1986

Chemistry of 2-triptycynylmethylene

David C. Pang

The University of Montana

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THE CHEMISTRY OF 2-TRIPTYCENYL METHYLENE

By

David C. Pang

B.S., National Chung-Hsing University, 1973
Presented in Partial Fulfillment of the Requirement
for the Degree of
Master of Science
UNIVERSITY OF MONTANA
1986

Approved by:

[Signatures]

Chairman, Board of Examiners

[Signature]
Dean, Graduate School

Date May 1, 1987

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The synthesis of sodium salt of tosylhydrazone of triptycene 2-carboxaldehyde \textit{68} was reported. The decomposition of \textit{68} was carried out by solution thermolysis, photolysis and vacuum pyrolysis. The resulting products were analyzed. The structures of the alkene dimer (\textit{cis}) \textit{69}, the alkene dimer (\textit{trans}) \textit{70}, triptycene 2-carboxaldehyde \textit{60}, the azine \textit{71}, the insertion products \textit{72} and \textit{76}, the sulfone \textit{73} and the sulfinate \textit{74} were identified and proved. The overall rearrangement scheme of certain constrained cycloheptatetraenylidenes and cycloheptatetraenenes was shown. The carbene \textit{62} was not involved in the carbon atom elimination reaction from constrained allene \textit{55}.

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This research was supported by the Petroleum Research Fund.
I am dedicating this thesis
to my father

Mr. C. M. Pang (May 7, 1924 – February 27, 1986)

May God rest his soul
CHAPTER 1

INTRODUCTION

A. Electronic Structure of Carbenes

The carbene, as one of the most reactive intermediates, has attracted much interest in organic chemistry. Carbenes may be defined as divalent, neutral carbon intermediates. More precisely, the carbene carbon is linked by two covalent bonds and possesses two nonbonding electrons which may have anti-parallel spins (singlet state) \(^1\) or parallel spins (triplet state) \(^2\).

\[
\begin{array}{c}
\text{1} \\
\text{11} \\
\end{array}
\begin{array}{c}
\text{2} \\
\text{1} \\
\end{array}
\]

Generally, the triplet state is more stable than the singlet state of a given carbene but there are exceptions. \(^2,3,4\)

The electrophilicity or nucleophilicity of singlet carbenes depends strongly on the ability of the adjacent groups to withdraw electrons from or supply electrons to the carbene carbon.

B. Generation of Carbenes

There are many ways to generate carbenes. \(^1,5,6,7,8\) The easiest approach is from thermolysis or photolysis of the sodium salt of the tosylhydrazones as illustrated below.
Ketones and aldehydes 3 can be converted into tosylhydrazones 4 with tosylhydrazide. By treating 4 with sodium hydride in tetrahydrofuran (THF), the sodium salt 5 can be obtained in good yield. Decomposition of 5 either thermally or photochemically, will give the corresponding diazocompound 6 which under the reaction conditions can be further decomposed to the carbenes 7.1,8

C. Reactions of Carbenes

The reactivities of the parent carbene, methylene, have been investigated extensively. Therefore, its reactions were used as typical carbene reactions.

1. Insertion Reactions of Carbenes

   a. Insertion into Carbon-hydrogen Bonds

      This is one of the most characteristic reactions of the singlet carbenes.9 The reaction is believed to proceed by a concerted "three-center" mechanism without a detectable intermediate as shown below.10
b. Abstraction Reactions of Triplet Carbenes

The reactions between carbenes and hydrocarbons form, in addition to the products of direct insertions, various compounds which are best accounted for by the radical character of the triplet carbenes.

Triplet carbenes can react with the hydrocarbon to form two free radicals which are responsible for the products formed as shown below.

\[
: \text{CH}_2 + \cdot \text{CH}_3 + \cdot \text{R} \rightarrow \text{R-CH}_3 + \text{CH}_3-\text{CH}_3
\]

2. Reactions with Multiple Bonds

a. Reactions with Olefins

Methylene adds easily to carbon-carbon double bonds to form cyclopropanes as shown below.\(^\text{11}\)

\[
: \text{CH}_2 + \overset{\text{C}}{\text{C}}=\text{C} \rightarrow \text{C-} \overset{\text{C}}{\text{C}} \overset{\text{H}_2}{\text{C}}
\]
Addition reactions of singlet carbenes are stereospecific. \textit{cis} additions. \textit{cis}-1,2-Disubstituted cyclopropane products were obtained from \textit{cis}-olefins and \textit{trans}-1,2-disubstituted cyclopropane products from \textit{trans}-olefins. The addition process will be non-stereospecific whenever a carbene reacts in its triplet state.

In the gas phase, the newly formed singlet carbene may collide many times and may be converted into the triplet state before it reacts with olefins. The mechanism for the addition reactions of singlet carbenes and triplet carbenes is shown below. The stereospecificity has been used to reflect the singlet state of the reacting carbene (not necessary its ground state).\textsuperscript{12}
b. Reactions with Dienes

The reaction between methylene and butadiene appeared to involve 1,2- rather than 1,4-addition and vinylcyclopropane was the major product as shown below.\(^\text{13}\)

\[
\begin{align*}
\text{CH}_2 & \quad \overset{\text{X}}{\text{:CH}} \quad \overset{\text{Y}}{\text{HC}} \\
\end{align*}
\]

\[\text{c. Reactions with Acetylenes}\]

The photolysis of diazomethane in the presence of acetylene gave allene and propyne instead of the expected cyclopene.

The formation of allene-1,1,-d\(_2\) (8) from acetylene-1,2-d\(_2\) (9) indicated that the allene arised by way of a cyclopropene intermediate as shown below.\(^\text{14}\)

\[
\begin{align*}
\text{D}\quad \text{C} & \equiv \text{C} \quad \text{D} \quad + \quad \text{:CH}_2 \quad \rightarrow \quad \left[ \begin{array}{c}
\text{D} \quad \text{C} \equiv \text{C} \quad \text{D} \\
\text{C} \\
\text{H}_2
\end{array} \right] \quad \rightarrow \quad \text{CH}_2\text{C} = \text{CD}_2 \\
& \quad + \quad \frac{8}{9} \\
\text{CH}_2\text{D} \equiv \text{C} & \equiv \text{C} \quad \text{D} \\
\end{align*}
\]

Trapping of the cyclopropene 10 was impossible even under favorable conditions of collisional deactivation. No spectral evidence for the presence of either cyclopropene or methyl-acetylene was obtained after photolysis of solid argon-acetylene-diazomethane deposits at 4 K. Allene was the major product.
d. Reactions with Aromatic Compounds

The photolysis of diazomethane in benzene solution gave 32% cycloheptatriene and 9% toluene.\textsuperscript{16,17} Cycloheptatriene had been obtained from the catalyzed reaction of diazomethane with benzene. Cuprous chloride, cupric chloride and cuprous bromide were the most efficient catalysts among 18 metals and metal salts employed; but these reactions probably proceed through a copper carbenoid mechanism.\textsuperscript{18}

3. Reactions with Molecular Oxygen

Molecular oxygen, as a ground state triplet, is frequently used as a radical scavenger.\textsuperscript{19} Its behavior toward carbenes provided a chemical method in evaluating the spin state of the carbenes at the moment of reaction. For example, the presence of oxygen in the photolysis of diazomethane left the characteristic insertion pattern of methylene unchanged, but eliminated the minor radical abstraction reaction. The sensitivity of methylene toward oxygen increased in the presence of a large excess of inert gas. This effect is attributed to the singlet-triplet transition of methylene brought about by many collisions with inert gas molecules. The stereospecificity of the addition of methylene to substituted alkenes increased if oxygen was allowed in the reaction media. This clearly indicated that the non-stereospecific addition of carbenes to olefins, originating from a radical-type character of the carbenes, was prohibited from taking place due to the existence of ground state triplet oxygen molecules.
D. Structure of Allenes

Allenes are compounds which contain C=C=C functional groups. The central carbon atom has sp-hybridization with the remaining two p-orbitals perpendicular to each other. The adjacent two carbon atoms have sp²-hybridization with one p-orbital remaining for each carbon. Each of these p-orbitals will overlap with one of the two p-orbitals from the central carbon atom. Therefore, the C-C-C angle is 180° and the two H-C-H planes are orthogonal. Because of their unique structural features, some allenes are chiral. It was this chirality which helped chemists in solving many structure problems.²⁰

E. Generation of Allenes

Allenes may be prepared by dehydrohalogenation of vinyl halides. For example, treatment of 1-chlorocycloheptene (11) with alcoholic KOH gave 1,2-cycloheptadiene (12).²¹ The intermediate dimerized immediately. The overall reaction is shown below.
F. Completely Conjugated, Cyclic Carbenes and Allenes

For the past twenty years, carbene chemists have focused on a series of carbocyclic, completely conjugated carbenes because of their inherent special structural features. The electrophilicity or nucleophilicity of a carbene depends strongly on the adjacent groups to withdraw electrons from or supply electrons to the carbene carbon. In the series of carbocyclic, completely conjugated carbenes, the electronic character of the carbene carbons can be altered by incorporating the empty p-orbital or the non-bonding electron pair on the carbene carbon of the singlet carbenes into the center aromatic system. For example, if the non-bonding electron pair is involved in the aromatic system, the resulting carbene should be electrophilic; if the empty p-orbital is an integral part of an aromatic system, the resulting carbene might be nucleophilic.

1. Cyclopropenylidene (13) and Cyclopropadiene (14)

\[ 
\begin{array}{c}
\text{13} \\
\text{14}
\end{array}
\]

The diphenyl derivative of 13 (17) was generated by base-induced \( a \)-elimination of the N,N-dimethylcarbamic acid from the carbamate 16 which was produced \textit{in situ} from the nitrosourea 15. The intermediate 17 showed the anticipated low electrophilicity (no tendency to react with typical alkenes) and apparent nucleophilicity (reactions with electron-deficient double bonds).
The generation of cyclopropenylidene itself (13) was achieved recently by flash thermolysis of a highly constrained compound 18. Its matrix isolation infrared spectrum was recorded. The lack of an electron spin resonance (ESR) spectrum of the matrix-isolated product ruled against the existence of a triplet species. No spectral evidence indicated the existence of 14.

2. Cyclopentadienylidene (19) and 1,2,4-Cyclopentatriene (20)

When diazocyclopentadiene was photolyzed at 4 or 77 K in a solid matrix, a triplet ESR spectrum was recorded which was attributed to the ground state of 19. When diazocyclopentadiene was photolyzed at room temperature, it showed typical singlet carbene chemistry. The derivatives of cyclopentadienylidene also showed
triplet carbene chemistry; however, the triplet carbene chemistry was also shown in solution.

Apparently, the time required for the singlet intermediates to react with the surrounding molecules must be comparable to the time required for the singlet intermediates to undergo intersystem crossing to the triplets. In MNDO calculations, two energy minima were found for planar singlet \( 19 \). These corresponded to \( \sigma^2 \) and \( \pi^2 \) carbenes, and surprisingly, the "anti-aromatic singlet" \( \sigma^2 \) was more stable than "aromatic" singlet \( \pi^2 \). It was found that non-planar anti-aromatic singlet \( \sigma^2 \) with \( C_s \) symmetry was the lowest energy \( 19 \), and the planar carbenes (both aromatic and anti-aromatic) were transition states and not even energy minima.

3. Cycloheptatrienyldiene (21) and 1,2,4,6-Cycloheptatetraene (22)

![Structures](image)

The \( C_7H_6 \) intermediate was readily available by thermolysis or photolysis of the sodium salt of tropone tosylhydrazone. More detailed description of the \( C_7H_6 \) chemistry will be discussed in Carbene Rearrangements and constrained cycloheptatrienyldienes and cycloheptatetraenes.
4. Cyclononatetraenylidene (23) and Cyclononapentaene (24)

In an attempt to generate 24, Waali and Allison reported the isolation of indene, and its formation was suggested as electrocyclic ring closure followed by hydrogen migration.\(^{33}\)

When lithium cyclononatetraenide (25) was allowed to react with 4-nitrobenzenesulfonyl azide, 9,9'-bisbicyclo[4.3.0]-cyclononatriene 26 was isolated in 33% yield.\(^{34}\) A possible reaction mechanism is shown below.

Recently, isotopic labelling studies showed that the symmetrical cyclononatetraenyl radical 27 was produced directly from 25. The carbene 23 was not involved in this reaction.\(^{35}\)
G. Carbene-Allene Rearrangement

Owing to the extra stability from aromaticity, it was originally believed that 21 might be stable enough to be isolated at liquid nitrogen temperature. W. M. Jones and his coworkers set out with the task to isolate 21 at liquid nitrogen temperature. When sodium salt of tropone tosylhydrazone (28) was pyrolyzed at 250°C under high vacuum, the diazo-compound 29 would be formed.22 Under the same reaction conditions, 29 would be further decomposed to give intermediate 22. A trap immersed in liquid nitrogen was connected to the end of the pyrolysis tube. At the end of the experiment a light colored solid was formed which when warmed up to -100°C changed to the dark-brown solid, heptafulvalene (30). The immediate precursor to the formation of 30 must be the light colored solid which they thought was 21. Encouraged by this preliminary result, it was thought that this might be a standard way to isolate many types of carbenes. In another experiment, they attempted to isolate phenylcarbene 31 at liquid nitrogen temperature. When the sodium salt of benzaldehyde tosylhydrazone (32) was pyrolyzed with the same procedures described above, 30 was found to be the only product.

This observation opened up a new chapter in carbene chemistry. Singlet carbenes generated in inert media stabilize themselves by undergoing either intramolecular rearrangement to give valence-satisfied products or intersystem crossing to give the lower energy triplets. Formation of 30 from pyrolysis of 32 in the gas phase strongly suggested that a ring-expansion rearrangement took place. Crow and Wentrup36 predicted, based on their results from the intraconversion of 2-pyridyl-
carbenes (33) and phenyl nitrenes (34) and N-scrambling in 2-pyridyl-
nitrenes, that 22 and 31 could be transformed into each other with the
ring contraction favored over ring expansion.

Inspired by the results from W. M. Jones and C. Wentrup, M. Jones
showed the interconversion of substituted phenylcarbenes and their fur-
ther rearrangement to methylphenylcarbene. This result clearly suggested that the rearrangement of 22 to 31 is reversible.

The interconversion of substituted phenylcarbenes was demonstrated by constructing molecules incorporating a carbene trap at a remote position within the same molecule. The carbene can only react with the internal trap if rearrangements occur. The internal trap chosen was a methyl group. It was anticipated that should interconversion of the tolylcarbenes occur, products from o-tolylcarbene (35) would be isolated no matter which of the isomers was used as the starting material as shown below.

\[
\begin{align*}
&\text{R = CH}_3 \\
&\text{37} \\
&\text{38}
\end{align*}
\]

It was expected that 35 would be trapped as benzocyclobutene (37) and that further rearrangement to methylphenylcarbene (36) would be signaled by the appearance of styrene (38).

The tolylcarbenes were generated in the gas phase by evaporating the corresponding diazo compounds at 0.5 torr through a 420°C furnace into a trap cooled in a dry ice-acetone slurry. o-Tolyl diazomethane (39) gave both 37 and 38 in a 2.8 ratio. Remarkably, m-tolyl diazo-
methane (40) and p-tolyldiazomethane (41) also gave 37 and 38 in a 0.8 ratio as shown below.

In order to account for the formation of the benzocyclobutene and styrene a reaction mechanism was proposed based on the known cyclization of vinylmethylene 42 to cyclopropene 43 and its reversal.38,39

(Scheme 1) Recently, Wentrup reported that phenyl carbenes may sometimes rearrange directly to the allene without the bicyclic intermediates.40 Therefore, a revised mechanism was shown in Scheme 2.
Scheme 1. Rearrangement scheme via bicycloheptatrienes.

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Scheme 2. Rearrangement scheme without bicycloheptatrienes.
Jones and his coworkers then took a second look at the mystery, then 57 years old, of how diphenylmethylene is thermally converted into fluorene. Staudinger and Endle had obtained fluorene from the gas phase pyrolysis of diphenylketene (44) in 1913 and suggested that diphenylmethylene was an intermediate and underwent H-migration to give fluorene (45). Rice and Michaelson obtained the same result from diphenyldiazomethane (46) as shown below.
It was pointed out by W. M. Jones that should H-migration be responsible for the formation of fluorene, then, one should observe the formation of 3-methylfluorene (47) from p-tolylphenyldiazomethane (48) while a multiple carbene-carbene rearrangement, proposed by Baron, Jones and Gaspar, would yield 2-methylfluorene (49) as shown below.
As a matter of fact, when p-tolylphenyldiazo methane was pyrolyzed at 350-375°C, only 47 was obtained and no detectable 42 was found. This observation strongly support the mechanism suggested by Baron, Jones and Gaspar (Scheme 1 and 2). Further evidence proving the validity of this mechanism came from the experiment by Hedaya and Kent. They carried out a 13C labelling experiment. p-Tolylaldehyde was labeled at the aldehydic carbon with 13C, and was converted to the sodium salt of tosylhydrazone by the usual procedures. The salt was pyrolyzed at 700°C in a low-pressure short contact time flow system, with no loss of label. Benzocyclobutene and styrene was formed in a 0.83:1 ratio. The position of the label in the benzocyclobutene was unequivocally established by proton NMR to be [4-13C]benzocyclobutene. The styrene was examined by 60- and 200-MHz proton NMR and 22.63-MHz 13C NMR and the result showed the label at the para carbon of the styrene (Scheme 3). This was exactly the results predicted by the Baron, Jones and Gaspar mechanism.

H. Constrained Cycloheptatrienyldienes and Cycloheptatetraenes

Untch discovered that the dehydrohalogenation of 1-, 2- or 3-chlorocycloheptatriene (50-52) with strong base gave an intermediate that showed the same properties as those derived from the standard carbene precursors.
Scheme 3. $^{13}\text{C}$ experiment results.

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This observation introduced an interesting possibility that the common intermediate from two different sources might have an allene structure, e.g. $22$, or possibly might best represent as an interconverting mixture of the isomers. Both INDO$^{45}$ and MNDO$^{46}$ calculations indicated that the allene is more stable than the carbene. The MNDO calculations also indicated that the planar singlet is not even an energy minimum but a transition state for the interconversion of the nonplanar, chiral $22$ and its enantiomer.$^{46}$
Therefore, all the chemistry attributed from a carbene might actually originate from an allene. By using the chirality of cycloheptatrienylidene, Jones\textsuperscript{47} also provided experimental evidence indicating the existence of the allene\textsuperscript{22}. Chapman\textsuperscript{48} and his coworkers also observed the IR spectrum of the allene\textsuperscript{22}.

Based on the nonplanar structure of the allene, if the bonds extruding from the carbons of allene could be constrained to the same plane, there is a good chance of observing pure carbene chemistry. In more general terms, if constraints were applied to C3-C4, C5-C6 and C7-C1 in allene, the stability of the allene should decrease and the chance of observing a planar carbene chemistry should increase.

\begin{center}
\includegraphics[width=0.3\textwidth]{structure.png}
\end{center}

The benzoannulated cycloheptatrienylidene\textsuperscript{53,49} has been generated and found to be ground state triplets, but this is probably best viewed as a constrained versions of diphenylmethylen\textsuperscript{54}e (54) also known as ground state triplet.

\begin{center}
\includegraphics[width=0.5\textwidth]{structures.png}
\end{center}

It is the current goal of this laboratory to synthesize the constrained seven-membered cyclic, completely conjugated carbenes or allenes without perturbing the electronic configuration of the central seven-membered ring via resonance.

23

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Recently, a partially constrained seven-membered cyclic intermediate, 4,5-(9,10-anthraceno)-1,2,4,6-cycloheptatetraene (55), was formed by thermolysis of its sodium salt of tosylhydrazone in diglyme at 125°C or by the reaction of its chloride with KOt-Bu at room temperature.

Both pathways gave triptycene (56) in 37% and 12% yield, respectively. Although there were reports showing elimination of carbon atoms from norbornadienyldiene (57) and quadricyclanylidene (58), elimination of a carbon atom in solution under such mild conditions is very rare.

It was later found that the oxygen containing solvent (THF) was actively involved in accommodating the carbon elimination reaction. Also, if air is in the reaction vessel, both triptyceny1 1-carboxaldehyde (59) and triptyceny1 2-carboxaldehyde (60) were observed (Scheme 4).
Scheme 4. Possible mechanism for carbon elimination reaction.
The presence of triptycene clearly indicated that a carbon atom was somehow eliminated. The presence of 59 and 60 indicated that the originally formed intermediates was rearranged to 1-triptycenyl methylene (61) and 2-triptycenyl methylene (62) which then reacted with molecular oxygen to give 59 and 60. It is the goal of this thesis to synthesize 62 and to determine its role in the reactions shown in Scheme 4.
CHAPTER 2

RESULTS AND DISCUSSION

A. Synthesis

\[ \text{Acyl-Cl, AlCl}_3 \]

1. Acyl-Cl, AlCl₃

2. H⁺

\[ \text{Br}_2, \text{NaOH} \]

1. \( \text{Br}_2, \text{NaOH} \)

2. H⁺

\[ \text{LiAlH(Ot-Bu)}_3 \]

SOCI₂

\[ \text{LiAlH(Ot-Bu)}_3 \]

\[ \text{NaH} \]

\[ \text{Na}^+ \text{NNTs} \]

\[ \text{Na}^+ \text{NNTs} \]

\[ \text{Cl} \]

\[ \text{Cl} \]

\[ \text{Cl} \]

\[ \text{Cl} \]
1. Preparation of Triptycene (56)\textsuperscript{59}

Commercially available 2-aminobenzoic acid (63) reacted with isoamyl nitrite at elevated temperature to form benzyne which, under the reaction conditions, underwent a 2 + 4 cycloaddition with anthracene to give 56.

2. Preparation of Triptycene 2-carboxaldehyde (60)\textsuperscript{54,55,56,57}

There are two methods reported in preparation of 60. The first method involved using readily available reagents in the laboratory. It was a multi-step reaction. The second method was a single step reaction.

a. Method I: Preparation of 60

Triptycene 56 reacted with acetyl chloride, in the presence of anhydrous aluminum chloride, at -20°C in tetrachloroethane. Acid hydrolysis gave the 2-acetyltriptycene (64).\textsuperscript{54} Oxidative cleavage of 64 using sodium hypobromite gave 65.\textsuperscript{55} The triptycene 2-carboxylic acid 65 was converted to the acylchloride 66 by the use of thionyl chloride. Finally, a selective reducing agent, lithium tri-t-butoxyaluminohydride\textsuperscript{56}, was used to reduce 66 to 60.

It was a tedious, four step process and the overall yield of 60 was quite low. Therefore, direct formylation of 56 (Method II) was adopted as the standard method for generation
of \textit{60}.

b. Method II: Preparation of \textit{60}

In this process, \textit{56} was reacted with dichloromethyl methyl ether in the presence of anhydrous aluminum chloride. After acid hydrolysis, \textit{60} was isolated.\textsuperscript{57} This reported method for the synthesis of \textit{60} from \textit{56} was attempted several times with poor yield (less than 10\%). A modified approach by reversing the sequence of addition of dichloromethyl methyl ether and anhydrous aluminum chloride improved the yield to 37\%.

3. Preparation of Tosylhydrazone of Triptycene 2-carboxaldehyde (\textit{67})

The aldehyde \textit{60} was converted to its tosylhydrazone \textit{67} by the use of tosylhydrazide in tetrahydrofuran (THF), (tosyl = p-toluenesulfonyl).

4. Preparation of Sodium Salt of Tosylhydrazone of Triptycene 2-carboxaldehyde (\textit{68})

The acidic proton of the tosylhydrazone \textit{67} was removed by reacting \textit{67} with sodium hydride in THF at room temperature.
B. The Solution Thermolysis of Sodium Salt (68)

\[ \text{Na}^+ \rightarrow 125^\circ \text{C diglyme} \]

\[ \text{68} \rightarrow \text{69} \]

\[ \text{68} \rightarrow \text{70} \]

\[ \text{68} \rightarrow \text{71} \]

\[ \text{68} \rightarrow \text{60} \]

\[ \text{68} \rightarrow \text{72} \]

\[ \text{68} \rightarrow \text{73} \]

\[ \text{68} \rightarrow \text{74} \]

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Thermolysis of the sodium salt \textsuperscript{68} was carried out at 125-130°C in diglyme. Preparative thin layer chromatography (PTLC) resulted in seven compounds which were identified by their high resolution nuclear magnetic resonance (NMR) spectra and high resolution mass spectra (MS). \textsuperscript{73} and \textsuperscript{74} were not identified on the basis of their high resolution MS.

1. The Alkene Dimer (cis) \textsuperscript{69}

Two groups of doublet of doublets at 7.02 and 7.38 ppm were assigned to the aromatic protons (H\textsubscript{A}, H\textsubscript{A'}, H\textsubscript{B}, H\textsubscript{B'}) with the AA'BB' pattern (J\textsubscript{A,A'} = 5.3, J\textsubscript{A,B} = 3.4). The two bridge head protons H\textsubscript{C} and H\textsubscript{C'} gave two singlets at 5.36 and 5.18 ppm. The broad singlet at 7.28 ppm was assigned to the isolated proton (H\textsubscript{D}). The broadening of this singlet was caused by the long-range coupling from the nearby protons. H\textsubscript{E} was found at 6.88 ppm as a doublet of doublets (J\textsubscript{E,F} = 7.6, J\textsubscript{E,D} = 1.5), and a doublet at 7.20 ppm came from H\textsubscript{F} proton (J\textsubscript{F,E} = 7.6). A plane of symmetry exists in this molecule, therefore, the alkene protons (H\textsubscript{G}) appeared as singlet at 6.36 ppm.
2. The Alkene Dimer (trans) 70

\[
\begin{align*}
H_A, H_A', H_B \text{ and } H_B' \text{ protons have AA'BB' pattern which were easily recognized at } 7.03 \text{ and } 7.36 \text{ ppm (} J_{A,A'} = 5.3, J_{A,B} = 3.4). \text{ The bridge head protons, } H_C \text{ and } H_C', \text{ had chemical shifts at 5.38 and 5.40. The difference of these two chemical shifts, } 0.02 \text{ ppm, is smaller than the difference of those in } 69, \text{ which is } 0.18 \text{ ppm. Also found was a broad singlet at } 7.54 \text{ ppm which was assigned to } H_O \text{ proton. A doublet of doublets at } 7.03 \text{ ppm assigned to proton } H_E (J_{E,F} = 7.6, J_{E,D} = 1.5) \text{ and a doublet at } 7.31 \text{ ppm came from } H_F (J_{F,E} = 7.6). \text{ An axis of symmetry exists in this molecule and the two alkene protons, } H_G, \text{ are chemically equivalent with a chemical shift at } 6.91 \text{ ppm.}
\end{align*}
\]

3. The Aldehyde 60

\[
\begin{align*}
32
\end{align*}
\]

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Oxygen molecule, a ground state triplet, has been used as an effective scavenger for triplet carbenes.\textsuperscript{19} It was believed that the thermally produced carbene was first formed as a less stable singlet species which, then, underwent intersystem crossing by colliding with the solvent molecules to give the stable triplet carbenes. It was this triplet carbene which reacted with the molecular oxygen to form the aldehyde 60.

The aromatic protons with AA'BB' pattern were located at 6.92 and 7.41 ppm (J\textsubscript{A,A'} = 5.3, J\textsubscript{A,B} = 3.4). The bridge head protons appeared as two closely located singlets at 5.51 and 5.52 ppm. A broad singlet at 7.89 ppm was assigned to H\textsubscript{D} proton. Owing to the deshielding effect of the aldehyde functionality, the H\textsubscript{E} proton was shifted downfield and merged with the H\textsubscript{F} proton signal at 7.53 ppm. The unique aldehyde proton, H\textsubscript{G}, appeared as a sharp singlet at 9.89 ppm.

4. The Azine 71

![Diagram](image)

Protons AA'BB' were located at 6.97 and 7.36 ppm as two groups of doublet of doublets (J\textsubscript{A,A'} = 5.3, J\textsubscript{A,B} = 3.4). Bridge head protons H\textsubscript{C} and H\textsubscript{C'} gave two sharp singlets at 5.44 and 5.47 ppm. A broad
singlet at 7.93 ppm was assigned to H₀ proton. A doublet of doublets at 7.35 ppm, which was partially merged with AA'BB' protons at 7.36 ppm was assigned to Hₜ. A doublet at 7.41 ppm was assigned to Hₜ proton (J = 7.6). The azine protons Hₒ appeared as a sharp singlet at 8.54 ppm which is typical for azine. This result was expected because of the strong deshielding effect from the neighboring nitrogen atom and because this is where all azine H's are found.

5. The Diglyme Insertion Product 72

\[ \text{The AA'BB' aromatic protons were assigned with chemical shifts at 6.98 and 7.36 ppm (Jₐ,ₐ' = 5.3, Jₐ,ₚ = 3.4). Two bridge head protons, Hₜ and Hₜ', were located 5.37 and 5.38 ppm. The H₀ proton, appearing at 7.24 ppm, was not deshielded like the one in aldehyde 60 or azine 71. Other results found were that the Hₜ proton appeared at 6.84 ppm as a broad doublet (Jₜ,ₚ = 7.6), the Hₜ proton was recognized as a doublet at 7.26 (Jₜ,ₚ = 7.6), and the two methoxy groups on a diglyme molecule showed two singlets at 3.18 and 3.30 ppm. The benzylic protons and the other protons from the diglyme molecule resulted in a complex signal between 3.26-3.60 ppm.} \]
6. The Sulfone 73

The aromatic protons with AA'BB' pattern were assigned at 7.00 and 7.37 ppm \((J_{A,A'} = 5.3, J_{A,B} = 3.4)\). Bridge head protons \(H_c\) and \(H_{c'}\) had different chemical shifts at 5.26 and 5.39 ppm. A broad singlet at 7.28 ppm was contributed by \(H_d\) proton. \(H_e\) proton had recognizable doublet of doublets at 6.77 ppm \((J_{E,F} = 7.6, J_{E,D} = 1.5)\). A doublet at 7.32 ppm was assigned to \(H_f\) \((J = 7.6)\). The benzylic protons \(H_{a_5}\) had the same chemical shift and showed as a sharp singlet at 4.17 ppm. The aromatic protons on the tolyl group were located at 7.03 and 7.35 ppm with the downfield value assigned to the protons ortho to sulfone functionality. The methyl protons were found as a sharp singlet at 2.39 ppm.

7. The Sulfinate 74
Aromatic protons AA'BB' still remained at similar regions as in previously reported compounds, 6.96 and 7.35 ppm. Bridge head protons, H_c and H_c', were located at 5.39 and 5.40 ppm as two sharp singlets. Also found was a broad singlet at 7.29 ppm assigned to the H_d proton. A broad doublet at 6.85 ppm originated from the H_e proton (J = 7.6). H_f proton had a chemical shift at 7.30 ppm as a doublet (J = 7.6). The two distinct doublets at 4.91 and 4.44 ppm were assigned to the benzylic protons, H_g and H_g', with germinal coupling constant of 11.0 Hz.

In sulfone 7, even though sulfur bonded tetrahedrally to four neighboring groups, no chirality existed in sulfone 7 since two of the groups were oxygen atoms. It has been possible to make the chiral sulfones by substituting one of the two oxygen atoms in sulfone 7 by oxygen. 56 The achiral character of sulfone 7 makes the benzylic protons in 7 chemical shift equivalent. It was shown clearly by their 1H NMR spectrum.

In the case of sulfinate 7, the sulfur atom was pyramidal bonded to three different groups; the unshared pair of electrons was treated as the fourth group which was different from those three groups. Therefore, the sulfinate 7 is a chiral compound. The chirality on the sulfur atom causes the benzylic protons to have different chemical shifts which also was shown by their NMR spectrum.
C. Mechanisms of Product Formation

The proposed mechanism for the formation of the alkene dimer (cis or trans) (69 and 70) is shown below.
On thermolysis, the sodium salt of the tosylhydrazone decomposed to give the corresponding diazocompound which was further decomposed to form the carbene. Electrophilic reaction of the carbene to the diazocompound formed the dimer precursor which then lost a molecule of nitrogen to give the dimer. Steric repulsion should favor the formation of the trans dimer.

The formation of aldehyde was the result of the reaction between triplet carbene and molecular oxygen. The reaction mechanism still remained to be found.

Two possible mechanisms can be used to explain the formation of azine. First, by dimerization of the diazocompound and second, by reaction of the carbene with the diazocompound.

First mechanism:
In the first mechanism, dimerization of 75 followed by elimination of one molecule of nitrogen gave the azine 71.

Second mechanism:

In the second mechanism, owing to the electrophilicity of the carbene 62, it can be readily attacked by 75 to give the azine 71. The actual reaction mechanism still remained as an open question.

Insertion reactions are typical reactions for singlet carbenes. It was believed that the insertion reaction was a concerted reaction.

Sulfone 73 and sulfinate 74 probably had similar origins. In the thermolysis reaction, sodium 4-toluene sulfinate, is the by-product. Three resonance structures can be drawn for this product. The arylcarbene 62 is a good electrophile which can react with the sodium 4-toluene sulfone to form an anionic species. During work-up the resulting anionic species was protonated to give the sulfone 73 and sulfinate 74 (Scheme 5).
Scheme 5. Formation of Sulfone 73 and Sulfinate 74

\[
\begin{align*}
\text{S} & \quad \text{O} \\
79 & \quad \text{R} & \quad \text{O} & \quad 80 \\
79=81 & \\
\end{align*}
\]

\[
\begin{align*}
62 & + 80 \rightarrow 78 \\
81 & \\
73 & \\
74 & \\
\end{align*}
\]

\[
\begin{align*}
\text{R} &= \text{CH}_3
\end{align*}
\]

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D. The Photolysis of Sodium Salt 68

\[ \text{Chemical Structures} \]

68 \xrightarrow{h\nu, \text{THF}} 71

41

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The photolysis of the sodium salt 68 was carried out in THF in an ice bath. The resulting products were isolated by PTLC and NO TRIPTYCENE was found. The result also showed the existence of alkene dimer (cis) 69, alkene dimer (trans) 70, aldehyde 60, azine 71 and insertion product 76. No 4-toluene sulfonyl 73 and 4-toluene sulfinic 74 were observed.

The insertion product 76 has the following structure.

Aromatic protons AA'BB' were located at 6.98 and 7.36 ppm as two sets of doublet of doublets (J\(\alpha,\alpha'\) = 5.3, J\(\alpha,\beta\) = 3.4). Two bridge head protons, H\(_c\) and H\(_c'\), gave two singlets at 5.38 and 5.37 ppm. A broad singlet at 7.25 ppm was assigned to H\(_d\) proton. A doublet of doublets at 6.81 ppm originated from H\(_e\) proton (J\(\varepsilon,\varphi\) = 7.6, J\(\varepsilon,\delta\) = 1.5). Proton H\(_f\) gave a doublet at 7.27 ppm (J = 7.6). Two groups of doublet of doublets at 2.81 and 2.63 ppm were assigned to the benzylic protons, H\(_g\) and H\(_g'\) (J\(g,\alpha'\) = 11.0, J\(g,\alpha\) = 8.2). Proton H\(_i\) gave a multiplet at 3.70 ppm. Proton H\(_j\) and H\(_j'\) also appeared as two multiplets at 3.84 and 3.96 ppm. The remaining protons H\(_k\), H\(_k'\), H\(_l\) and H\(_l'\) gave a multiplet at 1.82 ppm.
E. The Vacuum Pyrolysis of Sodium Salt

\[ \text{68} \xrightarrow{350 \text{ or } 450^\circ\text{C}} \text{Vacuum} \]

\[ \text{60} \]

\[ \text{77} \]
The pyrolysis experiment was carried out using the equipment shown in the Experimental Section. Thermolysis was defined as a thermo decomposition process carried out in a high boiling point solvent at atmospheric pressure. Pyrolysis was defined as a thermo decomposition process carried out without the use of a solvent and under high vacuum. This process usually employed a higher temperature than thermolysis.

Two pyrolysis temperatures were used, one at 450°C and the other at 350°C. No distinguishable difference on the yield of the products was observed. The results from pyrolysis indicated that this process was very destructive. The crude product accounted for only 10% of the overall yield. The isolated compounds were alkene dimer (cis) 69, alkene dimer (trans) 70, aldehyde 60 and anthracene 77. Again NO TRIPTYCENE was observed. The appearance of the anthracene is a very interesting observation. Its formation is the result of a retro Diels-Alder reaction.
CHAPTER 3

CONCLUSION

The results from these experiments clearly indicated that NO TRIP-TYCENE was formed from 62. Since no triptycene was formed, it implied that arylcarbene 62 did not undergo the ring-expansion reaction to form the allene 55. If ring-expansion reaction had occurred, based on the previous report from this lab, the formation of triptycene should have been observed. Referring to the rearrangement Scheme 4, the arylcarbene 62 did not undergo direct carbon elimination reaction to form triptycene.

The formation of the alkene dimers (cis and trans), an azine, the aldehyde and insertion products were typical results in line with the results from the decomposition of the sodium salt of tosylhydrazone of benzyl aldehyde. 52 The formation of sulfone 73 and sulfinate 74 was not observed in the thermolysis of similar compound. 53 It was possible that the thermolysis by-product, sodium p-toluene sulfinate, reacted with the highly reactive arylcarbene 62 followed by protonation during work-up to give the sulfinate 74.

The formation of sulfone 73 can be described by the reaction between arylcarbene 62 and the resonance structure 80 to form 78. Protonation of 78 during work-up gave the sulfone 73 as shown in Scheme 5.

The formation of anthracene in the gas phase pyrolysis of 68 probably came from a retro Diels-Alder reaction, which is thermally allowed according to the frontier orbital theory. 54 At high temperature, the reverse reaction is thermally possible and anthracene was observed.
Scheme 6. 270 $^1$H NMR Spectrum of Sulfone 73
Scheme 7. 270 $^1$H NMR Spectrum of Sulfinate 74
A. General

Proton nuclear magnetic resonance (NMR) spectra were produced on Bruker HX-270 spectrometer at 270 MHz. Chemical shifts were reported as ppm units downfield from tetramethylsilane (TMS). NMR solvent was CDCl$_3$ unless otherwise specified. Mass spectra (MS) were obtained from a VG Instrument 7070-HF (Chemistry Department, Montana State University, Bozeman, Montana). Photolyses were carried out with a Hanovia 450-W medium pressure mercury lamp with a Pyrex vessel in an ice bath. The pyrolysis column was constructed with a two foot long Vycor tube 1" wrapped with heating wire.

Material: Commercially available reagents were used as obtained with the following exceptions. Tetrahydrofuran was distilled over benzophenone ketyl under dry nitrogen atmosphere and stored under nitrogen over 4 Å molecular sieves. Preparative thin layer chromatography (PTLC) solvents were distilled. Column chromatography was performed using Merck silica gel (60-200 mesh). PTLC plates were prepared by using EM reagent silica gel 60 PF-254 and 366. Components were detected by their quenching of fluorescence under ultraviolet light at 254 or 366 nm.
B. The Synthesis of Triptycene

Anthracene (198.0 g, 90-95%, 1.0 mole) was mixed with 2.5 L methylene chloride in a 5 L three necked round bottom flask equipped with a reflux condenser, a 250 mL addition funnel and a stir bar. Isoamyl-nitrile (145.0 g, 1.2 mole) was added and the whole mixture was brought up to reflux. While refluxing, anthranilic acid (150.0 g, 1.1 mole, dissolved in 600 mL THF) was added in a 3 h period. Refluxed for 18 h, and an aliquot of solution withdrawn, checked with NMR, about 1/2 of the anthracene still remained. Cooled to room temperature, isoamyl nitrile 145.0 g more was charged to the 5 L round bottom flask and system brought to reflux and anthranilic acid 150 g in 400 mL THF was added in a 3 h period. Refluxed for 18 h, NMR indicated about 1/3 anthracene left. Cooled in ice-bath and flaky crystal formed. Filtered with a 600 mL sintered glass funnel. The crystal was un-reacted anthracene. The filtrate collected, solvents removed by rotary evaporator. The residue dissolved in 500 mL methylene chloride, heated to reflux, until all solid dissolved. Cooled in an ice-bath, more anthracene precipitated out. Repeated the same procedure one more time. Collected the filtrate, solvent removed by rotary evaporator and the residue recrystallized from ethanol. The NMR showed bridge-headed protons at 5.41 ppm, 2 multiplets at 6.96 and 7.37 ppm. The recrystallized material was dried with high vacuum overnight. Weight 148.75 g, 59% yield, m.p. 250-252°C (lit. m.p. 250-251°C).

NMR (90 MHz, CDCl₃): 5.40 (s, 2H, bridge-head)
6.95 (dd, 4H, aromatic, AA'BB')
7.36 (dd, 4H, aromatic, AA'BB')
C. The Synthesis of Triptycene 2-Carboxaldehyde

Direct formylation of triptycene:

Triptycene (7.3 g, 0.030 mole) was dissolved in 30 mL dried methylene chloride in a 100 mL round bottom flask. The vessel was immersed in an acetone bath cooled to -20°C with liquid nitrogen and maintained at this temperature by addition of liquid nitrogen occasionally.

While stirring, dichloromethyl methyl ether (Aldrich) (5.1 g, 0.044 mole) was added all at once and then AlCl₃ (5.9 g, 0.044 mole) was added in 10 mins period while temperatures were kept between -20°C and -25°C. After the addition of AlCl₃, the temperature was allowed to raise to 0°C in one hour. The dark mixture was poured over a 500 mL beaker containing 200 g ice and 20 mL diluted hydrochloric acid. Stirring was applied and the color of the solution changed to light yellow immediately.

The aqueous solution was extracted twice with chloroform, 100 mL each. The organic portions combined and washed twice with distilled water. The organic portion dried over molecular sieve for 18 h. The NMR spectrum of this crude material showed two closely located singlets at 9.83 and 9.84 ppm. Alumina column chromatography with CH₂Cl₂/petroleum ether = 1/4 = V/V as eluting solvent were used to further purify the aldehyde.

Three 150 mL fractions were collected. The first fraction contained the desired product contaminated with some starting material. The second fraction was mainly bis-aldehyde. The third fraction contained polymeric impurities. The first fraction was further purified by silica
gel column chromatography using $\text{CH}_2\text{Cl}_2$/pet ether = 1/4 = V/V. The product, 3.44 g, was obtained which corresponded to 37% yield.

The addition sequence of $\text{AlCl}_3$ and dichloromethyl methyl ether was reversed compared to the original procedures on the reference which led to low product yield. A crystalline product was not obtained. The identity of the product was confirmed by high resolution NMR spectrum (see Results and Discussion).

D. The Synthesis of Tosylhydrazone of Triptycene 2-Carboxaldehyde

Triptycene 2-carboxaldehyde (4.0 g, 0.014 mole) was dissolved in 30 mL anhydrous THF and p-toluenesulfonyl hydrazide (2.6 g, 0.014 mole) was added. The whole mixture was stirred at room temperature overnight. Solid collected by vacuum filtration, recrystallized from 95% ethanol got tosylhydrazone (2.01 g, 32%) m.p. 218-219°C.

E. The Synthesis of Sodium Salt

Tosylhydrazone (2.01 g, 0.0045 mole) was put in a 50 mL round bottom flask with 20 mL dry THF. To this was added sodium hydride (0.109 g, 0.0045 mole; 0.191 g of a 57% dispersion in mineral oil). Mixture stirred at room temperature for 1/2 h. The solid was washed with dry THF 20 mL twice and dried under vacuum overnight. Weight: 1.17 g, 55%.

F. The Solution Thermolysis of Sodium Salt

In a 100 mL round bottom flask, equipped with a thermometer, was added 50 mL of diglyme. The system was brought to 125°C with an oil
bath. The sodium salt (1.0 g, 0.0021 mole) was added all at once. Immediately color changed to pink, and 5 mins later to light yellow. The mixture was stirred for 2 h while the temperature was maintained between 125-130°C. After 2 h, the diglyme solution was cooled to room temperature. Solid was removed by vacuum filtration and the filtrate was poured into 100 mL H₂O. The water-diglyme mixture was cooled in an ice-water bath for 1 h and white precipitate formed. Since the white precipitate was unsuccessfully collected by vacuum filtration, the filtrate was put in centrifuge tubes. The white precipitate was spun down by centrifugation. After decanting the supernatant, the residue was dissolved in 100 mL chloroform. The solution was dried with 4 A molecular sieve overnight. Molecular seives were removed by filtration and filtrate was collected. Chloroform was removed by rotary evaporator. The residue weighed 0.54 g.

The mixture was separated and purified by PTLC with chloroform/pet ether = 2/1 = V/V. Weight (percent yield) = cis dimer $69 \quad 6$
trans dimer $70 \quad 18$
aldehyde $60 \quad 12$
azine $71 \quad 11$
insertion $72 \quad 8$
sulfone $73 \quad 5$
sulfinate $74 \quad 20$

G. The Photolysis of Sodium Salt $68$

In a 50 mL round bottom flask was added 25 mL anhydrous THF and sodium salt (0.5 g, 0.0011 mole). The outlet at the top of the flask was connected to a mini oil bubbler to indicate gas evolution. The flask was immersed in an ice water bath right next to the Hanova 450-W medium pressure mercury lamp. After 3-1/2 h of irradiation, nitrogen
evolution ceased. The photolysis was stopped. The sodium p-toluene-
sulfinate was removed by vacuum filtration. The filtrate was collected
and the THF removed by rotary evaporator. The residue was dried under
vacuum overnight. The residue weighed 250 mg.

The residue was separated and purified by PTLC with chloroform/pet
ether = 2/1 = V/V. Weight (percent yield) = cis dimer 62
trans dimer 70
aldehyde 60
azine 71
insertion 7
sulfone 73
sulfinate 74

H. The Vacuum Pyrolysis of Sodium Salt 68

Sodium salt 68 (0.5 g, 0.0011 mole) was packed into the closed end
of a L-shape Pyrex tube. This was attached to the upper end of the
Vycor pyrolysis column. The lower end of the column was attached to a
U-shape Pyrex tube and the U-shape tube was immersed in liquid nitrogen.
The other end of the U-shape tube was connected to the vacuum pump. The heating zone on the pyrolysis column was precalibrated to 450°C with a thermocouple. The pyrolysis was achieved by starting the heating and vacuum pumping for 1 h. The salt was tapped into the pyrolysis column in 1 h. The decomposition of the salt was evidenced by an increase in pressure from the evolution of nitrogen gas. At the end of the addition, power for the heating zone was turned off and cooled to room temperature. All the residue was washed out with 100 mL chloroform. Insoluble material was removed by vacuum filtration. Collected filtrate and chloroform was removed by rotary evaporator (crude weight 105 mg, 37.4%). The crude residue was separated and purified into four components by PTLC with chloroform/pet ether = 2/1 = V/V.

Weight (percent yield) = anthracene 77 4.2
cis dimer 69 1.5
trans dimer 70 4.1
aldehyde 60 2.7

A majority of the residue remained at the starting line. Proton NMR spectrum indicated polymeric material.
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