Studies towards constrained cycloheptatrienyliidene and/or cycloheptatetraene

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STUDIES TOWARDS CONSTRAINED CYCLOHEPTATRIENYLIDENE AND/OR CYCLOHEPTATETRAENE

BY
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B. S., California Polytechnic State University, 1986

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Studies Towards Constrained Cycloheptatrienylidene and/or Cycloheptatetraene.

Director: Dr. E. E. Waali

The syntheses of two constrained cycloheptatrienylidene and/or cycloheptatetraene intermediates were attempted. Both of the constrained intermediates required tropones to generate the desired precursors. Synthesis of the first constrained tropone, 62, was unsuccessful and the synthesis of a system having a 1,4-cyclohexano constraint was abandoned. Synthesis of the second constrained tropone 84 was successful. However, when the synthesis of the carbene and allene precursors was attempted, the tropone 84 failed to produce the desired products 85 and 89 in good yield. Two products isolated from attempted synthesis of the tosylhydrazone 85 were the chloroazulenes 87 and 88. The formation of the chloroazulenes introduces interesting mechanistic possibilities.
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Thanks are also to be extended to John Zepp, for always making sure the chemicals were well stocked and the lab spotless.

AH
Introduction to Carbenes and Allenes

I. Introduction

When the study of the cycloheptatrienyldiene (1) - cycloheptatetraene (2) C₇H₆ system began, it was felt that the carbene could prove to be unusually stable due to its ability to exist as the aromatic singlet 1b. However, after various experiments and molecular orbital calculations it was determined that carbene 1 might also exist as the allene 2. The chemistry observed from the system could be explained in terms of either the singlet carbene 1 or the allene 2. Molecular orbital calculations suggest that the allene is the true intermediate, with the carbene being a transition state between the two enantiomeric forms of the allenes 2a and 2b. However, the relative energies of the carbene/allene system 1 and 2 have not be determined experimentally, and the question still remains as to which isomeric form of this C₇H₆ system gives rise to the observed chemistry.

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I.A. Carbene Chemistry

Carbenes are short lived highly reactive intermediates having a divalent neutral carbon as the reactive center. If sp\(^2\) hybridized, the two nonbonding electrons can occupy the same sigma orbital, thus leaving a vacant p orbital (a singlet carbene), or they can occupy separate orbitals (a triplet carbene). If carbenes were linear, it would follow from Hund's rule that the triplet state would be the preferred ground state for carbenes. However, carbenes are not necessarily linear, and the separation of energy levels between the singlet and triplet states is dependent on the types of substituents adjacent to the carbene carbon. If the substituents are alkyl or aryl (i.e., groups that are electron donating rather than electron withdrawing) the triplet is usually the observed ground state. However, singlet carbenes are observed if carbene carbon is bonded to electron withdrawing groups. An illustrative example of this is the different ground states of CH\(_2\) and CX\(_2\). Halogens are sufficiently electronegative to lower the energy of the singlet state relative to the triplet, making the singlet state more stable than the triplet. The stabilization of the singlet due to the presence of electronegative substituents may occur via the electron withdrawing effects of the halogen's sigma system, thus stabilizing the two electrons occupying the sigma orbital of the carbene. Stabilization of the singlet may also occur
through an interaction between the occupied $p$ orbitals of the halogens and the vacant $p$ orbital of the carbene.\(^7\)

$$\begin{align*}
\text{S} & : R/\, C^\cdot \\
\text{t} & : R/\, \cdot C \\
\end{align*}$$

Predicting the ground state of carbenes only works if the substituents are fairly simple. More complex carbene systems must be studied either spectroscopically or by chemical trapping. Spectroscopic studies are usually run in inert, low temperature (77 K) matrices in order to isolate the carbenes.\(^8\) Chemical experimentation usually involves studying the product distribution resulting from the generation of carbenes either in solution or in the gas phase. The products produced by carbenes are indicative of the reacting state of the carbene, but not the ground state. The conventional methods of generating carbenes produce the singlet initially, the triplet ground states being reached via intersystem crossing (ISC).

I.A.1. Generation of Carbenes

The most common methods for the generation of carbenes usually involves either photolysis, or thermolysis of sodium salts of tosylhydrazones and diazo compounds.\(^1,9\)
Dehalogenation using a strong base is also a common method for generating carbenes.\textsuperscript{10} Generally, the formation involves fragmentation forming stable, neutral compounds such as $\text{N}_2$, CO and $\text{HX}$, leaving behind the carbene.\textsuperscript{11} A summary of the most common methods for carbene formation is listed in Table 1.

The initial step in the generation of carbenes from either photolysis or thermolysis of a sodium salt of a tosylhydrazone involves the cleavage of the tosyl group. The resulting diazo fragment is highly reactive, decomposing readily into a nitrogen molecule and the carbene intermediate. The thermodynamic driving force behind the decomposition to the carbene is the expulsion of the stable nitrogen molecule.
The initial decomposition of the sodium salt of the tosylhydrazone generates a diazo compound having a singlet exited spin state. Since spin states are conserved in decomposition, the carbene also has a singlet spin state when generated. If the triplet carbene is lower in energy than the singlet it can be reached via intersystem crossing. The triplet carbene can also be formed directly by photosensitizing the diazo compound.
TABLE 1: GENERATION OF CARBENES

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Na}^+$ $\text{R}_2\text{C} = \text{N} - \text{N} - \text{Ts} \xrightarrow{\Delta \text{ or } h\nu} \text{R}_2\text{C} + \text{N}_2 + \text{Na}^+\text{SO}_2\text{Ar}$</td>
<td>$\text{R}_2\text{C} + \text{N}_2 + \text{Na}^+\text{SO}_2\text{Ar}$</td>
<td>1</td>
</tr>
<tr>
<td>$\text{R}_2\text{C} = \text{N} + \text{N} \xrightarrow{\Delta \text{ or } h\nu} \text{R}_2\text{C} + \text{N}_2$</td>
<td>$\text{R}_2\text{C} + \text{N}_2$</td>
<td>9</td>
</tr>
<tr>
<td>$\text{R}_2\text{C} = \text{N} \xrightarrow{\Delta \text{ or } h\nu} \text{R}_2\text{C}$</td>
<td>$\text{R}_2\text{C}$</td>
<td>13</td>
</tr>
<tr>
<td>$\text{R}_2\text{C} = \text{C} = \text{O} \xrightarrow{\Delta \text{ or } h\nu} \text{R}_2\text{C} + \text{CO}$</td>
<td>$\text{R}_2\text{C} + \text{CO}$</td>
<td>14</td>
</tr>
<tr>
<td>$\text{R}_2\text{C} = \text{C} \xrightarrow{\Delta \text{ or } h\nu} \text{R}_2\text{C} + \text{R}_2\text{C} = \text{C} = \text{R}_2$</td>
<td>$\text{R}_2\text{C} + \text{R}_2\text{C} = \text{C} = \text{R}_2$</td>
<td>13</td>
</tr>
<tr>
<td>$\text{R}_2\text{C} = \text{C} \xrightarrow{\Delta \text{ or } h\nu} \text{R}_2\text{C} + \text{R}_2\text{C} = \text{O}$</td>
<td>$\text{R}_2\text{C} + \text{R}_2\text{C} = \text{O}$</td>
<td>13</td>
</tr>
<tr>
<td>$\text{R}_2\text{C} - \text{X} \xrightarrow{B^-} \text{R}_2\text{C} + \text{BH} + \text{X}^-$</td>
<td>$\text{R}_2\text{C} + \text{BH} + \text{X}^-$</td>
<td>10</td>
</tr>
</tbody>
</table>
I.A.2. Reactions of Carbenes

I.A.2.a. Dimerization

Dimerization reactions involving triplet carbenes are usually exothermic and rapid, similar to the dimerization of radicals. The dimerization of two triplets is more likely than the dimerization of two singlets since triplet carbenes are usually more stable and selective.

\[
\begin{align*}
R_2\text{C}^\text{N} + R_2\text{C}^\text{N} & \rightarrow R_2\text{C}^\text{CR}_2 \\
\end{align*}
\]

The formation of dimers from carbenes is often misleading. While it is an allowed process, reaction conditions are often such that the probability of one carbene finding another to react with is small, especially in the case of highly reactive singlet carbenes. It is more likely that a carbene would react with the more readily available diazo precursor. Such a reaction would also produce the dimerization product, as well as the azine product.

\[
\begin{align*}
R_2\text{C}^\text{N} + R_2\text{C}^\text{N} & \rightarrow R_2\text{C}^\text{CR}_2 + N_2 \\
\end{align*}
\]
I.A.2.b. Addition Reactions

The addition of carbenes to alkenes to produce cyclopropane rings is not only a synthetically useful method of producing strained ring systems, but also one of the most useful methods of distinguishing between singlet and triplet chemistry. Skell and Woodworth originally postulated that a singlet carbene could add in a concerted fashion, whereas a triplet could add in a step-wise manner. The triplet first forms a diradical. The diradical must then undergo intersystem crossing (ISC) before completing the addition reaction. If rotation is a faster process than ISC, the observed products from triplet addition would be a mixture of stereoisomers. A summary of Skell's Rule (as it is often referred to) would be that singlet carbenes add stereospecifically and triplet carbenes add nonstereospecifically to alkenes.

\[
R_2\text{C}^+ + \text{C} = \underset{\text{ISC}}{\text{C}} \rightarrow R_2\text{C} \quad \rightarrow \quad R_2\text{C}^+ \quad \rightarrow \quad R_2\text{C}^+ \]

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I.A.2.c. Insertion and Hydrogen Abstraction Reactions

One common reaction route for singlet carbenes is insertion into a sigma bond, either a C-C, C-H or X-H. The most important of these is the C-H insertion. Like addition reactions, the stereochemistry of the products is determined by the whether the triplet or singlet carbene is responsible for the observed chemistry. The triplet carbene appears to follow the mechanism shown in path a, the initial step being hydrogen abstraction followed by recombination of the radical pair. If the radical pair separates they may not recombine with each other but may undergo further radical reactions.

Singlets could either react in a concerted fashion, path b, or a stepwise manner, path c.

Although path c is a viable mechanistic pathway for singlet carbenes, it appears that path b is the usual route. Evidence for this pathway is the intramolecular...
insertion of the arylcarbene 3 predominantly in the strained, exo position, giving rise to 4. \footnote{19}

\[ \text{H}^-\text{C}^+\text{H}_2 \overset{3}{\rightarrow} \text{H}^-\text{C}^-\text{H}_2 \overset{4}{\rightarrow} \text{major} \]

The use of pathway c by singlet carbenes is seen in the reaction of methylene with CDCl$_3$, in which a chlorine is abstracted, probably following the formation of an ylide. \footnote{20,21}

\[ \text{H}_2\text{Cl}^- + \text{CDCl}_3 \rightarrow \text{H}^-\text{C}^-\text{Cl}^+\text{CDCl}_2 \rightarrow \text{H}_2\text{Cl}^- + \text{CDCl}_2 \]

Reactions involving carbenes and heteroatoms usually proceed with insertion of singlet carbenes between the heteroatom and the hydrogen bond, and triplet insertion between C-H bonds. Ether linkages are common formations when alcohols are used in the presence of singlet carbenes. The preference of singlet carbenes to heteroatom bonds may also be a result of ylide formation, as in the reaction of...
methylene with CDCl₃, above. ²³

\[ \text{H}_2\text{C} = \text{H} + \text{RCH}_2\text{OH} \rightarrow \text{RCH}_2\text{OH} \rightarrow \text{RCH}_2\text{OCH}_3 \]

**I.A.2.d. Rearrangement Reactions**

The most common rearrangement reaction is the 1,2-hydrogen shift of singlet carbenes, leading to the formation of an alkene. ²² 1,2 shifts of sensitized triplets are not common. Such a reaction would resemble a 1,2 shift of a free radical, a very rare reaction. The usual reactions of triplets are hydrogen abstraction, recombination reactions and addition to alkenes.

The singlet carbene 1,2 shift could occur via the shift of the hydrogen (or other group) into the vacant \( p \) orbital of the carbene. Aryl and alkyl groups can also migrate, but a hydrogen shift is favored. ²³

Another important type of carbene rearrangement is the interconversion of arylcarbenes. An illustrative example of
this is the formation of 6 upon the heating of the sodium salt of the tosylhydrazone of 2,7-diphenylcyclohept-2,4,6-triene 5.\textsuperscript{24}

Phenylcarbene also undergoes interconversion reactions, one of the products formed upon thermolysis of the sodium salt of the tosylhydrazone of benzaldehyde being heptafulvalene.\textsuperscript{25} Heptafulvalene is also the product of the cycloheptatrienyldiene/cycloheptatetraene intermediate. The discovery that phenylcarbene undergoes rearrangement to a seven membered ring created greater interest in this system. The rearrangements of phenyl carbene will be discussed in a later part of this thesis.
I.B. Allenes

Allenes contain a central, sp-hybridized, carbon that is simultaneously doubly bonded to two other carbons. The planes created by the substituents bonded to the two end carbons (the Y-C-H and X-C-H planes in the example below) of the allene center are held perpendicular to each other. Due to the presence of the π systems allenes tend to be nucleophilic.

An interesting and useful property of allenes is the possibility for optical activity. A dissymmetric plane exist for allene, allowing for the existence of enantiomers.

Since the cyclic and fully conjugated allene 2 is isomeric with the carbene 1, it is a central part of the
study of the C\textsubscript{7}H\textsubscript{6} carbene/allene system 1 and 2. The stability of cyclic allenes depends on ring size. There is no evidence experimentally or theoretically for the existence of any cyclic and fully conjugated allene system smaller than cycloheptatetraene. The unique relationship between the allenes and carbenes of cyclic conjugated systems will be discussed later.

Smaller, nonconjugated cyclic allenes such as 1,2-cyclohexadiene (9) are known to exist, but are not stable at room temperature because of ring strain.\textsuperscript{28} Conjugation as well as ring size play an important role in the stability of cyclic allenes. An example of such an effect can be seen by comparing 1,2-cyclononadiene (7) and 1,2,4,6,8-cyclononapentaene (8).\textsuperscript{29} The allene 7 is stable at room temperature, while 8 is not.

\begin{align*}
\text{7} & \sim \\
\text{8} & \sim \\
\text{9} & \sim
\end{align*}
I.B.1. Generation of Allenes

Allenes can be generated in a number of ways, but only a few are synthetically useful. Table 2 shows some of the more common methods used to generate allenes.

Table 2: The Generation of Allenes

\[ \text{H}_2\text{C} = \text{C} = \text{CH}_2 + \text{Zn, EtOH} \rightarrow \text{H}_2\text{C} = \text{C} = \text{CH}_2 \]

ref. 30

\[ \text{ref. 31} \]

\[ \text{ref. 32} \]
The synthetic method used to generate the fully conjugated cyclic intermediate cycloheptatetraene 2 is low temperature, base-promoted dehydrohalogenation of the chloride 10 and its isomers.\textsuperscript{31}

I.B.2. Reactions of Allenes

Allenes undergo reactions similar to alkenes. These include [2+2] cycloadditions, Diels-Alder reactions, and electrophilic attack. Allenes also react with carbenes to form cyclopropane rings having exocyclic double bonds. The following are examples of various allene reactions.\textsuperscript{33}

Reactions with carbenes:\textsuperscript{34}

\[ \text{CH}_2\equiv\text{C} \equiv\text{CH}_2 + :\text{CH}_2 \rightarrow \bigtriangleup \]
Diels–Alder Reactions\textsuperscript{35}
\[ \text{CH}_2=\text{C}=\text{C} \text{H}_2 + \text{CH}_2=\text{C}=\text{C} \text{H}_2 \rightarrow \text{cyclohexene} \]

2+2 Cycloadditions\textsuperscript{36}
\[ \text{CH}_2=\text{C}=\text{C} \text{H}_2 + \text{R}_2\text{C}=\text{O} \rightarrow \text{cyclobutane} + \text{cyclobutene} + \text{acrolein} \]

Electrophilic Attack\textsuperscript{35}
\[ \text{CH}_2=\text{C}=\text{C} \text{H}_2 + \text{HX} \rightarrow \text{CH}_2-\text{C}=\text{C} \text{H}_2 + \text{CH}_2-\text{C}=\text{C} \text{H}_2 \]

Addition of electrophiles to allenes might be expected to occur at the center carbon, since the carbocation produced would be stabilized via resonance.\textsuperscript{35} However, resonance stabilization could not take effect until the three \( p \) orbitals are parallel. Rotation about the \( C-C \) bond must therefore occur first. The transition state is thus unaffected by resonance stabilization. Attack of electrophiles on unsubstituted allene 11 most often occurs at the end carbon.\textsuperscript{35} Further substitution effects the preference of attack, tetramethyl allene 12 being attacked predominantly at the center carbon.\textsuperscript{35}
I.C. Cyclic, Fully Conjugated Carbenes and Allenes

As mentioned previously, cyclic and fully conjugated allenes and carbenes may be isomeric. Unfortunately, allene chemistry can often be interpreted in terms of the carbene. The use of molecular orbital calculations is often useful for predicting whether the carbene or the allene will have the lowest energy.

One of the most common methods used to calculate molecular orbital energies is MNDO\textsuperscript{37}. MNDO molecular orbital calculations are semi-empirical methods that are used to determine the minimum energy of a system. The method is called semi-empirical because the calculations use experimentally determined parameters. The technique calculates heats of formation, but error may be present in the calculation. The usefulness of the calculations is in comparing energies of similar intermediates. The calculations are useful for helping to verify lowest energy states as well as the relative stabilities of the possible intermediates. E.E. Waali and co-workers used this method
to study the energy relationships between a number of cyclic, fully conjugated, allene/carbene systems.\textsuperscript{38}

I.C.1. Cyclopropenyldiene/Cyclopropadiene

The smallest conjugated cyclic carbene system is cyclopropenyldiene (13). Its existence is only known from low temperature matrix isolation studies; no chemistry from 13 has been reported.\textsuperscript{39} However, chemistry from its diphenyl derivative 15 is known.\textsuperscript{40} The chemistry of diphenyl cyclopropenyldiene is characteristic of singlet carbenes, adding to dimethyl fumarate but not to cyclohexene.

A singlet, ground state carbene is predicted for the parent cyclopropenyldiene because the vacant p orbital can...
be incorporated into the $\pi$ system, making it 'aromatic' in nature. MNDO studies also predict a ground state singlet, finding the singlet to be more stable than the triplet by 28 kcal/mol.\textsuperscript{37}

There is no evidence for the existence of 1,2-cyclopropadiene (14). The required bond angle of the central allene carbon would be too strained.\textsuperscript{37}

I.C.2. Cyclopentadienyldene/1,2,4-Cyclopentatriene

Cyclopentadienyldene (17) shows singlet solution chemistry,\textsuperscript{41} but ESR studies have shown that the true ground state is the triplet carbene 18.\textsuperscript{42} Singlet reaction products are most likely a result of very fast reactions of the initially formed singlet carbene 17. If the reactions are rapid there may not be enough time for the singlet 17 to intersystem cross to the triplet 18.

\[
\begin{array}{ccc}
\text{17} & \text{18} & \text{19} \\
\sim & \sim & \\
\end{array}
\]

It appears from the MNDO calculations that the singlet carbene $17s_2$ having its lone pair of electrons occupying the $p$ orbital does not stabilize the carbene even though the lone pair of electrons could interact with the $\pi$ system in
the ring, creating an 'aromatic like' intermediate. The higher energy of this carbene may be a result of the added energy required for the electrons to occupy a higher energy orbital.

Theoretical calculations also find that the triplet is the ground state. MNDO calculations found four possible carbene intermediates, 17s1, 17s2, 17s3, and 18, all except for the 17s2 ('aromatic like') carbene having lower energy than the allene 19. The energy separation between the lowest energy singlet 17s3 and triplet 18 was calculated to be only 21 kcal/mol.

\[ \begin{align*}
&17S_1 \\
&\sim \\
&17S_2 \\
&\sim \\
&17S_3 \\
&\sim \\
&18 \\
&\sim \\
&19
\end{align*} \]

I.C.3. Cyclononatetraenylidene/Cyclononapentaene

The nine membered ring appears to be large enough to allow for the existence of both the allene and the carbene intermediates. Chemical experiments suggest that when the respective intermediates are produced by classical methods, chemistry unique to the expected intermediate is observed. When the carbene 20 is generated directly, the product is found to be a dimer 22 formed via the triplet intermediate 21. When the allene 23 is formed by dehalogenation,
electrocyclic ring closure occurs followed by hydrogen migration, producing indene (24)."
it was thought that it could exhibit singlet carbene chemistry due to the 'aromatic' character of the system, i.e., the lone pair of electrons existing in the sigma orbital while the vacant p orbital was incorporated into the \( \pi \) system of the ring, creating a \( 4n+2 \) \( \pi \) e system.\(^1\) Early chemical studies seemed to support this hypothesis.\(^1\)

Photolysis of the sodium salt of the tosylhydrazone 25 in the presence of an electron rich alkene showed no reaction, instead the dimer heptafulvalene (26) was formed. The intermediate did react with a more electron deficient alkene, dimethyl fumarate, to form 27, similar to diphenylcyclopropenylidene, a known singlet carbene.\(^1\)

Later results showed that cycloheptatrienylidene would add to styrene, and in work done by Jones and co-workers, a Hammett study of various styrenes showed that indeed the
intermediate was nucleophilic in nature. The \( \rho \) value was found to be +1.05.

\[ \text{reactions} \]

The possibility that the intermediate giving rise to the observed chemistry could be the allene 2 was first introduced by Untch, who found that upon dehydrohalogenation of 1-chlorocycloheptatriene (10) (in an attempt to produce the allene directly) the product observed was heptafulvalene (26), the same dimer formed from the photolysis of the sodium salt of the tosylhydrazone of tropone 25. This discovery introduced the possibility that both reactions involved the same intermediate, namely the allene 2. Untch explained this in terms of a [2+2] dimerization followed by thermally allowed electrocyclic ring closure to form heptafulvalene. Since allenes are known to be nucleophilic in nature, the previous chemistry attributed to cycloheptatrienylidene 1 could also be attributed to cycloheptatetraene 2.
Since the observation that cycloheptatetraene could be the reactive intermediate much work has been done, both experimentally and theoretically, trying to determine whether the allene 2 or the carbene 1 is lower in energy.\textsuperscript{47} Experimentally the two intermediates are often indistinguishable, although products that are most likely a result of the allene 2 have been observed. The Diels-Alder reaction of 28 with the deuterium labelled allene intermediate 27 could only occur through the chiral allene to produce the optically active product 29.\textsuperscript{48} The allene 2 has also been observed by low temperature IR.\textsuperscript{49}
Added support for the allene 2 having lower energy than the carbene 1 comes from theoretical calculations. Both MNDO and \textit{ab initio} studies show allene 2 to be at an energy minima, lying somewhere between 16 and 48 Kcal/mol below the singlet carbene.\textsuperscript{46b,c} According to Waali's MNDO study the allene is a true intermediate, while the singlet is only a transition state between the two enantiomeric forms of the allene.

A recent \textit{ab initio} study by Schaefer and co-workers concluded that there is an energy minimum for the singlet 1, suggesting that is indeed a true intermediate, but the depth of the energy well in which the singlet lies was not reported.\textsuperscript{46c} The study confirms that the allene 2 is of lower energy than the singlet 1. The same study found that the approximate energy difference between the singlet and triplet carbenes was within 5 kcal/mol, with the singlet having lower energy than the triplet. This seems to contradict ESR observations by both Chapman and Wentrup of the triplet carbene.\textsuperscript{50}

I.C.4.a. Phenyl Carbene Rearrangements

The C\textsubscript{7}H\textsubscript{6} carbene 1 or allene 2 intermediate gained importance when W. M. Jones and co-workers reported that phenyl carbene 30 underwent rearrangements to form heptafulvalene 26.\textsuperscript{25a} Rearrangements involving \textsuperscript{o}-, \textsuperscript{m}-, and \textsuperscript{p}-tolylcarbenes 31, 32, 33, were also reported by M. Jones,
Jr. and co-workers. The methyl groups were used as internal traps, producing benzocyclobutane 35 and styrene 36. Through this latter work, it was demonstrated that the ring expansion of phenylcarbene 30 to cycloheptatetraene (2) was reversible. When these papers were published, the observation were still being attributed to the singlet carbene 1. It now seems appropriate to explain the results of the rearrangement products in terms of the allene 2.
I.C.5. Constrained Cycloheptatrienyldiene and Cycloheptatetraene Systems

One way to alter the energy of carbene 1 with respect to allene 2 is to constrain the ring. A constraint could force the allene 2 into planarity, thereby stabilizing the singlet carbene. Constraining the system might thus give chemistry unique to the singlet carbene. Work done by Tivakornpannarai° and McCarthy° studied the effects constraining cycloheptatetraene with a 9,10-anthraceno bridge, see structures 37 and 38, below. This constraint was chosen because, unlike previously studied constraints, there are no aromatic rings conjugated with the seven membered ring. Conjugated aromatic rings may interfere with the intermediates by resonance perturbation of the system.°

![Structure 37 and 38](image)

I.C.5.a. Benzoannelated Systems

One of the benzoannelated systems studies is benzocycloheptatetraene (39).° The presence of the benzo group appears to drive the rearrangement equilibrium towards the more favorable naphthalene carbene 41, as seen from the
carbene additions products.\textsuperscript{53a}

I.C.5.b. 4,5-(9,10-anthraceno)cycloheptatetraene (38) and 3,4-(9,10-anthraceno)cycloheptatetraene (37)

The 9,10-anthraceno constraint used to alter the C\textsubscript{7}H\textsubscript{6} system in this lab differs from the previous constraints in that the aromatic rings should not perturb the system \textit{via} resonance effects. There are three possible positions for the constraint. This thesis will use nomenclature for the constraint based on the position of the constraint with
respect to the reactive center, as shown below.

Although the 9,10-anthraceno constraint does have a small degree of flexibility, it was felt that it would favor the cycloheptatrienyldiene enough to allow it to undergo reactions. Effective constraint favoring a carbene would presumably only occur in the α and γ positions. The β constraint of 37 should only reinforce allene chemistry.

I.C.5.b.i. 3,4-(9,10-anthraceno)cycloheptatetraene 37\textsuperscript{50}

The first of the series studied was the β carbene/allene 37, by Tivakornpannarai.\textsuperscript{51a,b} As mentioned above, such a constraint would be expected to reinforce
normal allene chemistry. It was studied as a model for the parent system. Some of the products observed from the allene/carbene intermediate 37, generated either by thermolysis or photolysis of the sodium salt of the tosylhydrazone 42 or by the dehydrohalogenation of the chloride 49, were unexpected. One product formed was the dimer 44, analogous to the dimer heptafulvalene (26) formed by the parent system. The formation of the dimer is most likely a result of the allene. Triptycene (45) was also formed from both reactions. The photolysis of the sodium salt of the tosylhydrazone 43 also produced some products typical of carbenes, namely the aldehydes 47 and 48, as well as the azine dimer 46. Base elimination of the chloride also showed formation of 50.
I.C.5.b.ii. 4,5-(9,10-anthraceno)cycloheptatetraene 38

The gamma constraint was studied by McCarthy.\textsuperscript{51} The products obtained from both the thermolysis and photolysis of the sodium salt of the tosylhydrazone 54 as well as dehydrohalogenation of the chloride 56 produced the dimer 55 analogous to heptafulvalene (26) formed by the parent system. Triptycene (45) was also formed. No products were isolated and identified that could be attributed solely to a singlet carbene intermediate.

\[ \sim 54 \sim \text{Na}^+ \]

\[ \sim 56 \sim Cl \]

The formation of triptycene form both the $\gamma$ and the $\beta$ constrained intermediates 37 and 38 was both unusual and unexpected. Its formation requires the net loss of a carbon atom, a rare if not unknown process in small systems under such mild conditions (the reactions were all carried out at room temperatures). Since both 37 and 38 give rise to carbon atom loss, it is possible they undergo a
rearrangement to a common intermediate that then gives rise to carbon loss. One possible mechanistic explanation could involve rearrangement to the carbene intermediates 51 and 52, below.\textsuperscript{50,51} The carbene could possibly be stabilized via through space stabilization of the aromatic rings. The carbon atom could then be extracted from the ring by the solvent, tetrahydrofuran (THF), to form the ylide 53. Support for the extraction of the carbon by THF comes from a study by Tivakornpannarai in which the gases evolved during a photolysis reaction were monitored by IR.\textsuperscript{50} Both CO and ethylene bands were observed.
Determining whether the aromatic rings play a role in the loss of a carbon atom would be possible by studying a similar constraint that lacks the aromatic rings. Two such systems to be studied are 57/58 and 59/60. This research will attempt to generate the allene and/or carbene with these types of constraints.
II: Results and Discussion

II.A. The Attempted Synthesis of 2,7-Dibromo-4,5-(1,4-cyclohexano)cyclohept-4-en-1-one

One of the essential precursors to fully conjugated, cyclic, seven-membered carbene and/or allene systems is cyclohepta-3,5,7-trien-l-one (tropone). Tropone (61) is the precursor for both the sodium salt of the tosylhydrazone 25 and the chloride 10.$^{1,34}$

![Chemical Reaction Diagram]

Synthesis of the 1,4-cyclohexano constrained tropone 62 has been previously reported in the literature (see Figure 2).$^{54}$ Some steps in Figure 2 appear to go in good yield, but the yields of some steps were not reported. The overall low yield of this sequence coupled with the high cost of the starting material, tropolone, rendered this synthetic
FIGURE 1: The Synthesis of Tropone 62
route to tropone 62 impractical.

The synthetic route attempted in this research to generate the tropone 62 was based on work done by McCarthy for the tropone 63 (see Figure 3, Reaction 1). This route involves the [3+4]-7 cycloaddition reaction between an oxyallyl cation and a diene. Cycloadditions utilizing oxyallyl cations as the electrophiles have long been used as a convenient method for forming seven membered rings by organic chemists. Such reactions are limited by the stability and relative electrophilicity of the oxyallyl cation as well as the nucleophilicity of the diene system. Less nucleophilic dienes require more electrophilic oxyallyl cations. One of the most electrophilic classes of oxyallyl cations is generated from polybromo ketones in the presence of either diiron nonacarbonyl or iron pentacarbonyl. Much of the work involving these types of oxyallyl cations was developed by Noroyri and co-workers.

The are two mechanistic pathways for [3+4]-7 cycloaddition reactions that should be considered. Pathway 'a' shows a concerted mechanism. Cycloaddition reaction undergoing a concerted mechanism would be expected to add stereospecifically. Pathway 'b' shows a stepwise mechanism. Cycloadditions undergoing a stepwise mechanism would not be expected to give stereospecific additions since rotation could occur in the intermediate prior to ring
FIGURE 2: Synthetic Route to the Dibromoketones 68 and 70.

\[
\text{67} + \text{Br}_2\text{CHCHBr}_2 \xrightarrow{\text{Fe}_2(\text{CO})_9} \text{67} + \text{55}
\]

\[
\text{63} \xrightarrow{\text{LIF, DMF}} \text{68} \xrightarrow{\text{Li}_2\text{CO}_3}
\]

\[
\text{69} + \text{Br}_2\text{CHCHBr}_2 \xrightarrow{\text{Fe}_2(\text{CO})_9} \text{69} + \text{55}
\]

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According to H. M. R. Hoffmann, strongly electrophilic oxyallyl cations prefer the stepwise mechanism shown in 'b'. A stepwise mechanism would be expected in the case of nonrigid dienes, since the double bonds would not necessarily be held in the same plane, a usual requirement in concerted reactions.

When the [3+4]-7 cycloaddition reaction between the diene 67 and the oxyallyl cation 66 was carried out, the yield of the dibromoketone 68 was very low (see Figure 3, Reaction 1). The overall yield starting from the diene 67 and going to the tropone 63 was only 15%. Although this yield is not a significant improvement over the previous method reported in the literature (analogous to the reaction sequence in Figure 2 except that anthracene was used in the Diels-Alder reaction with tropynone rather than 1,3-cyclohexadiene), the route is advantageous because it requires a fewer number of steps. The starting materials in
this route were also more readily available than the starting materials in the previous route.

The reaction of the diene 69 with the oxyallyl cation 66 failed to produce any of the dibromoketone 70 (see Figure 3, Reaction 2). Eight experiments outlining some of the variations in reaction conditions that were attempted in order to produce 70 are shown in Table 3 (in the Experimental Section). All of the reactions were run under nitrogen in dry benzene and were heated at reflux.

Some of the variations in the experimental conditions included changing the molar ratios of the various reactants, changing the order in which the reactants were added, and finally changing the reaction time. Reactions A and E involved generating an iron carbonyl complex with the diene 69 first, followed by the addition of tetrabromoacetone. The iron carbonyl complex was isolated and analyzed by NMR in reaction A prior the addition of tetrabromoacetone.

The failure of the reaction was either a result of a poor diene or an unstable oxyallyl cation. Work reported previously in the literature using tetrabromoacetone in [3+4]→7 cycloaddition reactions employed only very rigid dienes such as furan and cyclopentadiene. Dienes similar to 69 undergoing cycloaddition reactions with polybromoketones in the presence of diiron nonacarbonyl always had alkyl substituents adjacent to the carbocation centers. In order to try and determine the reason why
this reaction failed, a reaction was carried out between both dienes 67 and 69 and 2,4-dibromo-3-pentanone in the presence of diiron nonacarbonyl (see Figure 3). Isolation of the dimethylketones 71 (85%) and 72 (45%) suggested that the problem was with the oxyallyl cation, not with the diene. It appears that the oxyallyl cation generated from tetrabromoacetone is too unstable to undergo cycloadditions with the diene 69. Changing from diene 67 to diene 69 seems to effectively reduce the yield of dibromoketone from 15% to 0%.

After determining that the diene 69 would not react with the oxyallyl cation 66, the synthetic route outlined in Figure 3 was abandoned. A new synthetic route that involved the cycloaddition of the dienamine 76 with cyclopropenone was attempted (see Figure 4, Reaction 1). This route was based on similar work previously reported in the literature.

Problems with this route arose with the synthesis of the aldehyde 74. Boron trifluoride etherate was used to catalyze the rearrangement of the epoxide 73 to the aldehyde, following a similar procedure previously reported in the literature. The reaction went in low yield producing the conjugated aldehyde 95 along with 74. Attempted purification of the aldehydes by distillation resulted in their decomposition. The synthesis of the dienamine 76 was tried once, following a procedure
Figure 3: Synthesis of the dimethylketones 71 and 72
FIGURE 4: Attempted Synthesis of Tropone 62

\[
\text{CH}_2\text{C} = \text{C} + \text{CO}_2\text{H} \rightarrow \text{CH}_2\text{C} = \text{C} - \text{CO}_2\text{H} \rightarrow \text{Br}_2 - \text{E}_2\text{O} \rightarrow \text{CH}_2\text{C} = \text{C} + \text{CO}_2\text{H}
\]

\[
\text{CH}_2\text{C} = \text{C} + \text{C} = \text{C} \rightarrow \text{CH}_2\text{C} = \text{C} - \text{CO}_2\text{H} \rightarrow \text{CH}_2\text{C} = \text{C} + \text{CO}_2\text{H}
\]

\[
\text{CH}_2\text{C} = \text{C} + \text{CH}_3\text{C} = \text{C} \rightarrow \text{CH}_2\text{C} = \text{C} - \text{CO}_2\text{H} \rightarrow \text{CH}_2\text{C} = \text{C} + \text{CO}_2\text{H}
\]

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previously reported in the literature for the synthesis of
dienamines, but no products were isolated.$^61$

Due to the low yields of the aldehyde this route was abandoned. A few other routes to the aldehydes 74 and 75 were tried, but without success (see reaction 2 and 3 shown in Figure 4). The route may still be a valid synthetic pathway to the tropone 62, but it requires considerable synthetic development.

II.B. 4,5-(3,4-propano)cyclohept-2,4,6-trien-1-one (84)

The 1,4-cyclohexano constraint was probably the best type of saturated constraint for mimicking the 9,10-anthraceno constraint. Since a simple synthetic route into this system was not available, a different system was chosen, the 3,4-propano system. If carbon atom loss involves the interaction of the carbene carbon with the aromatic rings in 37/38, then no carbon atom loss would be expected from this allene/carbene system 59/60. If carbon atom loss is still seen, then the possibility of through space interaction between the aromatic rings and the carbene carbon would have to be ruled out.

One of the main advantages of the system was that a synthetic route had been reported in the literature.$^62$

Except for a few minor variations in the synthesis of the tropone 84, the procedure is the same as reported by Kende and Koch (see Figure 5).$^64$ The main variation was the use
FIGURE 5: Synthesis of the Tropone 84

CH₂CH₃₃CO₂H → CH₂CH₃₃CH₂OH → CH₂CH₃₃CH₂OMs

77 → 78 → 79

LiAlH₄ → MgCl₂ → NaNₐ₃Acetone

(CH₂)₄ONO + (CH₂)₄NO₂

82 + 81 → 80

a. RNH₃NO₂ or b. NaNₐ₂

CH₂CH₂CH₂CH₂I

83

1. 0.01W KOH K₂Fe(CN)₆

2. Citric Acid

84

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of NaNO₂ as a nitrating agent rather than a nitrating organic resin. A resin was used initially but found to be inefficient. The nitrating resin had to first be generated from the chloride, then washed with anhydrous benzene and finally dried under vacuum. The resin was found to produce not only the desired nitro compound 81, but also the nitrite ester 82 and the alcohol 79 in at least a 1:1 ratio. The use of NaNO₂ was not only a more convenient reaction but also gave a higher yield of the nitro compound with respect to the nitrite ester. It did not produce any of the alcohol 79.

The most efficient way to generate the tropone was to first dissolve the nitrophenol 83 in 1M KOH, then dilute the solution to 0.01M, followed by the addition of K₃Fe(CN)₆. After stirring for 30 minutes the reaction was quenched with an excess of citric acid.

Once the tropone was isolated and purified, the generation of the carbene and allene precursors was attempted. Various reactions were tried in attempts to form either the tosylhydrazone 85 or the chloride 86 (see Table 4). None of the desired products were ever isolated in pure form, although the reaction of the tropone 84 with purified thionyl chloride followed by the addition of tosylhydrazide produced what appears to be the tosylhydrazone 85 as well as a small amount of the chlorinated azulene 87. During the same reaction, a small
sample of the dichloride 89 was removed and a proton NMR obtained. The NMR spectra of the tropone 84, the dichloride 89, and the tosylhydrazone 85 are shown in Figure 7. The tosylhydrazone 85 was never successfully isolated and characterized. Thionyl chloride that had not been purified produced none of the tosylhydrazone but did produce a mixture of the chloroafulenes 87 and 88 in a 3.2:1 ratio (4% total combined yield). A more detailed description of their formation along with structure proofs and a possible mechanism will be presented in the following section.

The various experiments attempting to produce the tosylhydrazone 85 or the chloride 86 are presented in Table 4. It appears that the use of oxalyl chloride, usually the favored reagent for the formation of the dichloride 89, fails to yield any of the desired products. The reaction of the tropone 84 with oxalyl chloride was followed by the immediate addition of either tosylhydrazide or lithium aluminum hydride. Neither of the desired products were ever isolated from these reactions.
TABLE 3: Attempted generation of the Tosylhydrazone 85 and the Chloride 86

\[ \text{Ref. } 50a \]

\[ \text{Ref. } 51b \]

\[ \text{Ref. } 51b \]

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FIGURE 6: The Spectral Data for the Tosylhydrazone 85.

$^1\text{H}$: $H_b$ or $H_a$ 6.55 ppm (d)

$H_a$ or $H_b$ 6.39 ppm (d)

$H_c$ 2.68 ppm (t)

$H_c$ 1.88 ppm (t)
II.B.1. The Formation of Tri- and Tetrachloroazulene

The reaction of the tropone 84 with thionyl chloride that had not been carefully purified produced a small amount of the trichloroazulene 87 and a trace amount of the tetrachloroazulene 88 (the combined yield for the two was only 4%, and they were formed in a 3.2:1 ratio). Use of purified thionyl chloride (refluxed for 12 hr over sulfur followed by two fractional distillations, all under nitrogen\(^\text{66}\)) also produced the azulene 87. Neither of these species have been previously reported in the literature.

The formation of the azulene 92 could be explained in terms of the loss of a proton from the dichloride 89 followed by a disproportionation reaction or oxidation reaction (see Figure 9). The NMR taken of the dichloride 89 suggests that is being initially formed. The disproportionation of two 2,3-dihydro-6-chloroazulenes (91) would result in the formation of 6-chloroazulene (92) and (1H)-2,3-dihydro-6-chloroazulene (86), although there is no evidence of the chloride 86 in the NMR spectra.\(^\text{67}\) A number of oxidizing materials could have been present. These include air, the decomposition products of thionyl chloride (SOCl\(_2\) decomposes upon heating to temperatures above its bp to form S\(_2\)Cl\(_2\), SO\(_2\), and Cl\(_2\)\(^\text{68}\)), or sulfuryl chloride (present either as a contaminant in the thionyl chloride or formed from recombination of the decomposition products of thionyl chloride).
The formation of the trichloroazulene likely involves electrophilic aromatic substitution by either sulfuryl chloride or chlorine (thionyl chloride is not a good chlorinating reagent) on the five membered ring of 6-chloroazulene. Electrophilic attack occurs preferentially on the five membered ring of azulenes due to its greater negative charge density.\(^6\)

The formation of the tetrachloroazulene \(^8\) is likely to be the result of further chlorination of the trichloroazulene \(^7\). There are two possible positions for the fourth chlorine to attack, either at carbon 4 or carbon 5 (numbering the five membered ring first, the bridgehead carbons are numbered as 3a and 8a). However, according to charge densities carbon 5 is more susceptible to electrophilic aromatic substitution than carbon 4.\(^7\) It also follows by analogy to chlorobenzene chemistry that the chlorine on carbon 6 would direct electrophilic attack to the 5 position. It has also been shown that 1,2,3-triphenylazulene is brominated in the 5 position. Further bromination occurs in the 7 position, and subsequent brominations occur on the phenyl rings.\(^7\)

The reaction between purified thionyl chloride and tropone \(^8\) that was run under nitrogen showed only a trace amount of the trichloroazulene \(^7\) and none of the tetrachloroazulene \(^8\). Although an actual percent yield was not determined from this reaction, it was evident that the
FIGURE 7: Spectral Data for the Chloroazulenes 87 and 88.

87

\[ ^1H: \ H_b \text{ or } H_a \ 8.11 \text{ ppm (d, 10.68 Hz)} \]

\[ H_b \text{ or } H_a \ 7.23 \text{ ppm (d, 10.68 Hz)} \]

\[ H_a \ 7.81 \text{ ppm (s)} \]

88

\[ ^1H: \ H_d \text{ or } H_b \ 8.02 \text{ ppm (d, 10.68 Hz)} \]

\[ H_b \text{ or } H_d \ 7.43 \text{ ppm (d, 10.68 Hz)} \]

\[ H_a \ 8.51 \text{ ppm (s)} \]

\[ H_a \ 7.65 \text{ ppm (s)} \]
**FIGURE 8: Possible Mechanism for the Formation of 87 and 88**

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amount of the trichloroazulene formed was much less than in the reaction with thionyl chloride that had not been carefully purified. Whether this is due to the careful purification of the thionyl chloride, the absence of air, the lack of heating, or a combination of the these three factors cannot be known for certain.

II.C. Conclusions

The generation of the precursors necessary for the formation of the allene and carbene species with a saturated constraint was unsuccessful. The first system attempted failed in the reaction between the oxyallyl cation $66$ and the diene $69$ due to the instability of the oxyallyl cation in the presence of a poor diene system.

The second system attempted, using (1,3-propano)-cyclohept-2,4,6-trien-1-one, failed to produce the chloride $86$. The reaction of the tropone $84$ with purified thionyl chloride did produce a mixture of the trichloroazulene $87$ and what appears to be the tosylhydrazone $85$. It may be that tropone $84$ is so sensitive to oxidation (resulting in the formation of azulene) that the reaction must be run under very mild conditions.
III. EXPERIMENTAL

General: Nuclear magnetic resonance (NMR) spectra were run on a JEOL FX-90Q spectrometer (proton 89.56 MHz; carbon, 22.5 MHz). Proton spectra were also run on a Bruker HX-270 spectrometer (270 MHz). A few proton spectra were run on a EM-360 spectrometer (60 MHz). All proton chemical shifts were reported in ppm units downfield from tetramethylsilane. All carbon 13 chemical shifts were reported in ppm units relative to CDCl$_3$ at 77 ppm. Infrared (IR) spectra were run on a Beckmann Acculab 2. Mass spectra (MS) were obtained from a VG Instruments 7070-HF spectrometer (Chemistry Department, Montana State University, Bozeman, Montana). Melting points were obtained from a Meltemp melting point apparatus and were not corrected. Solvents were removed from reaction products by rotary evaporator at water aspirator pressure. Trace solvents were removed by mechanical pump. Preparative Gas Chromatography (GC) work was done on a Varian Series 1400 using a 10 % SE-30 1/4' column.

Materials: Commercially available materials were used without further purification unless otherwise specified. When necessary solvents were dried, distilled and stored over molecular sieves (4 A$^\circ$). Preparative thin layer chromatography (PTLC) plates were prepared using EM Reagent Silica Gel 60 PF-256 + 366 and were activated by drying at 100 °C for 2-4 hr. Packing materials used for column
chromatography were silica gel (60-100 mesh) and alumina (60-100 mesh), obtained from Aldrich.

2,3-Bis(methylene)bicyclo[2.2.2]octane (69).
Method A: The synthesis of 2,3-bis(methylene)-bicyclo-[2.2.2]octane was first attempted by a method similar to the one used to prepare the diene 67. The reaction of 1,3-cyclohexadiene (0.84 g, 0.0105 moles) with 1,4-dichloro-2-butene (4.73 g, 0.0378 moles) in a sealed tube. The tube was heated for 60 hours at 190 °C. None of the desired 2,3-bis(chloromethyl)bicyclo[2.2.2]octane was isolated. Only polymer was obtained.
Method B: 2,3-Bis(methylene)bicyclo[2.2.2]octane was successfully synthesized following the procedure developed by Bailey and Lawson (see Figure 10). The only change in the procedure was the reduction of the anhydride adduct 93 with LiAlH₄ to produce the diol 94. Reduction of the anhydride 93 occurs in an almost quantitative yield (97%). The overall yield based on 1,3-cyclohexadiene was 33%. Spectral data were identical to that previously reported in the literature.

^H (69) 5.24 ppm (s)
4.71 ppm (s)
2.34 ppm (s)
1.62 ppm (s)
FIGURE 9: Synthesis of the Diene 69

\[ \text{Cyclopentadiene} + \text{Maleic Anhydride} \rightarrow \text{Diene Intermediate} \rightarrow \text{LiAlH}_4 \rightarrow \text{Diene Product} \rightarrow \text{H}_2/\text{Pt} \rightarrow \text{Diene Product} \]

\[ \text{Diene Product} \rightarrow \text{Acetic Anhydride} \rightarrow \text{Diene Product} \]

\[ \text{Diene Product} \rightarrow \text{Maleic Anhydride} \rightarrow \text{Diene Product} \]

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1,1,3,3-Tetrabromoacetone.\textsuperscript{73,74}

The 1,1,3,3-tetrabromoacetone used in this research was prepared and purified according to the methods described in the literature.\textsuperscript{71,72}

2,7-Dibromo-4,5-(1,4-cyclohexano)cyclohept-4-en-1-one (70).

This procedure was based on methods previously reported in the literature.\textsuperscript{56} A typical procedure for the attempted synthesis of the dibromoketone 70 was as follows: In a three-neck, round bottom flask fitted with a reflux condenser, a nitrogen inlet and outlet, a dropping funnel, a magnetic stir bar and a thermometer, was placed a mixture of diiron nonacarbonyl (5.5g, 0.015 moles) and the diene (2.0 g, 0.015 moles) in 100 mL of dry benzene. The solution was heated to 60 °C. To this mixture, a solution of 1,1,3,3-tetrabromoacetone (5.6 g, 0.015 moles) in 25 mL of dry benzene was added dropwise over a period of 30 min. The mixture was stirred at 60 °C for 48 hours. Upon cooling to room temperature the solution was poured into 200 mL of saturated sodium bicarbonate and stirred vigorously for 30 min. Ethyl acetate (200 mL) was added and the solution stirred for an additional 30 min. The solution was then filtered over diatomaceous earth. The organic and aqueous layers were separated and the aqueous layer was washed with ethyl acetate (2 x 50 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent removed under reduced pressure. The resulting black
TABLE 4: Attempted synthesis of the dibromoketone 70

<table>
<thead>
<tr>
<th>Diene 69</th>
<th>CHBr₂C(O)CHBr₂</th>
<th>Fe₂(CO)₉</th>
<th>Rxn Time (hr)</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.</td>
<td>1</td>
<td>1'</td>
<td>1'</td>
<td>24</td>
</tr>
<tr>
<td>B.</td>
<td>1'</td>
<td>1</td>
<td>1'</td>
<td>48</td>
</tr>
<tr>
<td>C.</td>
<td>1</td>
<td>1'</td>
<td>1'</td>
<td>12</td>
</tr>
<tr>
<td>D.</td>
<td>2'</td>
<td>1</td>
<td>1'</td>
<td>2</td>
</tr>
<tr>
<td>E.</td>
<td>4</td>
<td>1'</td>
<td>1'</td>
<td>2</td>
</tr>
<tr>
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<td>H.</td>
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<td>72</td>
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* These two reagents were added together first. The third reagent was then added dropwise.
material was purified over silica gel using petroleum ether with increasing amounts of chloroform as the eluent. The NMR showed no identifiable products.

2,3-Bis(methylene)bicyclo[2.2.2]octane Iron Tricarbonyl Complex.

This procedure followed methods previously reported in the literature.58 Into a 250 mL three-neck, round bottom flask fitted with a condenser, a nitrogen inlet and outlet, a magnetic stirrer and a thermometer, was placed 4.6 g (0.01233 mol) of diiron nonacarbonyl in 30 mL of dry hexane. To this was added 0.8 g (0.0060 mol) of diene 69. The solution was heated to reflux and stirred under nitrogen for 2 hr. After cooling to room temperature the mixture was filtered over a pad of silica and the solvent was removed under reduced pressure. The crude material was chromatographed over alumina using hexane with increasing amounts of benzene as the eluents. The yield of pure product was 1.08 g (60%). Due to the presence of iron in the NMR sample a quantitative spectra was not obtained. The following proton NMR peaks were seen: 2.53 ppm (multiplet), 1.79-1.76 ppm (multiplet), 0.22 ppm (s), 0.19 ppm (s).

2,7-Dimethyl-4,5-(1,4-cyclohexano)cyclohept-4-en-1-one (72).

This procedure was based on methods previously reported in the literature.56 Into a three-neck, round bottom flask fitted with a condenser, a magnetic stirred, a nitrogen
inlet and outlet, and a thermometer, was placed 3.37 g (0.00929 mol) of diiron nonacarbonyl. The round bottom flask was then vigorously flushed with nitrogen. To this was added 0.5 g (0.0037 mol) of diene 69 in 10 mL of dry benzene followed by the addition of 2.27 g (0.00929 mol) of 2,4-dibromo-3-pentanone. The solution was heated to reflux and stirred under nitrogen for 46 hr. After cooling to room temperature the reaction mixture was poured onto 75 mL of saturated sodium bicarbonate and stirred for 15 min. Ethyl acetate was then added (300 mL) and the mixture stirred for an additional 15 min. The organic layer was separated and the aqueous layer washed with an additional 100 mL of ethyl acetate. The combined organic fractions were then dried over MgSO₄ and the solvent was removed under reduced pressure. The dark brown material was then chromatographed over silica gel using a 1:1 mixture of hexane/benzene as the eluent. The final yield of pure 72 was 0.4 g (49%).

\[ ^1H \ (72) \ 2.81 \text{ ppm (multiplet)} \]
\[ 2.11 \text{ ppm (multiplet)} \]
\[ 1.03 \text{ ppm (multiplet)} \]

\[ ^{13}C \ 135.6, 127.9, 44.6, 37.2, 25.32 \ (2 \text{ peaks}), \]

\[ \text{IR} \ 1700 \text{ cm}^{-1} \text{ strong, CO stretch} \]

2,7-Dimethyl-4,5-(9,10-anthraceno)cyclohept-4-en-1-one (71).

The 9,10-anthraceno constrained dimethyl ketone was prepared in the same manner as the 4,5-cyclohexano
constrained dimethyl ketone. The product was not purified and the yield of crude material was 92%.

^1H
7.28 ppm (multiplet)
5.86 ppm (s)
4.02 ppm (multiplet)
3.42 ppm (m)
2.08 ppm (d)

2-Epoxyethylene-3-methylenebicyclo[2.2.2]octan« (73).

The following procedure was based on methods previously reported in the literature. In a three-neck, round bottom flask fitted with a condenser, thermometer, dropping funnel and magnetic stir bar, was placed a solution of the diene 69 (3.4 g, 0.0254 moles) in 10.0 mL of methylene chloride. The solution was cooled in an ice bath to 0 °C. m-Chloroperbenzoic acid (4.4 g, 0.254 moles dissolved in 40 mL of methylene chloride) was added dropwise to the solution over a 20 min period. The solution was stirred at 0 °C for an additional 10 min. The solution was allowed to warm to room temperature after which the benzoic acid was removed by vacuum filtration. The solution was washed with saturated sodium bicarbonate (3 x 25 mL) followed by two washings with 25 mL of water. The organic material was dried over anhydrous magnesium sulfate and the solvent was removed. The epoxide was purified by vacuum distillation (25°C, 0.250 mm Hg). Spectral data are as follows:
\[ ^1H \ (73) \ 4.84 \text{ ppm (s)} \]
\[ 4.75 \text{ ppm (d)} \]
\[ 2.87 \text{ ppm (d)} \]
\[ 2.29 \text{ ppm (multiplet)} \]
\[ 1.68 \text{ ppm (multiplet)} \]

\[ ^{13}C \ 151.3, 104.6, 59.9, 56.1, 35.8, 33.62, 26.2, 24.9, 23.5, 21.9 \text{ ppm.} \]

\textbf{IR} \ 1250 \text{ CM}^{-1} \text{ strong, C-O-C stretch}

\textbf{bp} \ 25 \text{ °C}, 0.250 \text{ mm Hg}

2-Formyl-3-methylenebicyclo[2.2.2]octane (74) and 2-Formyl-3-methylbicyclo[2.2.2]oct-2-ene (75).

The following procedure was based on methods previously reported in the literature.\textsuperscript{62} In a three-neck, round bottom flask fitted with a condenser, thermometer, nitrogen inlet and outlet and a magnetic stir bar, was placed the epoxide 73 (1.8 mL) in 20 mL dry benzene and 5 mL methylene chloride. The solution was cooled to 0 °C. To this solution was added 0.2 mL of boron trifluoride etherate. The solution was then stirred for 15 min. After allowing the solution to warm to room temperature, it was washed two times with 25 mL portions of water. The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated. The products were purified by vacuum distillation (0.025 mm Hg, 1st drop: <35 °C; 2nd drop at 35
°C, rest polymerized). Only a crude proton NMR of the mixture containing both aldehydes 74 and 75 was obtained: 9.93 (s), 9.65 (d), 4.65-5.15 (multiplet), 3.86 (s), 3.83 (s), 2.25 (s), 1.55 ppm (s).

1-(1-Pyrrolidinyl)-2,3-(1,4-cyclohexano)1,3butadiene (76).

**Method A:** This procedure was based on methods previously reported in the literature.\(^6\) Synthesis of the dienamine 76 from the aldehydes 74 and 75 was only attempted once. The aldehyde was not purified prior to use in the following procedure. All attempted purifications of the aldehyde lead to decomposition.

In a three-neck round bottom flask fitted with a condenser, thermometer and a magnetic stir bar was placed approximately 1.0 g of the aldehyde. The solution was cooled to 0 °C in an ice bath. To this was added 2 mL of pyrrolidine and 5 g of CaCO₃. The solution was stirred for 3 hours. The calcium carbonate was then filtered and rinsed with dry benzene. The benzene and excess pyrrolidine were removed under reduced pressure. A solid brown material was recovered, but the proton NMR data did not show any of the desired product (i.e. if dienamine were present peaks would have been expected at approximately 6.2 ppm\(^6\)).

**Method B:** Synthesis of the dienamine was also attempted via the reaction of pyrrolidine (0.1195 g, 0.00144 moles) directly with the epoxide (0.216 g, 0.00144 moles) under
both acidic and neutral conditions. The reactions were run in NMR tubes and monitored over time by NMR. Formation of the dienamine not observed.

2-Carbomethoxy-3-methylbicyclo[2.2.2]octa-2,5-diene.

In an NMR tube was placed 0.1266 g (0.00158 mol) of 1,3-cyclohexadiene and 0.1559 g (0.00158 mol) of methyl 2-butynoate in CDCl₃. The tube was sealed under vacuum and heated to 140 °C over a 20 hr period. The NMR showed what appeared to be the retro Diels Alder product (o-methyl-toluate) of the cycloaddition (this observation was based on the appearance of a large peak in the aromatic region of the NMR spectra).

2-Carbomethoxy-3-methylbicyclo[2.2.2]octa-2-ene.

In a NMR tube was placed 0.1266 g (0.00158 mol) of 1,3-cyclohexadiene and 0.1582 g (0.00158 mol) of methyl crotonate in CDCl₃. The tube was sealed under vacuum and heated to 200 °C over a 46 hr period. The reaction was monitored over time by NMR and no change was observed.

4-(4-Methoxy phenyl)butan-1-ol (78).

The following procedure was based on methods previously reported in the literature.⁷⁴ To a 5 L round bottom flask fitted with a condenser, nitrogen inlet and outline, a dropping funnel, and a mechanical stirrer, was
added 1 L of THF followed by the careful addition of 38.2 g (1.005 mol) of lithium aluminum hydride. The organic acid 77 (150 g, 0.77 mol), dissolved in 1 L of THF, was then added dropwise through the addition funnel at such a rate as to maintain vigorous boiling. The solution was then stirred for 24 hr with gently refluxing. After cooling to room temperature, ethyl acetate (50 mL) was added to destroy the excess lithium aluminum hydride. The solution was then allowed to cool to room temperature and dilute sulfuric acid was added. The organic layer was separated, washed with 5% H₂SO₄ followed by washing with 10% NaHCO₃. The organic extract was then dried over MgSO₄ and the solvent removed under reduced pressure. The recovered product (105 g, 75%) was used in the next step without further purification.

**¹H (78)** 7.05 ppm (d)
6.78 ppm (d)
3.76 ppm (s)
3.55 ppm (t)
2.93 ppm (OH peak, broad singlet)
2.53 ppm (t)
1.58 ppm (multiplet)

4-(4-Methoxyphenyl)butyl methanesulfonate (79).

The following procedure was based on methods previously reported in the literature.⁷⁵ Into a 2 L three-neck, round bottom flask fitted with a condenser, magnetic stirrer,
nitrogen inlet and outlet, dropping funnel and a thermometer, was placed the alcohol 78 (68 g, 0.37 mol), triethylamine (57 g, 0.564 mol), and diethyl ether (500 mL). The solution was cooled to 0 °C in an ice bath. Methanesulfonyl chloride (42.42 g, 0.397 mol) was added dropwise at a rate that did not allow the temperature to rise above 10 °C. After the addition of the methanesulfonyl chloride was complete the solution was allowed to warm to room temperature and then stirred for an additional 3 hr. The mixture was then poured into 150 mL of ice water and the organic layer was separated. The organic extract was washed with 150 mL of 20% H₂SO₄, followed by washing with 200 mL of saturated NaHCO₃. The final wash was with 200 mL of brine solution. The organic fraction was then dried over MgSO₄ and the solvent removed under reduced pressure. The crude product (83.0 g, 85%) was used in the next step without further purification.

\( ^1H \) (79) 7.04 ppm (d)
6.79 ppm (d)
4.18 ppm (t)
3.74 ppm (s)
2.92 ppm (s)
2.56 ppm (t)
1.68 ppm (multiplet)
1-Iodo-4-(4-methoxyphenyl)butane (80).

Into a 2 L three-neck, round bottom flask fitted with a magnetic stirrer, a condenser and a dropping funnel, was placed NaI (96.6 g, 0.644 mol) and acetone (700 mL). The mesylate 79 (83.0 g, 0.322 mol) was added after the NaI was completely dissolved. The solution was then stirred for 2 hr. The salt was then removed by filtration and the acetone removed under reduced pressure. The material was dissolved in 200 mL of methylene chloride (the insoluble material removed by further filtration) and washed with 500 mL of water. The organic layer was then dried over MgSO₄ and the solvent removed under reduced pressure. The crude product (87.5 g, 94%) was used in the following step without further purification.

\[^1\text{H} (80)\] 7.08 ppm (d)
6.82 ppm (d)
3.78 ppm (s)
3.26 ppm (d)
2.55 ppm (t)
1.75 ppm (multiplet)

4-(4-Methoxyphenyl)-1-nitrobutane (81).

The organic resin (Amberlite IRA-90) was purchased as the chloride. It was converted to the nitrite by placing the chloride resin in a sonicator in 1 M NaNO₂ for approximately 30 min. It was then placed in a column and
rinsed with the NaNO₂ solution until it no longer gave a positive silver chloride test. It was then washed with water, followed by ethanol (95 %), followed by dry benzene. The solvent was then removed under vacuum.

**Method A:**\(^{64,65}\) Into a 1 L three-neck, round bottom flask, was placed 300 mL of dry benzene and 130.5 g (0.45 mol) of 1-iodo-4-(4-methoxy)phenylbutane 80. To this solution was added Amberlite IRA-900 ion exchange resin treated with NaNO₂. The mixture was then heated to reflux and the reaction followed by NMR. The reaction took approximately 5 days and the resin had be regenerated on the third day. When the reaction was complete the resin was removed by vacuum filtration and the solvent removed under reduced pressure. The reaction yield a mixture of the desired nitro compound 81 as well as the nitrite ester 82 and the alcohol 78. The components were separated by chromatographing over silica gel using petroleum ether with increasing amounts of chloroform as the eluent. The final yield of the nitro compound was 14.3 g (15%).

**Method B:** The following procedure was based on methods previously reported in the literature.\(^66\) In a 250 mL round bottom flask fitted with a condenser, nitrogen inlet and outlet, a thermometer, a magnetic stirrer and a dropping funnel, was placed the sodium nitrate (4.13 g, 0.0598 mol) followed by 70 mL of N,N-dimethylformamide. The iodide 80 (10.0 g, 0.0345 mol) was added to the mixture through the
dropping funnel at a fast rate. The solution was then stirred at room temperature for 2.5 hr. After stirring, the mixture was poured onto 300 mL of ice water layered with 50 mL of methylene chloride. The organic layer was separated and washed with a large excess of water in order to remove the DMF. The solution was finally washed twice with 10% sodium thiosulfate. The organic layer was dried over MgSO₄ and the solvent was removed under reduced pressure. The product was purified by chromatographing over alumina using petroleum ether with increasing amounts of chloroform as the eluents (6.0 g of 82 isolated, 83%).

Spectral Data for the Nitrite Ester 82:

\[ ^1H \]
\[
7.08 \text{ ppm (d)} \\
6.82 \text{ ppm (d)} \\
4.44 \text{ ppm (d)} \\
3.30 \text{ ppm (s)} \\
2.59 \text{ ppm (t)} \\
1.73 \text{ ppm (quintet)}
\]

\[ ^{13}C \]
\[
\text{(off resonance)} 157.8 \text{ (s)}, 133.4 \text{ (s)}, 129.1 \text{ (d)}, \ 113.6 \text{ (d)}, 73.1 \text{ (t)}, 54.9 \text{ (q)}, 34.1 \text{ (t)}, 27.38 \text{ (t)}, 26.0 \text{ ppm (t)}
\]

\[ \text{IR} \]
\[
1620 \text{ cm}^{-1} \text{ and } 1610 \text{ cm}^{-1} \text{ strong, O-NO stretch} \\
1500 \text{ cm}^{-1} \text{ strong, N=O stretch}
\]
Spectral Data for the Nitro compound 81:

\(^1\text{H}\)
- 7.09 ppm (d)
- 6.84 ppm (d)
- 4.35 ppm (t)
- 3.77 ppm (s)
- 2.60 ppm (t)
- 2.2-1.5 ppm (multiplet)

\(^{13}\text{C}\) 175.5, 132.8, 129.4, 113.8, 75.0, 54.9, 33.6, 27.8, 26.3 ppm.

IR 1540 cm\(^{-1}\) strong, \(\text{NO}_2\) asymmetric stretch
- 1370 cm\(^{-1}\) medium, \(\text{NO}_2\) symmetric stretch

4-(4-Hydroxyphenyl)-1-nitrobutane (83).

The following procedure was based on methods previously reported in the literature.\(^7\)

Into a 2 L round bottom, flask fitted with condenser, a magnetic stirrer, a nitrogen inlet and outlet, a low temperature thermometer, and a dropping funnel, was placed 500 mL of methylene chloride and 20.7 g (0.099 mol) of the 81. The system was vigorously flushed with nitrogen and cooled to \(-80^\circ\text{C}\) in a dry ice bath. Boron tribromide (49.63 g, 0.1981 mol) was added via a syringe to the dropping funnel (containing 100 mL of methylene chloride). The mixture was added dropwise at a fast rate. After addition of the boron tribromide, the solution was allowed to warm to room temperature and stirred for 5 hr. Water (200 mL) was then added to the solution and
the organic layer separated. The organic layer was dried over MgSO₄ and the solvent removed under reduced pressure. The dark brown product had a sharp odor characteristic of phenols. The yield was 12.4 g, 64%.

\begin{align*}
\text{H} & (83) & 7.04 \text{ ppm (d)} \\
& & 6.74 \text{ ppm (d)} \\
& & 4.86 \text{ ppm (OH peak, broad)} \\
& & 4.43 \text{ ppm (t)} \\
& & 2.54 \text{ ppm (t)} \\
& & 2.1-1.4 \text{ ppm (multiplet)}
\end{align*}

4,5-(1,3-propano)cyclohept-2,4,6-trien-1-one (84).\textsuperscript{64,67}

In a 5 L round bottom flask was placed 9.1 g (0.0467 mol) of the nitro phenol 83 dissolved in 200 mL of 1M KOH. To this was added 3 L of water. If the phenol oiled out of solution a small amount of ethanol was be added to help it dissolve. K₃Fe(CN)₆ (123 g, 0.374 mol) was then added and the solution stirred for 30 min. The reaction mixture was quenched with an excess of citric acid (76 g, 0.374 mol) and stirred for and additional 2 hr. The organic product was extracted with methylene chloride (3 x 200 mL) and the combined organic layers extracted with 200 mL of water. The organic layer was then dried over MgSO₄ and the solvent removed under reduced pressure. Purification was achieved by chromatography over alumina using petroleum ether with increasing amounts of chloroform as the eluents.
$^1$H (84) 7.23 ppm (d)

6.93 ppm (d)

2.98 ppm (t)

2.02 ppm (quintet)

4,5-(1,3-propano)cyclohept-2,4,6-trien-1-one tosylhydrazone (85).

Method A: The general procedure of Kirsme was followed.\textsuperscript{47a} Into a 250 mL round bottom flask fitted with a magnetic stirrer, a condenser, a thermometer, a nitrogen inlet and outlet, and a dropping funnel, was placed 0.8 g (0.0055 mol) of the tropone 84. To this was added 30 mL of dry methylene chloride and the solution cooled to 0 °C in an ice bath. The oxalyl chloride (5.4 g, 0.044 mol) was diluted with 20 mL of dry methylene chloride and added dropwise to the solution. The solution was stirred at 0 °C for 30 min, followed by an additional 30 min of stirring at room temperature. The solvent and excess oxalyl chloride was removed under reduced pressure. The dark brown material was taken up in 25 mL of absolute ethanol and stirred under nitrogen. Tosylhydrazide (1.02 g, 0.0055 mol) was added in small quantities to the solution. The mixture was stirred overnight at room temperature. The solution was then poured into a 1:1 mixture of methylene chloride and saturated sodium bicarbonate and stirred under gas was no longer evolved. The organic layer was then separated and the
aqueous layer washed two times with 100 mL of methylene chloride. The organic fractions were then combined and
dried over MgSO₄. The solvent was removed under reduced pressure. The NMR of did not show any of the desired product.

Method B: The general procedure of Chapman was followed.² Into a dry, 50 mL round bottom flask fitted with a
condenser, a magnetic stirrer and a nitrogen inlet and outlet, was added 1.33 g (0.0091 mol) of the tropone in 20 mL of absolute ethanol and 10 mL of chloroform. To this was added tosylhydrazide (1.86 g, 0.010 mol) and the solution stirred under nitrogen for 20 hr at room temperature. NMR did not show the formation of the tosylhydrazone.

Method C: This method was the same as method (B) except that a small amount of acid was added to the solution in hopes of catalyzing the reaction. Again, NMR did not show the formation of any product.

Method D: The general procedure of Jones was followed.² In a round bottom flask fitted with a condenser, cooled to 0 °C and containing 50 mL of freshly distilled thionyl chloride was added 0.63 g of tropone 84. The solution was refluxed on a steam bath for 5 min. The excess thionyl chloride was removed under reduced pressure and the residue taken up in 10 mL of absolute ethanol. Tosylhydrazide (0.81 g, 0.433 mol), dissolved in 10 mL of absolute ethanol, was then added and the solution stirred at room temperature for
half an hour. Any solid material formed was removed by filtration and the filtrate was poured into a mixture of 50 mL methylene chloride and 100 mL of saturated sodium bicarbonate. This solution was stirred vigorously for 15 min. The organic layer was then separated and the aqueous layer washed two times with 50 mL of methylene chloride. The combined organic fractions were then washed with water and dried over MgSO₄. The solvent was removed under reduced pressure. The only products isolated in this reaction were the tri- and tetrachloroazulenes 87 and 88 (4% combined yield of 87 and 88, in a ratio of 3.2:1).

Spectral Data for 1,3,6-trichloroazulene (87):

\[ ^1H \]
- 8.11 ppm (d)
- 7.61 ppm (s)
- 7.29 ppm (d)

\[ ^13C \]
- 135.02, 134.48, 133.18, 132.74, 131.55, 123.75 ppm

\[ ^1H \]
- Experimental: 229.9458
- Calculated: 229.9457

Spectral Data for 1,3,5,6-tetrachloroazulene (88):

\[ ^1H \]
- 8.51 ppm (s, 1H)
- 8.02 ppm (d, 1H)
- 7.65 ppm (s, 1H)
- (7, 43 ppm (d, 1H)
- 2.32 ppm (quintet, 2H)
Method E: The final attempt at making the tosylhydrazone 85 was carried out in a similar manner as method (D), except that the thionyl chloride was refluxed over sulfur for 12 hr under nitrogen followed by two fractional distillations (both under nitrogen). The tropone 84 was added directly to the freshly distilled thionyl chloride cooled to zero degrees in an ice bath, still under nitrogen. The mixture was allowed to warm temperature and stirred for an additional 30 min. The work up for the reaction was the same as in method d. The NMR of the crude material contains peaks that correlate well with the expected spectra of the tosylhydrazone. After the removal of the excess thionyl chloride under reduced pressures a NMR of the residue was run. This NMR also fit well with the expected spectra of the chloride salt. Attempted purification of the final product failed to produce any of the pure tosylhydrazone, but a TLC did show that the trichloroazulene 87 was formed in this reaction also.

Spectral Data for the chloride 89:

\[ ^1H \quad 8.54 \text{ ppm (d)} \]
\[ 8.29 \text{ ppm (d)} \]
\[ 3.46 \text{ ppm (t)} \]
\[ 2.61 \text{ ppm (quintet)} \]

Spectral Data for the Tosylhydrazone 85: (also containing
tosylhydrazide)

\[ {^1H} \text{NMR: 7.84 ppm (t), 7.33 ppm (q), 6.55 ppm (d), 6.39 ppm (d), 2.68 ppm (t); 2.45 ppm (s), 2.40 ppm (s), 1.88 ppm (multiplet)} \]

1-Chloro-4,5-(1,3-propano)cyclohept-1,3,5-triene and Isomers.

Method a: This method follows the general procedure of Tivakornpannarai.\textsuperscript{51b} Into a 250 mL round bottom flask fitted with a condenser, a dropping funnel, a nitrogen inlet and outlet, a magnetic stirrer and a thermometer was placed 1.0 g (0.0068 mol) of tropone 84 dissolved in 20 mL of dry methylene chloride. After cooling to 0 °C in an ice bath 0.90 g (0.0073 mol) of oxalyl chloride, diluted with 15 mL of dry methylene chloride, was added dropwise over a 20 min period. The solution was stirred at 0 °C for an additional 30 min then allowed to warm to room temperature and stirred for an additional 2 hr. Excess oxalyl chloride and the methylene chloride were removed under reduced pressure. The residue was taken up in 20 mL of dry THF and cooled to 0 °C. LiAlH\textsubscript{4} (0.52 g, 0.136 mol) was added slowly. After addition was complete the solution was refluxed for one hour. Water was then added to destroy the excess lithium aluminum hydride. The organic layer was separated and the aqueous layer washed twice with 100 mL of methylene chloride. The combined organic fractions were dried over
MgSO₄ and the solvent removed under reduced pressure. The NMR did not show any of the desired products.

**Method B:** This follows the general method of Tivakornpannarai. This reaction is similar to the above reaction except that the thionyl chloride had been refluxed for 12 hr over sulfur followed by two fractional distillations, all under nitrogen. The tropone was added directly to the thionyl chloride after the final distillation. The excess thionyl chloride was removed under reduced pressure and the attempted reduction of the chloride 89 was carried out as above except that the solution was not heated, but simply stirred at room temperature for 30 min. A PTLC of the final product showed unreacted tropone, but none of the desired product was observed.
IV. References


7. See reference 4, p.233.


17. See ref. 4, p. 192-93.


22. See ref. 4, p. 199.


35. See references 29, 35.


46. Untch, K., First International Symposium on the Chemistry of non-Benzeneoid Aromatic Compounds, Sedai, Japan, August, 1970. See also ref. 2.


57. The experimental conditions for the reaction were based on the methods reported in ref. 56 and 52.


63. The resin was prepared following the procedures reported in the following article: Gelbard, G.; Colonna, S. *Synthesis*, 1977, 113.

64. For a review on nitro compounds, including synthetic methods, see: Feuer, H., *The Chemistry of the Nitro and Nitroso Groups*, Wiley and Sons, New York, 1969.

65. Koch, K.; private communication. See also ref. 64.


67. For disproportionation reactions involving aromatic compounds see ref. 29 p. 611 and references cited therein.


74. We thank T. McCarthy for the generous gift of the 1,1,3,3-tetrabromoacetone.
