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THE CHEMISTRY OF 5,6-(9,10-ANTHRACENO)-1,2,4,6-
CYCLOHEPTATETRAENE

BY

Timothy J. McCarthy

B. A., Augustana College, 1983

Presented in partial fulfillment of the requirements

for the degree of

Master of Science

University of Montana

1988

Approved by

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The Chemistry of 5,6-(9,10-anthraceno)-1,2,4,6-cycloheptatetraene.

Director: Edward E. Waali *EEW*

The chemistry of 5,6-(9,10-anthraceno)-1,2,4,6-cycloheptatetraene (2) in solution was the focus of this research. Application of the 9,10-anthraceno bridge system as constraint at this position on the cycloheptatetraene ring was proposed to alter the chemical reactivity of the system in such a way as to favor carbene chemistry. Produced from the photolysis of the tosylhydrazone sodium salt 140 and the dehydrohalogenation of the chlorotriene 138, two products attributed to 2 were isolated. The dimer 141 was the product of dimerization followed by rearrangement. The formation of triptycene 112 was thought to be the result of rearrangement of 2 followed by solvent assisted carbon loss. A mechanism involving π - π interactions between a rearranged carbene system and the p-orbitals in the 9,10-anthraceno bridge system was hypothesized to be involved in facilitating carbon loss.

Varying the position of the constraint (in this case the 9,10-anthraceno bridge) on the seven membered ring does not produce dramatic differences in the chemistry in the system 59 - 60. The chemistry is best ascribed to the reactivity of the substituted allene 2.

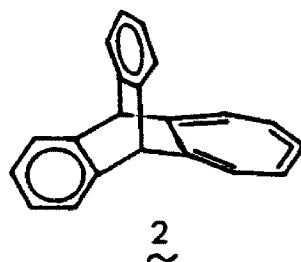
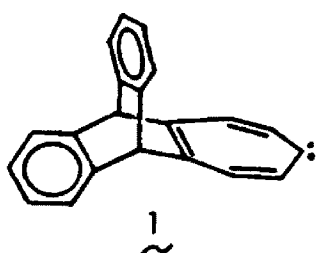
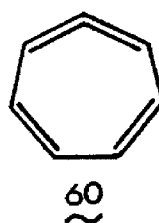
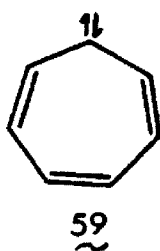


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I thank my wife and pal, Nancy, for her support and love during this research. This is at least half hers!

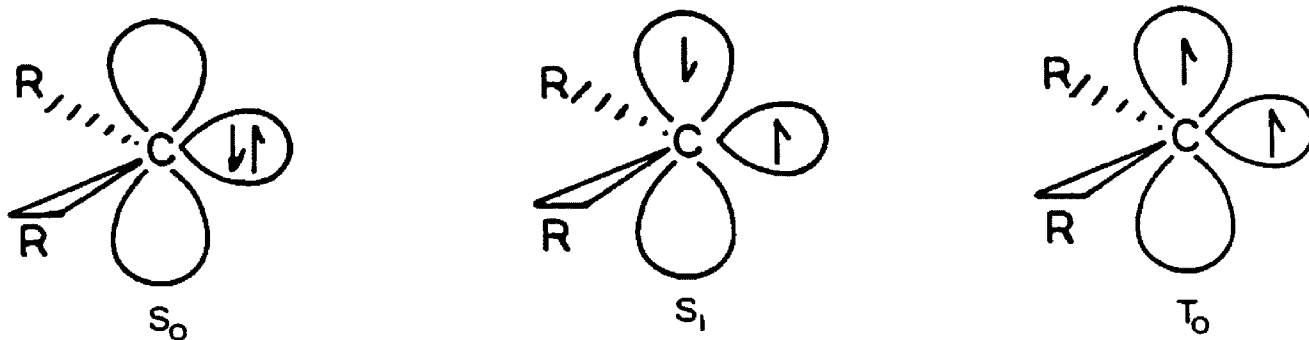
I. INTRODUCTION

The research described here involves the production and characterization of a constrained cycloheptatrienyliidene/cycloheptatetraene system in solution.

The introduction presents a brief review of some of the properties of carbenes and allenes, including completely conjugated three-, five- and seven-membered carbocyclic carbenes and their valence isomeric allene counterparts.

A. CARBENES

Carbenes differ from other intermediates in that they are divalent, neutral, highly energetic, short lived entities. Methylene ($R = H$) is the simplest of the carbenes and may exist as a singlet (S_0), excited singlet (S_1), or triplet (T_0) species.¹



The simplest molecular orbital (MO) bonding model for S_0 would assume the carbon as having sp^2 -hybridization with both electrons occupying the sp^2 -orbital, leaving the perpendicular p-orbital vacant. The H-C-H angle for S_0 would be expected to be less than 120° due to the non-bonding electron pair repulsion present. The S_1 state would have the two electrons paired but in both the available orbitals. The bond angle in S_1 would thus be expected to be greater than 120° , due to

less electron pair repulsion and because the two orbitals both have a single electron. Carbenes with two orbitals, each occupied by a single electron with identical spin, have a total spin quantum number (s) equal to one and a spin multiplicity ($2s + 1$) of three indicative of a triplet state. The two p-orbitals of the T_1 state with sp-hybridization, are degenerate and orthogonal, making the bond angle 180° . Spectroscopic studies have in fact shown that methylene, arylmethylenes and alkylmethylenes are ground state triplets with bond angles of $130-180^\circ$ and that their corresponding singlet states have angles between $100-110^\circ$.²

Predicting and determining the ground state characteristics of a system is very important in studies involving carbenes. The relative energies of the singlet and triplet states can be altered by the effects imposed on the system from various substituents linked to the carbene carbon.^{3,4} By reducing the bond angle at the carbene carbon the σ -orbital obtains more s-character and the singlet state may be stabilized. The character of the perturbation determines the relative energy differences between the singlet and triplet states, and therefore, which is the ground state. Alkyl groups have been found to have a negligible effect on the relative energy states and thus are very similar to the perturbation effects of hydrogen.⁵ The result is that dialkylcarbenes are also ground state triplets. Other substituents, however, such as those that are able to donate electrons to the carbene center, have been found to lower the energy of the singlet state relative to the triplet state. Therefore, carbene centers with halogen or oxygen substituents have singlet states that are stabilized relative

to their triplet states.⁶ Unsaturation next to a carbene center has also leads to ground state singlet characteristics.⁷

As more complex substituents are added to the carbene system, it becomes difficult to predict with confidence the nature of the ground state. Experimental procedures must therefore be employed to determine these energy relationships. Diphenylmethylene (DPM), for example, has been found to be a ground state triplet.⁸ The bond angle at the carbene carbon might be expected to be 180° with the two phenyl groups lying in the same plane. However, this is not the case, as the bond angle has been found to be about 150° with the phenyl groups twisted in relation to each other.

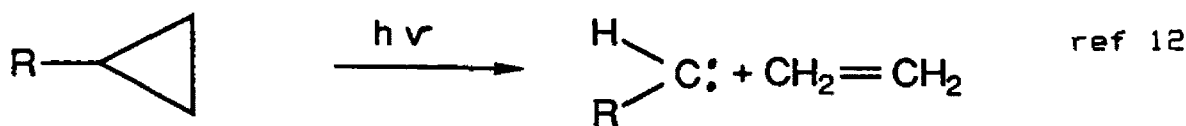
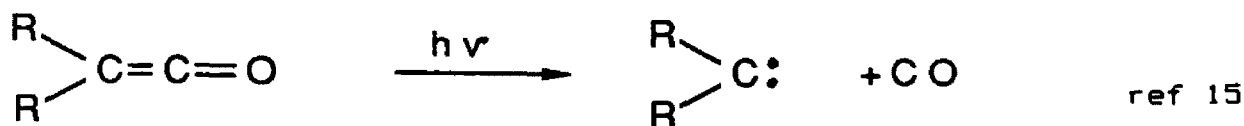
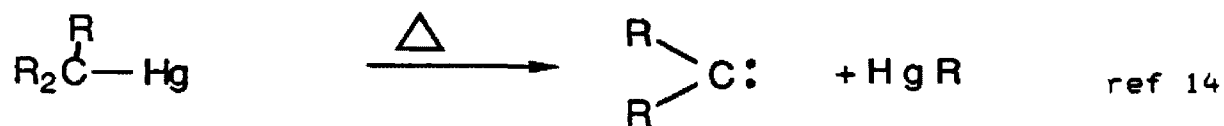
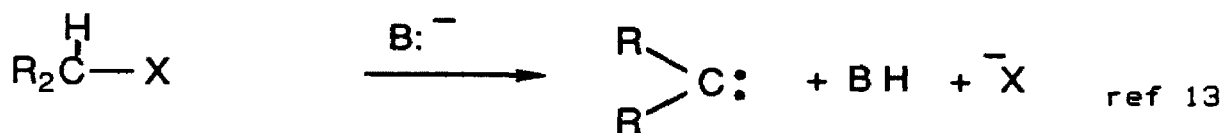
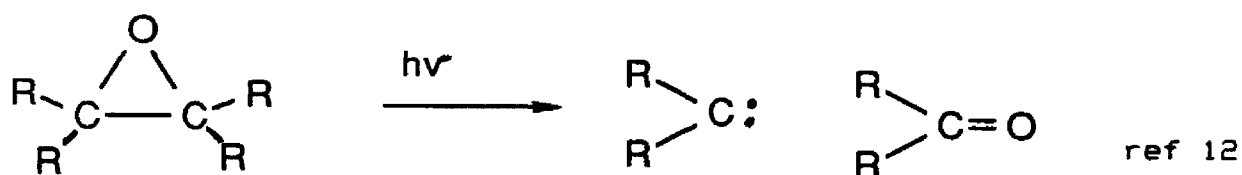
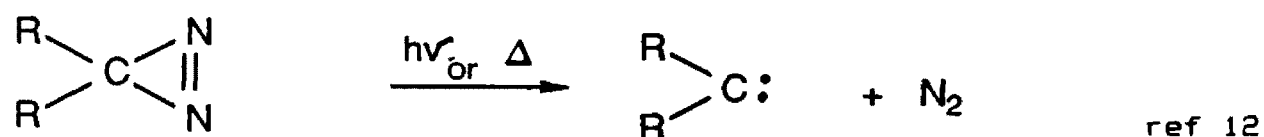
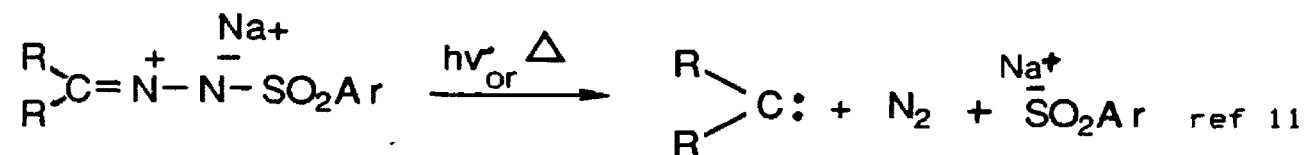
With an unfilled p-orbital, the singlet species is usually electrophilic in nature, seeking electron rich centers. This property can be measured directly by Hammett studies. A more qualitative understanding of an intermediate's electrophilicity may be obtained by observing its reactivity to electron-rich versus electron-poor alkenes.

Groups like oxygen, which have the ability to donate electrons to the carbene carbon, reduce its electrophilic character. Dimethoxycarbene, for example, has been found to be nucleophilic in its reaction with electron deficient double bonds.⁹ Nucleophilic character would be expected from such a species as the empty p-orbital would be removed from actively participating in electrophilic attack.

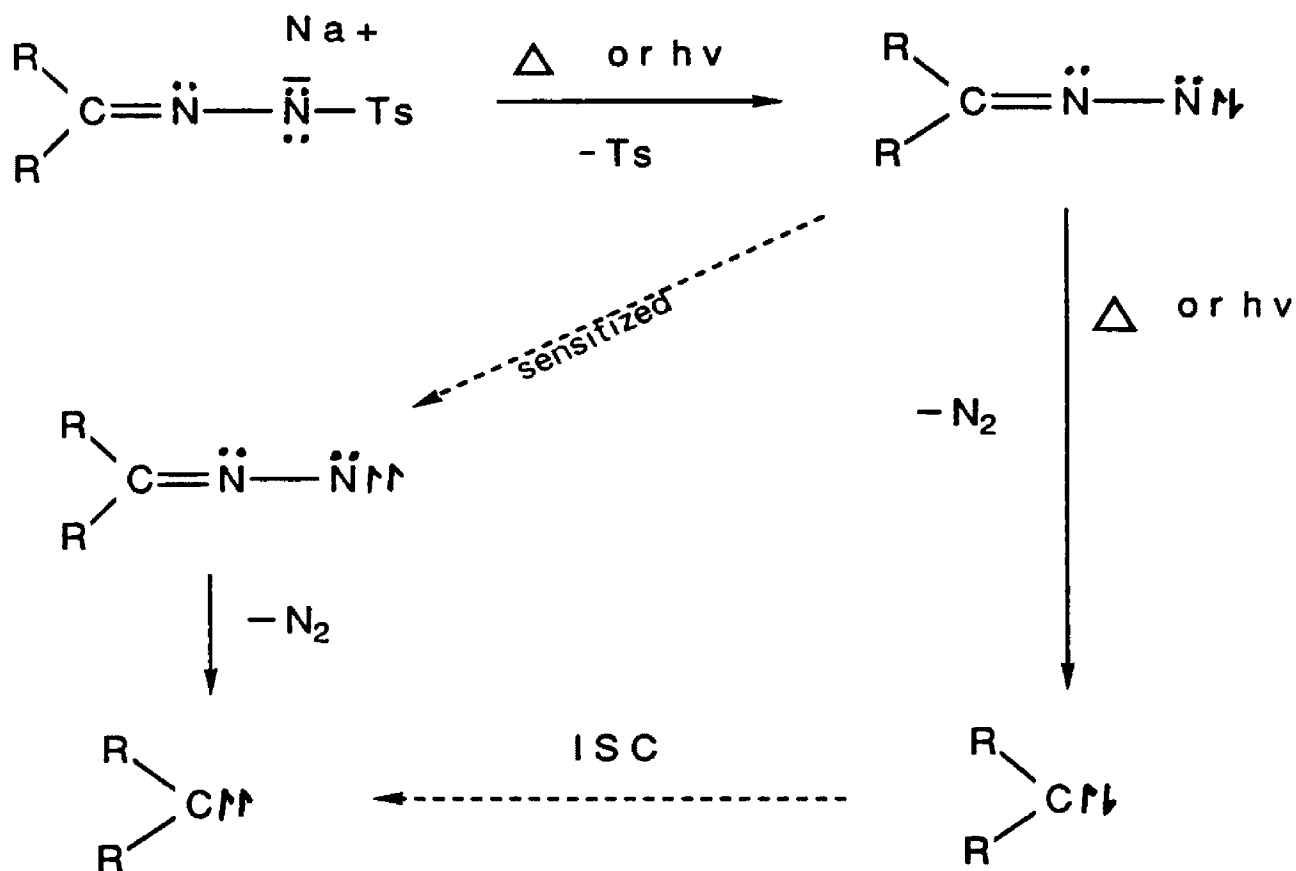
1. Generation of Carbenes

Some of the most general methods for making carbene intermediates are summarized in Table 1.

TABLE 1: GENERATION OF CARBENES

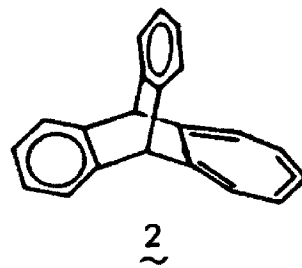
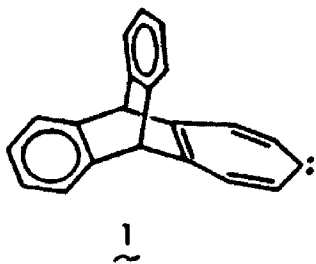


Upon photolysis or thermolysis of the sodium salt of the tosylhydrazone derivative, the tosyl group is initially cleaved to leave the highly reactive diazo group. Further decomposition results in the formation of a carbene intermediate and a nitrogen molecule.¹¹ Because of the great stability of the nitrogen molecule, its formation is the



driving force behind the decomposition of the diazo compound. Because spin is conserved in the decomposition, the carbene is formed in a singlet state which may decay to a lower energy triplet state.¹⁴ Although photosensitized decomposition may produce a triplet carbene directly,¹⁷ this was not attempted in this research.

The photolytic decomposition of the sodium salt of the ketone tosylhydrazone derivative (140) was used as one method to attain the cyclic carbene/allene intermediate $\frac{1}{2}$ studied in this research.

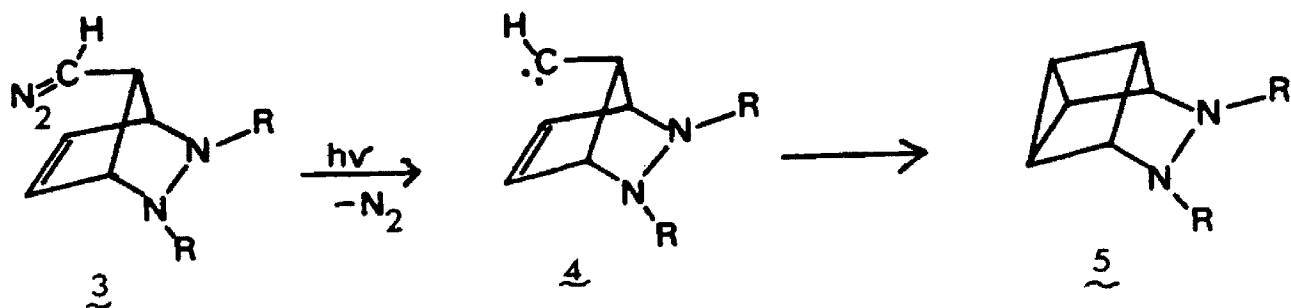


2. Reactions of Carbenes

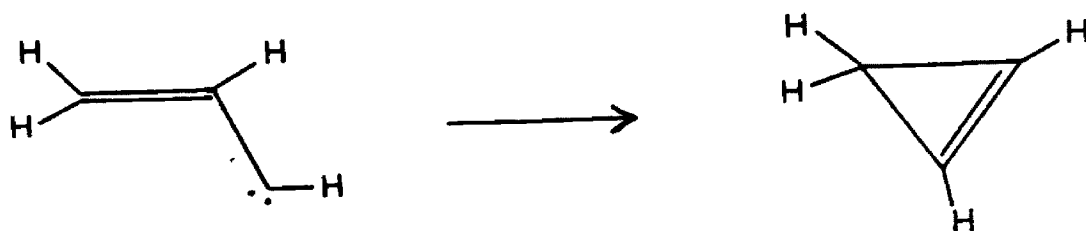
In carbene studies, determination of the lowest energy state, the energy separation between the singlet and triplet spin state and the spin state responsible for the chemistry observed is of great interest. Although a number of spectral techniques exist to observe the characteristics of carbene intermediates in inert matrices,^{18,19} most studies rely on the differences in the reactivity of the singlet versus the triplet intermediate species with other molecules in solution. The most characteristic reactions of carbenes are: additions to multiple bonds, insertions, hydrogen abstractions, and rearrangements.

a. Addition Reactions

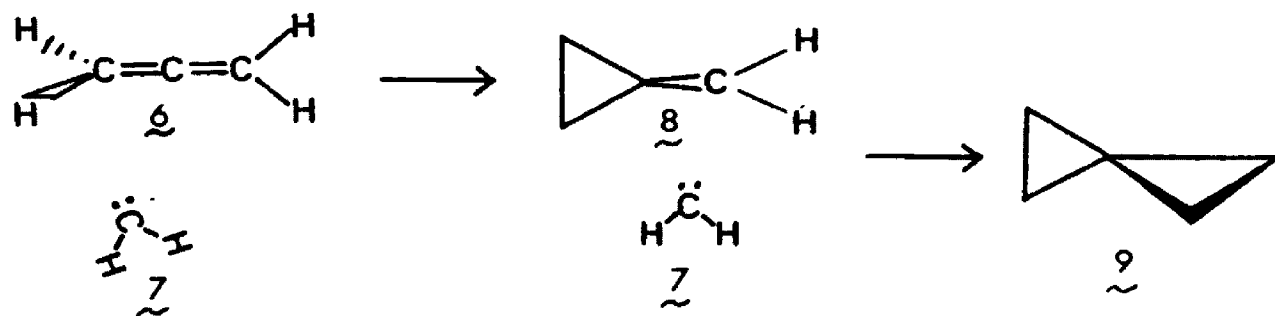
The [2+1] cycloaddition reaction of carbenes to alkenes produces cyclopropanes.¹⁹ This type of reaction has been synthetically applied to produce strained cyclopropane rings. Since the carbene is highly energetic, it has the ability to build highly strained molecules when intramolecular additions are performed, as is the case in the construction of the strained tetracyclic framework 5.²⁰



Carbenes centers adjacent to double bonds may also add to produce cyclopropanes.²¹

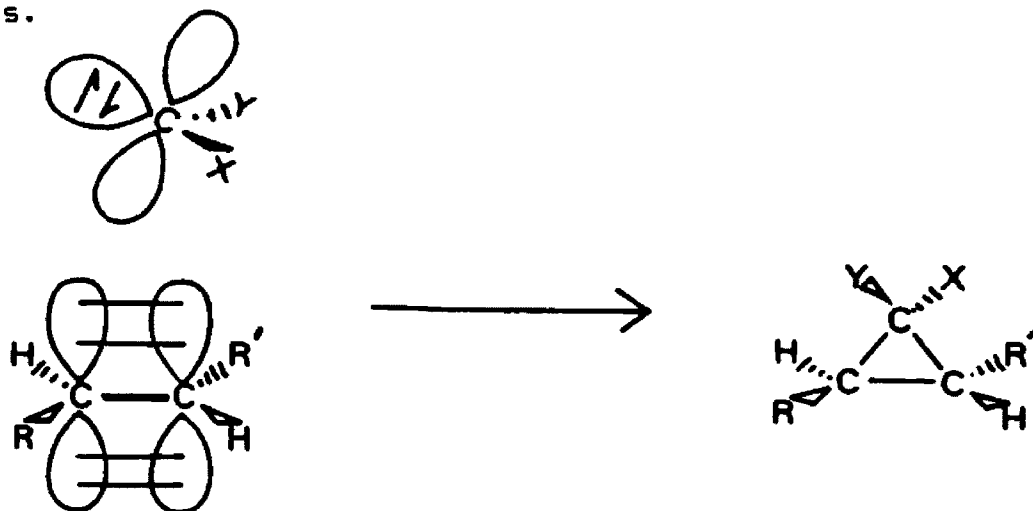


Addition may also occur with alkynes and benzene.²² A useful method for producing spiro-compounds involves the addition of a carbene to exocyclic double bonds. Spiropentane (9) has been produced from the addition of two equivalents of methylene (7) to allene (6).²³

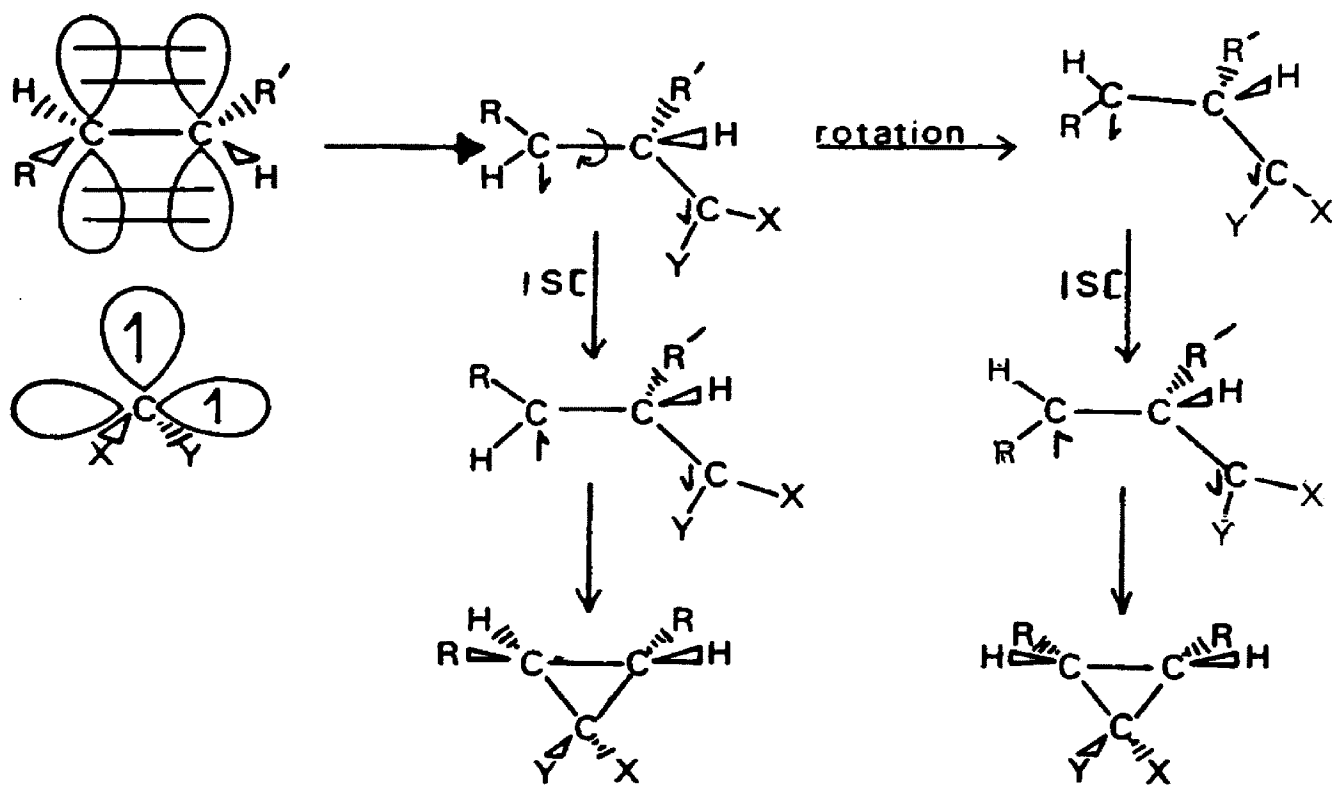


The mechanism by which addition occurs and the products that result, also provide a way of distinguishing between the singlet and triplet spin states of the carbene intermediate.^{6, 15, 19, 24} According to the Skell Hypothesis, singlet and triplet carbene species are postulated to differ both in their selectivity and in their stereospecificity of addition to double bonds. From this, the most reactive

spin state can be determined by studying the stereochemistry of the cyclopropane products. In general, the rule holds that addition of a singlet carbene to a double bond can occur in a one step mechanism in which the stereochemistry of the alkene is preserved. This concerted mechanism is allowed because the spin state is conserved as reactants go to products.



Triplet species on the other hand behave like diradicals, one electron must undergo spin inversion in order to produce a ground state cyclopropane singlet product. This line of thinking is an extension of the Pauli Exclusion Principle which states that an orbital may not contain two electrons with parallel spin. They must be spin paired. For this reason a step-wise mechanism is necessary. Because rotation about the single bonds present in the diradical is assumed to be faster than intersystem crossing (ISC), the stereochemistry of the alkene can be expected to be scrambled in the cyclopropane product. The use of stereospecificity as a test for the spin state of a carbene must be limited to those methods which do not produce the carbene in a highly excited singlet state (S_1). Cyclopropane addition products formed from the addition of a photolytically generated, highly excited singlet



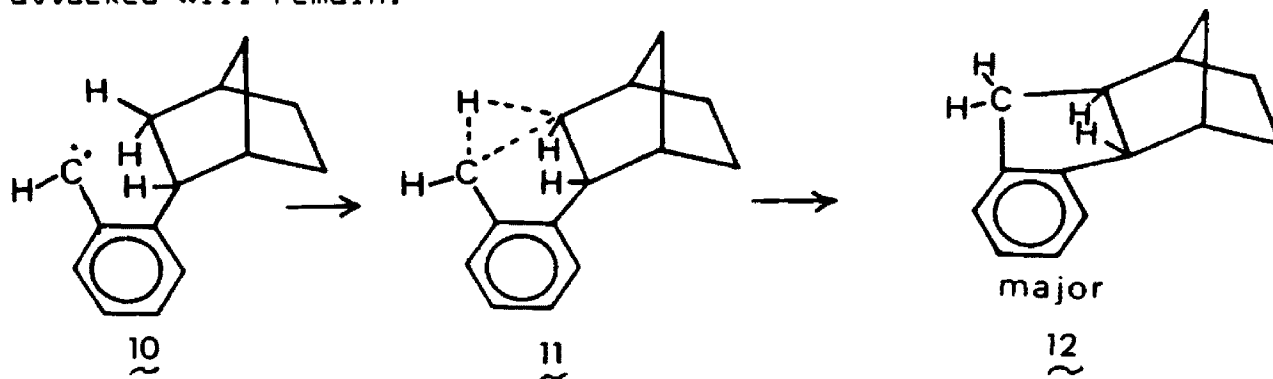
methylene carry excess vibrational energy. Although addition may initially be stereospecific, the cyclopropane product may undergo cis-trans isomerism after its formation, giving the appearance as if the triplet carbene was involved.^{15,25}

b. Insertion and Hydrogen Abstractions

An insertion reaction is a common singlet carbene reaction in which a carbene attacks a single bond in a concerted mechanism. Because of its ability to insert into 1°, 2°, 3°, aliphatic, allylic or vinyl C-H bonds indiscriminately, methylene was classed for a time, as "...the most indiscriminate reagent known in organic chemistry."²⁶ Insertion into the C-H bonds of pentane, 2-methyl-pentane and 3-methyl-pentane by methylene produced by the photolysis of diazomethane gave

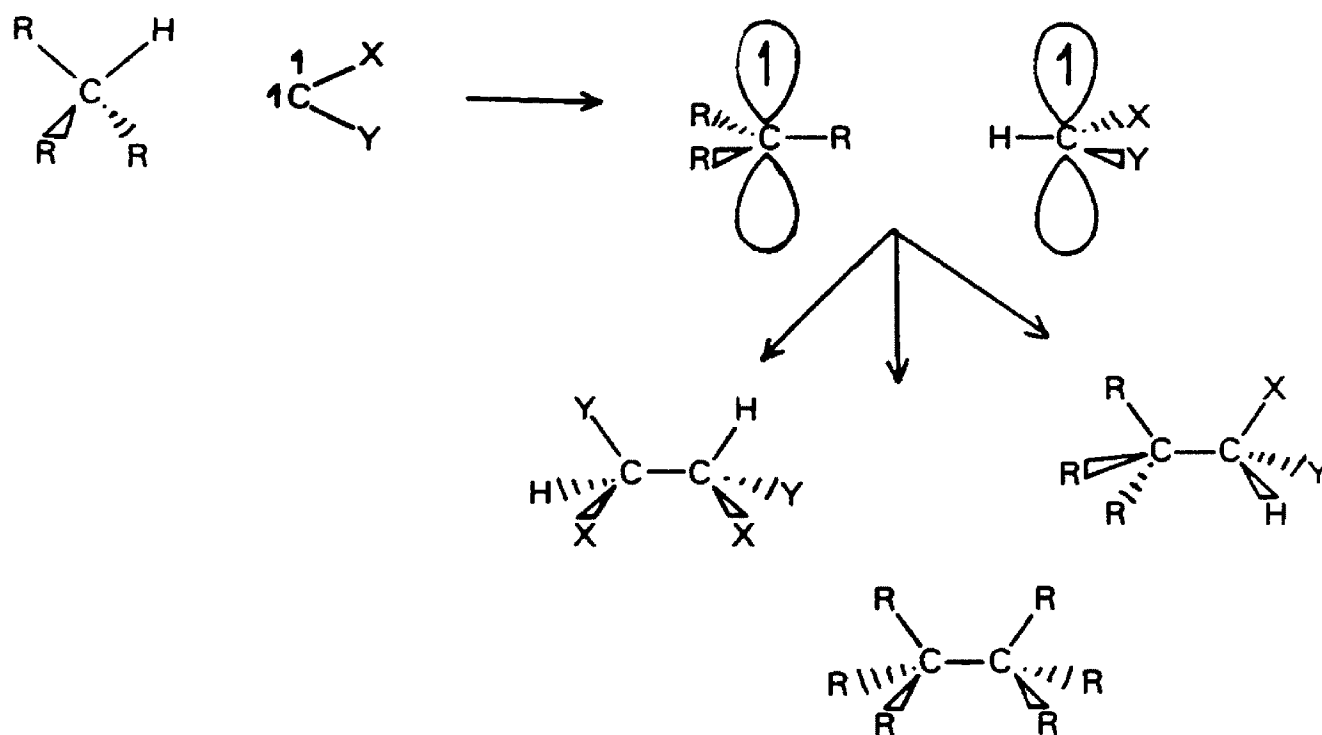
insertion products in the ratios expected statistically, showing its very random behavior.²⁶ Methylene produced in this manner is obviously not very synthetically useful. Methylene generated by other methods, and other types of carbenes are less reactive and show a corresponding increase in their selectivity, preferring to insert in the order tertiary > secondary > primary.²⁷

In an insertion reaction, a single bond is broken and the carbene carbon is inserted between the two atoms of the attacked single bond via a three-centered transition state. Because of the concerted nature of this reaction, any stereochemistry present in the molecule being attacked will remain.^{28,30}



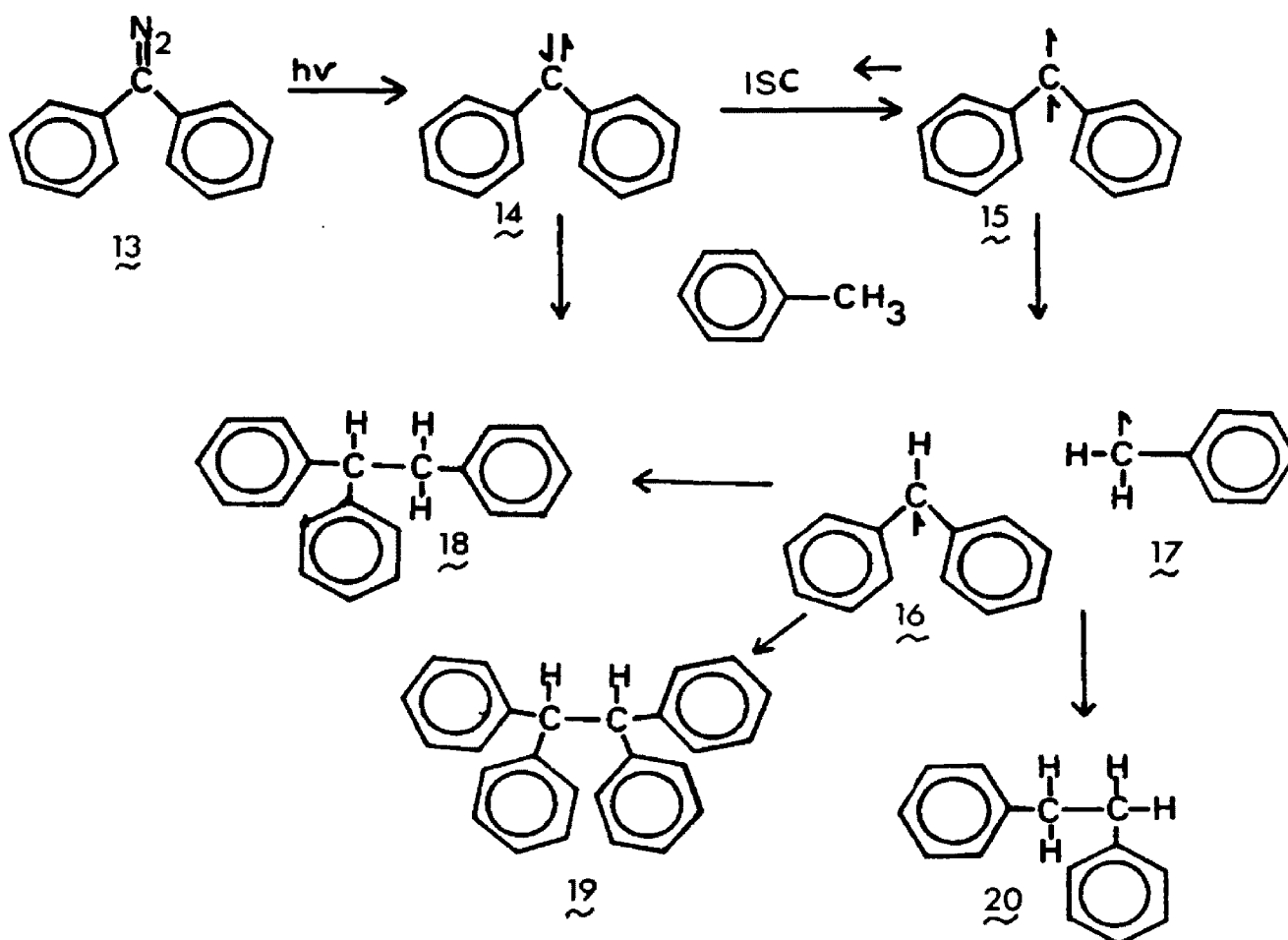
In an interesting study by Gutsche and co-workers,²⁹ this mechanism was given additional validity. They studied the intramolecular insertion yields that occurred on production of 10. They found that the greatest yield of insertion occurred where the molecule could orient itself so as to give the proper orientation for the three-centered transition state 11. The preferred pathway of attack being midway between the C-H atoms and perpendicular to the C-H bond thus produced 12 as the major product.

Kollmer³⁰ has completed calculations using modified CNDO molecular orbital programs to shed light on the mechanism of insertion and addition reactions of nucleophilic carbenes. Nucleophilic attack of cyclopropenylidene and methylene on a H_2 molecule is symmetry forbidden. These calculations indicate that the rate determining step for the reaction is an electrophilic phase whereby the hydrogen molecule approaches the carbene from above forming a three center bond with the empty p-orbital of the carbene. Then, in the nucleophilic stage, the hydrogen bond is broken and the HCH plane rotates to a tetrahedral configuration while the lone pair of the carbene populates the σ^* orbital of the hydrogen molecule. This indicates that the p-orbital is important in insertion reactions when dealing with σ^e nucleophilic carbenes where the p-orbital is allowed to react. The p-orbital of a carbene has a similar role in additions to double bonds.



In the presence of heteroatoms, insertion occurs preferentially between the heteroatom and the hydrogen bond to the exclusion of other possible insertion sites. Insertion reactions with alcohols thus produce ether linkages rather than alcohols.³¹

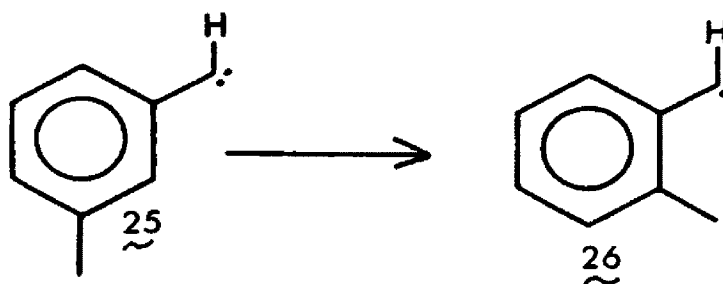
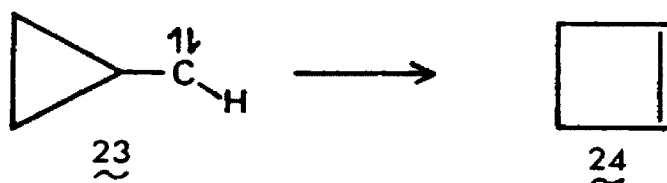
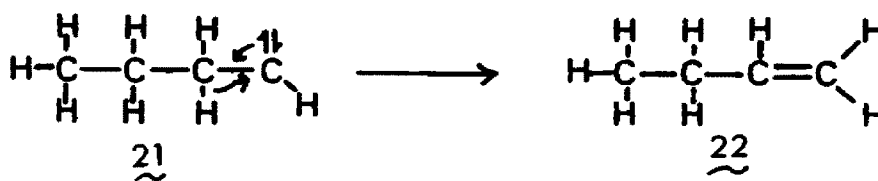
The reaction of a triplet carbene with a single C-H bond occurs by a non-concerted mechanism, as shown on the previous page. In this situation, the triplet carbene first pulls off a hydrogen from a solvent molecule to form two radicals which may then combine to form various recombination products. Alternatively, the radical may abstract another hydrogen. Any stereochemistry that was present at the abstraction site will be lost due to the formation of the two achiral radicals.



Abstraction products are very important in observing triplet carbene chemistry. In a study of the solution chemistry of diphenylmethylene (DPM) (14), it was found that triplet DPM (15) abstracts hydrogen from the solvent to give the two radical species 16 and 17, which then recombined to give the products 19 and 20.³²

c. Rearrangements

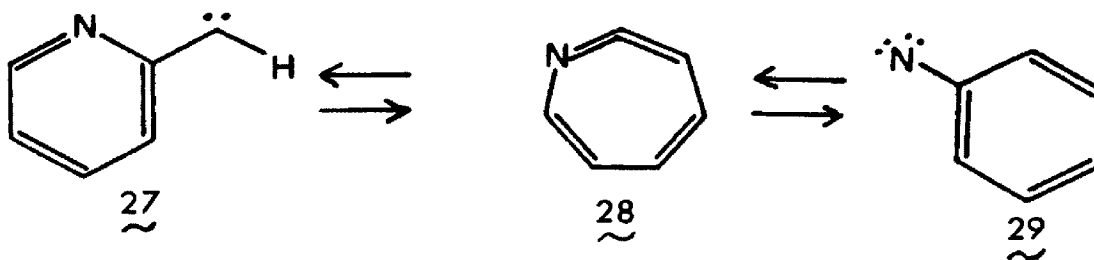
Shifts of a hydrogen to produce an alkene (ie. 22) as well as shifts of alkyl and aryl groups are very common in carbene reactions.³³



For example, the rearrangement of cyclopropylidene (23) has been found to expand to cyclobutene (24), while the rearrangement of m-tolylmethylene (25) has been found to give o-tolylmethylene (26).⁷²

The reversibility of rearrangements between carbenes and nitrenes was demonstrated from the inter-conversion of 2-pyridylmethylene (27)

and phenylnitrene (29).³⁵ This observation plays a vital function in the chemistry of large cyclic systems as will be described later.



3. Spin State Population

The method used to produce a carbene may affect the proportion of singlet to triplet species in a reaction. For example, both singlet and triplet spin states can be formed in the production of the methylene carbene by photolysis or photosensitized photolysis.¹⁷ The ratio of the singlet to triplet spin states is dependent upon the precursor that is used, the photolysis wavelength and the reaction cell conditions employed.³⁶

Addition of an inert material in large excess may result in the intersystem crossing (ISC) of singlet state intermediates present to the corresponding triplet state.³⁷ Doing this in the presence of an olefin increases the percentage of non-stereospecific product produced. This technique takes advantage of the fact that kinetically, intersystem crossing from a singlet to a triplet species is mononuclear and independent of concentration, while stereospecific addition is first order with respect to concentration. For example, methylene has been found to undergo stereospecific addition to olefins, indicating that singlet methylene was produced from the photolysis of diazomethane. Photolysis of diazomethane in the presence of a high pressure of an

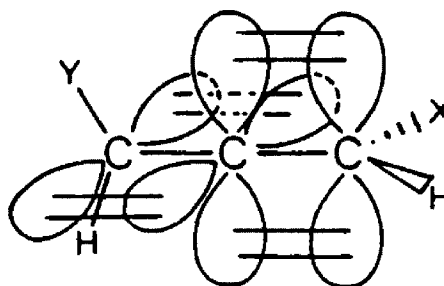
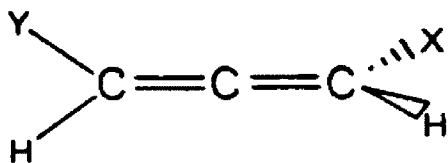
inert gas, however, has produced non-stereospecific addition products, indicating intersystem crossing to its triplet ground state.²⁴

Hexafluorobenzene, with its inert C-F bonds, in solution also brings about singlet decay.³⁰

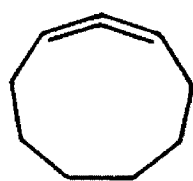
Triplet species quenching agents, such as O₂, may be employed in order to see addition reaction products solely attributable to the singlet species.²⁴

Solvent polarity has also been found to effect the ratio of stereospecific to non-stereospecific products. The polarity of the solvent affects the singlet-triplet energy gap resulting in the rate of spin inversion to be altered. The more polar singlet state is strongly stabilized in polar solvents, where as the less polar triplet experiences only a slight stabilization.³⁷

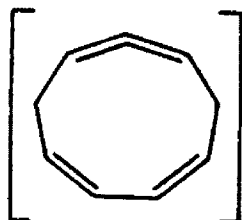
B. ALLENES



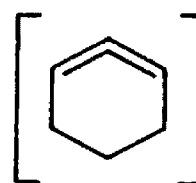
In the simple allene structure shown above, the central carbon is sp -hybridized, while the other carbons are sp^2 -hybridized. Overlap of one of the p -orbitals of the central carbon with a p -orbital of each of the outside carbons requires the substituents on each of the outside carbons to be orthogonal. Allene systems have an axial symmetry. When X or Y are different substituents, two enantiomeric forms are possible.⁴⁰ The stability of a cyclic allene system is dependent upon the



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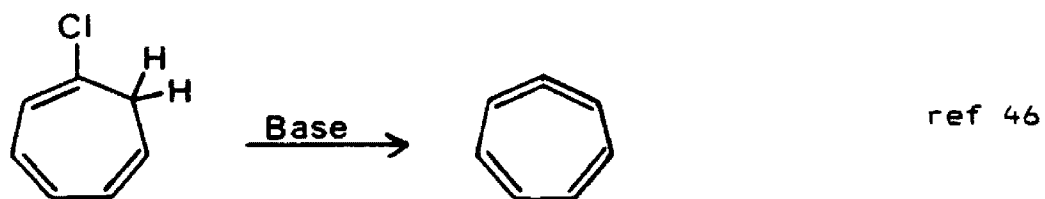
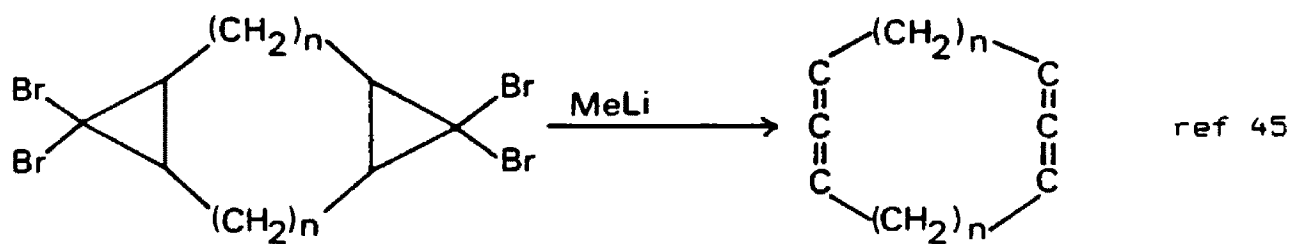
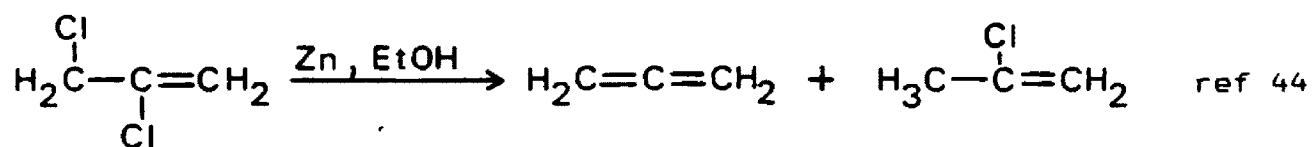
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size of the ring in which the allene moiety is contained as well as the amount of other saturation and functionality that is present in the system. At room temperature, 1,2-cyclononadiene (30) is isolable, however, neither smaller ring sizes such as 1,2-cyclohexadiene (32) nor the more highly saturated 1,2,4,6,8-cyclononapentaene (31) is stable under these same conditions.^{41,42}

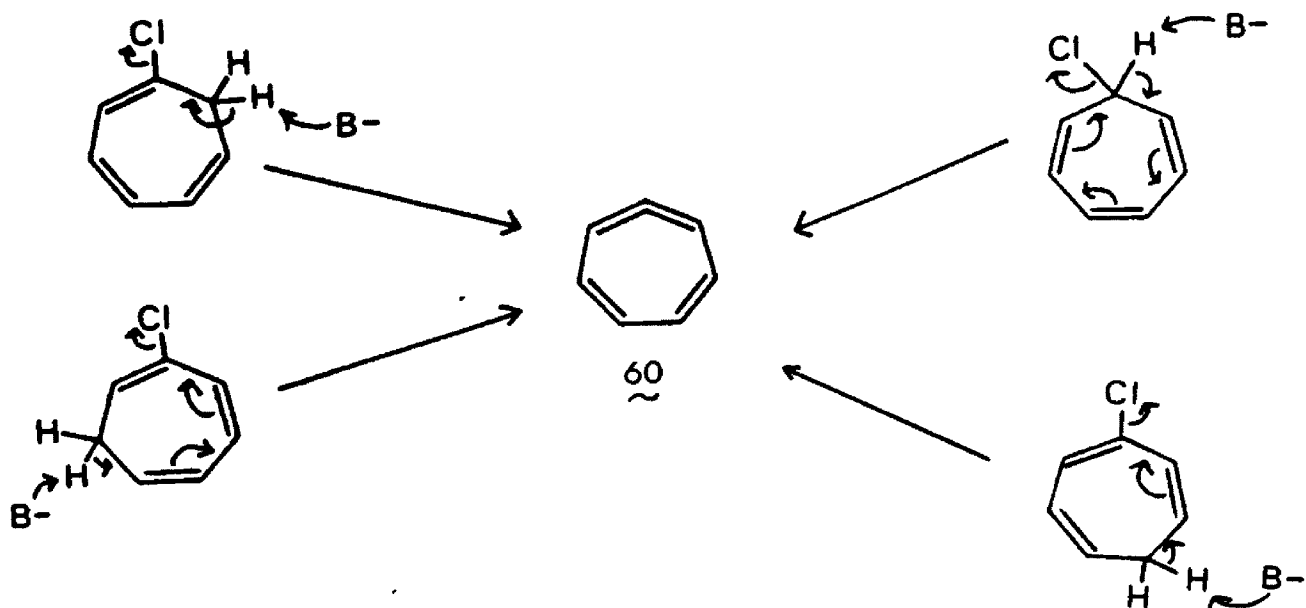
1. Generation of Allenes

There are many methods for producing allenenes, the most synthetically useful being the dehalogenation reactions of dihaloalkenes, dihalocyclopropanes and haloalkenes.⁴³ Table 2 shows some examples.

TABLE 2: GENERATION OF ALLENES



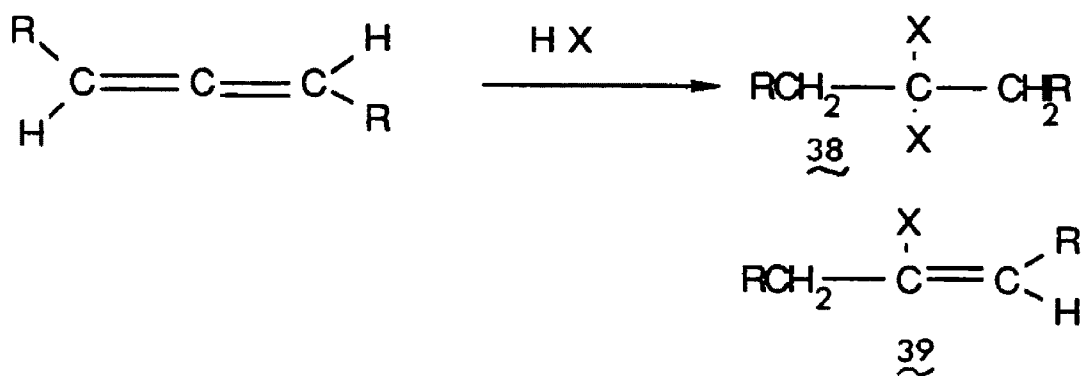
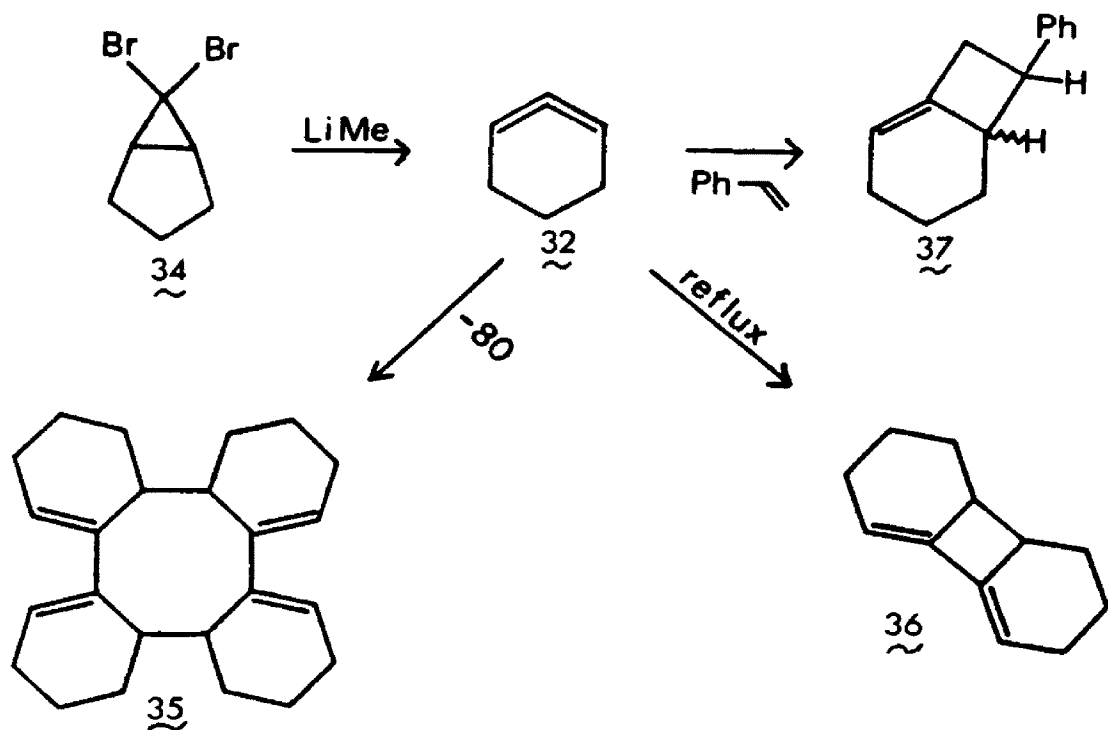
Low temperature, base promoted elimination from halo-alkenes produces an allene intermediate and the salt of the base and halide.⁴⁴ This method was used in this research to attain a substituted cyclic allene intermediate of 60 from the various chlorocycloheptatriene isomers 33a-d.



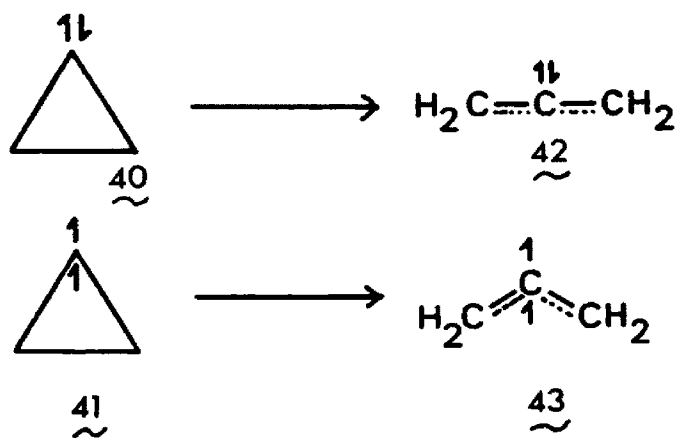
2. Reactions of Allenes

Allenenes have been shown to undergo 2+2 cycloadditions with alkenes to give cyclobutanes.⁴⁷ For example, 1,2-cyclohexadiene (32) undergoes 2+2 additions with styrene to produce 37 and with itself to produce the dimer 36 and tetramer 35.^{41,48} Allenenes also undergo electrophilic addition reactions such as hydrohalogenation to produce dihalopropanes and halopropenes like 38 and 39.⁴⁹

Pasto and co-workers⁴⁹ studied the singlet and triplet cyclopropylidene/allene system and their interconversion as might be related to their photochemistry. The energy barrier for the disrotatory ring opening (DRO) of the singlet (40) and triplet (41) cyclopropylidene species to their singlet (42) and triplet (43) allene counterparts was calculated to be 18 and 19 kcal/mole, respectively.



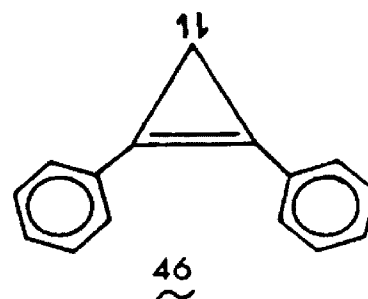
The realization that carbene and allenes may have an intimate relationship is very important in larger, fully conjugated systems such as the C_7H_6 system studied in this research.



C. CYCLIC, FULLY CONJUGATED, CARBENE/ALLENE SYSTEMS

When studying carbenes in fully conjugated cyclic systems, consideration of their valence isomeric allene forms can be very important. Molecular orbital calculations can be used to help in investigations where a number of possible intermediates are viable in a reaction scheme. MNDO molecular orbital calculations are semi-empirical methods for estimation of the energy of a molecular system. MNDO is considered semi-empirical because it relies on some experimentally determined parameters which are used in the calculations. The power of this technique is not that the energies calculated represent the exact energies of the system, but rather, the calculated energies give good relative energies which can be used for comparison of chemical species within a certain system. The comparisons can then provide information on the type of interactions that may be possible. Many investigators have found that the semi-empirical MNDO method is extremely useful when studying large carbene systems. E.E.Waali and co-workers⁵⁰ have used this method to study the energy relationships in a number of carbene/allene systems that are important in this report.

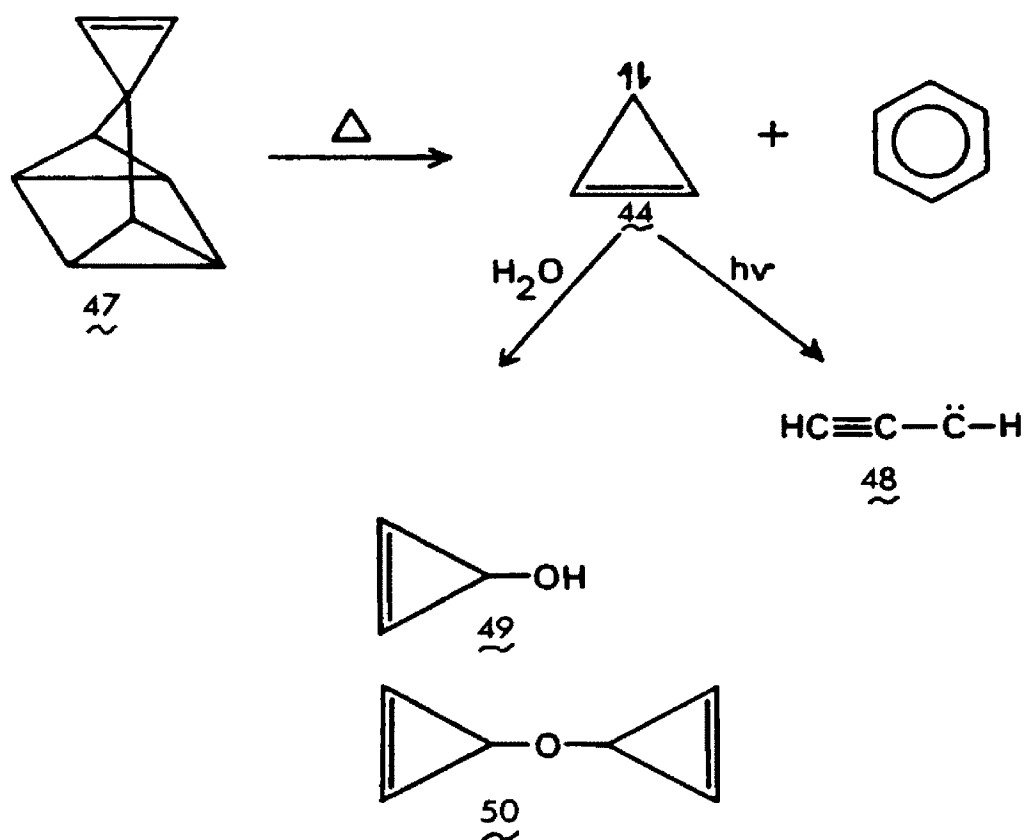
1. Cyclopropenylidene / Cyclopropadiene



MNDO calculations⁵⁰ show that the singlet ground state of cyclo-

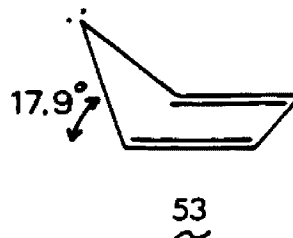
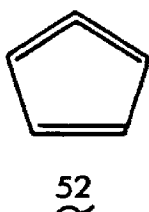
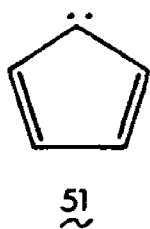
propenylidene (44) is 28 kcal/mol more stable than the corresponding triplet. The allene structure 45 was found to be too strained to be a reasonable possibility and therefore extremely unlikely to be observed.

Upon the vacuum flash pyrolysis of 47, the matrix isolation IR of cyclopropenylidene (44) was obtained.⁵¹ An ESR spectrum could not be observed. The presence of 44 was proven by irradiating the matrix isolated material and observing the known ESR signals of the isomer propynylidene (48) formed from the rearrangement of 44. If all of the moisture was not removed from the system the insertion products 49 and 50 were also observed. These data indicate that 44 has a singlet ground state that can best be described as a σ^2 carbene, where the two singlet electrons occupy the σ -orbital and the p-orbital remains empty.

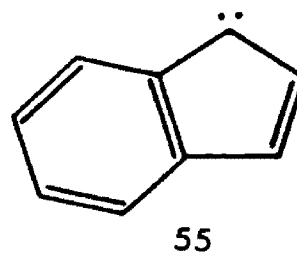
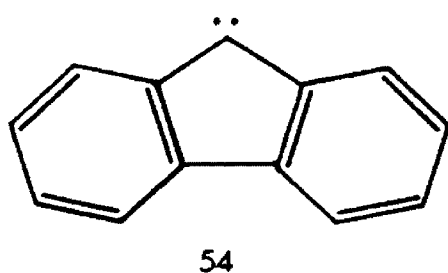


Diphenyl cyclopropenyli $\dot{\text{d}}$ ene (46) has also been made and its properties observed. It was found that it undergoes addition to electron deficient double bonds such as dimethyl maleate while failing to add to electron rich alkenes,⁵² indicating that 46 also acts as a nucleophilic σ^2 carbene species.

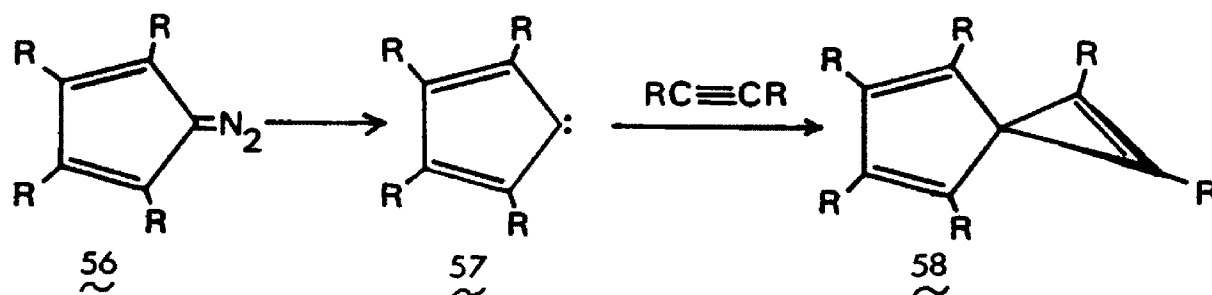
2. Cyclopentadienyli $\dot{\text{d}}$ ene / Cyclopentatriene



Cyclopentadienyli $\dot{\text{d}}$ ene (51) has been found to exhibit both singlet and triplet properties.⁵³ MNDO⁵³ shows two planar structures corresponding to σ^2 and π^2 carbenes, the σ^2 being more stable by about 6 kcal/mole. The allene 52 was again found to be a very unstable intermediate. The most interesting results from MNDO however, were from force constant calculations which indicated that the σ^2 configuration is a transition state while the π^2 configuration lies neither at an energy minimum nor a transition state maximum. The lowest energy singlet carbene was instead found to be the non-planar species 53 with the carbene carbon almost 18° out of the plane of the other four carbons. In fact, ESR measurements imply that the bonds to the divalent carbene carbon in indenyli $\dot{\text{d}}$ ene (55), fluorenyli $\dot{\text{d}}$ ene (54) as well as cyclopentadienyli $\dot{\text{d}}$ ene (51) are bent.⁵⁴ These same ESR measurements also show that all three are ground state triplets.

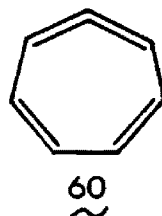
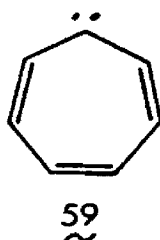


Production of 51 in solution at room temperature gives an intermediate which shows electrophilic singlet characteristics, having been found to add stereospecifically to cis or trans olefins,⁵⁵ and insert readily with little discrimination into saturated C-H bonds.⁵⁶ Both of these observations are indicative of singlet chemistry. Either a π^2 structure, with the two carbene carbons delocalized in the 6 electron aromatic system, or an anti-aromatic σ^2 structure could lend electrophilic characteristics. Electrophilic characteristics have been shown from studies of the room temperature, stereospecific [1+2] cycloaddition of 51 to *p*- and *m*-substituted styrenes. A Hammett value of -0.76 ± 0.10 was obtained.⁵⁷ In another study, photolysis of substituted diazocyclopentadienes 56 in the presence of alkynes produced spiro[2.4]heptatrienes 58 in which yields were increased by using electron rich alkynes, thus demonstrating the electrophilic nature of cyclopentadienylidene derivatives in solution.⁵⁸



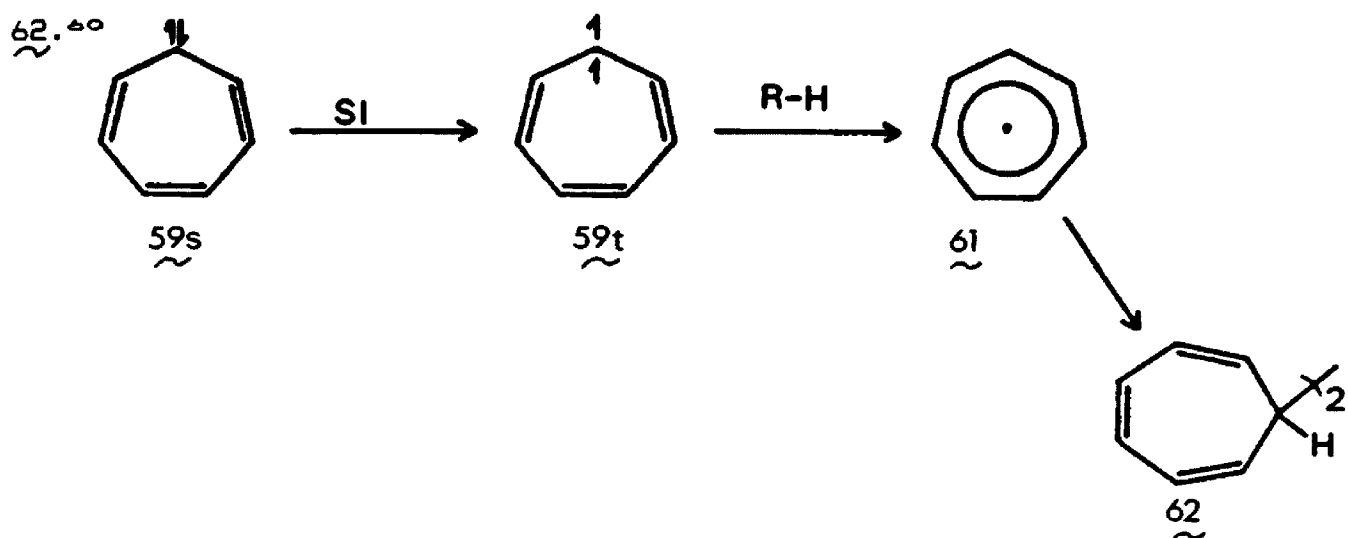
At room temperature, in solution both fluorenylidene (54) and indenylidene (55) have shown triplet behavior by producing 45% non-stereospecific addition products with 4-methyl-cis-2-pentene. The non-stereospecific percentage was increased to 75% in the presence of 90 mol% of hexafluorobenzene.³⁸ Non-stereospecific addition of the parent 51 however, could not be increased upon dilution with this inert solvent, indicating that the singlet carbene species 51 is very reactive and that the rate of decay to the triplet state is particularly slow.³⁵ The small (1-2%) non-stereospecific addition that was always present was attributed to stereospecific addition by a highly excited singlet followed by cis-trans isomerism.

3. Cycloheptatrienyliidene / Cycloheptatetraene



The question of aromaticity is also important when the carbene carbon is incorporated into a fully conjugated seven membered ring such as cycloheptatrienyliidene (59). If the two non-bonding electrons in the singlet state carbene 59s occupy the σ orbital, then the empty p-orbital on the carbene carbon would be incorporated into a six electron, $(4n+2)$ Hückel aromatic system similar to the tropylium ion. The triplet state, on the other hand, would be similar in π -electron density to the troyl radical. The presence of an ESR signal of 59t indicates that the triplet is or is within a few calories per mole of

the ground state.⁵⁷ Abstraction products have also been observed in solution from the triplet species 59t to produce the bitropyl molecule



If this system is aromatic, there is not much additional stabilization that is lent to the system from being in the σ^2 singlet state. The nucleophilic characteristics of the C_7H_6 system may however be indicative of a σ^2 singlet state. Hammett investigations give it a value of $+1.05 \pm 0.05$.⁴¹ The stereochemistry of its addition to double bonds has in fact been found to be completely stereospecific, implying the existence of either 59s or 60.⁴²

Most of the chemistry of the C_7H_6 system described above has been in terms of the completely conjugated planar carbene 59. Recent MNDO calculations reveal that this system is even more complicated.⁵⁰ It is now apparent that early work in this system led to the incorrect conclusion that cycloheptatetraene (60) was too strained to be a viable intermediate.⁴³ Figure 1 (page 27) shows calculated ΔH_f values along the reaction coordinate for the interconversion of 60 and 59. MNDO shows that the planar singlet 59s is not an energy minimum, but rather a transition state for the conversion of the nonplanar chiral allene

60s with its enantiomer.

The heat of formation of the allene 60s was determined to be 23 kcal/mole lower than the carbene 59s. Calculations looking at the triplet states in this system indicate that the triplet allene 60t is not an energy minimum and transforms into the planar triplet carbene 59s with no activation energy.

Any authentic carbene chemistry observed from the C_7H_6 system is therefore likely only from its triplet state. It is more likely still that the chemistry observed in this system reflects the reactivity of the more stable cycloheptatetraene 60s. More recent ab-initio calculations⁴⁴ conflict with these MNDO calculations but the following evidence is consistent with the MNDO work.

MINDO/3 calculations⁴⁵ and experiments⁴⁶ looking at the rearrangement reaction profile for phenyl carbene (63) found no evidence for 59 and instead found that the allene isomer 60 was formed directly.

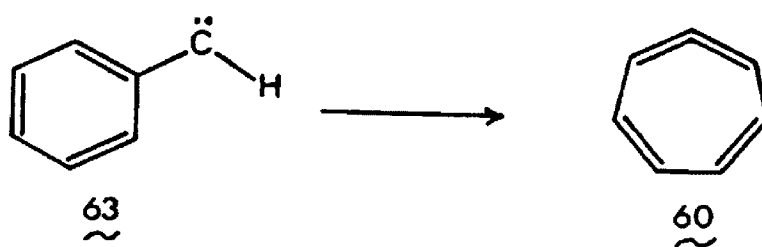
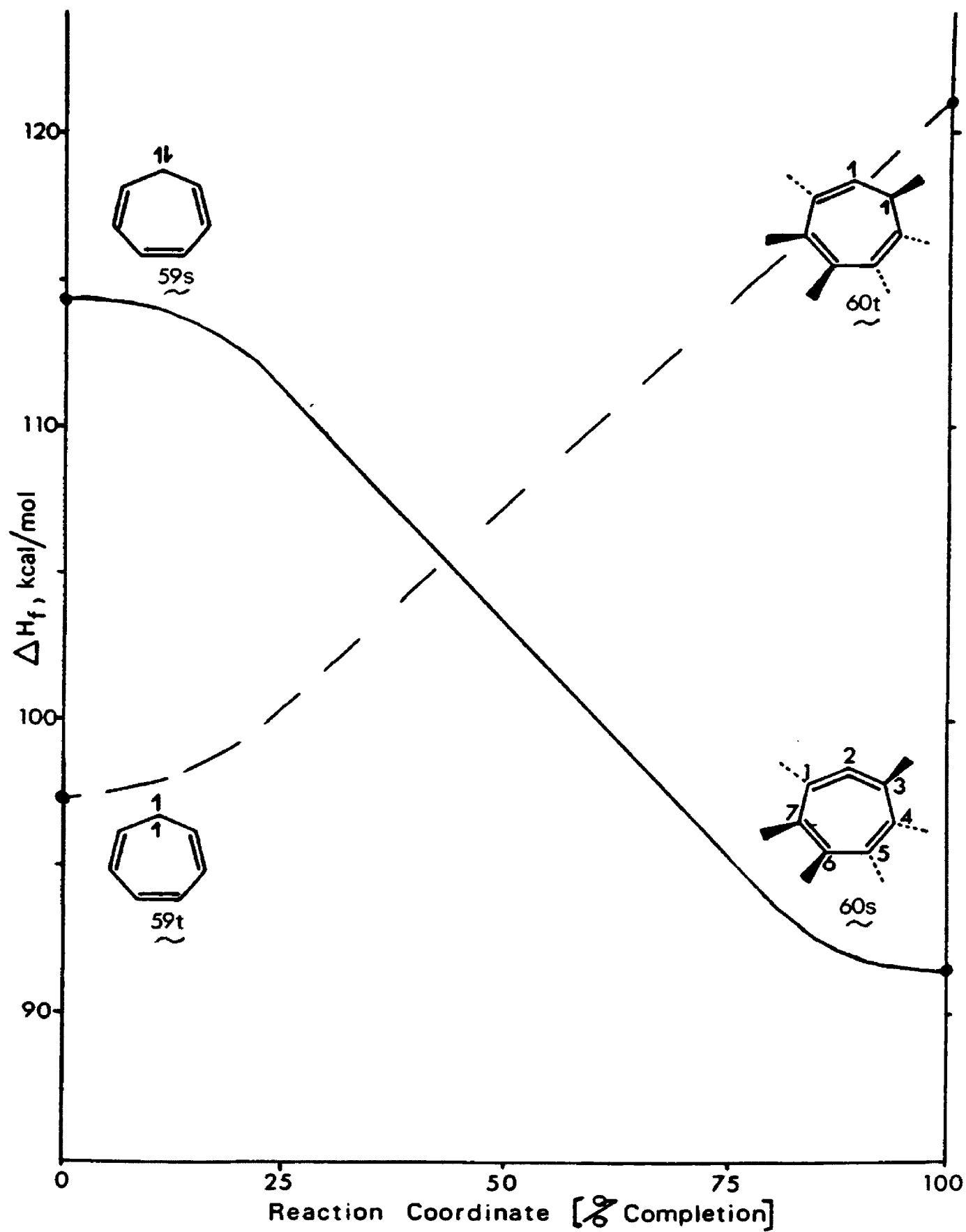
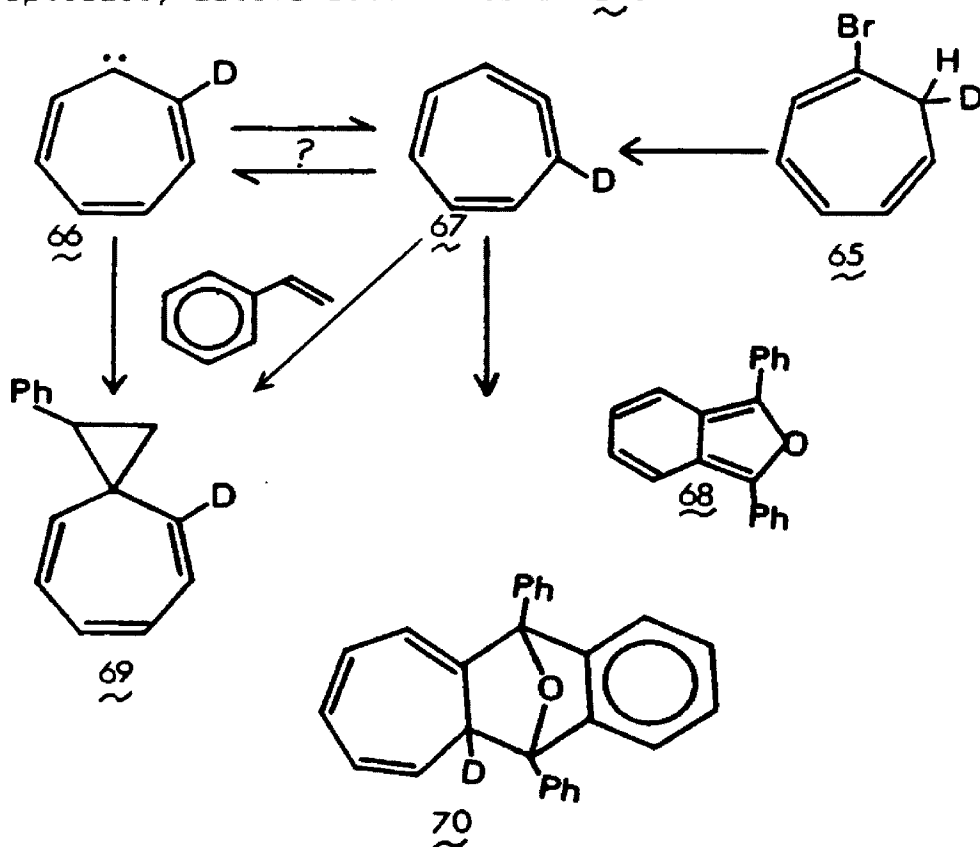


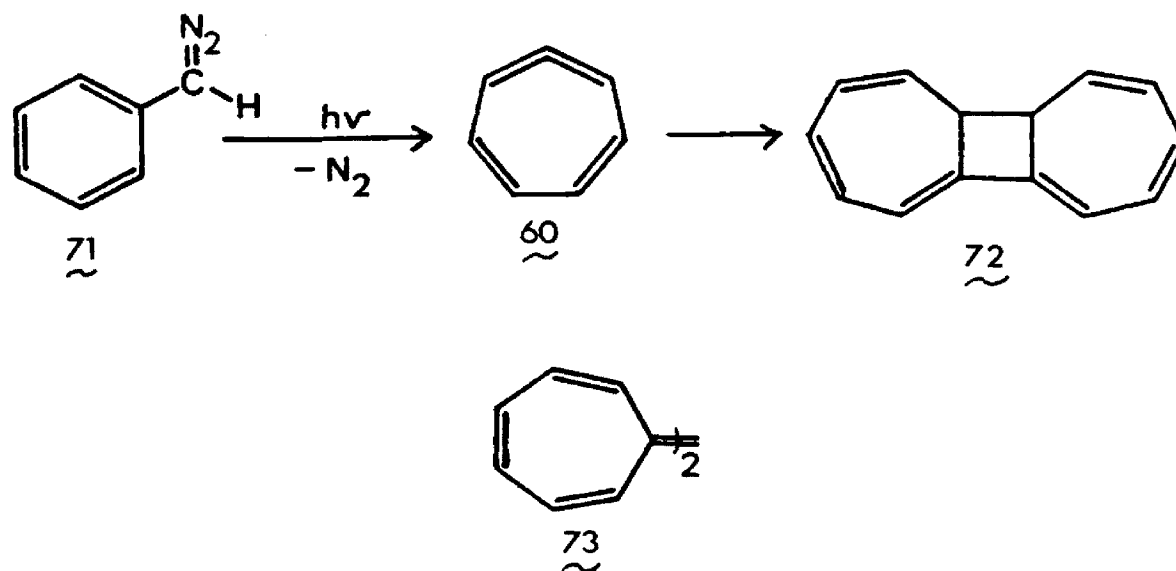
FIGURE 1: CALCULATED ΔH_f VALUES vs. REACTION COORDINATE ($59 \leftrightarrow 60$)



Harris and Jones⁶⁷ have found definitive evidence for the chirality of the allene 67 by observing an optically active Diels-Alder adduct 70 which could only have been obtained from the addition of an achiral diene to the reaction mixture of intermediates containing a chiral, optically active allene isomer 67.

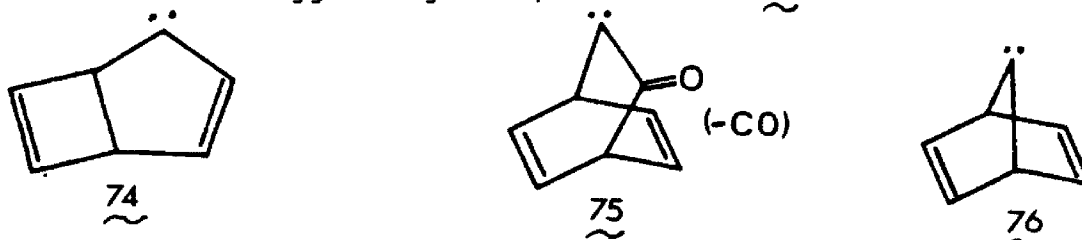


The matrix isolated IR and UV spectrum of 60s has been observed.⁶⁸ Investigators have also reported that upon the production of the phenyl carbene intermediate, a beige product was produced at liquid nitrogen temperatures which then decomposed upon warming to the black heptafulvalene dimer 73.^{63,69,70} This beige material has since been attributed to the 2+2 addition dimer of the allene 72.⁷¹ This is additional evidence that 63 rearranges directly to the allene 60 rather than the carbene 59.



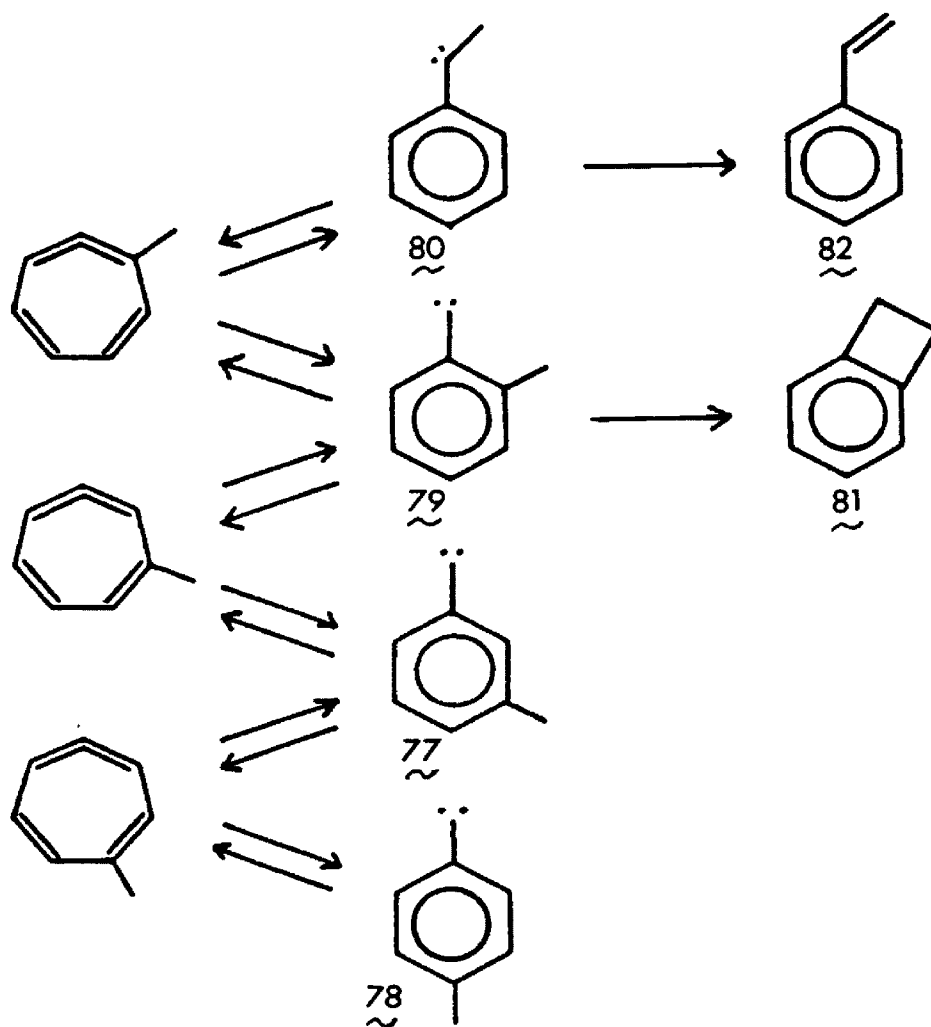
Allenes are known to show nucleophilic characteristics. The Hammett study⁶¹ of the cycloheptatrienylidene/tetraene system may thus be a measurement of the nucleophilicity of 60 rather than 59.

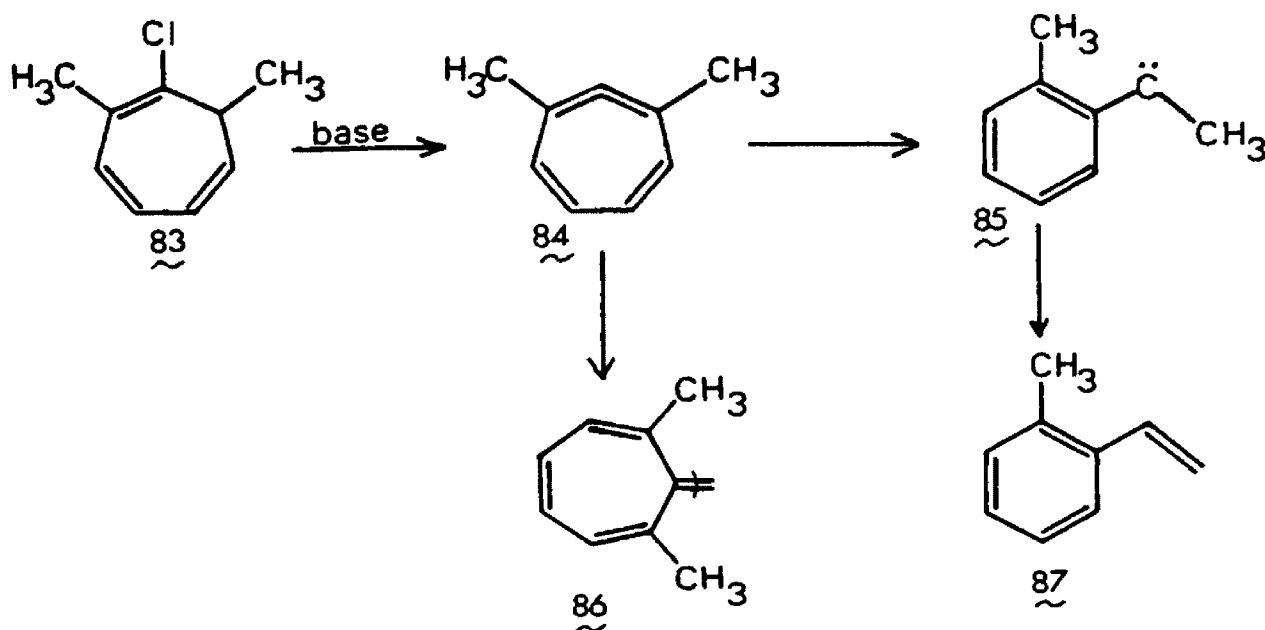
A number of other intermediates have since been shown to be included in the C_7H_6 energy surface, including; 74, 75 and 76. All three intermediates have been shown to rearrange directly to 60 with no evidence suggesting the presence of 59.



The production of o-, m- or p-tolylcarbene (77-79) and phenyl methyl carbene (80) in the gas phase results in the formation of benzocyclobutene (81) and styrene (82). These results were originally interpreted as implying the reversibility of the interconversions of phenyl carbenes and cycloheptatrienylidenes in the gas phase.^{7e} It is best now to consider the interconversion and reversibility to be the relationship of the substituted allenes and substituted phenyl carbenes, as pictured.

In solution the production of phenylcarbene (63) fails to produce the heptafulvalene dimer 75 expected after rearrangement. By retarding the dimerization reaction, however, rearrangement can be promoted in solution. Upon the production of 84 in solution, equal amounts of the substituted styrene 87 and the dimer 86 were produced.⁷⁹





The chemistry of this C_7H_8 system is very interesting, complicated, and, at times, confusing. What can be done to this system to alter its chemistry from the parent system? The research in this lab was aimed at physically constraining the C_7 -ring of 60 to planarity by holding the C3-C4, C4-C5 or C5-C6 bonds (as numbered on the allene) in the same plane by applying a rigid structure to the ring. The primary goal of this constraint was to alter the energy relationships of the parent system (as theoretically represented in Figure 1) and thus encourage chemical behavior different from that of the parent system.

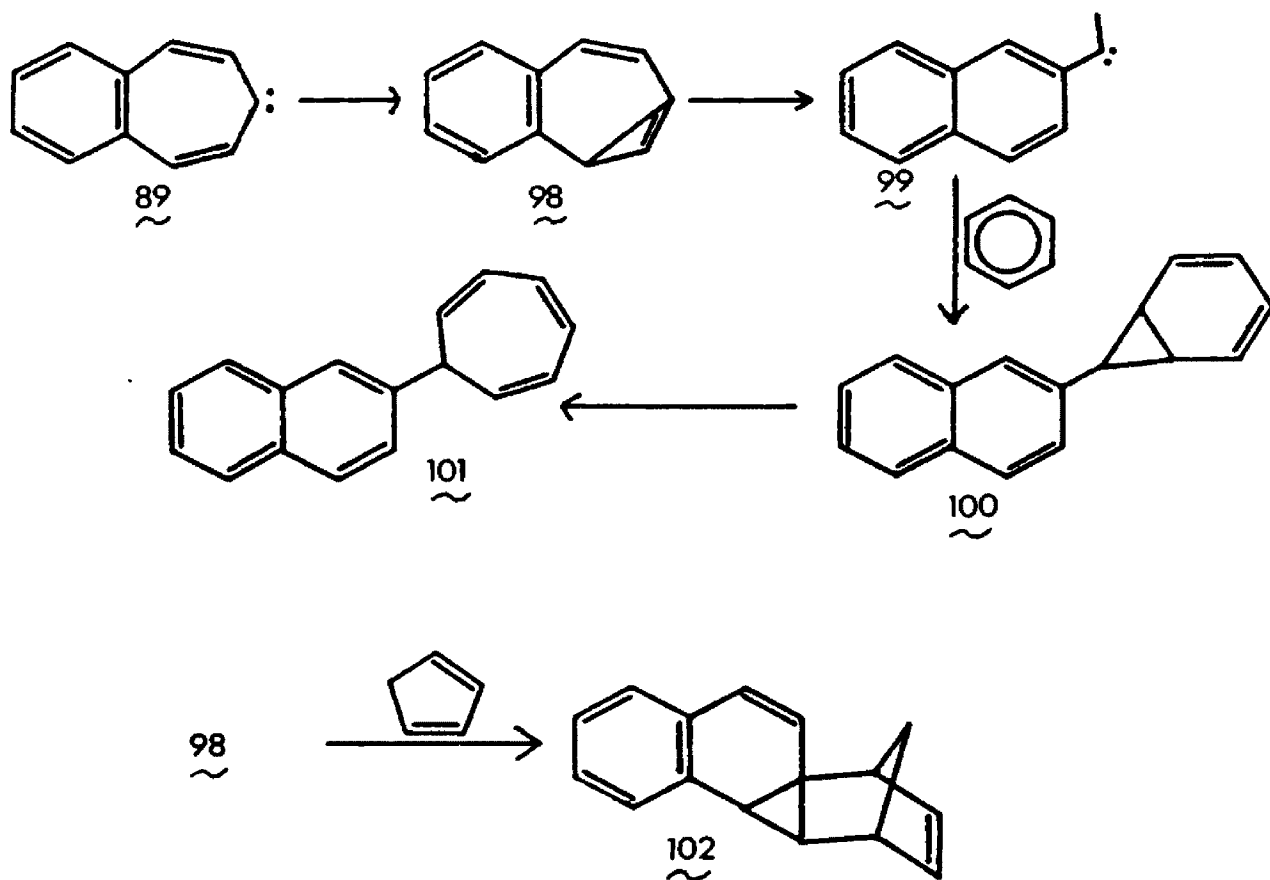
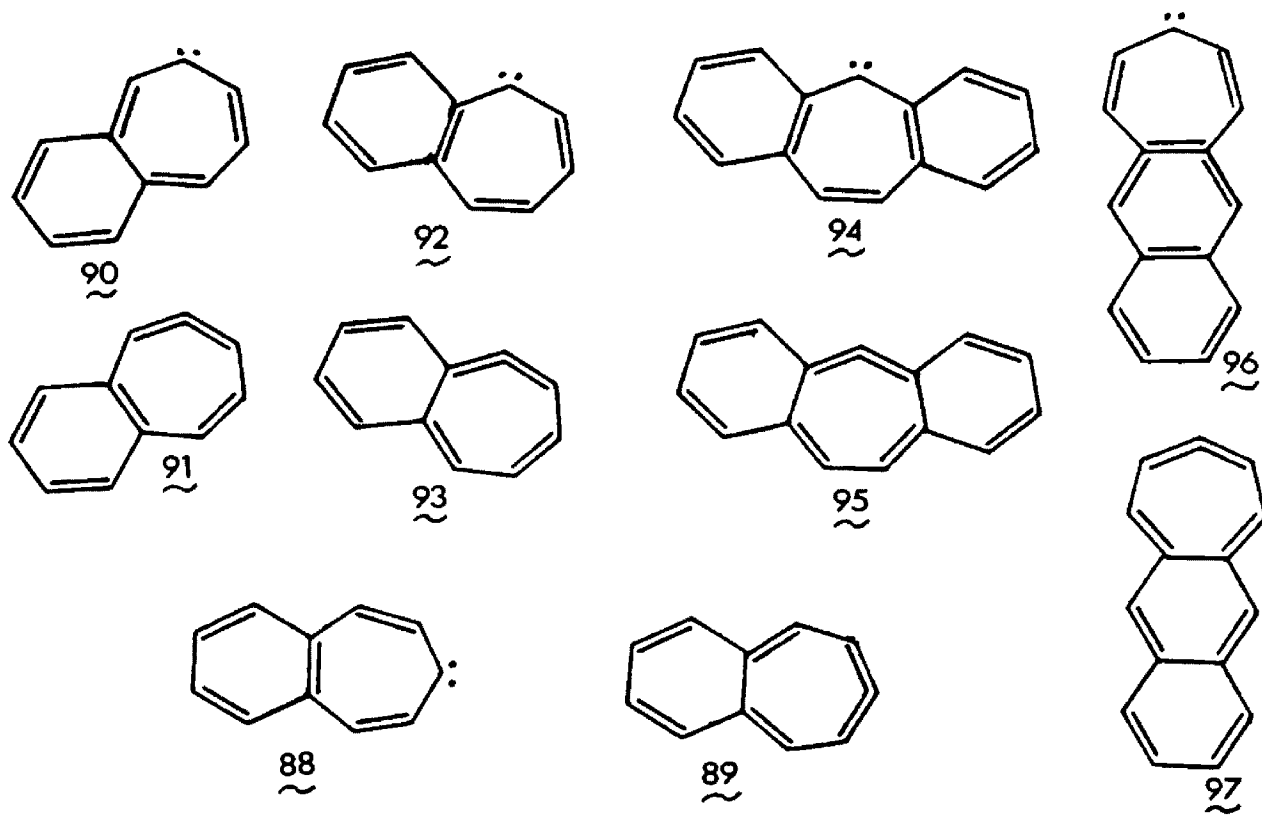
Referring to Figure 1 (see page 27), the allene should be stabilized relative to the carbene when constraint is at the C4-C5 positions (β -systems).⁷⁴ The carbene should be stabilized relative to the allene form when constraint is applied to either the C3-C4 (α -systems) or the C5-C6 (γ -systems) positions. C4-C5 substitution of the ring is by no means overwhelmingly constraining, since in both the allene and carbene isomers, the C4 and C5 bonds out of the ring lie on the same side of the plane of the ring. The constraint in the β -system therefore, is

much less constrictive than in the α - and γ -systems where constraint forces bonds which originally lie on opposite sides of the ring in the allene isomer into the same plane. The constraint in the α - and γ -systems would be expected to perturb the energy relationships of the C_7H_6 parent system to a much greater extent. Triplet chemistry could therefore be expected to be more likely in these systems than in the β -systems. Constraint, however, is not the only factor that influences these energy relationships as the number of constraining groups, the amount and type of resonance and solvent interactions all have a role in influencing these relationships.

a. Benzoannelated Systems

Benzoannelated systems which offer constraint of the cycloheptatetraene system, such as those shown below, have been investigated. These suffer, however, in that they provide significant resonance perturbation to the system.^{73,74,77} For example, annelation of phenylcarbene and cycloheptatetraene shifts the equilibrium between the two toward the annelated phenylcarbene.⁷⁵ The rearrangement of 89 to 99 is therefore driven by the aromatization that results in the process.^{73,74}

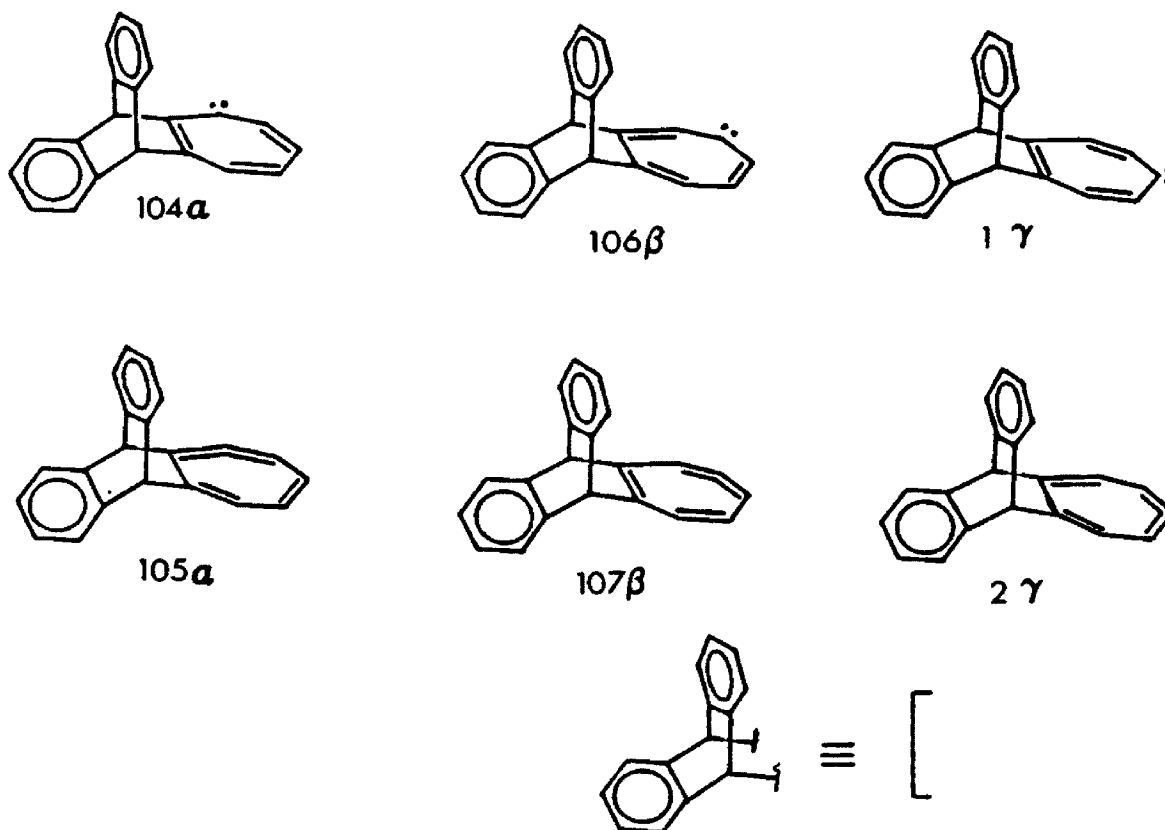
Production of 89 in benzene gave naphthocycloheptatriene (101), whose formation can best be explained from a rearrangement followed by addition into benzene followed by an additional rearrangement.⁷⁵ The existence of the bicycloheptatriene intermediate 98 has been shown since the cyclopentadiene Diels-Alder adduct 102 has been trapped.⁷⁴



This is different from the parent C_7H_6 system where no bicycloheptatriene intermediate has been trapped or observed spectroscopically.

MNDO calculations indicated that in every case the benzoannellated allene species to be lower in energy than the corresponding carbene.⁵⁰ Only in the dibenzo and naphtho derivatives 94/95 and 96/97 were the energy differences small enough to allow for isomerization to the carbene species. The observed solution chemistry of these systems was best explained in terms of their singlet species,⁷⁷ although both are ground state triplets as determined by ESR spectroscopy.

b. 9,10-Anthraceno Bridged Systems



The 9,10-anthraceno bridge applies constraint to the C_7H_6 system without applying resonance perturbations. This constraint was thought to be the only way to see any chemistry that could be attributed to an

authentic cycloheptatrienyliene species. Although physical constraint such as this was not overwhelming, it was enough to alter the chemistry of the parent system.

i. The β -system; C4-C5 constraint, 106/107

This intermediate system was produced and its reactivity characterized by Tivakornpannarai.⁷⁸

Figure 2 shows the various reaction products that were found upon the production of this carbene/allene intermediate. The chemistry of this intermediate was explained in terms of the allene intermediate 107. The formation of the hydrocarbon 115 was interesting because it indicated the presence of the triplet carbene 106. The only logical explanation for its formation was for 106 to abstract two hydrogens successively from the solvent.

Figure 3 shows a rearrangement scheme representing the interconversion of the substituted arylcarbenes and cycloheptatetraenes of the α , β and γ -systems. The isolation of the aldehydes 113 and 114 was indicative of rearrangement of the allene 107 to the arylcarbenes 116 and 117, followed by intersystem crossing to their more stable triplet states and reaction with oxygen (present in trace amounts). These rearrangements are analogous to the high temperature gas phase chemistry of the C_7H_6 parent system, and the solution chemistry of other substituted systems.⁷⁹

The finding of triptycene (112) in significant yields was surprising because its formation via carbon loss under mild conditions in solution was virtually unheard of before.

FIGURE 2: REACTION PRODUCTS FROM THE β -SYSTEM

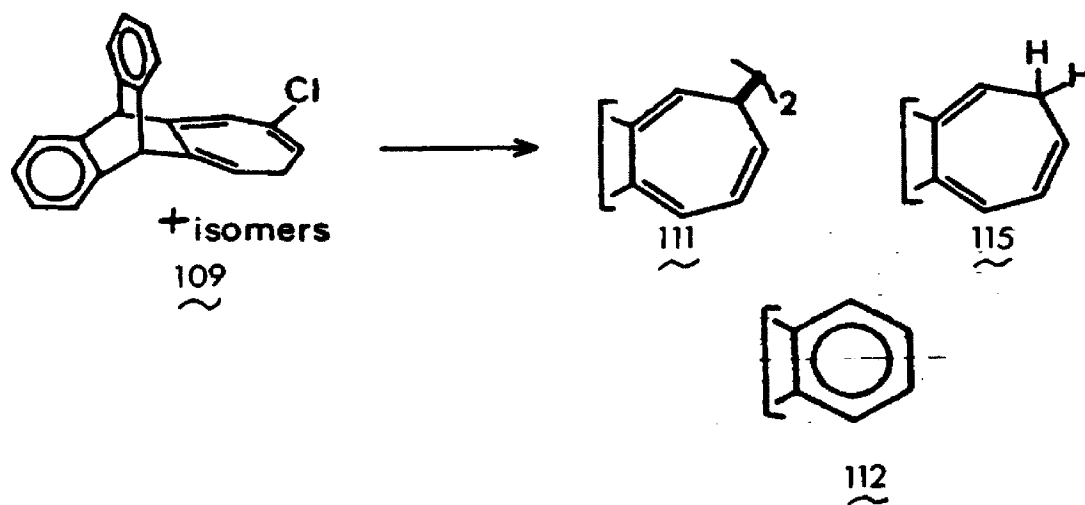
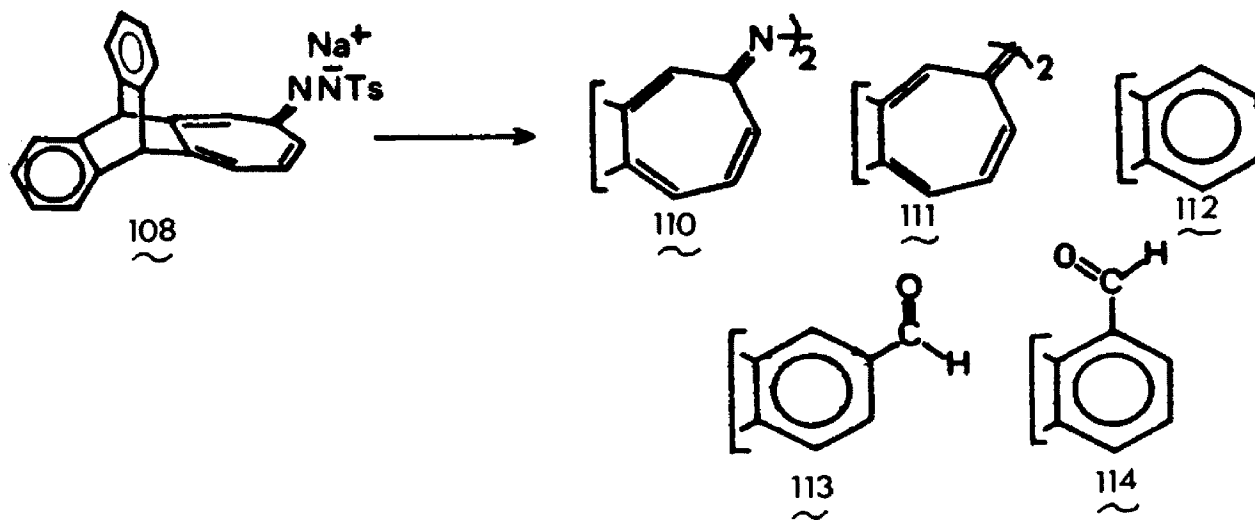


FIGURE 3: REARRANGEMENT SCHEME: INTERCONVERSION α , β AND γ -SYSTEMS

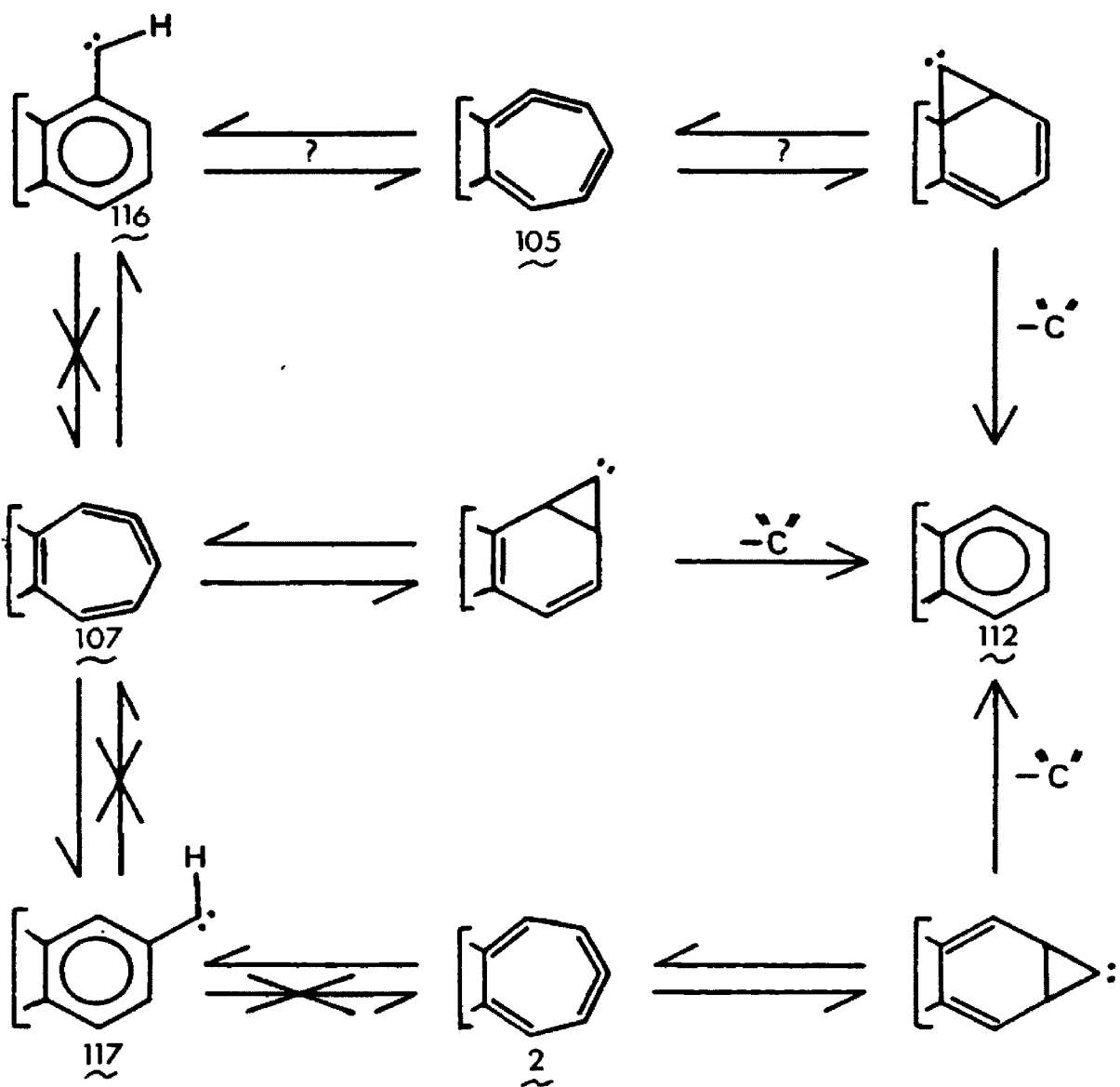
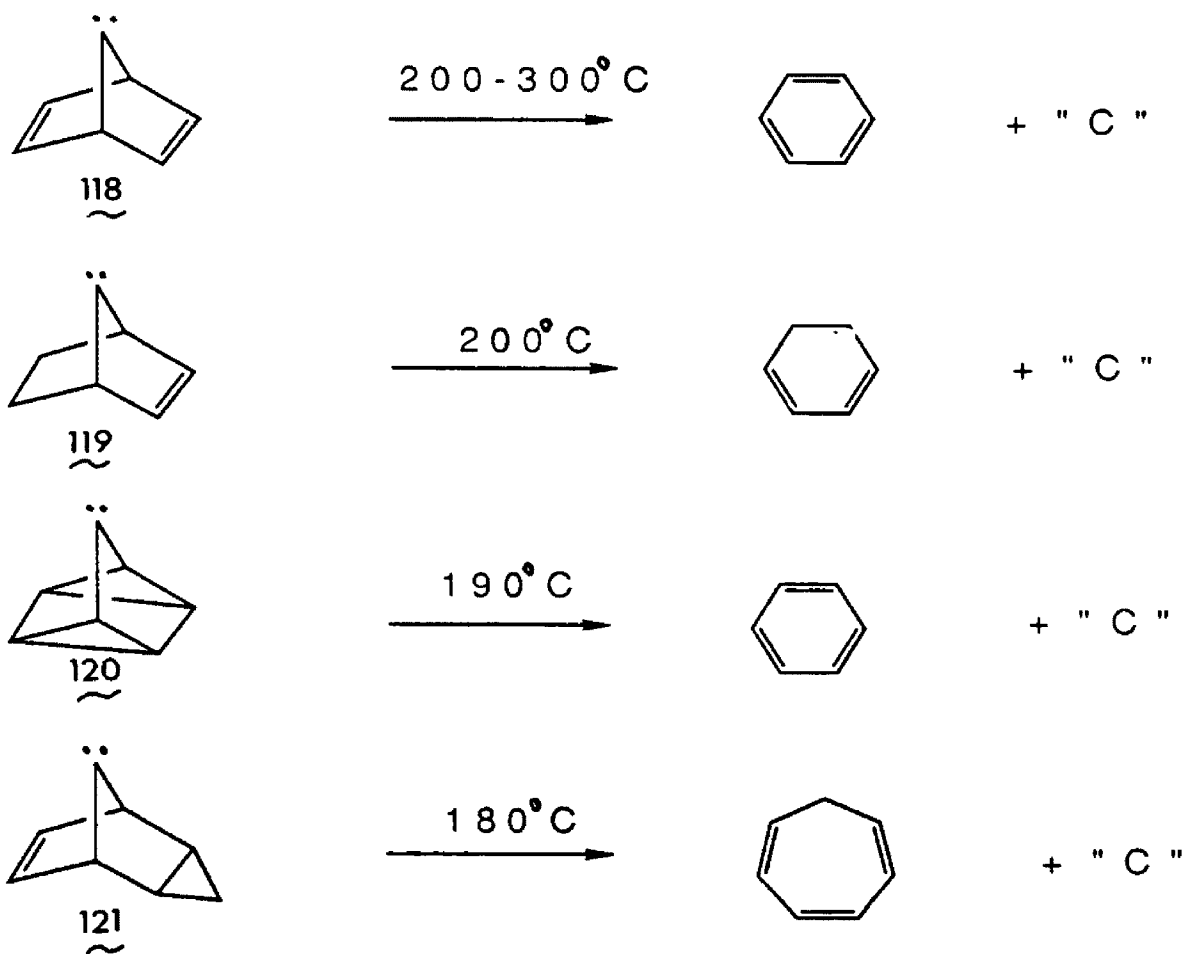


Figure 4 shows other systems exhibiting carbon loss. Carbon loss has been observed from quadricyclanylidene 118 and norbornadienylidene 119, but under the much more vigorous conditions of vacuum pyrolysis at 200-300° of the corresponding tosylhydrazones.⁷⁹ Carbon loss has also been observed from 129 and 121 during the vacuum thermolyses of their corresponding tosylhydrazone salts.

The finding of the hydrocarbon 115 and triptycene 112 was interesting in that it was not expected from the constraint and reaction conditions that were applied. The observation of triplet derived products was perplexing since it was thought that cycloheptatrienylidene chemistry would be much less likely with this constraint than without it. With these interesting, but ambiguous results, the unique synthesis of the γ -system was carried out and its chemistry under similar reaction conditions was observed.

FIGURE 4: OTHER CARBENES EXHIBITING CARBON LOSS



II. RESULTS AND DISCUSSION

The following chapter discusses the synthesis of the γ -intermediate, the resultant isolated products and the relationship with the results of the β -system.^{7a}

A. SYNTHESIS OF PRECURSORS TO THE γ -SYSTEM, 1/2

Only one method was found in the literature to synthesize the tropone 124, a necessary precursor to the carbene/allene system 1/2. This method involved the trapping of the intermediate tropyne 152 with anthracene 131. This was reported to produce 124 in only 12% overall yield.⁸⁹

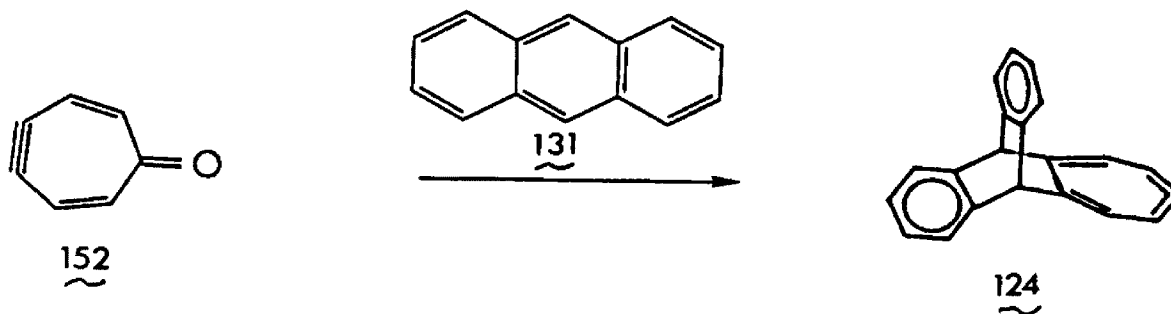
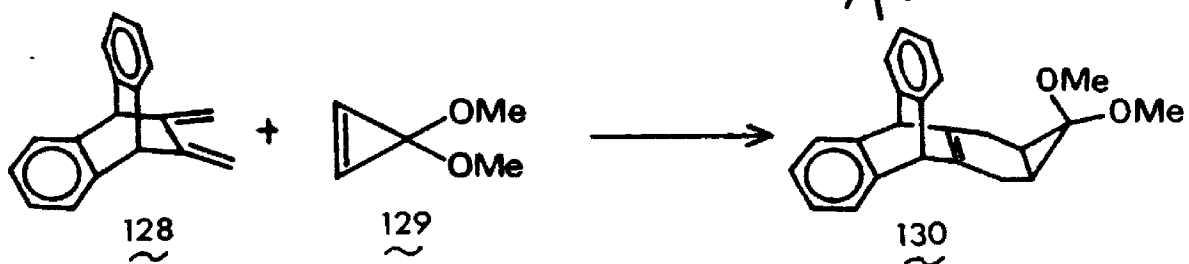
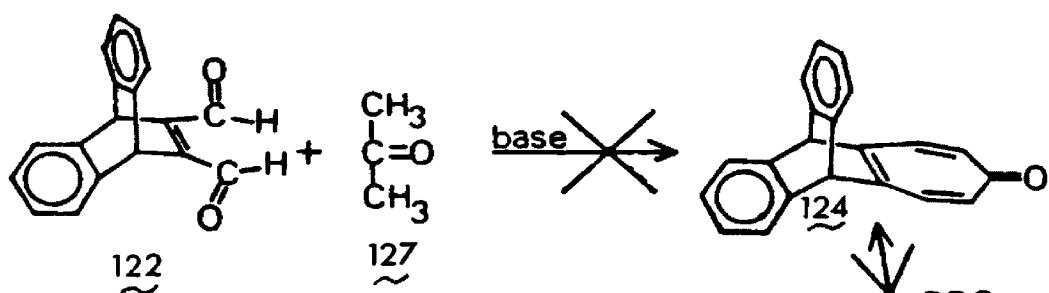
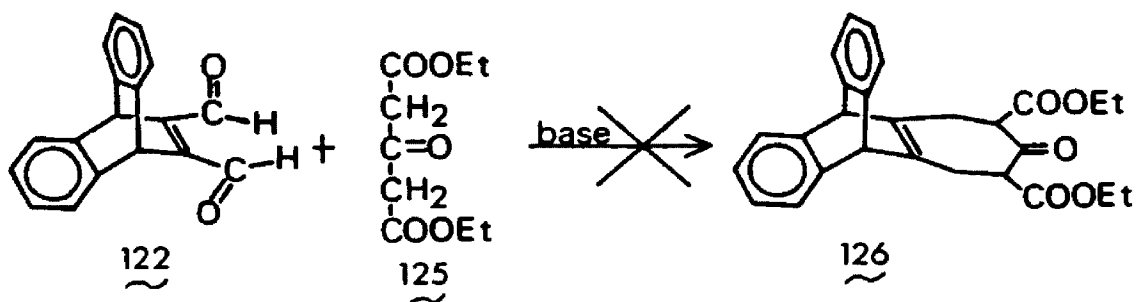
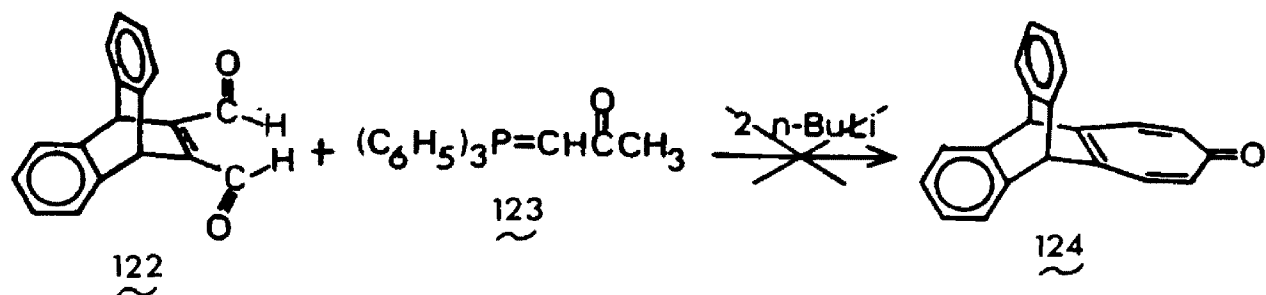


Figure 5 shows a number of different reaction paths that were attempted in the making of the tropone 124. The dialdehyde 122 was made in 40% yield using known procedures.⁸⁹ Reactions one through three show various condensation reactions designed to eventually give 124. Reaction one involved the production of a ylide anion from 123 and two equivalents of n-butyl lithium.⁹¹ The ylide was designed to undergo a double condensation reaction with 122 to give the tropone 124.⁹² Reactions two and three were designed to take advantage of the acidic hydrogens alpha to the carbonyl in compounds 125 and 127.

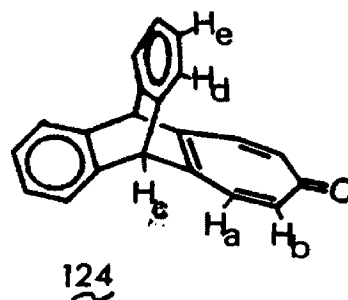
FIGURE 5 : ATTEMPTS TO GENERATE THE TROPONE 124



These reactions also designed to undergo condensation reactions with 122 failed.⁶³ Reaction four involved the Diels-Alder addition of the diene 128,⁶⁴ with 3,3-dimethoxycyclopropane (129)⁶⁵ to produce the 7,7-dimethoxy-3-norcarene 130.⁶⁶ Treatment of 130 with dichlorodicyanoquinone (DDQ), followed by acid catalyzed hydrolysis, however, failed to give the desired product, the tropone 124.

Figure 6 shows the method that was used to obtain the tropone 124 in 9% overall yield. The dichloro-adduct 132 obtained from the reaction of anthracene (131) with 1,4-dichloro-2-butene, was treated with two equivalents of potassium *t*-butoxide to give the diene 128 in 84% overall yield.⁶⁴ The next reaction relied on the unique properties of the oxyallyl-Fe(II) complex 135. Produced from the reaction of tetrabromoacetone (133) and diiron nonacarbonyl (134),⁶⁷ the oxyallyl complex 135 was able to act as a two electron dienophile. Producing 135 in the presence of the diene 128 resulted in the formation of the dibromoketone-adduct 136 in 25-50% yield. Double dehydrohalogenation was affected by treating 136 with lithium chloride or lithium fluoride in a buffered solution of lithium carbonate and dimethylformamide (DMF) in only 10-14% yield.⁶⁸ The following spectral data is identical with what has been reported for the tropone 124.⁶⁹ The ¹³C-NMR data has not been reported previously.

¹H-NMR; 5.35 ppm (s, H_c, 2H)
 6.83 - 7.23 ppm (m, H_a + H_b, 4H)
 6.96 - 7.07 ppm (m, H_d, 4H)
 7.33 - 7.45 ppm (m, H_e, 4H)



^{13}C -NMR; 58.24 ppm C_5 (d)

123.79 ppm C_7 (d)

125.68 ppm C_8 (d)

136.57 ppm C_3 (d)

140.47 ppm C_2 (d), 143.18 ppm C_6 (s),

152.34 ppm C_4 (s), 186.30 ppm C_1 (s)

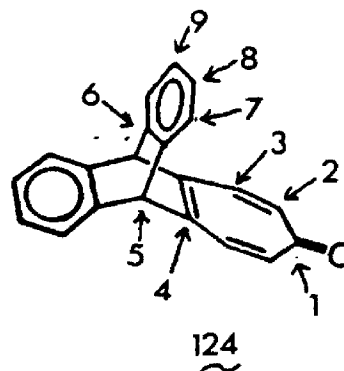
m.p.; 158 - 160°C (dec.)

MS; calculated: 282.10452

observed: 282.104775

IR (KBr pellet); 124 shows distinctive tropone stretching bands.

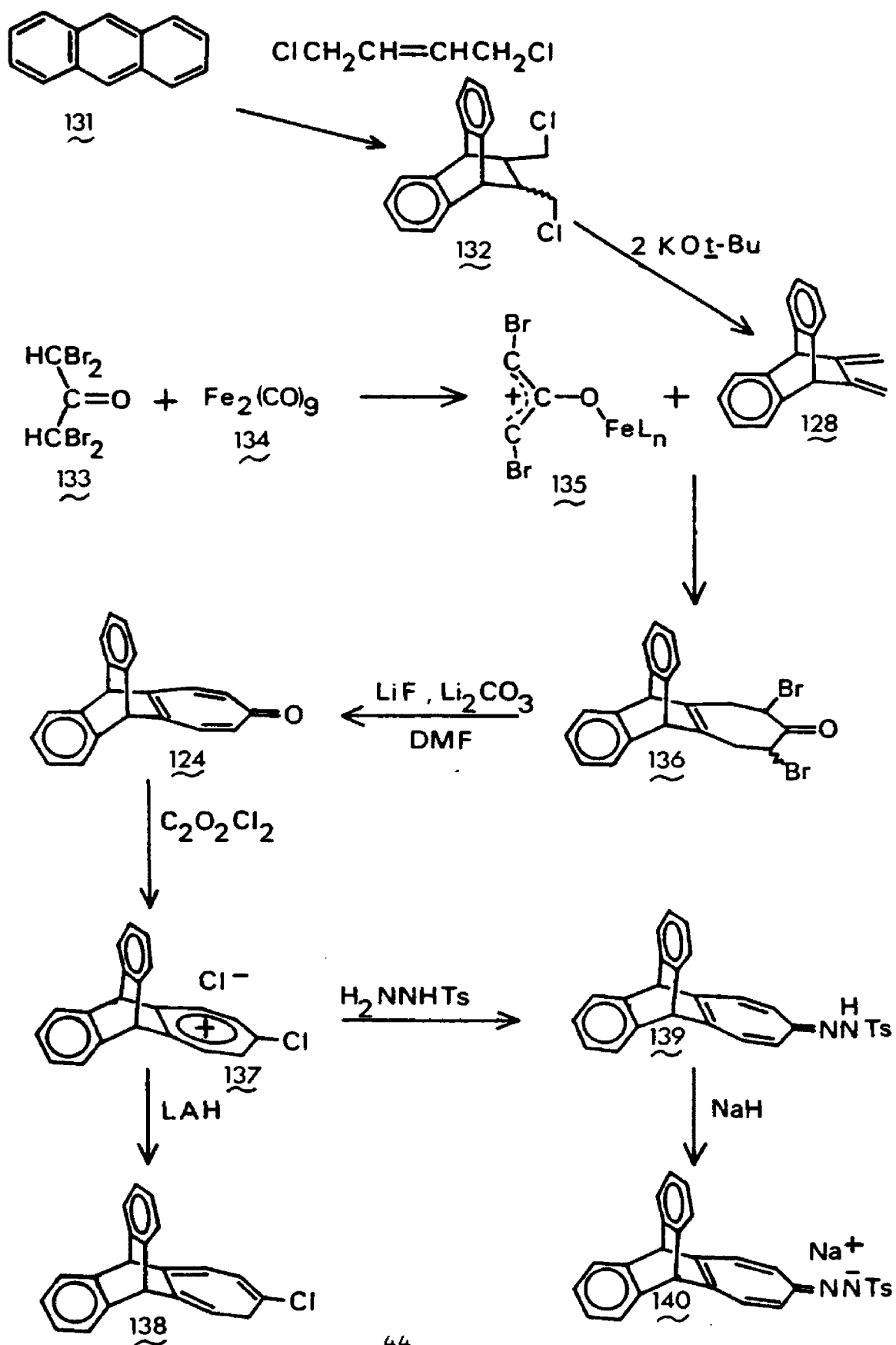
$\text{C}=\text{C}$ stretch - 1563 cm^{-1} $\text{C}=\text{O}$ stretch - 1615 cm^{-1}



Treatment of the tropone 124 with oxalyl chloride followed by *p*-toluenesulfonyl hydrazide resulted in the formation of the tosyl-hydrazone derivative 139 in 43% yield. The sodium salt 140 was then made in 57% yield by treating 139 with sodium hydride.

Treatment of the tropone 124 with oxalyl chloride followed by lithium aluminum hydride (LAH) resulted in the formation of the chlorotriene 138 and its isomers in 80% yield.

FIGURE 6: SYNTHESIS OF γ -SYSTEM PRECURSORS



B. GENERATION OF THE γ -INTERMEDIATE, 1/2

Photolysis of the sodium salt 140 as well as the dehydrohalogenation of the chlorotriene 138 (+ isomers) with potassium t-butoxide both in solution at 25°C were used as methods to access the γ -intermediate energy surface.⁴⁴ Table 3 shows the reaction conditions as well as the yields for the products that were isolated and identified. Figure 6 shows the various product structures that were identified from the production of the γ -intermediate in solution.

TABLE 3: REACTION CONDITIONS AND PRODUCT YIELDS, γ -SYSTEM

PRECURSOR	REACTION CONDITIONS	PRODUCT YIELDS *			
		<u>1141</u>	<u>1112</u>	<u>1144</u>	<u>1143</u>
<u>138</u>	K <u>t</u> -OBu, THF, 23 C, N ₂ .088M	35	9	0	0
<u>138</u>	K <u>t</u> -OBu, THF, 23 C, N ₂ .044M	10	30	0	0
<u>138</u>	K <u>t</u> -OBu, THF, 23 C, N ₂ .100M	*	4	0	0
<u>140</u>	h ν , THF, 23 C, N ₂ .024M	24	12	0	0
<u>140</u>	h ν , THF, 23 C, N ₂ .0124M	*	6	0	0

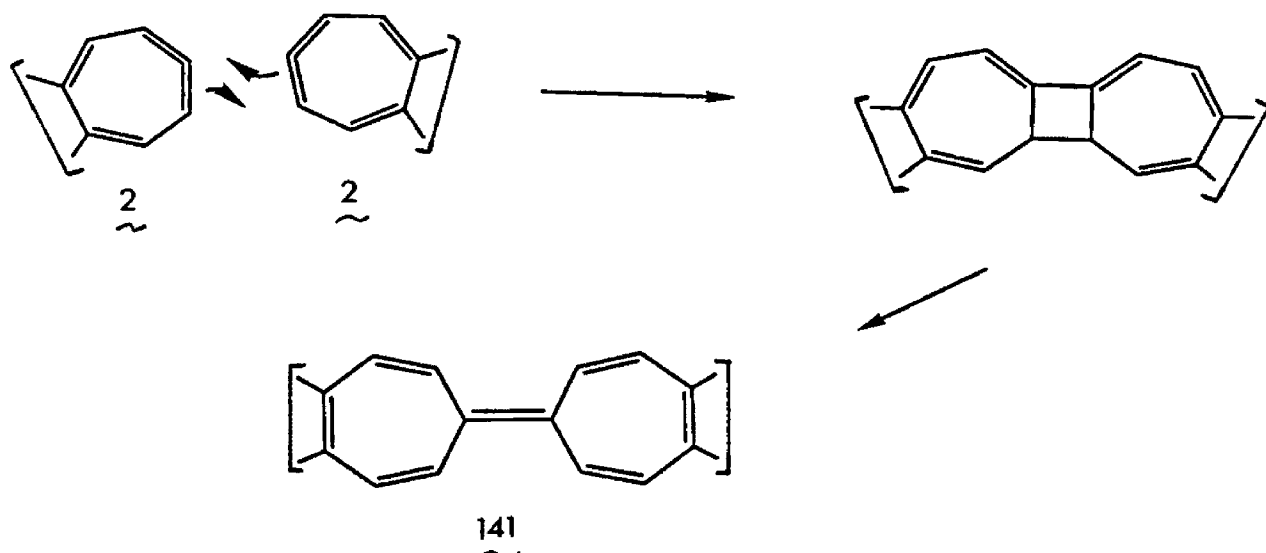
* Dimer present but decomposed before isolation.

The azine 142 expected from the decomposition of 140 was not obtained. This is in sharp contrast to the β -system where as much as 30% of the azine 110 was isolated.

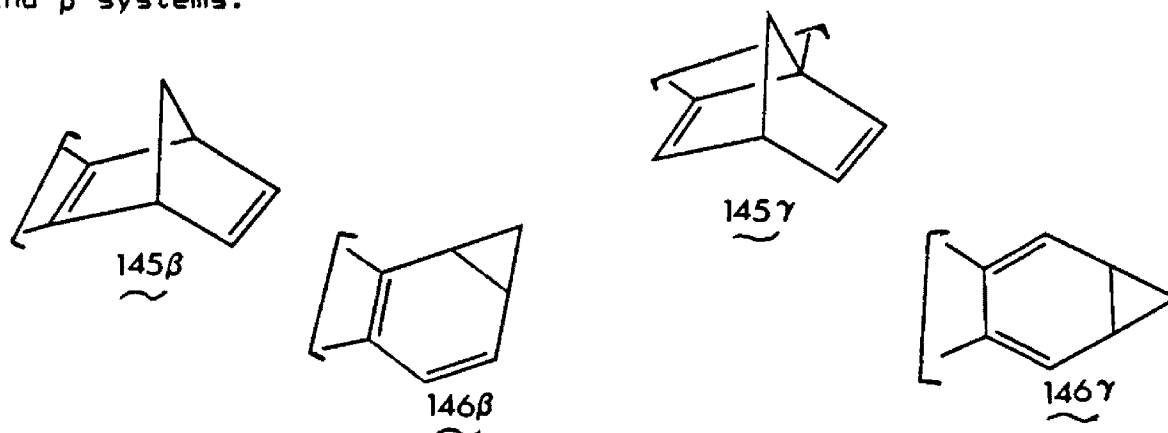
Conspicuously absent from the isolated products was the hydrocarbon 144. The inability to isolate 144 was probably the result of two factors. First, although a number of products could be seen by TLC in many cases not enough of the material could be isolated to give useful NMR spectra. This type of isolation method was therefore anticipated to give an error in determining the yield. Alternatively,

the absence of 144 may indicate the absence of the γ -carbene entirely. In support of this notion was the fact that carbene abstraction products were also absent. These observations show that the γ -system was still best explained in terms of its allene species 2. The allene 2 was therefore used in explaining the remaining isolated products.

The dimer 141 was a product of the 2+2 cycloaddition of the allene followed by rearrangement to the heptafulvalene product 141.



Triptycene 112 was found in every experiment. The formation of 112 must require rearrangement of the allene 2 as well as 107 to a species which could make loss of a carbon atom energetically more favorable. The substituted norcaradienylienes 145 or norbornadienylienes 146 were postulated as possibilities for carbon loss from the γ - and β -systems.²⁰



Since it was highly unlikely that a free carbon atom was produced, it was further postulated that the carbon loss in the β -system was facilitated by assistance from the nucleophilic solvent, THF. The zwitterion 147 was assumed by Tivakornpannarai⁷⁹ to decompose to give detectable amounts of ethylene and carbon monoxide. This mechanism was also used to explain products isolated in the present work.

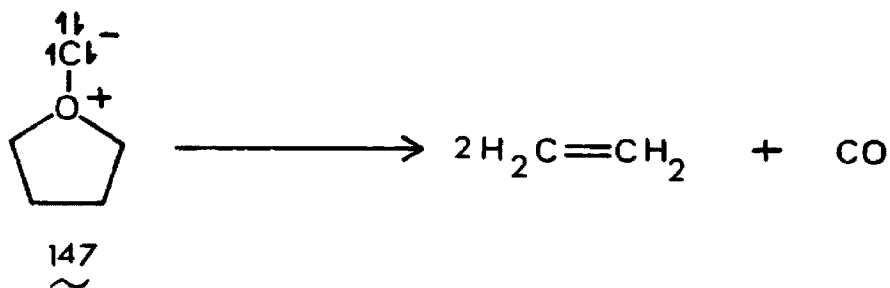
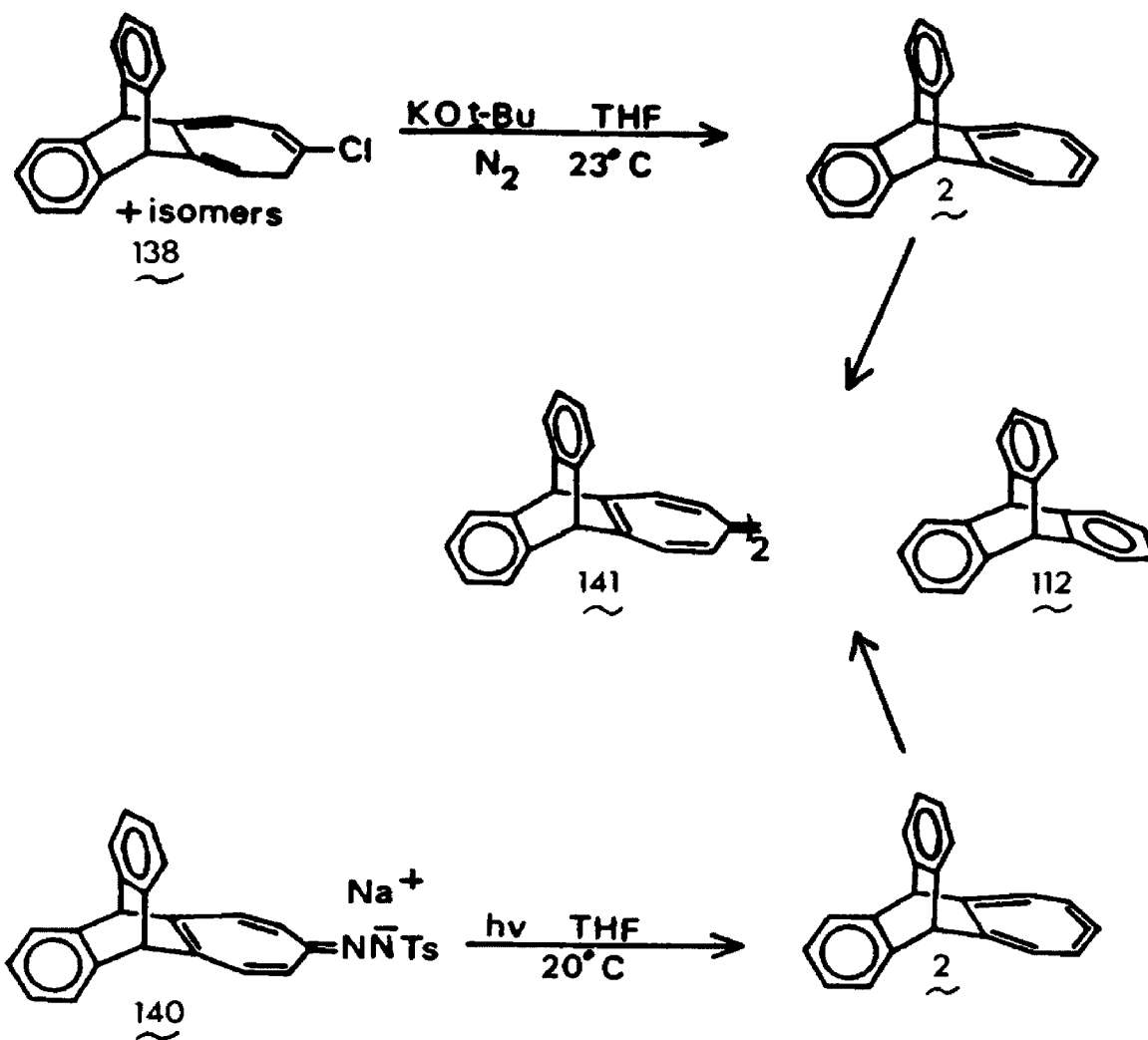
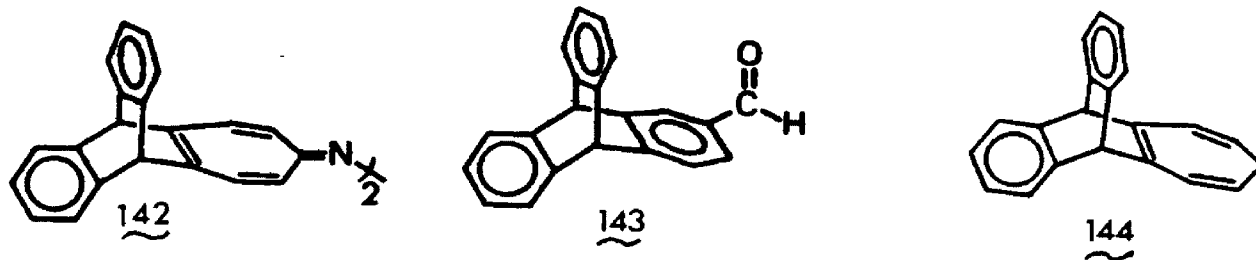


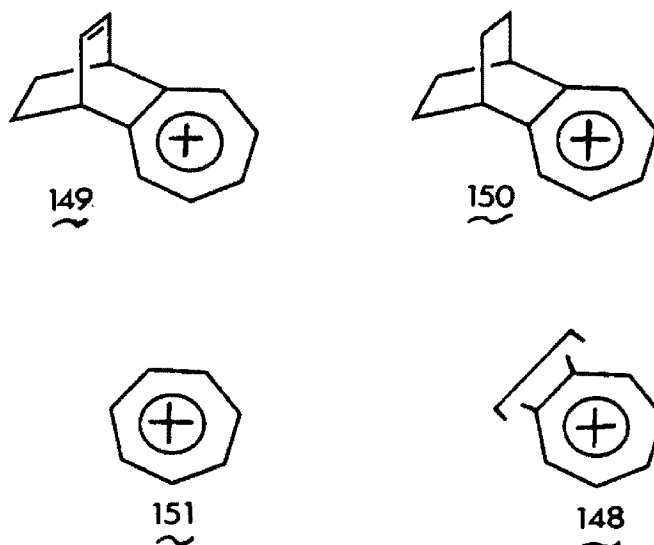
FIGURE 7: PRODUCTS ISOLATED FROM PRODUCTION OF THE γ -INTERMEDIATE.



NOT ISOLATED



A third influence which may have helped bring about carbon loss could be the interaction of the π -system of the aromatic rings in the 9,10-anthraceno bridge with the π -system of the seven membered ring. Intramolecular charge transfer (CT) interactions such as these have been observed in similarly substituted systems with the tropylium ion.⁹⁰



The CT interactions in 148 and 149 were observed as broad long wavelength absorptions in their electronic spectrum at 300-450 nm which was absent in 150, and the unsubstituted tropylium 151. Nakazawa and co-workers⁹¹ additionally noted that although these interactions are strong, the donor and acceptor are not on parallel planes, resulting in minimized overlap of the orbital systems. It is therefore not illogical to expect increased π -interaction between the benzene rings with either of the substituted norcaradiene 145 or norbornadiene 146 isomers. Either would have increased orbital overlap as a result of their geometry which allows their carbene carbon orbitals to more

efficiently interact with the π -orbitals of the benzene ring. At this point however the importance of these interactions is only hypothetical.

Interestingly, triptycene (112) was not observed upon production of either of the arylcarbenes (116 or 117) from their corresponding tosylhydrazone salts.^{78, 98} The lack of carbon loss products or other products attributable to either of the β - or γ -allenes when starting with 116 or 117 was interpreted as the presence of the equilibrium toward the constrained aryl carbene. Refer to the rearrangement scheme represented in Figure 3.

The aldehydes 113 and 114 observed from the rearrangement from the β -allene were not observed from the γ -allene. This finding was rationalized as indicating the presence of oxygen in the β -system reactions. Their absence in the γ -system reactions however, might be an indication of the absence of oxygen in the reaction flasks rather than the inability of the γ -allene to rearrange. Since products attributable to the aryl carbene were never detected, no positive evidence can be claimed for the existence of an equilibrium with the γ -system.

As a result of these studies a number of conclusions were drawn about the influence of the constraint on the parent C_7H_6 .

1. Based on the MNDO calculations of the parent system as represented in Figure 1, we expected a difference in the chemistry between the β - and γ -systems. The β -system was expected to yield products attributable to the allene species. The γ -system was expected to display

products more characteristic of the carbene species. From the above results it seems that the position of constraint using the 9,10-anthraceno bridge system is of little consequence, with both the β - and γ -systems best described in terms of their allene forms. This conclusion does not seem surprising considering the fact that even benzoannulated systems were best described in terms of their allene forms. These systems have the added resonance influence which is absent in the 9,10-anthraceno bridged systems. It is concluded that systems which physically constrain the parent system, as in this research, do not significantly alter the energy relationships of the parent system.

2. Both of the γ - and β -allenes exhibited carbon loss. Triptycene 112 was found in every run. Earlier studies concluded this to be important in the observation of carbon loss.^{7a} Rearrangement to a system allowing the loss of a carbon atom was also deemed to be a necessary requirement based on thermodynamic arguments.

3. Having never been seen in a system under such mild conditions a further requirement for observing carbon loss might be CT interactions of the bridge system benzene π -orbitals with a norcaradienylidene or norbornadienylidene isomer. Although this is purely speculation, further investigation involving completely saturated constrained systems will show the importance of these interactions.

4. Yields of triptycene 112 increased concurrently with a yield decrease of the heptafulvalene dimer 141 upon increased solvent

dilution. This result is in accord with a bimolecular mechanism for both the formation of the dimer 141 and triptycene 112. The formation of 141 is a function of the concentration of the allene 2 to the second power ([allene]²) while triptycene formation is probably first order with respect to the allene. Therefore, greater dilution favors triptycene formation at the expense of the dimer.

III. EXPERIMENTAL

General: The following analytical methods were used throughout this research. Nuclear magnetic resonance (NMR) spectra were produced on a JEOL FX-90Q spectrometer: Proton, 89.56MHz; Carbon, 22.50MHz, as well as a few on a Bruker WM-250 (250MHz) instrument at Montana State University. Chemical shifts were reported as ppm units down-field from tetramethylsilane. Infrared (IR) spectra were taken on a Nicolet MX-1 FT-IR spectrometer. Mass spectra (MS) were obtained from a VG Instruments 7070-HF (Chemistry Department, Montana State University, Bozeman, Montana). Melting Points (m.p.) were obtained on a Meltemp melting point apparatus and were not corrected. All photolyses were carried out with a Hanovia 450 watt medium pressure mercury immersion lamp, using a Pyrex reaction vessel. Volatile solvents were removed by using a rotary evaporator at water aspirator pressure. Trace solvent impurities were removed using a mechanical pump. Percent yields were based on isolated material from PTLC or column chromatography techniques.

Materials: Commercial materials were used as obtained. Tetrahydrofuran, diglyme and benzene were distilled over benzophenone ketyl under nitrogen atmosphere and stored over molecular sieve. Dimethylformamide (DMF) was distilled after drying with anhydrous magnesium sulfate and stored over molecular sieve. Preparative thin layer chromatography (PTLC) plates were prepared by using EM Reagent Silica Gel 60 PF-256 + 366 and were activated by drying at 100° C for 2-4 hours. Chromatography components were visualized by observing their quenching of fluorescence under ultraviolet light either at 254 or 366

nm. Column chromatography was performed using Merck Silica Gel (60-200 mesh) and alumina (60-200 mesh).

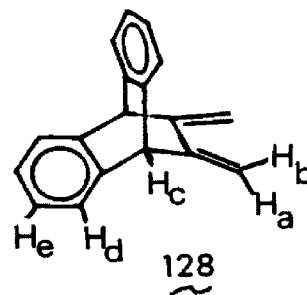
11,12-dimethylene-9,10-dihydro-9,10-ethanoanthracene 128⁸⁴

A mixture of anthracene (35.6 grams, 0.2 moles) and 1,4-dichloro-2-butene (100ml, 1.3 moles) was heated at 164° C in a three necked flask fitted with a condenser, magnetic stir bar, thermometer and nitrogen inlet for three days. The cooled black solution was eluted through a short column of silica gel using dichloromethane/hexane (1:2) as eluent. The solvent was removed and the excess dichlorobutene was removed by distillation at reduced pressure. The resulting solid was recrystallized from petroleum ether; 53.42 grams (88%) of the dichloride 132 was recovered. The NMR data that was obtained was consistent for a mixture of cis- and trans-11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene: AA'BB' aromatic multiplet from 7.07 to 7.36 ppm, a pair of bridgehead doublets (which vary in intensity depending upon the relative amount of cis versus trans isomer in the sample) at 4.41 and 4.54 ppm and multiplets at 2.82-3.38 ppm and 1.65-1.86 ppm.

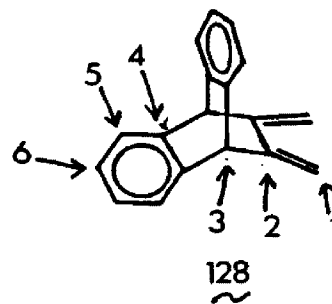
To a stirred solution of the dichloride 132 (8.86 grams, 0.029 moles), dimethylsulfoxide (80ml) and tetrahydrofuran (20ml) cooled to 0° C in a three-necked flask fitted with a condenser, was added two equivalents of potassium t-butoxide (6.5 grams, 0.058 moles) in small portions. The resultant green solution was stirred for 12 hours at room temperature. The solution was then poured into 200ml of ice water and extracted with methylene chloride (5 x 50ml). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent removed. The solid material was purified by column chromatography

using silica gel and chloroform/ petroleum ether (1:3) as eluent. The solvent was removed. The solid material was then recrystallized from hexane affording 6.32 grams (94.6%) of 11,12-dimethylene-9,10-dihydro-9,10-ethanoanthracene (128). Spectral data is identical with that found in the literature.²⁴

<u>¹H</u>	5.12 ppm	(s, H _a , 2H)
	4.86 ppm	(s, H _c , 2H)
	5.28 ppm	(s, H _b , 2H)
	7.04-7.18 ppm	(m, H _d , 4H)
	7.22-7.36 ppm	(m, H _e , 4H)



<u>¹³C</u>	55.22 ppm	(C ₃ , offres.- d)
	105.22 ppm	(C ₁ , t)
	123.27 ppm	(C ₅ , d)
	126.25 ppm	(C ₆ , d)
	141.74 ppm	(C ₄ , s)
	143.85 ppm	(C ₂ , s)



m.p. 156-158° C

MS calculated: 230.10962
observed: 230.10896

1,1,4,4-tetrabromoacetone 133²³

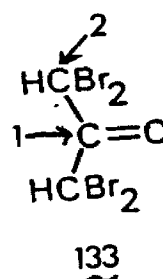
CAUTION: These brominated products are severe eye and skin irritants!

In a three necked flask fitted with a reflux condenser, nitrogen inlet, thermometer and addition funnel, a four fold molar excess of bromine (292.8 grams, 94.5ml, 1.83 moles) was added over a period of

two hours to a mixture of acetone (35ml, 0.46 moles) and 48% hydrobromic acid (50ml) cooled to 0° C. The resulting mixture was then allowed to stir overnight at room temperature. Water (380ml) was then added to the solution and stirred vigorously for thirty minutes. The organic layer was isolated and washed successively with saturated aqueous sodium bicarbonate (2 x 50ml) and sodium bisulfite solutions (4 x 50ml) then dried over anhydrous calcium chloride pellets.

A vacuum distillation apparatus was set up and the crude product was fractionated. The desired product 133 (137 grams, 80%) was collected at 129-131° C, 7mm Hg. Repeat distillations yielded quality material. Spectral data was identical with that reported in the literature.⁹³

<u>¹H</u>	6.38 ppm (s, H _a , 2H)
<u>¹³C</u>	183.2 ppm (C ₁ , s)
	34.0 ppm (C ₂ , d)
<u>mp</u>	37-39 C
<u>bp</u>	129-131° C / 7mm Hg



4,5-(9,10-anthraceno)-2,4,6-cycloheptatriene-1-one 124⁸⁹

In a three necked flask fitted with a reflux condenser, nitrogen inlet, magnetic stir bar and thermometer a mixture of diiron nonacarbonyl 134 (7.35 grams, 0.0202 moles) and the diene 128 (9.3 grams, 0.0404 moles) in 75ml benzene was heated to 60° C. To this mixture a solution of the tetrabromoacetone 133 (9.34 grams, 0.025 moles) in 15ml benzene was added carefully over a period of thirty minutes. Upon this addition a gas (CO) is vigorously evolved. The mixture was stirred

at 60° C for an additional two hours. Upon cooling to room temperature the solution was poured into 200ml of a saturated aqueous sodium bicarbonate solution and stirred vigorously for fifteen minutes. To this was added 200ml ethyl acetate and the mixture was stirred for an additional fifteen minutes. The dark green precipitate was removed by filtration through a pad of diatomaceous earth. The organic and aqueous layers were separated and the aqueous layer washed with ethyl acetate (2 x 50ml). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent removed to give a dark brown material. Chromatography of the brown material using silica gel and chloroform/Hexane as eluent gave 136 of sufficient purity. Proton NMR analysis revealed a sharp bridgehead singlet at 4.74 ppm, aromatic multiplets from 6.89 ppm to 7.03 ppm and 7.02 ppm to 7.30 ppm, aliphatic hydrogen multiplets from 4.63 ppm to 4.77 ppm and 2.88 ppm to 3.53 ppm.

Dehydrohalogenation of was affected by treating the dibromketone 136 (2.22 grams, 0.0045 moles) in anhydrous dimethylformamide (20ml) with lithium fluoride (0.13 grams, 0.005 moles), lithium carbonate (0.37 grams, 0.005 moles) and powdered soft glass (200mg). The mixture was stirred and heated at 120-130°C for two hours in a three necked flask fitted with condenser, nitrogen inlet, magnetic stir bar and thermometer. The mixture was allowed to cool to room temperature diluted with water (100ml) and then extracted with methylene chloride (5 x 50ml). The combined organic layers were washed with water (5 x 500ml) and brine solution (50ml) then dried over anhydrous magnesium sulfate. The solvent was then removed and the resulting brown material

subjected to column chromatography on alumina using ethyl acetate/hexane (2:1) as eluent. The tropone 124 was recrystallized from benzene/hexane to give an overall yield of 14.7% at best. Spectroscopic data are given on page 42 and 43.

4,5-(9,10-anthraceno)-1-chloro-1,3,5-cycloheptatriene 138

The general procedure that was followed was that of Tivakornpan-narai.⁷⁸ In an oven dried three necked flask fitted with magnetic stir bar, nitrogen inlet, condenser, thermometer and addition funnel, a stirring solution of the tropone 124 (1.00 grams, 0.00354 moles) and methylene chloride (50ml) was cooled to 0° C. A mixture of oxalyl chloride (0.635 grams, 0.005 moles) and methylene chloride (20ml) was then added to the cooled solution over a twenty minute period. After stirring for an additional twenty minutes at 0° C, the mixture was allowed to warm to room temperature. Stirring was continued for an additional thirty minutes. The solvent was then removed and the residue taken up in tetrahydrofuran (10ml). This solution was cooled to 0° C and lithium aluminum hydride (0.500 grams, 0.0132 moles) was added in one portion and vigorously stirred. The mixture was allowed to warm to room temperature and stirred for an additional twenty minutes. The excess lithium aluminum hydride was destroyed with water (50ml) after which the mixture was extracted with methylene chloride (5 x 25ml). The combined organic layers were and dried over anhydrous magnesium sulfate, the solvent was then removed. The yellow material was recrystallized from petroleum ether to give 0.862 grams (80.5%) of the chloride 138 (major) plus its alkene isomers. Spectral data was

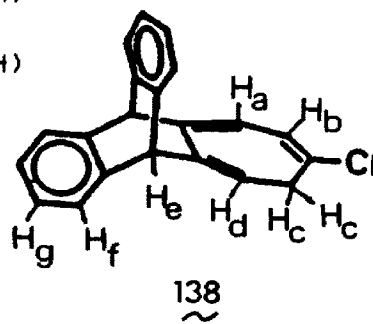
consistent with this molecule.

^1H	4.92 ppm (s, H_a , 2H)
	2.69 ppm (d; $J = 6.56$ Hz, H_c , 2H)
	5.45 ppm (t; $J = 6.56$ Hz, H_d , 1H)
	6.06 ppm (d; $J = 6.78$ Hz, H_e , 1H)
	6.30 ppm (d; $J = 6.78$ Hz, H_b , 1H)
	6.99 - 7.09 ppm (m, H_f , 4H)
	7.23 - 7.35 ppm (m, H_g , 4H)

mp 161-166.5° C

MS calculated: 302.08635

observed: 302.08259

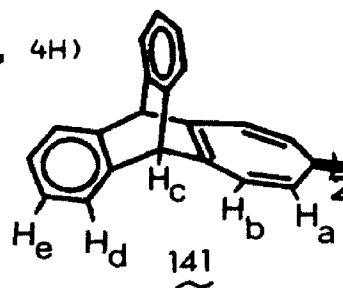


Treatment of the Chlorocycloheptatriene 138 with KOt-Bu

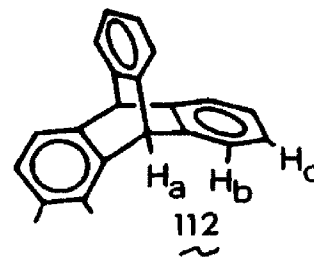
The general procedure followed that of Tivakornpannarai.^{7a} In a three necked flask fitted with a thermometer, condenser, nitrogen inlet and a 90° side arm adapter with small 5ml flask attached, was added dry tetrahydrofuran (30ml) and the chlorocycloheptatriene 138 (0.800 grams, 0.00264 moles). The side arm flask containing the potassium t-butoxide (0.533 grams, 0.00475 moles) was then rotated upward so that all of the solid fell into the chloride solution. The resultant brown solution was stirred at room temperature for an additional ninety minutes. After cooling, water (20ml) was added and then extracted with methylene chloride (3 x 25ml). The organic layers were washed once with water, dried over anhydrous magnesium sulfate, and solvent removed. Column chromatography on alumina and preparative thin layer chromatography

using methylene chloride/ petroleum ether (1/4) as eluent were used to separate and purify the dimer 141 and triptycene 112. Yields of the remaining experiments are presented in Table 3. The instability of the dimer 141 inhibited the acquisition of additional spectroscopic data. The proton NMR is consistent with a symmetrical dimer. Its R_f value and color was also consistent with the diene 111 found from the β -system.^{7e} The spectroscopic data for triptycene 112 was identical with that in the literature.^{74,78,7a}

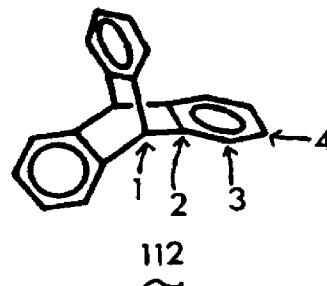
dimer <u>141</u>	^1H	4.82 ppm (s, H_c , 4H)
		5.51 ppm (d; $J=11.4$ Hz, H_b , 4H)
		6.08 ppm (d; $J=11.4$ Hz, H_a , 4H)
		6.90-7.09 ppm (m, H_d , 8H)
		7.11-7.37 ppm (m, H_e , 8H)



triptycene <u>112</u>	^1H	5.41 ppm (s, H_a , 2H)
		6.91-7.05 ppm (m, H_b , 6H)
		7.11-7.37 ppm (m, H_c , 6H)



^{13}C	54.08 ppm (C_1 , d)
	123.54 ppm (C_3 , d)
	125.05 ppm (C_4 , d)
	145.25 ppm (C_2 , s)
<u>mp</u>	251-253° C
<u>MS</u>	calculated: 254.10962
	observed: 254.11218



Tosylhydrazone derivative of the Tropone 139

In a three necked flask fitted with magnetic stir bar nitrogen inlet, condenser, thermometer and addition funnel, a stirring solution of the tropone 124 (1.085 grams, 0.00384 moles) in methylene chloride (20ml) was cooled to 0 C. To this was added a solution of oxalyl chloride (1.08 grams, 0.0085 moles) in methylene chloride (10ml) over a twenty minute period. After stirring for an additional twenty minutes at 0° C, the mixture was allowed to warm to room temperature, and stirring was continued for an additional thirty minutes. The solvent was then removed and the residue taken up in absolute ethanol (25ml). To this solution was added p-toluenesulfonyl hydrazide (0.715 grams, 0.00177 moles) in small portions with vigorous stirring. The mixture was stirred for twelve hours and then concentrated to 15ml and poured with rapid stirring, into a one to one mixture of methylene chloride and saturated aqueous sodium bicarbonate solutions (150ml). The organic layer was separated and the aqueous layer washed once with methylene chloride (25ml). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent removed. Recrystallization of the crude product from absolute ethanol/chloroform gave 0.748 grams (43.2%) of the tosylhydrazone derivative 139. This compound had not been reported previously.

<u>¹H</u>	2.34 ppm (s, H _a , 3H)
	5.35 ppm (s, H _b , 2H)
	6.65 ppm (s, H _c , 1H)
	6.18-6.78 ppm (d, H _d , 2H)
	6.94-7.03 ppm (d, H _e , 2H)

7.06-7.45 ppm (m, H_r, 8H)

7.28 ppm (d, H_g, J= 8.24 Hz, 2H)

7.72 ppm (d, H₁, J= 8.25 Hz, 2H)

mp 213-215.5 C

MS calculated: 450.14036

observed: 450.14101

Sodium salt of the tosylhydrazone derivative 140

The general procedure followed was that of Tivakornpannarai⁷⁸. In a three-necked flask fitted with magnetic stir bar, reflux condenser and nitrogen inlet, a solution of the tropone tosylhydrazone 139 (1.06 grams, 0.00235 moles) and dry THF (30ml) was flushed with nitrogen for thirty minutes. To this was added sodium hydride (0.113 grams of a 50% dispersion in mineral oil; 0.0565 grams, 0.00235 moles), and stirring was continued at room temperature for 45 additional minutes. The resulting precipitate was vacuum filtered and washed with dry THF (4 x 5ml). The purple-red salt 140 (0.633 grams, 57%) was pumped dry by mechanical pumping for ten hours and stored in a refrigerated desiccator, evacuated with N₂ and wrapped in foil until used.

Photolysis of the sodium salt 140

The photolysis apparatus was as follows: A 5 gallon tank with a magnetic stirrer was used as a water bath. A water line was placed in the tank to allow a slow steady stream of water to circulate. The overflow was directed to a sink. Both photolysis reaction vessel and

lamp jacket were emersed in this cooling tank which was kept at 20 C during the reaction by adjusting the flow of water into the tank. The lamp cooling jacket containing the medium pressure mercury lamp was flushed with nitrogen prior to the beginning of an experiment and a constant flow of water around the jacket was maintained. The reaction vessel itself consisted of a three necked 100ml Pyrex 14/20 flask fitted with a mechanical stirrer, nitrogen atmosphere and a thermometer.

The sodium salt 140 (0.51g, 0.00108 moles) and 87 ml of dry THF were placed into the reaction vessel immersed in water kept at 20 C. With vigorous stirring the mixture was irradiated for three hours at which time the reaction mixture was poured into 50ml of water and then extracted with chloroform (4 x 25). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent removed. The residue was then chromatographed through grade 3 alumina eluting with petroleum ether and ethyl acetate, increasing the eluant ethyl acetate percentage by 10% every 150ml. The dimer 141 and triptycene 112 were recovered. Yields are recorded in Table 3.

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