this exhibited an absorption at 2270 cm⁻¹. This would confirm that an acylium cation had been formed, as typically cations of this type exhibit the carbonyl absorptions in this region. For example the phenylmethylacylium cation, with a SbF₆⁻ counter ion, has been reported to absorb at 2279 cm⁻¹.95
The BCl₃ complex of N,N-dimethyl-7-cycloheptatrienylcarboxamide, 42 / 43, rearranged at 0° very slowly to give the BCl₃ complex of N,N-dimethylphenylacetate, 64. No formation of the acylium cation 60 was observed in this reaction. A complex with a pmr spectrum identical to that of the rearrangement product of 42 / 43, could be prepared by reacting N,N-dimethylphenylacetaldehyde, 65, with BCl₃ in a CD₂Cl₂ solution. A 94% yield of the amide 65 was obtained on reaction of the solution of rearrangement product of 42 + 43 with water or dimethylamine, Table 9.
Table 9: Products obtained on quenching complexes and thermally rearranged materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Quenching agent</th>
<th>Product a</th>
</tr>
</thead>
<tbody>
<tr>
<td>37</td>
<td>Me₂NH</td>
<td>35 (100%)</td>
</tr>
<tr>
<td>32</td>
<td>Me₂NH</td>
<td>35 (100%)</td>
</tr>
<tr>
<td>42 + 43</td>
<td>water or Me₂NH</td>
<td>41 b</td>
</tr>
<tr>
<td>57 (58%) + 60 (42%)</td>
<td>Me₂NH</td>
<td>58 (70%)</td>
</tr>
<tr>
<td>57 (60%) + 60 (40%)</td>
<td>EtoH</td>
<td>58 (58%) + 52 (42%)</td>
</tr>
<tr>
<td>60 + 63</td>
<td>EtoH</td>
<td>58 (13%) + 52 (87%)</td>
</tr>
<tr>
<td>64</td>
<td>water or Me₂NH</td>
<td>65 (94%)</td>
</tr>
</tbody>
</table>

a) yield determined by comparison with internal hexamethylbenzene

b) no other product detected by pmr.
Both the distribution of the rearrangement products and the rate of rearrangement of 27 were found to be dependent on the ratio of the ester to Lewis acid used. Thus as is shown in Table 8, when the ratio of BCl₃ to 35 was increased the rate of the rearrangement of 57 was enhanced and also the relative amount of the acylium cation 60 produced was increased, Table 10.

Table 10: Products of thermal rearrangement of 27

<table>
<thead>
<tr>
<th>ester to Lewis acid ratio</th>
<th>temp °C</th>
<th>57</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0.9</td>
<td>20</td>
<td>93</td>
<td>7</td>
</tr>
<tr>
<td>1:2</td>
<td>20</td>
<td>77</td>
<td>23</td>
</tr>
<tr>
<td>1:8</td>
<td>20</td>
<td>42</td>
<td>58</td>
</tr>
</tbody>
</table>

a) the ratio of the products was determined by integration of the pmr spectra

It is important to note however, that the enhanced rate cannot be accounted for simply by the increase in the amount of the acylium cation produced, but that the rate of formation of 27 was also increased by the addition of BCl₃.

While the formation of acylium cations from protonated carboxylic acid derivatives is well known, in this case 60 was not formed from 57. Thus when a solution of 57 prepared by reaction of 58 with BCl₃, or by thermal rearrangement of 27, was heated for 1 hour to 50° no formation of 60 was detected by pmr. The acylium cation 60 must therefore be a primary rearrangement product of 27.

A reaction sequence which can account for these experimental observations is outlined in the Scheme 3. The starting norcaradiene can be considered to be in an equilibrium with the cyclobutyl zwitterion 66.
Scheme 3: Thermal rearrangement of 27
and this could undergo a 1,2 hydride shift to give 67. Comparable cyclobutyl cations have been suggested as intermediates in the ring contraction reactions of certain homotropylium cations. The energy difference between 66 and 67 might not be all that great as the cyclohexadienyl cation in 67 is forced to be twisted by the fused cyclobutane ring and some homodiencylic stabilization of the positive charge in 66 is possible. Rigidity of the system would make it difficult for the appropriate geometry for this hydride shift to be attained. For these reasons the transformation of 66 to 67 might well be the slow step in such a rearrangement.

The rate of isomerization of 37 and the product distribution were found to be dependent on the ratio of the Lewis acid to the ester used. As the ester is almost completely complexed under the reaction conditions, this would suggest that a further isomerization pathway is available which involves a second molecule of BCl₃. In the suggested intermediate 66, the positive charge is removed from the ester oxygen and this could interact with a further molecule of Lewis acid to give 70. The rate of the hydride shift which leads from 70 to 68 could well be expected to be faster than the comparable shift linking 66 to 67 as a result of the additional positive charge in the complex 70.

There are two possible reaction pathways open for 68. Elimination of one Lewis acid molecule would lead to 67 which would probably rapidly aromatize to 57. Competing with this reaction could be the fragmentation of 68 into 69, BCl₄, and methyldichloroborinate, followed by rearrangement of 69 into the acylium cation 60. A comparable ring opening of cyclobutanone cations similar to 69 have been reported. The suggested mechanistic scheme can account for the product
distribution and the kinetics of isomerization of 27 under different conditions, Tables 8 and 10. Scheme 3 is also consistent with the observed rates of isomerization of 39 and 42/43. The overall rate of isomerization of these complexes would not only be a function of the rates of the slow hydride shifts, but would also be dependent on the several pre-equilibrium steps involved. In the amide case, the amount of the norcaradiene form present in equilibrium with the cycloheptatriene is substantially smaller than with 27, and this factor might be at least partially responsible for the slower rate of isomerization encountered with the amide complexes 42/43. It is interesting to note that no acylium cation was produced on isomerization of these complexes. The absence of 60 in the rearrangement products of 42/43 might be due to the fact that the elimination of (Me) 2 N-BCl 3 from an intermediate similar to 68, is relatively slow so that rearrangement to a nitrogen analogue of 67 prevails. This explanation is consistent with the poor leaving ability of the NR 3 + group in E 1 elimination reactions. 100

The borontribromide complex 29 was observed to rearrange much more rapidly than the BCl 3 analogue, 27. This increase in the rate of isomerization could be attributed to a different position of equilibrium between the norcaradiene and bicyclooctadiene cation when BBr 3 is used as a Lewis acid. Furthermore, the higher Lewis acidity of BBr 3 would alter the equilibrium between species comparable to 66 and 70 in favour of the latter.

It would seem that both the proportion of the norcaradiene form present in the tautomeric mixtures of these cationic systems and also the ease of their rearrangement to benzenoid compounds are directly

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It seems there's a typo in the sentence: "It would seem that both the proportion of the norcaradiene form present in the tautomeric mixtures of these cationic systems and also the ease of their rearrangement to benzenoid compounds are directly..." It should say "It would seem that both the proportion of the norcaradiene form present in the tautomeric mixtures of these cationic systems and also the ease of their rearrangement to benzenoid compounds are directly..."
related to the ability of the C-7 substituents to stabilize the positive charge. This being the case it is not surprising that it has proved to be impossible to detect any unsubstituted, diarylsubstituted or mono-oxyxsubstituted 7-norcaradienyl carbonium ions in this or earlier work, as it would be expected that cations of this type would aromatize very rapidly even at low temperatures. No evidence was found for the formation of heptafulvene, tropylium or homotropylium cations (Scheme 1) in the thermal rearrangement of the norcaradiene complexes.

The 7-cycloheptatrienylcarbinyl and the 7-norcaradienylcarbinyl cations are just two of a family of cations with the molecular formula $C_8H_9^+$. A common entry into this or related substituted series of cations is the addition of an electrophile to cyclooctatetraene, and very frequently the end products of such addition reactions have been reported to be substituted benzenes. Ganelin and Pettit have found some evidence for the intermediacy of seven-membered ring compounds in these rearrangements and they suggested that the initial cation produced is the homotropylium cation, $\text{[7]}$, Scheme 4. The homotropylium cation which in certain reactions can be trapped to give cyclooctatriene products, was thought to rearrange to the cycloheptatrienyl cation, $\text{[7]}$, Scheme 4. The results described in this present thesis would seem to indicate that yet another cation, the 7-norcardienyl methyl cation, is also involved in this rearrangement sequence and that it can lead, possibly via a bicyclo [4.1.0] octadienyl cation, to benzenoid materials. It should be pointed out that there are other possible rearrangements pathways from homotropylium cations.
Scheme 5: Rearrangements of cations C₈H₉⁺

Synthesis of 3-substituted-1,4-cycloheptadienes

As was discussed earlier, 3-methoxycarbonyl-1,4-cycloheptadiene, 4₄₄, was required as a precursor of the zwitterion 4₅₅. Since no report of the preparation of this ester was found in the literature, a new synthetic route to 4₄₄ had to be designed. Surprisingly, the synthesis of 4₄₄ was not as straightforward as one might have expected for such an ostensibly simple, low molecular weight compound.
The first attempted approach to \( \text{44} \) involved the preparation of the cycloheptadiene anion, \( \text{73} \), and the reaction of this anion with a potential source of a carboxy group, Scheme 5.

\[
\text{\chem{\includegraphics[width=0.4\textwidth]{diagram.png}}}
\]

Scheme 5: Attempted synthesis of \( \text{44} \)

The cycloheptadiene anion \( \text{73} \) has been described before\textsuperscript{104-106} and has been used to obtain 5-substituted 1,3-cycloheptadienes.\textsuperscript{104,106a} Dark red solutions of \( \text{73} \) were prepared by abstraction of a proton from 1,3- or 1,4-cycloheptadiene, \( \text{74} \), with strong bases such as \( \text{KNH}_2 \), \( \text{tBuLi} \), or \( \text{iPrLi} \), or directly from cycloheptatriene by reacting it with two equivalents of lithium dissolved in liquid ammonia.

Several different trapping reactions were attempted in attempts to obtain \( \text{44} \). Reaction of \( \text{73} \) with an excess of solid carbon dioxide gave two isomeric cycloheptadienes and a mixture of carboxylic acids. The carboxylic acids were reacted with \( \text{CH}_2\text{N}_2 \) and the mixture of esters so formed was separated by vpc into 7 fractions. Although not all of these
fractions were identified, in no case were the spectral data compatible with \( \text{NH}_3 \). Ter Borg has reported somewhat similar results.\(^{105}\)

\[
\begin{array}{c}
\text{CO}_2 \\
\text{in NH}_3
\end{array} \xrightarrow{} \begin{array}{ccc}
\text{COOH} & + & \text{COOH} \\
25\% & + & 30\% & + & 8\%
\end{array}
\]

Reaction of \( \text{73} \) with ethylchloroformate led to a similar mixture of esters.

As cycloheptatriene can be reduced with lithium in liquid ammonia, a similar reduction\(^{107}\) of cycloheptatriene-7-carboxylic acid was attempted, eq. 27, however once more a complex mixture of esters was obtained upon treatment of the product with diazomethane.

\[
\begin{array}{c}
\text{COOH} \\
\text{Li/NH}_3
\end{array} \xrightarrow{} \begin{array}{c}
\text{COOH}
\end{array}
\]

In view of the complexity of these reactions involving anionic species a milder, more specific route was sought. Allred and Hinshaw have reported that the azocompound \( \text{75} \) decomposes thermally at 25° to give 1,4-cycloheptadiene and nitrogen, eq. 28.\(^{108}\)

\[
\begin{array}{c}
\text{N} \\
\text{25°} \\
\text{N}
\end{array} \xrightarrow{} \text{COOH}
\]

75
It appeared likely, that a similar reaction of 76 would produce the desired ester 44 in a pure form and under very mild conditions.

\[
\begin{array}{c}
\text{COOMe} \\
\text{[Diagram of 76]} \\
\text{?} \\
\text{COOMe}
\end{array}
\]

Since 75 was prepared by hydrogenation of the Diels-Alder adduct of cycloheptatriene and 4-phenyl-1,2,4-triazoline-3,5-dione, \textit{6d,109} a similar route was employed for preparation of 76 (Scheme 6 and 7).

The addition of 77, prepared "in situ" by oxidation of 72 with leadtetraacetate, to 7-substituted cycloheptatrienes proceeded rapidly at low temperatures to give a high yield of the tetracyclic compound 78. The structure of 78 was established from its spectral data, elementary analysis, and the subsequent chemical reactions. The stereochemistry at the carbon bearing the substituent R was determined from the magnitude of the coupling constant between the bridgehead cyclopropyl hydrogens, and the proton adjacent to the ester group, \( J = 3.0 \text{ Hz} \). A coupling of this magnitude is clearly indicative of the proposed geometry, \textit{78,68}.

The cycloheptatrienes entered the Diels-Alder reaction only in the norcaradiene form. No adduct such as 81, derived from the cycloheptatriene form, was detected.

The adduct 78 was hydrogenated at atmospheric pressure using a Pd/C catalyst to give 80 in a high yield. The resonance of the
bridgehead cyclopropyl protons of 78 and 80, R=COOMe, appear at almost the same position (2.19 and 2.11 δ respectively) in their pmr spectra, however the proton geminal to the ester group resonated at 1.41 δ in 78 and at 1.87 δ in 80. The shift of the resonance of this proton by 0.45 ppm on saturation of the double bond indicates that the proton was located in the shielding region of the double bond and further confirms the assignment of the stereochemistry of the cyclopropyl ring.
Hydrolysis of 80 with alcoholic potassium hydroxide yielded the hydrazo compound 83 and aniline. Shorter reaction times led to the recovery of partially hydrolyzed product, compound 82.

\[
\text{80} \quad \xrightarrow{\text{KOH/Methanol, 4 hr}} \quad \xrightarrow{\text{1. HCl}} \quad \xrightarrow{\text{2. CuCl}_2} \quad \text{83}
\]

\[
\text{80} \quad \xrightarrow{\text{KOH/Methanol, 24 hr}} \quad \xrightarrow{\text{2 CO}_2} \quad \xrightarrow{\text{1. HCl}} \quad \xrightarrow{\text{2. CuCl}_2} \quad \text{83}
\]

\[
\text{83} \quad \xrightarrow{\text{1. HCl}} \quad \xrightarrow{\text{2. CuCl}_2} \quad \text{84}
\]

\[
a) \quad R_1 = \text{COO}^- \quad R_2 = \text{COOH} \\
b) \quad R_2 = \text{CH(OMe)}_2 \quad R_2 = \text{CHO}
\]

Scheme 7: Synthesis of 84

Compound 83 was found to be sensitive towards oxygen and when exposed to air, it was rapidly converted into a dark gluey polymeric material. Thus in a typical reaction, 83 was not isolated but the reaction mixture was dissolved in nitrogen saturated water, acidified to pH 4 and treated with 2 equivalents of CuCl₂. The role of cupric
chloride was two-fold; it oxidized 83 into 76, and subsequently reacted with this azocompound to form the stable 84. The copper complexes such as 84 could be prepared in reasonable quantities and stored as stable precursors of 1,4-cycloheptadienes, such as 44.

Treatment of 84 with aqueous base liberated 76. The azo compound 76 was thermally unstable and when heated to $35^\circ$ eliminated nitrogen and gave substituted cycloheptadienes, Scheme 8. The structure of the product was found to depend on the base used. Thus if the copper complex 84a was decomposed with a 0.1 N KOH solution, only the conjugated acid 85 was eventually isolated, however, 86 was the sole product of the reaction when 1 equivalent of potassium carbonate was used as a base.

\[ \text{[76a]} \xrightarrow{35^\circ} - \text{N}_2 \]
\[ \xrightarrow{0.1 \text{ N KOH}} \]
\[ \xrightarrow{\text{K}_2\text{CO}_3} \]

Scheme 8: Synthesis and rearrangement of 44
The synthesis was then completed by acidification of the solution to pH 2.5, extraction of the organic acid with ether and subsequent esterification with diazomethane to give 44. The ester 44 was found to be rather unstable, and at room temperature it rearranged to the conjugated ester 87, with the half life of about 12 hours.

A similar reaction sequence was used to prepare 3-dimethoxy-methyl-1,4-cycloheptadiene, 88. However, since the acetal group of 88 is acid sensitive the last step of the synthetic procedure had to be modified. Instead of preparing the copper complex, the solution of 83b obtained from hydrolysis was directly oxidized with air to 76b. The thermolysis of this azocompound at 35° afforded 88, eq. 29.

\[
\begin{align*}
83b & \xrightarrow{O_2 \text{ (air)}} \begin{bmatrix} \text{CH(OMe)}_2 \end{bmatrix} & 35^\circ & \begin{bmatrix} \text{N} \\ \text{N} \end{bmatrix} & \xrightarrow{-N_2} \begin{bmatrix} \text{CH(OMe)}_2 \end{bmatrix}
\end{align*}
\]

(29)

Scope and Evaluation of Synthesis Scheme 5-7

The reaction sequence outlined in Schemes 5-7, may appear to be a cumbersome synthesis of such simple compounds as 44. However, in spite of the number of steps and intermediates involved, it is a reasonably fast and efficient procedure. For example the yield of the Diels-Alder adducts is in vicinity of 80%, and both the hydrogenation and esterification steps proceed fairly rapidly with almost 100% efficiency. The hydrolysis, decarboxylation, nitrogen cleavage and esterification,
80→44 (Schemes 6 and 7), gave typically a combined yield of 35%, thus making the overall yield of 44 from cycloheptatriene 35 about 29%.

Variously substituted cycloheptadienes can be prepared by the appropriate choice of starting cycloheptatriene, or by modification of the cyclopropyl substituent of 80. For example treatment of 80b, prepared from 7-dimethoxymethylcycloheptatriene 61, with aqueous acid, eq. 30, converted the acetal quantitatively into the aldehyde 89. The difficult preparation of the unstable 7-formylcycloheptatriene 46 was thus avoided.

Similarly, 20 could be prepared by reacting 80 with MeLi and subsequent hydrolysis and oxidation reactions, Scheme 6 and 7.

The 1,4-cycloheptadienes were found to be thermally unstable and to rearrange readily into the corresponding 1,3-isomers, eq. 31. The rate of this rearrangement appeared to depend on the electron-withdrawing power of the substituent. For example the following order of stabilities of 3-substituted-1,4-cycloheptadienes was qualitatively
observed: \( H \rightarrow C(\text{Me}_2)\text{OH} = \text{CH(O\text{Me}_2)} > \text{COO}^- > \text{COOMe} > \text{COOH} > \text{CHO} \). Thus for example while \( \text{ester} \) can be heated to \( 60^\circ \) without a noticeable rearrangement, ester \( 44 \) rearranged rapidly above \( 40^\circ \) and the corresponding acid was even more thermally labile. The attempted synthesis of \( 3\)-formyl-1,4-\( \text{cycloheptadiene} \) from \( \text{ester} \) resulted in isolation of the conjugated isomer, even when the synthesis was carried out in a cold room at \( +4^\circ \). The rate of rearrangement, eq., eq. increased drastically in the presence of strong acids or bases. The advantage of the synthesis outlined in Schemes 5 to 7 is that the 1,4 dienes are prepared at low temperatures.
CHAPTER III

PREPARATION OF SUBSTITUTED HOMOTROPYLIDENES

A major difficulty in investigation of the effect of a substituent on a position of the CHT/NCD equilibrium is the large thermodynamic preference for one of the isomers. The doubly degenerate homotropylidene system does not possess this inherent structural disadvantage and for this reason it was decided to study the effect of a substituent on the equilibrium between 28 and 29. The electronic structure of 3,4-homotropylidene is very similar to that of cycloheptatriene and norcaradiene and consequently it was felt that the homotropylidene system would serve as a good model for the CHT/NCD equilibrium.

\[ \text{28} \quad \text{29} \]

3,4-Homotropylidene (28, R=H) is just one member of a series of related fluxional systems which can undergo degenerate Cope transformations. Also included in this series are bullvalene, 21, bullvalone, 22, barbaralane, 23, barbaralone, 24, semibullvalene, 25, and several compounds derived from azabullvalene, 26.

\[ \text{91 - 96, 28} \quad (X \text{ is indicated on the next page}) \]
Not all of these systems are equally suited for use as models for the CHT/NCD equilibrium. For example, substituted bullvalenes can undergo a 1209600 fold degenerate rearrangement and the substituent can be scrambled around the entire molecule.\textsuperscript{118}

Fluorobullvalene \textsuperscript{21} R=F was found to exist predominantly as the isomer "a" just as might be expected on the basis of the theoretical calculations of the related semibullvallene system.\textsuperscript{141,58} However, determination of the composition of the equilibrium mixture in \textsuperscript{21} R=F was
hampered by the availability of additional sites for the fluorine. Moreover, all bridged homotropylidenes are only capable of monosubstitution on C-4 or C-8 and thus steric effects resulting from disubstitution can not be readily studied. Therefore the preparation of substituted 3,4-homotropylidenes which do not possess these disadvantages was attempted.

While the synthesis of 1,4-homotropylidenes was being attempted, several studies of the effect of a substituent on bridged homotropylidenes have been reported. The deuterium and methyl substituted barbalones were investigated by Schleyer and co-workers. They showed that deuterium was preferentially located on the sp\(^3\) rather than on the cyclopropyl carbon. The reverse situation was found with the methyl substituted system in which the methyl group was largely located on the cyclopropyl carbon. It should be pointed out however, that the bridging carbonyl group could be attenuating or modifying the effects of these substituents.

\[
\begin{array}{c}
\text{R = Me} & 77\% \\
\text{R = D} & 46\% \\
\end{array}
\]

Another doubly degenerate system of this type, semibullvalene, has been extensively studied by Paquette and co-workers. All the substituted compounds they were able to prepare existed predominantly as 95a.
While the equilibrium position for the systems bearing electron-withdrawing substituents, such as Ph or CN, is that expected on the basis of Hoffmann's \(^{44}\) and Dewar's \(^{58}\) calculations the interpretation of the effect of alkyl substituents is much less simple. In its interaction with semibulvallene the methyl group would be expected to be a net electron donor \(^{120}\) and to have a bond strengthening effect on the fused cyclopropane bond. For example, it has been observed that a methyl group bonded to a cyclopropane ring causes a shortening of the \(\beta\) and lengthening of the \(\alpha\) cyclopropyl C-C bonds. \(^{121}\) The results obtained with \(^{95}\) do not seem to follow this pattern.

Semibulvallene is the only bridged homotropylidene which has been used for a systematic investigation of substituent effects. However the range of substituents studied so far is rather narrow and for example, it does not include any strongly electron-donating substituents. Furthermore, due to the considerable strain intrinsic to a semibulvallene molecule, \(^{95}\) might not be the ideal model for a CHT/NCD system. Thus the synthesis of the substituted homotropylidenes still appears to be desirable.
Attempted Synthesis of Substituted 3,4-homotropylidenes

Three routes to substituted homotropylidenes have been investigated:

a) Addition of a carbene to cycloheptatriene.

\[
\text{R'} \quad + \quad :\text{CHR}'' \quad \rightarrow \quad \text{R}'' \quad \text{R'}
\]

b) Elimination of nitrogen from 9,10-diazatetracyclo [3.3.2.0₂,₄.0₆,₈]dec-9-ene.

\[
\text{R} \quad \xrightarrow{-\text{N}_2} \quad \text{R}
\]

c) Introduction of a second double bond into substituted bicyclo[5.1.0]oct-2-ene.

\[
\text{R} \quad \xrightarrow{-\text{HX}} \quad \text{R}
\]

Work on each of these routes is discussed in separate sections.

ADDITION OF A CARBENE TO CYCLOHEPTATRIENE

The first reported synthesis of unsubstituted 3,4-homotropylidene involved the addition of :CH₂ to cycloheptatriene. The reported yield of the desired product was low and this method involves a rather difficult separation of 3,4-homotropylidene from its 1,2- isomer.

The adoption of this method for the preparation of substituted
homotropylidenes could be achieved by the use of either a substituted cycloheptatriene or a substituted carbene (or carbenoid). Some preliminary experiments on both these routes were carried out.

\[
\text{R}^1 + \text{CHR}'' \rightarrow \text{R}^1-\text{CHR}''-\text{R}^2
\]

a. \( \text{R}^1 = \text{COOEt}, \quad \text{R}'' = \text{H} \)
b. \( \text{R}^1 = \text{H}, \quad \text{R}'' = \text{COOEt} \)

**Simmons-Smith Reaction on 7-ethoxycarbonylcycloheptatriene**

One useful method of converting an olefin into a cyclopropane is the Simmons-Smith reaction.\(^{122}\) This reaction is particularly suitable for alkenes which are flanked by a group which can function as a Lewis base and coordinate with the attacking carbenoid species.\(^{123}\) However when this reaction was attempted with 7-ethoxycarbonylcycloheptatriene a whole range of products was obtained. The products were separated by preparative vpc and tentatively identified on the basis of their spectroscopic properties, Scheme 9. It is possible that a small amount of the desired 3,4-homotropylidene was present in one of the fractions, however it could not be successfully isolated.

It will be noted that the bis adduct \(^97\) has been formulated as arising from a norcaradiene precursor. Similar adducts have been reported as products from the catalysed decomposition of ethylidiazoacetate in benzene.\(^{124}\) In view of the results described previously with the
Scheme 9: Simmons-Smith reaction with 7-ethoxycarbonylcycloheptatriene

Lewis acid complexes of 35, it is possible that similar copper or zinc complexes are formed during these carbenoid reactions.

**Addition of \( \cdot \text{CHCOOEt} \) to Cycloheptatriene**

The copper catalysed reaction of ethyldiazocetate in cycloheptatriene, eq. 32 has been previously reported to give only one monoadduct, namely 98.\(^{125}\) This reaction was reinvestigated however, even though monoadduct species were detected, it was not possible to isolate them in a pure state and characterize them.

\[
\begin{align*}
\text{Cycloheptatriene} + \text{N}_2\text{CHCOOEt} & \xrightarrow{\text{hv or Cu}} \text{Cycloheptatriene} \cdot \text{COOEt} + \text{Cycloheptatriene} \\
& \text{(32)}
\end{align*}
\]
This seemingly simple approach to substituted 3,4-homotropolidenes was not further investigated.

ELIMINATION OF NITROGEN FROM 9,10-DIAZATETRACYCLO[3.3.2.0^2,4.0^6,8]DEC-10-ENE

The ready synthesis of compounds such as 78a, discussed in the previous chapter of this thesis, suggested that they might serve as a convenient precursor for substituted 3,4-homotropolidenes. Thus as is shown in Scheme 10, the addition of a further cyclopropane to 78a, followed by hydrolysis, decarboxylation, oxidation and nitrogen elimination would be expected to yield 28. Several closely related synthesis of multi-cyclic systems have been reported.108,116,126

![Scheme 10: Possible synthesis of 28](image)

In spite of seemingly good literature precedence for such a synthetic route to 28, it did not prove possible to achieve the first stage of this sequence, namely the cyclopropylation of the double bond of 78a. Attempts to add a methylene using a Simmons-Smith procedure,122
to add :CHCOOEt by using ethyldiazoacetate,\textsuperscript{127} and to add :CCl\textsubscript{2} using Seyferth's Ph-Hg-CCl\textsubscript{3} reagent,\textsuperscript{128} all failed. Similarly it was not possible to induce diazomethane to undergo a 1,3-dipolar addition to the double bond of 78a.\textsuperscript{129}

One difficulty in working with 78a, was its very low solubility which caused these attempted cyclopropylation reactions to be carried out either in very dilute solutions or as heterogeneous mixtures. In order to circumvent this inconvenience, the preparation of the diester 99 was attempted, eq. 33.

\[
\begin{array}{c}
\text{COOMe} \\
\text{35}
\end{array} + \begin{array}{c}
\begin{array}{c}
\text{R} = \text{COOEt}
\end{array}
\end{array} \xrightarrow{} \begin{array}{c}
\text{COOMe}
\end{array} + \begin{array}{c}
\text{COOMe}
\end{array}
\]

The reaction of 35 with diethylazodicarboxylate gave two compounds, the adduct 99, derived from the norcaradiene form and the cycloheptatriene adduct, 100. The ratio of the two products formed was found to be dependent on the temperature at which the Diels-Alder reaction was carried out. For example when the reaction was performed at 50\degree it the ratio of 99 to 100 was 1.7 : 1 however this ratio increased to 5.7:1 when the reaction was allowed to proceed slowly at -5\degree. The products of this reaction were separated by column chromatography. The tricyclic compound 99 was isolated in a pure form, however 100 appeared to be a mixture of different stereoisomers, probably involving the ester group on the three carbon bridge.
Temperature Dependence of the pmr Spectra of 99

When the pmr spectrum of 99 was recorded at +90° the absorptions of all the protons, except those at C-1 and C-5, appeared as sharp signals with a well-defined fine structure. Only one set of signals was recorded for the two ethyl group under these conditions. In the pmr spectrum obtained at +35° all the resonances except those of the methoxy group, appeared to be broadened. Despite the limited solubility of 99 at low temperatures, at -50° it would seem that two sets of signals corresponding to two ethyl groups were present, Figure 8. This temperature dependence of the pmr spectrum of 99 is similar to that observed for the related 2,3-diazabicyclo[2.2.2]octanes, such as 101, and can reasonably be accounted for on the basis of the pyramidal inversion of the ester group about the nitrogen atoms.

![Diagram of 99 and 101](image)

Reaction of 99 with Diazomethane

The 1,3-dipolar addition of diazomethane to 99 was attempted, however, this compound again was found to be very resistant to this type of reaction. Thus when 99 dissolved in ether was treated with a 10 fold excess of diazomethane at -5° for one month, although the pmr spectrum
indicated that the double bond of 22 had reacted, no adduct could be isolated. No significant amount of N₂ was developed when the intractable, honey-like product of this reaction was either heated¹³¹,¹¹⁶ or irradiated.¹²⁶,¹⁰⁸

\[
\begin{align*}
\text{N-R} & \quad \text{CH₂N₂} \\
\text{N-R} & \quad 3 \text{ days, 87\%} \\
\end{align*}
\]

(34)

\[
\begin{align*}
\text{N-R} & \quad \text{CH₂N₂} \\
\text{N-R} & \quad \rightarrow \\
\text{N-N} & \quad \rightarrow \\
\end{align*}
\]

(35)

It is not clear why 78 and 22 seem to be so resistant to the addition of diazomethane, considering that the reactions of similar compounds, eq. 34¹⁰⁸ and eq. 35¹²⁶ have been reported to take place readily.

INTRODUCTION OF A SECOND DOUBLE BOND INTO SUBSTITUTED BICYCLO[5.1.0] OCT-2-ENES

Cyclohepta-2,4-dienones can be prepared by a variety of methods. The parent compound itself can be obtained from cycloheptatriene although the overall yields reported thus far are not very high.¹³² 2,6,6-Trimethylcyclohepta-2,4-dienone 102, eucarvone, can be readily prepared from carvone¹³³ and this more readily available cycloheptadienone was used as a model compound in many of the subsequent reactions.

As shown in the Scheme 11, the conversion of a cyclohepta-2,4-diene into a 3,4-homotropyliidene species formally requires but two steps. These are the conversion of the 2,3-double bond into a cyclopropane and
Scheme 11: Conversion of 86 into 3,4-homotropyliene

the subsequent replacement of the ketone function by a double bond.

Corey has in fact shown that eucarvone, 102, when treated with
(CH₃)₂SOCH₂ gives eq. 36 and there would seem no reason why this
reaction could not be applied to other cycloheptadienones. Substituted
ylid reagents are available and it was thought that it should also be
possible to form a functionalized cyclopropane by a comparable reaction.

The Synthesis of 2,4-cycloheptadienone, 104

The seemingly easiest route to this material is that shown in
Scheme 12. However, as was mentioned earlier, the overall yield of 104
from cycloheptatriene, 3%, is not that good. It has been found that
minor changes in the reaction procedures can increase the overall yield
to some 11% and permit batches of several grams of cycloheptadienone to be prepared at a time. The changes made are indicated in Scheme 12 and in the experimental section.

**Scheme 12: Synthesis of 2,4-cycloheptadienone, 104**

**Cyclopropylation of cycloheptadienones**

The bicyclic ketone 103 was prepared from eucarvone using the procedure described by Corey, eq. 36. A comparable reaction with the parent compound 104 also resulted in the formation of a bicyclic ketone, however 105 was in this case only a minor product, eq. 37.
The main product of reaction eq. 37 was a colourless material with a molecular weight \(m/e = 216.115\) corresponding to a dimer of 104. The ratio of aliphatic to olefinic resonances in the pmr spectrum of this compound was found to be 3:1, and only one carbonyl absorption at 1709 cm\(^{-1}\) was observed in its ir spectrum. One structure compatible with these data is 106. The tricyclic dione 106 could be formed by two consecutive Michael additions\(^{137}\) of 104 catalyzed by the strongly basic ylid, Scheme 13. The structure of this product was not rigorously established.

\[
\begin{array}{c}
104 + (\text{CH}_3)_2\text{S}=\text{CH}_2 \rightarrow \begin{array}{c}
\text{cyclic structure}
\end{array} \\
\text{104} \rightarrow \text{107} \quad \text{base}
\end{array}
\]

Scheme 13: Dimerization of 2,4-cycloheptadiene

A room temperature reaction of 104 with the resonance stabilized ylid 108\(^{138}\) gave a 37% yield of two products, eq. 38 in ratio of 1:2.3. The two compounds were separated on an alumina column and further purified by vpc.
Although the addition of a $\alpha$CR$_2$ element in the reaction of ylids with dienones is known to proceed preferably in the $\alpha,\beta$ position$^{134}$, the formation of a bis adducts under more strenuous conditions$^{138}$ indicates that the $\gamma,\delta$ double bond is not completely inert. Thus the reaction of 104 with the ylid could possibly give four products; 109, 110, and two stereoisomers of 111.

The solid compound with a shorter retention time was identified as a 2,3-addition product on the basis of its spectral properties. The uv spectrum of this compound, $\lambda_{\text{MeOH}} = 202$ nm, is not compatible with the structure 111 as $\alpha,\beta$ unsaturated ketones absorb typically around 230 nm$^{139}$. The uv absorption maxima of $\alpha$-cyclopropyl ketones has been found to depend on the geometry of the molecule. The reported values vary between 197 and 220 nm for the saturated systems$^{140}$, while the introduction of a double bond substituent on the cyclopropane ring can cause a bathochromic effect of some 3-15 nm$^{140,141}$. 
The pmr spectrum of this product contained olefinic and aliphatic proton resonances in a relative amount of 2:7 in addition to the signals attributable to the ethoxy group. While the resonances of the $\beta$ hydrogens of $\alpha,\beta$ unsaturated cyclic ketones typically occur at a considerably lower field than those of the $\alpha$ hydrogens, this addition product displayed only one narrow band in the olefinic region of the pmr spectrum.

The other product obtained was a liquid, the elementary analysis and the spectral data of which were consistent with both structures, 109 and 110.

While it seems certain that the products of reaction eq. 38 are 109 and 110, determination of the stereochemistry at C-8 proved to be difficult. It is tentatively assumed that the larger fraction with the longer retention time, has the less crowded exo structure, 110.

Formally one would expect that two different isomers of 28 could be formed from 109 and 110. However the stereochemical identity of the two carbons residing in the plane of symmetry of the rapidly rearranging
system 28/29 would be lost, if the Cope rearrangement occurred via both chair-like and boat-like transition states,\textsuperscript{143,144} Scheme 14.

![Scheme 14: Synthesis of 28 from 109 and 110](image)

It was therefore expected that the mixture of both of the isomers, 109 and 110 could be used for preparation of 28.

**Transformation of Carbonyl Function to a Double Bond**

The number of different procedures described in the chemical literature for the introduction of a double bond into a molecule is immense and this perhaps testifies to the difficulties that can be encountered with this type of reaction. Basically, starting with a ketone function, there are some four different general types of reaction sequences that have been employed. These are:

a) Reduction to alcohol and an ionic type elimination of water or some other molecule after suitable derivatization of the alcohol.

b) Reduction to alcohol, formation of an ester or a related derivative, and a thermal, concerted elimination.
c) Reaction of the ketone with a hydrazine; its subsequent conversion to a diazo compound, elimination of nitrogen followed by a hydrogen shift to give the olefin.

d) Formation of an enol ester derivative from the ketone and appropriate cleavage of the enol ester group.

Each of the above mentioned routes has been investigated and the results of these studies are given in the subsequent sections of this chapter.

**Reduction to Alcohol, Ionic Elimination**

1. **Reduction**

The carbonyl group of 103 has been previously reduced using lithium aluminium hydride.\(^{150}\) Since this reagent would also reduce the ester group in compounds such as 109 and 110, the reduction of the carbonyl group of these bicyclo[5.1.0]oct-5-en-2-ones was attempted with sodium borohydride. However, instead of formation of the alcohol in high yield as would be expected,\(^{145}\) esters of boric acid were obtained as the principal products. Thus 103 on treatment with NaBH\(_4\), gave a high yield of 113 Similarly the esters 109 and 110 were largely converted to boric esters on reaction with NaBH\(_4\).

The formation of the esters of boric acid during the borohydride reduction of hindered ketones has been previously noted\(^{117-119}\) and their hydrolysis has sometimes proved to be difficult.\(^{116}\) It was found that the alcohol 112 could be liberated from the corresponding boric ester 113 by treating it with MeOH/H\(^+\),\(^{146}\) H\(_2\)O/H\(_3\)O\(^+\),\(^{147}\) or NH\(_4\)OH.\(^{148}\) The last mode of reaction was found to be most convenient.

Alternatively 103 could be reduced with Li (BuO)\(_3\)AlH,\(^{149}\) eq. 39.
Since this reagent is normally unreactive towards ester groups under the conditions used, this procedure would also be expected to be suitable also for reduction of 109 and 110.

Bellamy and co-workers have recently reported that they were unable to dehydrate 112 by either direct or indirect methods. For example treatment of 112 with P₂O₅ in benzene or with polyphosphoric acid or the pyrolysis of the corresponding acetate, were all reported to result in complete destruction of the bicyclic structure and formation of a number of products. As the conditions of these reactions were rather strenuous, some milder reactions were attempted in this work.

The direct dehydration of 112 was attempted by injection of the alcohol on a gas chromatographic column filled with neutral alumina.
under a variety of conditions (temperature, length of column, flow rate). The product of the reaction was invariably a mixture of benzenoid compounds which was not further analyzed.

In an attempt to introduce a better leaving group, 112 was reacted with methane sulfonylchloride (MsCl) in 2,6-lutidine using similar conditions to those used with other alcohols. The product of this reaction was decomposed with sodium ethoxide, or with lutidine at 70°. A major reorganization of the compound occurred in both cases, leading to at least 16 products none of which constituted more than 25% of the mixture. A similar result would seem to have been obtained by Bellamy upon reacting 112 with POCl₃ in pyridine.

A very efficient dehydrating agent, bis(hexafluoro-2-phenyl-2-propyloxy) diphenylsulfurane, 118, was recently developed by Martin. Sulfurane 118 was reported to dehydrate secondary alcohols in seconds at room temperature. Moreover it was reported that while the acid catalyzed dehydration of 119 led only to ring opened products, 31% of 120 was formed on reacting 119 with the sulfurane 118, eq. 40.

The addition of 118 to a chloroform solution of 112 caused an immediate reaction as was shown by the drastic change in the pmr spectrum of the solution. However the vpc analysis of the products obtained once more indicated that many products were formed. Five major fractions were
collected and were shown to be hexafluoro-2-phenyl-2-propanol, \( 121 \), di-phenylsulfoxide, \( 122 \), and three different hydrocarbons. The mass spectra of these hydrocarbons indicated that they were isomers with a molecular formula corresponding to \( C_{11}H_{18} \). The pmr spectra of these compounds were incompatible with the structure of trimethyl-3,4-homotrotylidene, \( 123 \), and the materials were not further identified.

Dehydration of \( 112 \) was also attempted by treating it with \( SO_2Cl_2 \) in pyridine, \(^{154}\) with tosylchloride in pyridine \(^{155}\) and by heating it with iodine. \(^{156}\) None of these reactions led to isolation of \( 123 \).
Pyrolysis of Esters of 112

In an attempt to avoid the formation of the seemingly rearrangement prone cationic intermediates, the dehydration of 112 was attempted by the pyrolysis of some of its ester derivatives. Eliminations of this type are generally considered to occur in a concerted fashion and structural changes in the rest of molecule are less likely to be encountered.\textsuperscript{157}

The pyrolysis of the acetate of 112 has been recently attempted by Bellamy.\textsuperscript{150} Neither this reaction, not the pyrolysis of corresponding boric ester\textsuperscript{158} investigated in this work, led to the formation of 123. The temperature required for pyrolysis of esters depends on the nature of the ester group. For example while the acetate of 112 was pyrolysed at 460\degree,\textsuperscript{150} the pyrolysis of xanthates (Chugayev reaction) typically occurs at 100-200\degree.\textsuperscript{157} As it was expected that 123 would survive this temperature, the Chugayev reaction was attempted with 112.

\begin{equation}
\begin{aligned}
112 & \xrightarrow{\text{MeLi, CS}_2, \text{MeI}} \xrightarrow{220^\circ} \text{11 products} \\
\text{124}
\end{aligned}
\end{equation}

Xanthate 124 was prepared from 112 and purified by distillation at reduced pressure. The thermal decomposition of 124 did not take place until it was heated to 220\degree and then a mixture of some 11 products was obtained. Three major constituents of the reaction mixture were isolated but neither of these had pmr spectrum compatible with the structure 123.

Scheme 15 summarizes all the types of dehydration attempted.
Ionic eliminations:
1. $\text{Al}_2\text{O}_3$ 150-250$^\circ$
2. $\text{SO}_2\text{Cl}_2$/pyridine
3. $\text{TsCl}$/pyridine
4. $\text{MsCl}$/pyridine
5. Sulfurane 118 reaction
6. $\text{I}_2$
7. polyphosphoric acid
8. $\text{P}_2\text{O}_5$/benzene
9. $\text{POCl}_3$/pyridine

Concerted eliminations:
10. xanthate pyrolysis
11. boric ester pyrolysis
12. acetate pyrolysis

reactions 1-6, 10 and 11, this work
reactions 7-9 and 12 Bellamy

Scheme 15: Attempted dehydration of 112.

Fragmentation of 6-diazo-4,4,7-trimethylbicyclo[5.1.0]oct-2-ene

The difficulties encountered with the dehydration of 112 stimulated the investigation of alternative routes for transformation of a ketone function in a double bond. In one such alternative procedure, the ketone is first converted into a tosylhydrazone and the sodium salt of the latter is then thermally decomposed to yield, after liberation of
nitrogen, the desired olefin.\textsuperscript{159-161} This reaction probably involves the intermediacy of a carbene\textsuperscript{159} or a carbanion\textsuperscript{160,161} rather than a rearrangement prone carbonium ion and it seems to be suitable for cyclopropyl ketones. For example, vinylcyclopropane was prepared in a good yield from the methyl vinyl ketone using this procedure,\textsuperscript{160} eq. 41

\begin{equation}
\text{CH}_3

\begin{align*}
\text{CH}_3 & \rightarrow \text{CH}_2
\end{align*}
\end{equation}

Tosylhydrazone \textsuperscript{125} was prepared by reaction of \textsuperscript{102} with a 10\% excess of \textit{p}-toluenesulfonylhydrazide. This hydrazone, \textsuperscript{125}, was reacted with NaH in refluxing benzene to give a single product which was shown to be the acetylene \textsuperscript{126}. The structure of this new product was assigned on the basis of its spectral data (ir, uv, high resolution mass spec., single and double irradiation pmr and cmr experiments) which are given in full in the experimental section.

\begin{tikzpicture}

\begin{scope}[scale=0.6]

\node (a) at (0,0) {102};
\node (b) at (2,0) {125};
\node (c) at (4,0) {126};
\node (d) at (4,2) {TsNHNH\textsubscript{2}};
\node (e) at (4,-2) {N-NHTs};

\draw[->] (a) -- (b);
\draw[->] (b) -- (c);
\end{scope}

\end{tikzpicture}

In a parallel reaction, the tosylhydrazone \textsuperscript{127} prepared from \textsuperscript{104} was heated at reduced pressure with NaH in refluxing parafin and the single volatile product was condensed in a cold trap. Again an acetylene (\textsuperscript{128}) was the only product. The identity of \textsuperscript{128} was established from its
spectroscopic data and by its hydrogenation to give a product whose ir spectrum and vpc retention times on two different columns were identical with those of n-octane.

Cleavage of the Enol Ester Group

A simple two step procedure for preparation of olefins from ketones was developed by Ireland. In this method the ketone is first converted to an enol ester of tetramethylphosphorodiamic acid (TMPD) and the ester group is then removed by a reduction with dissolving metal in liquid amine or ammonia, to give a high yield of the olefin.

In the analogy with Ireland's method, the enolate was prepared by reacting with (iPr)₂NLi and immediately reacted with tetramethyldiamidophosphorochloridate. The product of this reaction was a white solid, the pmr spectrum of which was consistent with the structure. The crude material was dried and without further purification treated with an excess of Li in liquid ammonia.
The vpc analysis of the reduction product revealed that it was composed mainly (95%) of two components with a similar retention time. These major constituents were separated by preparative vpc and investigated by spectroscopic methods. The pmr spectrum of each one of these compounds contained a complex resonance between δ 0.9 and 2.2 and a signal of smaller area between δ 5.0 and 6.0. Integration of the pmr spectra revealed that the ratio of aliphatic to olefinic resonances was approximately 15:1 and 8.6:1 respectively. A molecular ion m/e = 150.1408, corresponding to a molecular formula of C_{11}H_{18}, was found in the high resolution mass spectrum of both of these compounds.

While the identity of the last two compounds has not been definitely established, structures such as 132 or 133 are possible. It is clear that the Birch reduction not only removed the HMPD group, but also saturated one of the double bonds of 123, which possibly occurred as an intermediate. As isolated double bonds are not normally reduced under these reaction conditions, it is possible that base catalysed isomerization of the double bonds is occurring to give a conjugated diene.
Conclusion

The plethora of products encountered in these attempted dehydrations that involved cationic intermediates, probably results from the adjacent vinylcyclopropyl system. Opening of the cyclopropane would not only relieve the strain energy inherent in this three-membered ring \(^{164}\) but would also lead to a relatively stable allyl cation, \(^{134}\).

\[
\begin{align*}
\text{OR} & \quad \rightarrow \quad \text{further reactions} \\
\text{134}
\end{align*}
\]

The structural features of the derivatives of \(^{112}\) mentioned above possibly cause the ester pyrolysis reaction to proceed by a polar mechanism. For example, even though the pyrolysis of xanthates is usually assumed to be a concerted process with a six-membered transition state, \(^{135}\) being involved, eq. 42, a polar mechanism, eq. 43, is also conceivable. This might be especially favoured, if it is enhanced by release of the strain energy of the cyclopropyl ring and by the stability of the carbonium ion formed in the process.

\[
\begin{align*}
\text{OCS}_2\text{Me} & \quad \rightarrow \quad \text{O} \quad \rightarrow \quad + \text{HSCOSMe} \\
\text{135}
\end{align*}
\]

\[
\begin{align*}
\text{OCS}_2\text{Me} & \quad \rightarrow \quad \text{HSCOSMe} \\
\text{135}
\end{align*}
\]
The thermal decomposition of tosylhydrazone salts usually gives olefins as the major products, \textsuperscript{160,161} however formation of acetylenes has been reported in the case of \(\alpha\)-oxiranyl and certain \(\alpha\)-cyclopropyl-tosylhydrazones.\textsuperscript{163} For example, the hydrazone \textsuperscript{136} decomposes to a mixture of the olefin \textsuperscript{137} and acetylene \textsuperscript{138}.\textsuperscript{159}

\[
\text{COOEt} \quad \text{N-NHTs} \quad \text{COOEt} \quad \text{N-NHTs} \quad + \quad \text{N-NHTs} \quad + \quad \text{N-NHTs}
\]

The difference in behaviour of \textsuperscript{136} and the hydrazones \textsuperscript{125} and \textsuperscript{127} could be caused by the stabilizing effect of the vinyl group on the anionic intermediate formed on opening of the cyclopropane ring of the latter compounds.

\[
\text{127} \quad \text{base} \quad \text{Ts} \quad \text{N=N} \quad \text{N=N} \quad \text{N=N} \quad \text{N=N} \quad \text{N=N} \quad \text{N=N}
\]

It is interesting to note that a 3,4-homotropylidene was actually prepared by the last route attempted, the enol ester cleavage reaction. The enol ester \textsuperscript{131} is in fact 3,4-homotropylidene and should be capable of undergoing a valence tautomerism, eq. \textsuperscript{44}.
Although the resonances attributable to the ester function cover a large part of the pmr spectra of 131 and render this particular type of ester unsuitable for variable temperature pmr studies, it should be possible to form some simpler ester derivatives. As a substituent on the central carbon of a homotropylidene should not affect the position of the equilibrium between the two possible valence tautomers, perhaps further work in this area might be directed towards the preparation of such derivatives as the enolacetates or enol ethers of 129.
CHAPTER IV

DIAMAGNETIC SUSCEPTIBILITY MEASUREMENTS OF SOME
CYCLOHEPTATRIENES AND A NORCARADIENE

As was mentioned in Chapter 1 of this thesis, Doering originally suggested that cycloheptatriene and norcaradiene were but two resonance forms of a single homoaromatic molecule.\(^5\) Although such a structural representation was subsequently rejected in the light of evidence which demonstrated that these two molecules were valence tautomers, it is still possible that each individual tautomer could possess some homoaromatic delocalization.

Before discussing the existing evidence regarding the possible aromaticity of these systems, it is advisable to review carefully what is meant by this term. While there is no common agreement about the definitions of the terms aromatic or aromaticity, it is generally recognized that this property is somehow related to the thermodynamic stability of a molecule and its ability to sustain an induced diamagnetic ring current. This latter phenomenon has been used by several authors as a basis for a definition of aromaticity. For example Garratt\(^{165}\) would define an aromatic molecule as being -

"a cyclic system which exhibits a diamagnetic ring current and in which all the ring atoms are involved in a single conjugated system."

Inextricably linked to the problem of the definition of aromatic character, is also the problem of establishment of criteria for both its
presence and also its importance in a molecule. Suggested criteria include reactivity, thermodynamic stability, various spectroscopic properties, bond lengths, and the presence of an induced diamagnetic ring current when the molecule in question is placed in a magnetic field. As most of these criteria are dependent upon a comparison of the properties of the molecule with a "wisely chosen non-aromatic molecule", frequently the pronouncement of a compound as being aromatic is a highly subjective thing. One reason that a definition based on an induced magnetic ring current would seem to be gaining increased favour among organic chemists is that it provides a physical property which can be experimentally determined. Indeed Jackman has gone one stage further in the definition of aromaticity in suggesting that the magnitude of the induced diamagnetic ring current is a measure of the degree of aromaticity of a molecule.

It has been suggested that the presence and magnitude of an induced diamagnetic ring current can be evaluated from proton magnetic resonance experiments by an analysis of the chemical shifts of the resonances of various, appropriately placed nuclei. This is difficult to do however, as once more model compounds are required. Such a procedure for example, is used in the Chapter 2 of this thesis and the success of an argument of this type is only good as the model compounds chosen. In this present chapter the question of the aromaticity of cycloheptatriene and norcaradiene is reexamined using a technique which enables the diamagnetic susceptibilities of these compounds to be measured directly.

Earlier in this thesis it was proposed that the zwitterions \( \text{37} \) and \( \text{32} \) were aromatic molecules and that they were capable of sustaining
an induced diamagnetic ring current. It was suggested that the aromatic character of these zwitterions, which derives from a mixing of the molecular orbitals of the diene and cyclopropyl moieties, was enhanced by the presence of a $\pi$ electron accepting C-7 substituent. It is interesting to examine the possible aromaticity of some neutral norcaradienes which do not have strongly electron withdrawing substituents on C-7.

In 1963 Vogel and Günther reported the synthesis of norcaradiene 12, the bicyclic form of which is stabilized by the three carbon bridge between C-1 and C-6. On the basis of an analysis of its pmr spectrum, these authors concluded that 12 is not an aromatic molecule. They proposed however that the Co(0) complex of 12, 139, was aromatic. The upfield positions of the resonances of the bridge protons, and the downfield position of the resonances of olefinic protons in 139 were assumed to be at least partially caused by a ring current induced in the six membered ring. This rationalization contains one obvious discrepancy.

The resonances of both of the two methylene bridge protons of 12 moved upfield on complexation of 12 to give 139 by about the same amount (1.6 ppm). As was pointed out earlier (Table 6) semiempirical calculations indicate that the endo proton is expected to be shielded by the ring current of such a six membered ring, however the same type of calculations reveal that the exo-proton should be little affected. The equal difference in the chemical shifts of the two bridge protons of 12 ($\delta_{ex} - \delta_{en} = 1.66$ ppm) and 139 ($\delta_{ex} - \delta_{en} = 1.61$ ppm) seems to indicate that no change in the degree of aromaticity has in fact occurred upon complexation of 12. The upfield shift of the resonances of both of the methylene protons of 139 as compared to 12 may well be caused
by the different distribution of the electron density in the chromium complex 139 and in the free ligand 12. The question of the aromaticity of these compounds can not be considered to be resolved.

The geometry of the cycloheptatriene molecule was discussed earlier and it was concluded that the compound exists in a boat form. Despite its nonplanar conformation, some evidence for the homoaromaticity of this compound has been obtained. For example the resonance energy of 1, determined by comparison of the heats of hydrogenation of 1 and 1,3-cycloheptadiene, is 7 Kcal/mol., about 20% of that of benzene.169

The diamagnetic susceptibility of 1170 and more recently the effect of 1 as a solvent on the chemical shift of a solute,171 also seem to indicate the presence of an induced diamagnetic ring current in a molecule of

As mentioned in Chapter 2, there is a striking difference in the chemical shifts of the C-7 proton of 35 and the C-3 proton of 44. Examination of these chemical shifts reveals, that the "normal" value is that found for 44, while the resonance of the C-7 proton of 35 appears to be at an unexpectedly high field. For example, the value of the chemical shift of the proton attached to a tertiary carbon substituted with two vinyl groups and one ester function can be calculated from Schoolery's equation172 as δ 4.4.

\[
\begin{align*}
\text{35} & \quad \delta 2.48 \\
& \quad \text{COOME}
\end{align*}
\]

\[
\begin{align*}
\text{44} & \quad \delta 4.23 \\
& \quad \text{COOME}
\end{align*}
\]
It could be argued that the high field position of C-7 proton resonance of 25 is caused by the magnetic anisotropy of the C-3, C-4 double bond in the boat conformation 35a. However, using the results of calculation of Tillieu83 and Pople84 for the long range shielding of a double bond, the resulting shielding effect on the C-7 proton of 25 is found to be less than 0.2 ppm.

Alternatively, the position of the C-7 proton resonance of 25 could be explained in terms of a deshielding caused by an induced ring current in 35.

\[ \text{COOME} \quad \text{MeOOC} \]

35a 35b

**Measurement of Diamagnetic Susceptibility Exaltation**

The diamagnetic susceptibility of a compound may be readily determined using a two-compartment nmr tube and a high resolution nmr spectrometer.173, 174 In order to determine whether the susceptibility includes a contribution from the induced ring current, it is necessary to evaluate the expected susceptibility in the absence of any ring current. Following the early work of Pascal,175 it has been shown that the molar magnetic susceptibilities of organic compounds are approximately additive functions of their constituent groups, and several systems have been devised for estimation of susceptibilities based on this fact. While the molar susceptibilities, \( x_M \), so estimated are usually very close to the
measured susceptibility, $\chi_M$, for non-aromatic compounds, benzenoid and other aromatic compounds exhibit somewhat larger susceptibilities than those predicted using an incremental system. The difference in the calculated and measured susceptibilities has been defined as the diamagnetic susceptibility exaltation $\Lambda$. The presence of a diamagnetic susceptibility exaltation can be taken as a criterion of aromaticity and the magnitude of the exaltation can be related to the degree of the delocalization within the molecule.  

$$\Lambda = \chi_M - \chi_m.$$ 

A series of cycloheptatrienes and related compounds were prepared and their volume magnetic susceptibilities $\kappa$ were determined using the Douglass and Fratiello method. The densities of the investigated compounds were determined at the same temperature as that measured in the probe of the NMR instrument ($36^\circ$). From the experimentally measured separations, densities and from molecular weights of the compounds, the diamagnetic susceptibilities per gram, $\chi$, and molar diamagnetic susceptibilities, $\chi_M$, were calculated. This procedure is illustrated for example with cycloheptatriene: The calibration of the reference assembly with eight standard solvents (see the Experimental Section for details) gave a calibration equation for volume magnetic susceptibility, $\kappa$, and reference peak separation, $n$ (Hz): $10^6 \cdot \kappa = 0.008655 \cdot n + 0.2314$

Measured separation (Fig. 8), $n = 39.35$ Hz

Measured density ($35^\circ$), $\rho = 0.8743$ g/cm$^3$

$$\kappa = (0.008655 \times 39.35 + 0.2314) \cdot 10^{-6} = 0.572 \cdot 10^{-6}$$
\[ \chi = \kappa / \rho = 0.572 / 0.8743 = 0.6540 \times 10^{-6} \text{ cm}^3 / \text{g} \]
\[ \chi_M = \chi \cdot M = 0.6540 \times 92.14 = 60.2 \times 10^{-6} \text{ cm}^3 / \text{mol.} \]

The pertinent data for all the other compounds are compiled in Table 11.

The calculated diamagnetic susceptibilities were obtained using the semiempirical increment system of Haberditzl.\textsuperscript{177} A typical calculation for cycloheptatriene is shown in Table 12.

**Table 12: Calculation of \( \chi_M' \) of cycloheptatriene:**

<table>
<thead>
<tr>
<th>element</th>
<th>No. of elements</th>
<th>increment</th>
<th>sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>7</td>
<td>0.15</td>
<td>1.05</td>
</tr>
<tr>
<td>C\textsuperscript{*} - H</td>
<td>6</td>
<td>3.2</td>
<td>19.2</td>
</tr>
<tr>
<td>C\textsuperscript{<em>} - C\textsuperscript{</em>}</td>
<td>5</td>
<td>2.4</td>
<td>12.0</td>
</tr>
<tr>
<td>C\textsuperscript{*} - C</td>
<td>2</td>
<td>2.6</td>
<td>5.2</td>
</tr>
<tr>
<td>C\textsubscript{2} ( \equiv ) C\textsubscript{2}</td>
<td>3</td>
<td>2.2</td>
<td>6.6</td>
</tr>
<tr>
<td>C\textsubscript{2} - H</td>
<td>2</td>
<td>3.8</td>
<td>7.6</td>
</tr>
</tbody>
</table>

\[ \chi_M' \text{ (cycloheptatriene) } = 51.7 \text{ cm}^3 / \text{mol.} \]

*indicates \( \text{sp}^2 \) hybridization; subscript represents the number of atoms (other than H) attached directly to the carbon atom; \( \pi \) indicate a \( \pi \) bond; the increments have units of \( \text{cm}^3 / \text{mol.} \)

Some difficulties were encountered in calculation of \( \chi_M' \) for 7-cyanocycloheptatriene, since the increment for the C\( = \)N bond has not been reported. Using the reported diamagnetic susceptibilities of
Table 11: Separations, densities, mol. weights, and experimentally determined diamagnetic susceptibilities

<table>
<thead>
<tr>
<th>Compound</th>
<th>$n$ (Hz)</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>mol. weight (g/mol.)</th>
<th>$\kappa \times 10^{-6}$</th>
<th>$\chi \times 10^{-6}$ (cm$^3$/g)</th>
<th>$\chi_M \times 10^{-6}$ (cm$^3$/mol.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycloheptatriene$^a$</td>
<td>1</td>
<td>39.35</td>
<td>0.8743</td>
<td>92.14</td>
<td>0.572</td>
<td>0.654</td>
</tr>
<tr>
<td>7-methoxycarbonylcycloheptatriene$^c$</td>
<td>35</td>
<td>10.90</td>
<td>1.0419</td>
<td>150.12</td>
<td>0.606</td>
<td>0.581</td>
</tr>
<tr>
<td>7-methylcycloheptatriene$^b$</td>
<td>140</td>
<td>102.93</td>
<td>0.8432</td>
<td>106.17</td>
<td>0.597</td>
<td>0.709</td>
</tr>
<tr>
<td>7-methoxycycloheptatriene$^b$</td>
<td>141</td>
<td>102.37</td>
<td>0.9131</td>
<td>122.17</td>
<td>0.592</td>
<td>0.648</td>
</tr>
<tr>
<td>7-cyanocycloheptatriene$^b$</td>
<td>142</td>
<td>106.44</td>
<td>1.0026</td>
<td>117.15</td>
<td>0.628</td>
<td>0.626</td>
</tr>
<tr>
<td>7-dimethoxymethylcycloheptatriene$^c$</td>
<td>143</td>
<td>107.80</td>
<td>0.9958</td>
<td>166.17</td>
<td>0.640</td>
<td>0.634</td>
</tr>
<tr>
<td>7-t-butylicycloheptatriene$^c$</td>
<td>144</td>
<td>109.38</td>
<td>0.8484</td>
<td>148.24</td>
<td>0.654</td>
<td>0.771</td>
</tr>
<tr>
<td>2-methoxycarboxyl-1,3-cycloheptadiene$^a$</td>
<td>87</td>
<td>45.82</td>
<td>1.0731</td>
<td>152.12</td>
<td>0.628</td>
<td>0.585</td>
</tr>
<tr>
<td>2-methoxycarboxyl-1,3-cycloheptadiene$^b$</td>
<td>87</td>
<td>45.78</td>
<td>1.0731</td>
<td>152.12</td>
<td>0.627</td>
<td>0.584</td>
</tr>
<tr>
<td>bicyclo 4.1.0 dec-2,4-diene$^c$</td>
<td>12</td>
<td>114.37</td>
<td>0.9495</td>
<td>134.21</td>
<td>0.698</td>
<td>0.735</td>
</tr>
<tr>
<td>bicyclo 4.1.0 dec-3-ene$^c$</td>
<td>145</td>
<td>116.48</td>
<td>0.9169</td>
<td>136.23</td>
<td>0.717</td>
<td>0.782</td>
</tr>
</tbody>
</table>

a. the calibration equation: $\kappa = 0.008655 \times n + 0.2314$, reference toluene, $\text{CH}_3$ resonance

b. the calibration equation: $\kappa = 0.008616 \times n + 0.2325$, reference toluene, $\text{CH}_3$ resonance

c. the calibration equation: $\kappa = 0.008830 \times n - 0.3119$, reference nitromethane
several nitriles it was possible to estimate the value of the \( \text{C} = \text{N} \) bond increment as the difference between the measured values of \( \chi_M \) and the sum of all other increments involved.

Table 13: Calculation of the increment of \( \text{C} = \text{N} \) bond

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \chi_M )</th>
<th>Calculated susceptibility in absence of ( \text{C} = \text{N} ) increment</th>
<th>( \text{C} = \text{N} ) increment</th>
</tr>
</thead>
<tbody>
<tr>
<td>butyronitrile</td>
<td>49.4</td>
<td>40.6</td>
<td>8.8</td>
</tr>
<tr>
<td>propionitrile</td>
<td>38.5</td>
<td>29.6</td>
<td>8.9</td>
</tr>
<tr>
<td>benzonitrile(^b)</td>
<td>65.2</td>
<td>56.6</td>
<td>8.6</td>
</tr>
</tbody>
</table>

a) ref. 178; the increments have units of \( 10^{-6} \) cm\(^3\)/mol.
b) increment of 51.6\(^177\) was used for the phenyl group.

A value of 8.8 was used as the increment of a \( \text{C} = \text{N} \) bond in the calculation of \( \chi_M \) of 142. The measured and calculated molar diamagnetic susceptibilities, and the exaltations \( \Lambda \) are compiled in Table 14.

**Discussion of Diamagnetic Susceptibility Exaltations**

As the data in Table 14 show, the reproducibility of this nmr instrument technique of measuring diamagnetic susceptibilities would appear to be fairly good. Thus the value of \( \chi_M \) for cycloheptatriene determined in this work (50.2 x \( 10^{-6} \)) and that reported by Dauben\(^{170} \) (59.8 x \( 10^{-6} \)) are close and well within the error limits of this type of measurement (±0.5 x \( 10^{-6} \), the values are given in units of cm\(^3\)/mol.).

While the calculation of \( \chi_M \) has been shown by Dauben\(^{170} \) and others\(^{183} \) to be reliable for hydrocarbons and alcohols, the incremental values associated with other functional groups are less well defined.
Table 14: Diamagnetic exaltation data

<table>
<thead>
<tr>
<th>compound to synthesis</th>
<th>$x_M^{\pm 0.5}$ $10^{-6}$ cm$^3$/mol.</th>
<th>$x_M'$ $10^{-6}$ cm$^3$/mol. cm$^3$/mol.</th>
<th>$\Lambda$ $10^{-6}$ (lit.)$^{170}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60.2</td>
<td>51.7</td>
<td>8.5</td>
</tr>
<tr>
<td>25</td>
<td>this work</td>
<td>87.3</td>
<td>77.8</td>
</tr>
<tr>
<td>140</td>
<td>179</td>
<td>75.2</td>
<td>63.8</td>
</tr>
<tr>
<td>141</td>
<td>179</td>
<td>79.1</td>
<td>67.3</td>
</tr>
<tr>
<td>142</td>
<td>180</td>
<td>73.4</td>
<td>61.5</td>
</tr>
<tr>
<td>143</td>
<td>61</td>
<td>106.8</td>
<td>94.0</td>
</tr>
<tr>
<td>144</td>
<td>181</td>
<td>114.3</td>
<td>99.5</td>
</tr>
<tr>
<td>87</td>
<td>this work</td>
<td>88.9</td>
<td>87.3</td>
</tr>
<tr>
<td>12</td>
<td>182</td>
<td>98.7</td>
<td>90.1</td>
</tr>
<tr>
<td>145</td>
<td>168</td>
<td>106.5</td>
<td>101.2</td>
</tr>
</tbody>
</table>

cycloheptene - 0.4
1,3-cycloheptadiene 0.3
1,3-cyclohexadiene - 0.7
benzene 13.7

However, as is shown in the Table 14, the difference in $x_M$ and $x_M'$ for the cycloheptadiene 87 is only $1.6 \times 10^{-6}$ and this does not greatly differ from zero as would be obtained ideally for a non-aromatic molecule. (All values of $\Lambda$ are given in units of cm$^3$/mol.)

It is interesting to note that all the substituted cycloheptatrienes exhibit a greater $\Lambda$ than the parent compound 1. There seems to be no correlation between the electronic requirements of the substituent
and the $\Lambda$ value of the cycloheptatriene. Thus the exaltations of cycloheptatrienes 140 and 141, with electron donating C-7 substituents, are the same as that of 142 which bears at C-7 a powerful electron withdrawing substituent. There appears to be some indication that $\Lambda$ could depend on the size of the C-7 substituent. For example cycloheptatrienes substituted at C-7 with a bulky substituent, 143 and 144, have the values of $\Lambda$ greater than 140 or 141, which in turn have $\Lambda$ greater than 1. However it should be pointed out that compounds such as 142 and 35 do not seem to fit in with this general trend.

One possible explanation for this apparent variation in $\Lambda$ with substituent size could be that the C-7 substituent, which preferentially occupies the pseudoequatorial position, is changing the conformation of the cycloheptatriene and so affecting the amount of delocalization. Perhaps the most important feature of these results is however the general magnitude of $\Lambda$ found in these systems. Thus the magnitudes of the exaltations determined for cycloheptatrienes are comparable to that measured for benzene and substituted benzenes. This clearly indicates that cycloheptatriene and its substituted derivatives can be regarded as aromatic molecules.

Dauben and co-workers have determined that the $\Lambda$ of cyclopropane ring is $5.1^{170}$ If a correction of this value is applied to the $\Lambda$ found for the norcarene 145, the corrected exaltation ($\Lambda$ corr. (145) = 5.3 - 5.1 = 0.2) is then very close to zero, just as expected for a non-aromatic compound. If a similar correction is applied to the exaltation of the norcaradiene 12, the corrected value of $\Lambda$ ($\Lambda$ corr. (12) = 8.1 - 5.1 = 3.0) is again small and would suggest that there is little induced
ring current set up when 12 is placed in a magnetic field. It would seem that this norcaradiene can not be considered to be an aromatic molecule but predominantly exist as noninteracting diene and cyclopropane moieties.

In Chapter II some chemical shift evidence was presented for the aromaticity of norcaradienes 27 and 29. Unfortunately, the solubility of these zwitterions in common solvents prevented determination of their \( \Lambda \) values, and thus the aromaticity of these systems can not be evaluated by this method. In future work in this area it would be interesting to determine the susceptibility of some norcaradienes such as 7,7-dicyanonorcaradiene which do possess electron withdrawing substituents on C-7, to test the suggestion made in Chapter II concerning the role of the substituent in enhancing the interaction of the cyclopropane and diene molecular orbitals in these systems.
CHAPTER V

EXPERIMENTAL SECTION

INSTRUMENTAL

The proton magnetic spectra of all new compounds were recorded using a frequency sweep mode with a Varian HA 100 spectrometer. The chemical shifts were determined using a Varian V4 315 frequency counter and are reported in ppm downfield from tetramethylsilane. A Hewlett-Packard 201C audiogenerator was employed for the double irradiation experiments. Varian A60 and T60 spectrometers were used for routine recording of pmr spectra. The cmr spectra were recorded on a Brucker BNC-12 instrument.

The variable temperature pmr spectra were measured with Varian HR 100 or A60 spectrometers equipped with variable temperature probes, controlled by Varian V6040 temperature regulators. Probe temperature was measured using a copper-constantan thermocouple inserted in a nonrotating nmr tube and connected to a Leeds-Northrup 8692 potentiometer.

TMS was used as an internal standard and locking signal in all carbon tetrachloride solutions. In the solutions containing strong Lewis acids, chloroform, taken as $\delta 7.30$ served as the internal standard. The chemical shifts are reported in units of $\delta$, followed by the multiplicity, relative area of the signals, and in some cases also coupling constants and assignment in brackets.

The infrared spectra were recorded on Perkin-Elmer 521 and 337.
spectrometers calibrated with a polystyrene film and are reported in units of cm\(^{-1}\). The ultraviolet spectra were recorded on a Cary 14 spectrometer.

Vapour phase chromatography was performed on a Varian Aerograph A90-P3 (preparative) and Aerograph 204 (analytical) instruments using helium as the carrier gas at 150 ml/min for the preparative and 50 ml/min for the analytical experiments. The term "SE-30 column" refers to a 10' x \(\frac{1}{4}\)" copper column containing 15% SE-30, the expression "carbowax column" to a 10' x \(\frac{1}{4}\)" copper column filled with 15% carbowax, and the term "analytical carbowax column" is used for a 10' x 1/8" copper column made with 5% carbowax. Chromosorb W, 60-80 mesh was used in all cases as the solid phase.

High resolution mass spectra were obtained on a Consolidated Electrodynamic Inc. Model 21-110b mass spectrometer. All melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. Elementary analyses were performed by Galbraith Laboratories in Knoxville, Tennessee.

MATERIALS

Deuterated methylene chloride, chloroform, boron trichloride and boron tribromide, used for preparation of the complexes, were purified by distillation onto phosphorous pentoxide and were subsequently distilled again immediately before use. Chloroform was washed with water, sulfuric acid, 0.1 N sodium bicarbonate, water, dried over P₂O₅ and distilled twice. CF₂ClH and SO₂ were doubly distilled before use. Aluminum trichloride was sublimed twice at reduced pressure and stored in a dry box. SbCl₅ TiCl₄ and SnCl₄ were distilled before use. Fluorosulfuric
acid was distilled from a small amount of NaF at atmospheric pressure and subsequently redistilled. The purified acid was stored in sealed glass ampules. SbF$_5$ was distilled at 15 mm Hg and also stored in sealed ampules. All liquid chromatography was performed on columns filled with Basic or Neutral Alumina Activity I, supplied by Fisher Scientific Company. Pentane used in the protonation experiments was purified by a treatment with concentrated H$_2$SO$_4$, followed by washing with water, drying over MgSO$_4$ and two distillations.

TECHNIQUES

Protonation

Protonations were carried out in a similar manner to that previously described.$^{132}$

Preparation of Borontrihalide Complexes

All manipulations were carried out under high vacuum conditions. The starting organic compound (ca. 30 mg) was weighed into a small reaction vessel which contained a magnetic stirrer, was fitted with a sealed on nmr tube, and could be attached to a vacuum line through a suitable high vacuum stopcock. The reactor, Figure 9, was cooled and CD$_2$Cl$_2$ (1 ml) was transferred from a reservoir where it had been stored over P$_2$O$_5$. The organic material was dissolved and then a weighed amount of the appropriate Lewis acid was slowly distilled in while the solution was being stirred and maintained at -78°C. On completion of the addition, the reactor was separated from the vacuum line and the appropriate amount of the solution transferred to the nmr tube which was then sealed. During this transfer the apparatus was kept at -78°C.
Figure 9: Reactor used for preparation of $\text{BX}_3$ complexes
For the uv determinations, a similar technique was used except that a larger reaction vessel with an attached 0.2 cm uv cell was employed.

**Preparation of Other Complexes**

The following procedure was applied for preparation of all complexes except those using BCl\(_3\) or BBr\(_3\) as Lewis acids. Approximately 10% excess of the Lewis acid was placed in a thin wall nmr tube and cooled in a dry-ice/acetone bath. The material to be complexed (15 mg) was dissolved in 0.5 ml of CDCl\(_3\) or other solvent, and using a small pipet this solution was in a nitrogen atmosphere slowly poured down the cooled wall of the nmr tube containing the acid. After waiting several minutes for the temperatures to equilibrate the contents of the nmr tube were mixed by vigorous shaking.

**Ir Spectrum of Benzylcarboxonium ion, 60**

The BBr\(_3\) complex 39 was prepared in usual fashion and the thermal rearrangement was allowed to occur in the probe of an nmr spectrometer. When the acylium cation was fully developed, the solution was transferred into a wider tube in a dry box and the volatile components were removed under a high vacuum at room temperature. The residue in the tube was mixed with nujol, placed between two nujol covered KBr plates and its ir spectrum recorded. A reasonably intense absorption was observed at 2270 cm\(^{-1}\). The KBr cell was opened and the material was exposed to the atmosphere for 8 minutes. In the ir spectrum recorded after this time, there was no absorption at 2270 cm\(^{-1}\) and a new signal was found at 1700 cm\(^{-1}\).
Thermal Rearrangement of Complexes

A sealed nmr tube containing a solution of one of the complexes was inserted into a precooled probe of the pmr spectrometer and the spectrum was recorded. The temperature of the probe was then gradually increased while the pmr spectrum was scanned periodically until a rearrangement was observed by the appearance and disappearance of certain resonances. The rate of the rearrangement was measured at such temperatures that the half life of the complex was approximately 30 minutes. The spectrum was obtained at known time intervals and the relative amounts of the starting complex and rearrangement products determined by comparison of the peak heights of the various methoxy resonances. Pseudo first order kinetics were observed in all cases.

Neutralization of Complexes

An excess of gaseous \((\text{CH}_3)_2\text{NH}\) was passed into the \(\text{CD}_2\text{Cl}_2\) solution of the zwitterions at \(-78^\circ\). The resulting mixture was treated with water and the organic material was extracted three times with ether. The combined ether extracts were dried over \(\text{MgSO}_4\) and the solvent removed in vacuo prior to analysis by vpc and pmr. Hexamethylbenzene was used as an internal standard in some of the reactions in order to quantitatively measure the recovery of the starting compounds.

Measurement of Diamagnetic Susceptibility

Volumetric diamagnetic susceptibilities were determined by method of Douglass and Fratiello.\(^{173}\) This method requires the use of precision bored concentric sample tubes, which were obtained from Wilmad Glass Company. The sample of unknown susceptibility was placed
in the central tube, and the reference compound in the surrounding annular region. The pmr spectrum of the non spinning assembly was recorded and the resonance signal of the reference sample was found to be split into two peaks, Figure 10. The separation of the two peaks is proportional to the diamagnetic susceptibility of the sample.

A Varian HR 100 spectrometer operated in a no-lock mode was used for these measurements. Since it is not possible to completely eliminate any drift of the magnetic field under these conditions, the error caused by the drift was reduced by scanning the signal 12 to 18 times alternately in the forward and backward direction, and calculating the average separation.

As this method of determination of the diamagnetic susceptibility is not an absolute one, the sample cell and the spectrometer were calibrated with a series of compounds of known susceptibility. The compounds used for this calibration were: methylene iodide, bromoform, methylene chloride, water, toluene, acetonitrile, ethanol and nitromethane. It was found to be necessary to tune up the spectrometer to a very high degree of field homogeneity and to calibrate the spectrometer and measure the unknown diamagnetic susceptibilities of the samples in one sitting. To check that no change in the calibration had occurred during the course of the measurements, the susceptibilities of several standards were redetermined at the end of the series of measurements.

A plot of the known susceptibilities of these compounds versus the separation of the CH$_3$ resonance of nitromethane or toluene (used in the outer part of the sample cell) gave a straight line. Least
Figure 10: Separation of the CH$_3$ resonance of toluene, observed for three of the standards
square analysis of the data gave the following three equations for three different sets of measurements:

\[ \kappa = 0.008655 \cdot n + 0.2314 \]
\[ \kappa = 0.008616 \cdot n + 0.2325 \]
\[ \kappa = 0.008830 \cdot n - 0.3119 \]

Toluene was used as the reference in case 1 and 2, and nitromethane was the standard in the third series of measurements. The change of the standard was necessary because the resonances of the measured compounds in some cases coincided with those of the standard. The correlation coefficient was in each case at least 0.999 and the standard deviation in \( \kappa \) less than 0.004.

The magnetic susceptibility per gram, \( \chi \), is given by

\[ \chi = \kappa / \rho \]

where \( \rho \) is density of material in g/cm\(^3\).

The molar susceptibility is given by

\[ \chi_M = M \cdot \chi \]

where \( M \) is the molecular weight of the substance. The units of \( \chi_M \) are \( 10^{-6} \text{ cm}^{-3}/\text{mole} \), \( \kappa \) is in units of \( 10^{-6} \).

A Lipkin bicapillary pycnometer (0.25 ml, Ace Glass Company), calibrated with water, was used to measure the density of the liquids. The solvents used for calibration of the spectrometer were carefully purified by established methods and finally distilled through a 20" column filled with glass helices under a constant flow of helium. The purified standards were stored in the dark under helium.
REATIONS AND SYNTHESES

7-Methoxycarbonylcycloheptatriene (35)
7-cyanocycloheptatriene (10 g) was refluxed under N₂ in MeOH
(150 ml) containing concentrated H₂SO₄ (30 g) for 30 h. The bulk of the
solvent was removed in vacuo and the residue poured into H₂O (400 ml).
The solution was extracted with petroleum ether (30-60°) (3 x 100 ml),
the extract dried over MgSO₄, and the solvent removed in vacuo to give
the crude ester. Distillation gave 9.0 g (80%) of 35 (b.p. 60°/0.5 Torr)
containing a small amount of methyl phenylacetate (2%). Pure material
was obtained by preparative vpc at a temperature below 130°.

N,N-Dimethyl-1,3,5-cycloheptatriene-7-carboxamide (41)
An excess of gaseous dimethylamine was added to a 10% solution
of 7-chlorocarbonylcycloheptatriene in anhydrous ether. The dimethyl-
amine hydrochloride formed was filtered off and the filtrate concentra-
ted in vacuo to give a brown oil. This was chromatographed on neutral
alumina eluting with ether to give a colorless solid. Recrystalliza-
tion from pentane gave 41 as colorless crystals (m.p. 64.5°) which
slowly became colored on standing. Nuclear magnetic resonance spectral
data are given in Table 4.

9-Methoxycarbonylbicyclo[6.1.0]nona-2,4,6-triene (54)
Compound 54, prepared by ester exchange of the corresponding
ethyl ester, had properties identical to those previously reported.

Reaction of the Rearrangement Products of 37 with EtOH
Ethanol (2 ml) was slowly added to a CD₂Cl₂ solution of the
rearrangement products of \( \text{37} \) at \(-78^\circ\). Water (10 ml) was added, the mixture extracted with ether (3 x 5 ml), and the extract dried over MgSO\(_4\). Evaporation of the ether gave an oil which was analyzed by both pmr and also analytical vpc using authentic samples of \( \text{38} \) and \( \text{39} \) for comparison purposes. The two esters, \( \text{38} \) and \( \text{39} \) in the quenched material were separated by preparative vpc and the pmr spectra of the isolated compounds were identical in all respects to that of the authentic samples.

**Reaction of 7,8-Epoxy-1,3,5-cyclooctatriene with Lewis acids**

Powdered Al\(_2\)Cl\(_6\) (8.9 mg, 0.07 mmol.) was mixed with 0.15 ml CD\(_2\)Cl\(_2\) and cooled in a dry-ice/acetone bath. A solution of the epoxide (8 mg, 0.07 mmol.) in CD\(_2\)Cl\(_2\) (0.2 ml) was added slowly and the suspension mixed by vigorous shaking. The pmr spectrum of the mixture, recorded at \(-75^\circ\), consisted of absorptions at \( \delta 7.3 \) (large relative area) and \( \delta 3.11, 3.90, \) and \( 4.90 \).

A solution prepared in a comparable manner from the epoxide (210 mg) and Al\(_2\)Cl\(_6\) (245 mg) in CH\(_2\)Cl\(_2\) (10 ml) was poured into a cooled (-20\(^\circ\)) and stirred mixture of water (5 ml), methanol (5 ml), and Na\(_2\)CO\(_3\) (0.5 g). The mixture was then allowed to warm up to room temperature, diluted with water (10 ml) and extracted with ether (3 x 10 ml). The ether layer was washed with water dried over MgSO\(_4\) and the ether was removed in vacuo to give 47 mg of a colourless oil. This product was identified by comparison of its pmr and ir spectra with the spectra of authentic compounds as the phenylacetaldehyde and dimethylacetal of phenylacetaldehyde\(^6\) in a ratio of 2 to 1. Attempted separation by vpc, carbowax, 130\(^\circ\), gave the same two compounds and also 2-styryl methyl ether. This
latter compound was shown to be a decomposition product of the di­methylacetal of phenylacetaldehyde by injection of a sample of authentic acetal into a vpc column under comparable conditions.

Reaction of Phenylacetaldehyde with \( \text{Al}_2\text{Cl}_6 \) and Subsequent Neutralization of the Complex

Phenylacetaldehyde (45 mg, 0.42 mmol.) was reacted with \( \text{Al}_2\text{Cl}_6 \) (53 mg, 0.42 mmol.) in CDCl\(_3\) (2 ml) in a directly comparable manner to that outlined above. The pmr spectrum of the solution had absorptions at 7.3 (large relative area) \( \delta \) 3.90 and 3.11.

The CDCl\(_3\) solution of this complex was reacted with a MeOH/H\(_2\)O/\( \text{Na}_2\text{CO}_3 \) mixture as described above to yield after extraction, drying and evaporation of the solvent, phenylacetaldehyde and the dimethylacetal of phenylacetaldehyde in a ratio of 2 to 1.

Preparation and Trapping of the 1,4-Cycloheptadiene anion, 73

a) Cycloheptatriene (10 g, 0.1 mol.) was dissolved in liquid ammonia (150 ml) and lithium (1.4 g, 0.20 mol.) was added in small pieces to the vigorously stirred solution. The liquid was dark blue at first but after several minutes it turned dark red as the anion 73 was formed. The reaction mixture was stirred for 2 hours at \(-40^\circ\) and then poured onto a large excess of crushed dry-ice. The dry-ice was allowed to evaporate and the volatile portion of the residue removed in vacuo at room temperature. This distillate (3.8 g) was separated by vpc (SE-30 column, 50\(^\circ\)) into two fractions which were shown to be the 1,3- and 1,4-cycloheptadiene (in ratio of 1 to 3.7) by comparison of their pmr spectra with those of the authentic materials. The
involatile residue was dissolved in water (20 ml), acidified with HCl, and extracted with ether (3 x 10 ml). The combined ether extracts were washed with water (3 x 10 ml), dried over MgSO₄, and treated with diazomethane (made from N-methyl-N-nitrosourea¹⁸⁵). The ether was removed and the residual product distilled under reduced pressure to give 2.7 g of a mixture of esters. This oil was separated by preparative vpc (carbowax column, ¹⁶⁰°) into seven fractions. These fractions were further purified by reinjection on the same column. The spectral properties of the isolated esters are given in the Table 15.

Table 15: Spectral properties of the esters obtained from ⁷³

<table>
<thead>
<tr>
<th>fr. ret.</th>
<th>relative</th>
<th>λ</th>
<th>chemical shifts in δ</th>
</tr>
</thead>
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<tr>
<td>No. time</td>
<td>amt. (%)</td>
<td>max (nm)</td>
<td>(and integration)</td>
</tr>
<tr>
<td>by vpc</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>4.2</td>
<td>6</td>
<td>230</td>
</tr>
<tr>
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<td>4.4</td>
<td>6</td>
<td>230</td>
</tr>
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<td>243</td>
</tr>
<tr>
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<tr>
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</tr>
<tr>
<td>7</td>
<td>11.0</td>
<td>34</td>
<td>270</td>
</tr>
</tbody>
</table>

b) 1,3-cycloheptadiene (0.2 g, 1.9 mmol.) was mixed in a nmr tube at -78° with hexane solution of tBuLi (0.9 ml, 2.2 N) and dry
tetrahydrofuran (THF, 0.5 ml) was added. The two solvents were miscible at first but after standing 15 minutes at that temperature two layers separated. The dark red lower layer contained the anion \(73\) in THF as was shown by its pmr spectrum.\(^{103-105}\) The upper hexane layer was removed and the THF layer was poured into cold stirred methylchloroformate (1 ml). Water (7 ml) was added and the mixture was extracted with ether (3 x 3 ml). The extract was washed with water (2 x 5 ml), dried over MgSO\(_4\), the ether was removed in vacuo, and the residue distilled. The pmr spectrum of the oil so obtained contained a sharp singlet \(\delta 1.0\) and broad multiplets at \(\delta 1.4-2.6\) and \(5.5-6.0\). The resonances of the ethyl group at \(\delta 1.4\) and \(4.2\) were split into several different sets of signals of unequal size. There were no sharp absorptions at \(\delta 2.3\) and \(5.9\) which are characteristic of \(\text{H}_4\). Injected onto a vpc column (carbowax, 140\(^\circ\)), the material separated into four peaks which were not further identified.

**Reduction of 7-Cycloheptatrienecarboxylic Acid**

A solution of 7-cycloheptatrienecarboxylic acid (0.9 g, 6 mmol.) in ether (2 ml) was mixed with liquid ammonia (60 ml), and sodium (0.4 g) was added in small pieces to the stirred solution maintained at -75\(^\circ\). After 15 minutes ammonium chloride (2 g) was added and the ammonia was allowed to evaporate at room temperature. The residue was dissolved in 15 ml of water, acidified with HCl, and extracted with concentrated HCl (3 x 5 ml). The extract was washed with water (2 x 10 ml), dried over MgSO\(_4\) and treated with \(\text{CH}_2\text{N}_2\). The solvent was then removed in vacuo and the residue was distilled at reduced pressure.
The distillate (0.4 g) was separated by vpc (carbowax column, 150°) into 5 fractions. The pmr and the ir spectra of the major fraction (66% of the product by vpc, ret. time 6.5 min.) were found to be identical with those of 85. The minor fractions were not identified.

**Synthesis of 4-Phenyl-9-methoxycarbonyl-2,4,6-triaza-
tetracyclo [5.3.2.03.08.10]dodec-12-en-3,5-dione, 78a**

A mixture of 4-phenyl-1,2,4-triazoline-3,5-dione, 72, (4.25 g, 24.7 mmol.) and 25 (4.0 g, 24.4 mmol.) in CH₂Cl₂ (120 ml) was cooled in a dry-ice/acetone bath to -60°. A solution of lead tetraacetate (14.5 g, 33.7 mmol.) in methylene chloride (120 ml) was added at once to the rapidly stirred solution. The temperature of the mixture was allowed to rise to +20° and the stirring continued for four additional hours. The solvent removed in vacuo and the residue was washed with 0.1 N HNO₃ (100 ml), 0.1 N NaOH (100 ml) and water (100 ml). The remaining brown material was dissolved in boiling methanol (400 ml), treated with charcoal, and the volume was reduced to 300 ml. On cooling this solution to room temperature 6.07 g of 78a crystallized and was filtered out. An additional 0.7 g of material was obtained as a second crop, bringing the total yield of 78a to 82%. The product was recrystallized from methanol to give pure 78a, m.p. 187°. Pmr (CDCl₃): 1.41 (t, 1, J = 3.0 Hz, H-9); 2.19 (m, 2, H-8, 10); 3.67 (s, 3, OMe); 5.23 (m, 2, bridgehead protons); 6.15 (t, 2, J = 3.7 Hz, olefinic protons); 7.40 (s, 5, Ph). Ir (KBr): 1770, 1730, 1417, 1323, 1240. Anal. calcd for C₁₇H₁₅N₃O₄: C, 62.77; H, 4.62; found: C, 62.76; H, 4.72.
Synthesis of 9-Methoxycarbonyl-4-phenyl-2,4,6-triazatetracyclo [5.3.2.0^4.6.0^8.10] dodeca-3,4-dione, 80a

The olefin 78a (3 g) was mixed with dioxane (100 ml) and partially dissolved. Palladium catalyst (5% Pd/C, 185 mg) was added and the mixture was vigorously stirred in a hydrogen atmosphere at 760 Torr. One equivalent of H\textsubscript{2} was consumed in 10 min to give 80a. (All the solid material dissolved during this reaction). Recrystallized from MeOH 80a melted at 156°. Pmr (CDCl\textsubscript{3}): 1.55-2.22 (m, 7, cyclopropyl and methylene protons); 3.66 (s, 3, OMe); 4.7 (broad s, 2, bridgehead protons); 7.47 (m, 5, Ph). Ir (KBr): 1775, 1720, 1500, 1440, 1410, 1250. Anal. calcd for C\textsubscript{17}H\textsubscript{17}N\textsubscript{3}O\textsubscript{4}: C, 62.38; H, 5.23; found: C, 62.53; H, 5.26.

Synthesis of 4-Phenyl-9-dimethoxymethyl-2,4,6-triazatetracyclo [5.3.2.0^4.6.0^8.10] dodec-12-ene-3,5-dione, 78b

The compound 78b was prepared from dimethoxymethylcycloheptatriene using the same procedure as that described above for the preparation of 78a. Yield: 73%. M.P.: 158°. Pmr (CDCl\textsubscript{3}): 0.97 (d of t's, 1, H-9); 1.76 (m, 2, H-8, 10); 3.33 (s, 6, OMe); 4.26 (d, 1, C-9 substituent); 5.22 (m, 2, H-1,7); 6.17 (t, 2, olefinic protons); 7.42 (s, 5, Ph). Ir (KBr): 1773, 1755, 1605, 1500, 1398. Anal. calcd for C\textsubscript{18}H\textsubscript{19}N\textsubscript{3}O\textsubscript{4}: C, 63.33; H, 5.63; found: C, 63.12; H, 5.70.
Synthesis of 4-Phenyl-9-dimethoxymethyl-2,4,6-triazatetracyclo[5.3.2.0^4,6.0^8,10]dodeca-3,5-dione, 80b

Olefin 78b was reduced in a directly comparable manner to that described above for reduction of 78a, to give a 100% yield of 80b:

Pmr (CDCl_3): 1.41 (t, 1, H-9); 1.60-2.20 (m, 6, H-8,10,11,12); 3.34 (s, 6, OMe); 4.22 (broad s, 2, bridgehead H's); 7.3-7.7 (m, 5, Ph).

Ir (KBr): 1750, 1696, 1500, 1430, 1410. Anal, calcd for C_{18}H_{21}N_{3}O_{4}: C, 62.93; H, 6.18; found: C, 62.85; H, 6.18. M.p.: 121°.

Synthesis of 9-Ethoxycarbonyl-4-phenyl-2,4,6-triazatetracyclo[5.3.2.0^4,6.0^8,10]dodeca-12-en-3,5-dione, 78c

7-Ethoxycarbonylcycloheptatriene was used as the starting material and the procedure used was the same as that described for the preparation of 78a. Yield: 73%. M.p.: 172.5°. Pmr (CDCl_3): 1.26 (t, 3, Me); 1.45 (t, 1, H-9); 2.23 (d of d's, 2, H-8,10); 4.14 (q, 2, CH_2); 5.25 (m, 2, bridgehead H's); 6.18 (t, 2, olefinic H's); 7.42 (s, 5, Ph). Ir (KBr): 1770, 1719, 1500, 1415, 1241. Anal, calcd, for C_{18}H_{17}N_{3}O_{4}: C, 63.71; H, 5.05; found: C, 63.81; H, 5.13.

Synthesis of 9-Ethoxycarbonyl-4-phenyl-2,4,6-triazatetracyclo[5.3.2.0^2,6.0^8,10]dodeca-3,5-dione, 80c

Starting with 78c the procedure used was the same as that described above for the preparation of 80a. Yield: 95%. M.p.: 156°. Pmr (CDCl_3): 1.27 (t, 3, Me); 1.60-2.20 (m, 7, H-8-12); 4.15 (q; 2, CH_2); 4.73 (broad s, 2, bridgehead H's); 7.32-7.62 (m, 5, Ph).
Ir (KBr): 1770, 1720, 1502, 1409, 1320, 1255. Anal, calcd for C_{18}H_{19}N_{3}O_{4}: C, 63.34; H, 5.61; found: C, 63.23; H, 5.52.

Synthesis of 6,7-Diaza-3-dimethoxymethyltricyclo[3.2.2.0²⁴]nonanyl-6-phenylcarboxamide, 82b

The acetal 80b (0.42 g) was refluxed for 4 hr in methanol (10 ml) containing KOH (0.5 g). The solvent was evaporated at reduced pressure the residue was extracted with CH₂Cl₂ (3 x 10 ml) and the extract was dried over MgSO₄. On removal of the solvent in vacuo 0.16 g of 79a was obtained. This material was three times recrystallized from ether/CH₂Cl₂ to give a pure product, m.p. 157-5°(N₂ sealed capillary). Yield of crude product: 35%. Pmr (CDCl₃): 1.00-1.95 (m, 7, H-2,3, 4,8,9); 3.37 (s, 6, OMe); 3.50 (m, 2, H-1,5) 4.10 (d, J=5 Hz, 1, C-3 substituent); 4.67 (broad s, 0.7, NH); 7.0-7.8 (m, 5, Ph); 8.86 (broad s, 0.7, NH). Ir (KBr): 3305, 3220, 1670, 1605, 1520, 1450. Anal, calcd for C_{17}H_{23}N_{3}O_{4}: C, 64.95; H, 7.39; found: C, 64.70; H, 7.25.

Synthesis of the Copper Complex of 6,7-Diazatricyclo[3.2.2.0²⁴]nonane-3-carboxylic acid 84a

A solution of 80a (2.85 g, 8.81 mmol.) in methanol (15 ml) containing KOH (3 g, 65 mmol.) was refluxed for 24 hr in a nitrogen atmosphere. The reaction mixture was cooled and dissolved in water (500 ml). The solution was titrated with 10% HCl to pH 4 and CuCl₂ (3 g, 22.3 mmol.) was dissolved in the mixture. After 30 min the green solution started turning red and during the following 15 hr crystals of ochre-red 84a accumulated on the bottom of the vessel. The complex
was filtered out and thoroughly washed with acetone and ether. Compound 84a was found to be insoluble in common solvents but to readily decompose in presence of bases. Yield: 1.5 g (64%). M.p.: 147° (decomposition). IR (KBr): 1697, 1470, 1340, 1280.

Synthesis of 3-Methoxycarbonyl-1,4-cycloheptadiene, 44

Copper complex 84a (0.9 g, 3.22 mmol.) was mixed with water (20 ml) containing K₂CO₃ (0.089 g, 6.44 mmol.). The red solid immediately turned brown and a slow development of gas was observed. After 1 hr of stirring bulky precipitate was filtered off and the filtrate was heated to 35°, until the production of nitrogen was completed (12 hr). The solution of 86 so obtained was cooled to 2° acidified with HCl to pH 3 and extracted with ether (3 x 15 ml). The ether extract was dried with MgSO₄ and immediately esterified with a slight excess of diazomethane. The solvent was removed in vacuo and the residue was distilled to give 44, 0.29 g (55%). B.p., 30°/0.1 Torr. PMR (CDCl₃): 2.25 (m, 4, H-6,7); 3.68 (s, 3, CH₃); 4.2 (m, 1, H-3); 5.79 (m, 4, H-1,2,4,5). IR (neat): 1725, 1465, 1415, 1295. Kept at room temperature 44 slowly rearranged to 87 (followed by pmr). Attempts to separate 44 from 87 on a short alumina column caused a complete rearrangement of 44 to give 87. PMR (CDCl₃): 1.85 (m, 2); 2.35 (m, 4); 3.54 (s, 3); 5.80 (d of t's, 1); 6.19 (broad d, 1); 6.91 (t, 1).

Rearrangement of 1,4-Cycloheptadiene-3-carboxylic acid, 86, to 1,3-Cycloheptadiene-2-carboxylic acid, 85

An ether solution of 86 was prepared from 84a as described above. The solution was dried over MgSO₄ and the solvent was removed in vacuo,
to give 86 as a colourless oil. Pmr (CDCl₃): 2.24 (broad s, 4, H-4,5); 4.16 (m, 1, H-1); 5.78 (broad s, 4, H-2,3,6,7); 11.2 (s, 1, acidic OH).

Ir (neat): 2500-3500, 1715, 1421, 1289.

Pure 86 was heated for 1 hr at 45° to give 85 as a yellow oil. Pmr (CDCl₃): 1.85 (m, 2, H-4,5); 2.38 (m, 4, H-3); 5.91 (d of t's, 1, H-6); 6.35 (d of d's, 1, H-7); 7.26 (t, 1, H-2); 11.2 (s, 1, OH). On irradiation at 2.38 the signal at 7.26 collapsed to a singlet, that at 5.91 to a doublet and the absorption at 1.85 collapsed to a broad singlet. J₂,₃=5.3 Hz, J₆,₇=11.5 Hz; J₅,₆=4.5 Hz; J₅,₇=1.0 Hz.

Synthesis of 3-Dimethoxymethyl-1,4-cycloheptadiene, 88

A solution of acetal 80b (2.0 g, 5.8 mmol.) in methanol (15 ml) containing KOH (1.5 g, 27 mmol.) was refluxed under N₂ for 48 hr. Deoxygenated water (30 ml) was added and the mixture extracted with methylene chloride (3 x 15 ml). The combined extract was dried with MgSO₄ and the solvent was removed in vacuo, to give an oil, pmr (CDCl₃): 1.05-2.02 (m, 7); 3.35 (s, 6); 4.20 (m, 4); 3.55 (s, 2); 6.9 (m, 5). This product was dissolved in CH₂Cl₂ and the solution was exposed to air for 8 hr. Development of gas was observed during this time. The solvent was removed in vacuo, and the mixture of 88 and aniline so obtained was separated on a short column of basic alumina eluting with ether. Yield of 88, 0.47 g (48%). Pmr (CDCl₃): 1.80-2.50 (m, 4, H-6,7); 3.25 (s, 6, OMe); 3.39 (m, 1, H-3); 4.17 (a, 1, H-8); 4.36-4.80 (m, 4, H-1,2,4,5). Anal, calcd for C₁₀H₁₆O₂: C, 72.26; H, 9.70; found: C, 71.97; H, 9.77.
4-Phenyl-2,4,6-triazatetracyclo[5.3.2.0\textsuperscript{4}.0\textsuperscript{8}.0\textsuperscript{10}]dodeca-3,5-dione-9-carbaldehyde, 89

Acetal 80b (0.8 g) was dissolved in acetone (30 ml), aqueous 37% HCl (0.5 ml) was added and the solution was kept for 30 min. at room temperature. At the end of this time NaHCO\textsubscript{3} (0.5 g) was slowly added and the solvent was removed in vacuo. The white residue was triturated with methanol, the inorganic salt removed by filtration and the solvent evaporated in vacuo to yield the crude 89 (0.65 g, 95%).

Three recrystallizations from CCl\textsubscript{4}/acetone mixtures gave pure 89, M.p.: 204°. Pmr (CDCl\textsubscript{3}): 1.50-2.30 (m, 7, H-8-12); 4.72 (broad s, 2, H-1,7); 7.28-7.62 (m, 5, Ph); 9.72 (s, 1, H-8). Ir (KBr): 1770, 1710, 1600, 1500, 1411, 1259. Anal. calcd for C\textsubscript{16}H\textsubscript{15}N\textsubscript{3}O\textsubscript{3}: C, 64.63; H, 5.08; found: C, 64.60; H, 5.00.

9(2-Hydroxy-2-propyl)4-phenyl-2,4,6-triazatetracyclo[5.3.2.0\textsuperscript{4}.0\textsuperscript{8}.0\textsuperscript{10}]dodeca-3,5-dione, 80 R = C(Me)\textsubscript{2}OH

Methyllithium (4 ml, 1.3 N in hexane) was added to a vigorously stirred solution of 80c (1.4 g, 4.10 mmol) in dry 1,4-dioxane (100 ml). After 15 min, water (15 ml) was added and the volume of the solution was reduced to 30 ml in vacuo. Additional water (20 ml) was added, the mixture neutralized with 10% HCl and extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 x 20 ml). The organic layer was dried over MgSO\textsubscript{4} and reduced to 10 ml. Addition of CCl\textsubscript{4} (10 ml) caused precipitation of 0.2 g of white product. This material was recrystallized from CH\textsubscript{2}Cl\textsubscript{2}/CCl\textsubscript{4} mixtures.
Attempted Preparation of 3-Formyl-1,4-Cycloheptadiene

a) Acetal $S_{Ob}$ (1 g) was hydrolyzed and treated with $CuCl_2$ in the same manner as described above for the preparation of $S_{4a}$, to give $S_{4b}$ (0.3 g, 33%). M.p.: 120-122° (decomposition). Ir (KBr): 1695, 1619, 1401. Complex $S_{4b}$ (0.2 g) was added to a 5% solution of $K_2CO_3$ (10 ml) the mixture was stirred for 3 hr at $+4\degree$, and extracted with three 5 ml portions of methylene chloride. The combined extract was dried with $MgSO_4$ and the solvent was removed in vacuo to give $S_{6b}$ (0.15 g). Pmr (CDCl$_3$, -20°): 1.2 (m); 1.9 (broad s); 5.6 (broad s); 9.3 (d), and absorptions of much smaller area at 5 1.7-2.9; 6.0-6.6 and 6.8. The CDCl$_3$ solution of $S_{6b}$ in an nmr tube was kept at 35° for 5 hr. Development of gas was observed during this time and $S_{6b}$ was converted into 2-formyl-1,4-cycloheptadiene. Pmr (CDCl$_3$): 1.65-2.20 (m, 2, H-6); 2.2-2.9 (m, 4, H-5,7); 6.05-6.60 (m, 2, H-3,4); 6.78 (t, 1, H-1; 9.37 (s, 1, -CHO).

b) Compound $S_{8}$ was reacted in a similar manner as described above for $S_{8b}$. The product obtained from this reaction had a pmr spectrum identical with that of 2-formyl-1,4-cycloheptadiene, described above.

c) Acetal $S_{8}$ (20 mg) was dissolved in ether (4 ml) and stirred for 30 min at $-5\degree$ with 3 drops of 37% aqueous HCl. The ether solution was then washed with 5% NaHCO$_3$ solution (5 ml) and water, dried with $MgSO_4$ and the solvent was removed in vacuo. All these operations were performed below $+4\degree$. The pmr spectrum of the product so obtained was again identical with that of 2-formyl-1,3-cycloheptadiene.
Synthesis of 3(2-Hydroxy-2-propyl)1,4-cycloheptadiene, 90

The title compound was prepared from 80, R=C(Me)\textsubscript{2}OH using a similar procedure to that used for the synthesis of 44. The products were separated on a short alumina column eluting with ether and the final fraction was distilled, (60°/0.5 Torr) to yield 90 (30%). Pmr (CCl\textsubscript{4}): 1.18 (s, 6, Me); 1.54 (s, 1, OH); 2.21 (m, 4, H-6,7); 3.15 (m, 1, H-3); 5.66 (m, 4, H-1,2,4,5). Ir (neat): 3400, 1170, 1370, 1450. Anal, calcd for C\textsubscript{10}H\textsubscript{16}O: C, 78.90; H, 10.59; found: C, 78.70; H, 10.71.

Simmons-Smith Reaction with 7-Ethoxycarbonylcycloheptatriene

Zinc copper couple\textsuperscript{122} (0.6 g), anhydrous ether (10 ml), CH\textsubscript{2}I\textsubscript{2} (2.2 g, 42 mmol.), and the title ester (0.3 g, 21 mmol.) were heated under nitrogen for 48 hr. (The progress of the reaction was followed by periodic analysis of samples by vpc). The reaction mixture was filtered and the solid residue washed with ether. The combined ether solutions were washed with saturated aqueous ammonium chloride solution (twice), 10% sodium bicarbonate solution, and water, dried with MgSO\textsubscript{4} and the solvent was removed in vacuo. The colourless oil so obtained was distilled and separated by vpc (carbowax column, 180°) into nine components. The first four constituents of the mixture were identified as methylene iodide ethylbenzoate, 3-, and 7-ethoxy-carbonylcycloheptatriene by comparison of their respective pmr spectra and vpc retention times with those of authentic materials.\textsuperscript{186} Fraction 5, was purified by two subsequent vpc separations. Mass spectrum, m/e = 192 (calc for C\textsubscript{11}H\textsubscript{14}O\textsubscript{2} = 192); pmr (CCl\textsubscript{4}): 0.15-0.40 (m,2); 0.75-1.16
Insufficient material was present in the fraction 9 for it to be analyzed.

Decomposition of \(N_{2}CHCOOEt\) in Cycloheptatriene

Ethylidiazooacetate\(^{187}\) (10 g, 88 mmol.) and cycloheptatriene (16 g, 176 mmol.) in \(CH\_2Cl\_2\) were irradiated in a Srinivasan-Griffin photochemical reactor, fitted with 3500 \(\AA\) lamps for three days, during which time 900 ml of \(N\_2\) were released. Anhydrous CuCl\(_2\) (0.1 g) was added to the solution and further 600 ml of \(N\_2\) was rapidly evolved. The solvent was removed in vacuo and the residue was distilled under reduced pressure to give two fractions. The first fraction, b.p. 72\(^{\circ}\)/0.2 Torr, was by vpc (carbowax column, 150\(^{\circ}\)) separated into two components the pmr and ir spectra of which were identical with those reported for ethyl fumarate\(^{188a}\) and ethyl maleate.\(^{188b}\) The second fraction, b.p. 72-78\(^{\circ}\)/0.2 Torr (2.5 g, was chromatographed on a 25 cm basic alumina column eluting with petroleum ether to give a small amount of ethyl fumarate and maleate and an oil (1.5 g), uv, \(\lambda_{\text{max}}^{\text{MeOH}} = 262 \text{ nm}\); pmr (CCl\(_4\)):

\[
\begin{align*}
&1.35 (t, 3); 1.5-2.9 (m, 5); 4.13 (q, 2); 5.5-6.4 (m, 4). \text{ Analysis of this oil by vpc on an analytical carbowax column showed it to consist of two materials, the first, retention time 32 min, 13\%, and the second, retention time 35 min, 87\%.}
\end{align*}
\]
The ester 35 (3.0 g, 20 mmol.) and diethylazodicarboxylate (2.5 g, 20 mmol.) were dissolved in ether (5 ml) and heated for 12 hr at 50°. The ester was then removed in vacuo and the product mixture separated on a 20 cm basic alumina column eluting with 10% ether in pentane. The first fraction contained a small amount of 35.

The second fraction consisted of 99, a viscous, honey-like material. Pmr (CDCl₃+CS₂) 35°: 1.12-1.42 (m, 7); 1.75-2.23 (broad s, 2); 3.59 (s, 3); 4.05 (broad, 4); 5.12, (broad s, 2); 6.18 (broad s, 2). +90°: 1.27 (d of t's, 7); 2.08 (q, 2, J=2.7 Hz); 3.62 (s, 3); 4.20 (d of q's, 4, J=7.0 Hz); 5.20 (m, 2); 6.18 (t, 2, J=4.0 Hz). Ir (neat): 1750, 1730, 1515, 1460, 1325. Anal, calc for C₁₅H₂₀N₂O₆: C, 55.52; H, 6.21; found: C, 55.70; H, 6.26. The third fraction to be eluted consisted of a mixture of 99 and 100. This was further separated on an alumina column, eluting with 10% ether in petroleum ether to give 100 containing some 8% 99 (estimated by pmr). Pmr (CDCl₃): 1.27 (d of t's, 7); 3.62 (s, 0.8); 3.78 (s, 0.78); 3.81 (s, 0.1); 4.0-4.5 (m, 4); 5.5-7.3 (m, 4). There were two methoxy resonances in this spectrum (in addition to that of 99). This pmr spectrum was not temperature dependent in the range of 0° to 60°. The ratio of 99 to 100, estimated from integration of the pmr resonances of respective CH₃ groups, was found to be 1.7:1.0. A similar reaction was carried out at 0°, with the reaction time of 48 hr. The ratio of 99 to 100 was estimated to be 5.7:1.0.
Synthesis of 2,4,6-Cycloheptatrienone (tropone)

A solution of potassium dihydrogen phosphate (61 g, 0.45 mol.) in water (100 ml) and a solution of cycloheptatriene (83 ml, 0.9 mol., 91% J.T. Baker Chemical Co. product containing 7% toluene) in dioxane (750 ml) were placed in a 2 l flask equipped with a mechanical stirrer and a reflux condenser. Selenium dioxide (100 g, 0.9 mol., J.T. Baker Chemical Co.) was added at once and the mixture was stirred under N₂ and heated to 92° using an oil bath for 15 hr. The mixture was cooled, filtered and the solid material was washed with CH₂Cl₂, the combined filtrate and washings were treated with water (200 ml) and extracted with CH₂Cl₂ (4 x 300 ml), the extract was dried (MgSO₄) and the solvent was removed in vacuo to yield a dark brown product. Distillation through a short Vigreux column gave tropone (47 g, 49%), b.p. 75°/1 Torr with identical spectral properties to those previously reported.¹³⁵

Synthesis of 3,5-cycloheptadienone

A solution of tropone (40 g, 0.3 mol.) in dry ether (500 ml) was slowly added to a well stirred mixture of lithium aluminium hydride (LAH) (10 g, 1.14 equivalent) and ether (0.5 l) in a 3 l flask equipped with a mechanical stirrer and cooled in an ice bath. When all tropone solution had been added the mixture was stirred, 30 min, and the excess of LAH destroyed by the slow addition of ethyl formate (50 ml) dissolved in ether (200 ml). Water (15 ml) and 10% KOH solution (11 ml) were added dropwise and the reaction mixture was stirred until a granulated precipitate was formed (20 min.). The reaction mixture was filtered, the precipitate was washed with ether, and the solvent was
removed at a reduced pressure. Distillation yielded 19.7 g (49%) of colourless 3,5-cycloheptadienone, b.p., 45°/5 Torr. The spectral properties of the ketone were identical with those reported previously. 189

Synthesis of 2,4-Cycloheptadienone, 104

3,5-Cycloheptadienone (8 g) was dissolved in HFSO₃ (90 ml) and the solution was kept at room temperature until rearrangement was complete. 132 Water (500 ml) and petroleum ether (200 ml) were mechanically stirred in a 2 l beaker cooled with a salt ice bath while a solution of 10% NaOH (150 ml) and the HFSO₃ solution were slowly added simultaneously in such a manner that the mixture was basic at all times. The thick mixture formed in this process was filtered and the two layers of filtrate separated. The water solution was extracted with ether (4 x 125 ml) and the combined ether solution dried over MgSO₄. The solvent was removed at atmospheric pressure through a 25 cm Vigreux column and the residue was distilled. B.p. 40°/0.2 Torr. Yield: 3.4 g (43%). The physical and spectroscopic properties of the product were identical with those reported for 104. 132

Synthesis of Bicyclo[5.1.0]oct-5-en-2-one, 105

A solution of 104 (1.5 g, 12.3 mmol.) in dimethylsulfoxide (4 ml) was slowly added to a solution of dimethylsulfoxonium methylide, prepared from trimethylsulfoxonium iodide (2.7 g, 12.3 mmol.) and NaH (0.38 g of 50% dispersion in oil) in dimethylsulfoxide (15 ml), kept at +5°. After completion of the addition (2 hr), the reaction mixture was allowed to warm up to room temperature and stirred at
this temperature for 2 hrs. The reaction mixture was poured into water (80 ml) and extracted with ether (5 x 50 ml). The combined extract was washed with water (2 x 50 ml), dried over MgSO₄ and the solvent removed in vacuo. A colourless solid material crystallized from the residual oil (0.23 g, 60%). Recrystallized from methanol, this material melted at 170°. Mass spectrum, m/e: 216.1150; calcd for C₁₄H₁₆O₂: 216.1150; uv, λ_max = 255 (ε = 654), local maximum at λ = 245 (ε = 616) and λ = 268 (ε = 390). IR (KBr): 3030, 1709, 1118, 1045. Pmr (CDCl₃): 1.55-1.78 (m, 3); 2.10-2.93 (m, 9); 5.64-6.19 (m, 4).

Distillation of the remaining liquid gave 0.6 g (16%) of colourless distillate, b.p., 70°/0.5 Torr. Injected on a preparative column, the material gave rise to a single peak with retention time of 10 min (150°, carbowax column). IR (neat): 1700, 1445, 1360. Pmr (CCl₄): 1.00-2.74 (m, 8); 5.70 (m, 1); 5.96 (d of d's, 1). Double irradiation experiment:

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Synthesis of 8-Ethoxycarbonylbicyclo[5.1.0]oct-5-en-2-ones, 109 and 110

Ethoxycarbonylmethylenedimethylsulfurane, \(^{190}\) (CH₃)₂S=CHCOOEt, (3.2 g, 21.3 mmol.) was added to a solution of 10₄ (2.5 g,
21.3 mmol.) in tetrahydrofuran (6 ml) and the solution was kept at room temperature for 24 hrs. (The progress of the reaction was followed by monitoring changes in the pmr spectra of small, periodically withdrawn samples). After 24 hrs, the solvent was removed in vacuo and the product distilled. The first fraction (0.94 g, 35%, b.p., 25°/0.4 Torr) contained some 85% of 104 and 15% of monoadduct (estimated by pmr). The second fraction (1.6 g, 37%, b.p., 104°/0.2 Torr) was essentially pure monoadduct. This fraction was separated by vpc (carbowax column, 155°) into component "A", ret. time 8 min 40 sec, and component "B", ret. time 9 min 20 sec. The ratio of A:B was 1:2.3. The two components were also separated on an alumina column eluting with a petroleum ether/ether mixture.

The first fraction was recrystallized three times from a pentane/ether mixture (50:1) at -20° and purified by vpc (carbowax column). The white solid obtained in this manner had the following properties: M.p., 52°. Ir (KBr): 1725, 1678, 1425, 1360, 1305 and 1185. Pmr (CCl4): 1.25 (t, 3, J=7 Hz); 2.02-2.62 (m, 7); 4.10 (q, 2, J=7 Hz); 5.60-6.00 (m, 2). Uv, \( \lambda_{\text{max}} \text{MeOH} = 202 \). Anal, calcd for C11H14O3: C, 68.02; H, 7.26; found: C, 68.17; H, 7.25.

The second fraction from the liquid chromatography was purified by vpc and had the following properties: Ir (neat): 1725, 1668, 1425, 1307, and 1175. Pmr (CCl4): 1.25 (t, 3, J=7 Hz); 1.63 (t, 2, J=4.5 Hz); 1.94-2.22 (m, 2); 2.22-2.72 (m, 3); 4.12 (q, 2, J=7 Hz); 5.37 (d, 1, J=12 Hz); 6.49 (d of d's of d's, 1, J=12,2.8 and 2.8 Hz). Irradiation at δ 2.1 reduces the signal at δ 2.60 into a singlet, and
the resonance at δ 6.49 into a doublet. Anal, calcd for C_{11}H_{14}O_3: C, 68.02; H, 7.26; found: C, 68.28; H, 7.32.

**Synthesis of 1,4,4-Trimethylbicyclo[5.1.0]oct-5-en-2-ol, 112**

a) NaBH₄ reduction of 103:

Sodium borohydride (4.5 g, 128 mmol.) was added to the solution of 103 (3.0 g, 18.4 mmol.) in EtOH (10 ml) containing 30% aqueous KOH (0.5 ml). The mixture was stirred and refluxed under nitrogen for 30 min., cooled to 25°, and poured into 30 ml of water. The water solution was extracted with ether (3 x 15 ml) the combined ether extracts dried over MgSO₄, and the solvent was removed in vacuo. Only a small amount (0.2 g) of the volatile alcohol 112 could be distilled out of the extract (80°, 0.2 Torr). Alcohol 112, recrystallized from CCl₄, had a m.p. of 48-60°. M.p. of twice sublimed material was 49-62°. Pmr (CCl₄): 0.36 (d of d's, 1, J=5.5 and 3.5 Hz); 0.67 (d of d's, 1, J=3.5 and 9.3 Hz); 0.97 (m, 1); 1.05 (s, 3); 1.10 (s, 6); 1.43 (d of t's, 1, J=13.5 and 1.5 Hz); 1.71 (broad s, 1, disappeared if shaken with D₂O); 2.16 (d of d's, 1, J=10 and 1.5 Hz); 3.33 (d of d, 1, J=10 and 1.5 Hz); 4.97 (d of m's, 1, J=11.7 Hz); 5.43 (d of d's, 1, J=11.7 and 2.8 Hz). Ir (KBr): 3310, 1459, 1448, 1340, 1142. Anal, calcd for C_{11}H_{18}O: C, 79.46; H, 10.91; found: C, 79.21; H, 10.66.

The involatile portion of the reaction product, 113, was a colourless viscous material which readily solidified at room temperature. The pmr spectrum of this material resembled that of 112 except that the resonance at δ 3.33 was shifted downfield by 0.6 ppm, to δ 3.93. Ir (neat): 3390, 1650, 1300-1500, 1035. Two procedures for liberation of 112 from this material are described below.
The solid boric esters (the nonvolatile portion of the reaction products, (0.5 g) was dissolved in MeOH (150 ml) the solution was acidified with 37% HCl (0.5 ml) and refluxed 5 min. The bulk of solvent was removed in vacuo, fresh alcohol and HCl were added and the procedure repeated three times. The distillation of the product of this reaction yielded 112 (0.2 g).

The second portion of the boric ester (0.5 g) was dissolved in methanol (15 ml) and treated with 35% \( \text{NH}_4\text{OH} \) (8 ml). After standing at room temperature for 1 hr the bulk of solvent was removed in vacuo, 50 ml of water was added and the mixture was extracted with ether (3 x 15 ml). The combined ether extracts were dried over \( \text{MgSO}_4 \), the ether removed in vacuo, and the residue distilled to give 112 (0.3 g).

b) \( \text{LiAl(OBu)}_3\text{H} \) Reduction of 103

A solution of 103 (1.3 g, 7.9 mmol.) in ether (5 ml) was slowly added to a stirred mixture of \( \text{LiAl(OBu)}_3\text{H} \) (2.5 g, 10 mmol.) and ether (20 ml) cooled to 0°. The reaction mixture was refluxed under nitrogen until all ketone was reduced. (Progress of reaction was followed by examining the carbonyl absorption in the ir spectra of small samples removed from the reaction mixture). After 22 hr virtually all ketone was reduced, heating was discontinued, water (0.3 ml) added and the mixture was agitated for 30 min. The white precipitate was filtered off, washed with ether, the ether solutions combined and the solvent removed in vacuo. The residue was distilled at reduced pressure to give 112 (0.29 g, 97%).
Synthesis of Bicyclo[5.1.0]oct-5-en-2-ols, 116

Sodium borohydride (0.8 g, 20 meq.) was added to a solution of 105 (0.36 g, 3 mmol.) in 3 ml of 50% EtOH and the mixture was refluxed under N₂ for 90 min. The solution was poured into water (10 ml) acidified with HCl to pH 2, and extracted with ether (3 x 15 ml). The combined organic extracts were washed with water, dried over MgSO₄ and the solvent was removed in vacuo. Vacuum distillation of the residue gave 0.15 g (42%) of colourless 116. Pmr (CDCl₃): 0.7-2.7 (m, 12); 3.7-4.3 (d of m's, 1); 5.3-5.9 (m, 2). Ir (neat): 3320, 3009, 2710, 1420, and 1370. Injected on a SE-30 column (110°) this material gave rise to two peaks in ratio 3.6:1 with retention times 10 min 35 sec and 11 min 45 sec respectively. Anal. of the mixture, calcd for C₈H₁₂O: 77.38; H, 9.74; found: C, 77.12 H, 9.90.

Attempted Dehydration of 1,4,4-Trimethylbicyclo[5.1.0]oct-5-en-2-ol, 112

a) On alumina:

Alcohol 112 was injected in 0.01 ml portions onto a 1/8" x 1' preparative gc column filled with a neutral alumina (activity I). The temperature was varied from 150 to 250° and flow rate of helium between 300 and 1500 ml/min. At lower temperatures and flow rates the bulk of material remained on the column. At higher temperatures the retention times were of order of 60 sec and only the benzenoid products (pmr) were collected. These products were not further analyzed.

b) Reaction of 112 with SO₂Cl₂ in pyridine:

The procedure described in ref. 154 was followed directly. The alcohol was recovered.
c) **Reaction of 112 with Methanesulfonylchloride in 2,6-Lutidine:**

A solution of 112 (0.28 g, 0.17 mmol.) in 2,6-lutidine (5 ml) was cooled to 0° and the solution of mesylchloride (0.3 ml, 0.27 mmol.) in 2,6-lutidine (2 ml) was added. The mixture was stirred at 50° for 30 min, then poured into water (50 ml) and the organic material extracted with ether (3 x 20 ml). The combined ether extracts were washed with dilute HCl and water, dried over MgSO₄ and the solvent removed in vacuo. The residue was divided into two equal portions. One of them was heated for 60 min at 70° in 2,6-lutidine (3 ml), and the other was treated for 5 min with an ethanol solution of EtONa (5 ml, 10%) at room temperature. Both reaction mixtures were worked up with water and ether, the products were distilled and injected on analytical gc column (carbowax, 130°). The distillate obtained by either route gave rise to at least 15 peaks which had almost identical retention times and relative amounts in the two cases. None of the peaks represented more than 20% of the mixture. The retention time of the last fraction was identical with that of 112 (18.5 min).

d) **Reaction of 112 with bis(2-henylhexafluoro-2-propyloxy)dimethylsulfurane, 118:**

The solid sulfurane 118 (3.9 g, 5.98 mmol.) was added to the solution of 112 (0.87 g, 5.27 mmol.) in dry, ethanol free chloroform (10 ml). The pmr spectrum of the mixture recorded shortly after dissolution of 118, was totally different from that of the starting 112. Some of the chloroform was evaporated in vacuo and the mixture was analysed by vpc (5% 30 column, programmed temperature increased from 95 to 150°C). Some 16 different peaks were observed and the major ones
of these were collected. The first and last of these fractions were identified as 2-phenylhexafluoro-2-propanol and diphenylsulfoxide by comparing their gc retention times, ir and pmr data with those of authentic materials. Fractions 2, 3 and 4 with retention times at 95° of 7.5, 11 and 13 min, each displayed in their mass spectrum molecular peaks (m/e=148) corresponding to formula C_{11}H_{16}, and had the following spectral properties: Fraction 2: Pmr (CDCl$_3$): 1.07 (s, 6); 2.07 (s, 3); 5.20 (d of d's, 2); 5.93-6.40 (m, 3). Ir (neat): 1450, 1375, 1357. Fraction 3: Pmr (CDCl$_3$): 0.98 (s, 3); 1.08 (s, 3); 1.65 (d of d's, 3); 2.1-3.5 (m, 4); 4.82 (m, 2); 5.68 (s, 2). Ir (neat): 1670, 1463, 1450, 1358. Fraction 4: Pmr (CDCl$_3$): 1.06 (s, 6); 1.22 (s, 1); 1.95 (s, 1); 1.98 (s, 3); 2.30 (s, 2); 4.73-5.00 (m, 5). Ir (neat): 1600, 1460, 1352, and 1293.

e) Reaction of 112 with p-Toluensulfonylchloride in Pyridine

Tosylchloride (0.46 g, 2 mmol.) was added to the solution of 112 (0.2 g, 1.2 mmol.) in dry pyridine (5 ml) and the mixture was stirred at room temperature for 3 hr. The solution was cooled below +5° and the remaining tosylchloride was decomposed by adding 0.1, 0.2 and 0.4 ml of water in 5 min intervals. Water (20 ml) was added and the mixture was extracted with ether (3 x 5 ml). The combined extract was washed with 10% HCl (5 ml), water (2 x 10 ml), dried over MgSO$_4$, and the solvent was removed in vacuo to give the starting alcohol (0.3 g, 70%).

f) Heating of 112 with I$_2$

No change in the pmr spectrum of 112 was observed when this compound was treated with I$_2$ at temperatures up to 110°.
Pyrolysis of Esters of 112

The xanthate of 112 was prepared from 112 (1.6 g, 10 mmol.) MeLi (10 ml of 1.5 N solution), carbon disulfide (1.5 g, 20 mmol.) and MeI (2.1 g, 15 mmol.) using a procedure previously described for a different alcohol. The distilled xanthate (b.p., 100°/0.1 Torr) had the following pmr data: Pmr (CDCl₃): 0.6-1.0 (m, 3) 1.18 (s, 3); 1.21 (s, 6); 2.6 (s, 3); 5.4 (m, 2) and a broad resonance between δ 1 and 2. This material was heated under nitrogen at 250° for 60 min in a flask equipped with a cold trap. The pressure was then reduced to 15 Torr and the volatile products were collected in the cold trap. Analysed by vpc (preparative carbowax column, 120°) this distillate produced 11 peaks with retention time between 3.5 and 16 min. Three largest of these comprised about 20% of the mixture each.

The boric ester obtained by a NaBH₄ reduction of 102 vide supra was heated to 180° at 0.2 Torr. No distillate was collected in the cold trap.

Synthesis of Oct-7-yn-1,3-diene, 128

Tosylhydrazine (0.47 g, 2.5 mmol.) was added to a solution of 104 (0.25 g, 2.0 mmol.) in MeOH (1 ml), and the mixture refluxed under nitrogen for 30 min. (Ir spectra of a sample removed after 30 min revealed that the carbonyl absorption at 1708 cm⁻¹ was replaced completely by a C = N stretch at 1595 cm⁻¹). The solution was dried over MgSO₄ and the solvent was removed in vacuo. The solid residue was mixed with melted parafin (20 ml) containing sodium hydride (0.2 g, 4.2 mmol. of 50% mixture with parafin) in a flask
equipped with stirrer, and a reflux condenser. A water pump was joined to the top of the condenser through a cold trap and the pressure was maintained at 15 Torr. The temperature of the flask was increased to the boiling point of the parafin (190°), and maintained at this level for 1 hr. During this time 15 mg (7%) of 128 was collected in the cold trap. The product gave only one peak (ret time, 3 min, 20 sec) when injected on a SE-30 column at 90°. Pmr (CCl₄): 1.78 (t, 1, H-8); 2.00-2.54 (m, 4, H-5,6); 4.98-5.28 (m, 2, H-1,1'); 5.38-5.60 (m, 1, H-4); 5.98 (t, 1, H-3); 6.55 (d of t's, 1, H-2); J₁₂ =10.5; J₁₁' =16.8; J₂₃ =10.5; J₃₄ =10.5; J₆₈ =2.5 Hz. Ir (neat): 3310, 3097, 2120, 1420. Uv, λmax = 227 nm, log ε = 4.37

Reduction of oct-7-en-1,3-diene, 128 (7 mg) with hydrogen at 30 psi, in MeOH (1 ml) using a Pd/C catalyst gave a product which had and identical ir spectrum and retention times on both, the carbowax and SE-30 column with that of authentic n-octane.

Synthesis of 5,5-Dimethylnon-7-yn-1,3-diene, 126

Tosylhydrazine (1.9 g, mmol.) was added to the solution of 102 (1.6 g, 10 mmol.) in MeOH (15 ml), and the mixture refluxed for 30 hr. (Ir spectra of small samples were examined periodically). The solution was then dried over MgSO₄ and the solvent was removed in vacuo, to give tosylhydrazone 125 (3.2 g, 88%).

Crude 125 (0.9 g, 3 mmol.) was dissolved in benzene (50 ml) and a 7 fold excess of sodium hydride (1.5 g, of a 53% dispersion in oil) added. The solution was refluxed for 6 hr, and during this time
the initially clear solution developed a white precipitate. The mixture was washed with water (50 ml), dried over MgSO₄, and the solvent was removed through a 1' column filled with glass helices at atmospheric pressure. Distillation of the residue gave 0.31 g (70%) of pure 126. This material gave only one peak when analysed by vpc (SE-30 column, 95°) with retention time 11.6 min. Uv, λ_max^MeOH = 229 nm, log ε = 4.58. Fmr (CDCl₃): 1.28 (s, 6, H-7); 1.83 (t, 3, H-6); 2.25 (q, 2, H-5); 5.07-5.28 (m, 2, H-1,1'); 5.46 (d, 1, H-4); 5.95 (t, 1, H-3); 6.86 (d of t's, 1, H-2).

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J₁,₂ = 12; J₁',₂ = 16; J₂,₃ = 11; J₃,₄ = 12; J₅,₆ = 12 Hz. Cmr (CDCl₃, in ppm downfield from TMS): C-1, 118.14; C-2, 129.06, 133.48, 140.02; C-3, 129.14; C-4, 129.06; C-5, 37.25; C-6, 34.43; C-7, 8, 3.57; C-8, 0.13; C-9, 0.13; C-10, 28.67. Ir (neat): 3090, 3000, 2980, 2917 and 1460. Mass spec., m/e: 148.1252; calcd for C₁₁H₁₆, 148.1252.

Reduction of 1,4,4-Trimethylbicyclo[5.1.0]oct-2,5-dienyl-2-tetramethylphosphorodiamidate, 131

The enol ester 131 was prepared from 102 using the procedure used previously for preparation of similar enol esters. Unpuri-

fied, dry 131 (1.2 g, 4.2 mmol.) was added to a solution of lithium (0.29 g, 40 catoms) in a mixture of liquid ammonia (120 ml) and tetra-
hydrofuran (12 ml), kept at -78°. The mixture was stirred and the temperature was maintained at -40° for 60 min. The blue solution was
then discoloured by addition of sodium benzoate (1.2 g) and ammonium chloride (0.8 g). After evaporation of the ammonia, the residue was dissolved in water (20 ml) and the water solution was extracted with CH$_2$Cl$_2$ (3 x 5 ml). The organic solution was washed with 10% NH$_4$Cl and water and dried over MgSO$_4$. The solvent was removed through a short column at atmospheric pressure and the residue was distilled to give 0.39 g, 65% of colourless liquid. Injected on an SE-30 column (90°) this material separated into five components. The two major components were collected.

Component "A" with a ret. time of 18 min, 58% of the mixture (determined by gc) had the following properties: m/e, 150.1408; calculated for C$_{11}$H$_{18}$: 150.1408. Ir (neat): 3022, 2960, 2925, 2870, 1360. Pmr (CDCl$_3$): 0.9-2.2 (m, 15); 5.2-5.8 (m, 1).

Component "B": ret. time 21.5 min, represented 37% of the mixture: m/e, 150.1408. Ir (neat): 2960, 2918, 1440, 1361; Pmr (CDCl$_3$): 0.91 (s, 6); 1.22-1.55 (m, 4); 1.72 (s, 3); 2.08 (m, 4); 5.23 (t, 1).
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