

AN ABSTRACT OF THE THESIS OF

KARL EDWARD SWENSON for the degree of DOCTOR OF PHILOSOPHY

in Chemistry (Organic) presented on November 26, 1979

Title: VINYLCARBENE INTERMEDIATES IN SOME CYCLIC SYSTEMS

Redacted for Privacy

Abstract approved:

Dr. Peter K. Freeman

Certain α,β -unsaturated ketones when treated with tosylhydrazine give a 3-tosyl adduct of the tosylhydrazone. An elimination reaction using potassium tert-butoxide in tert-butyl alcohol and THF has been developed to convert these 3-tosyl adducts to the α,β -unsaturated tosylhydrazone. Four α,β -unsaturated tosylhydrazones have been prepared by this method.

A series of carbenes of various unsaturated, bridged cyclic systems are generated by pyrolysis or photolysis of the metal salt of the corresponding tosylhydrazone. The first example, 2-carbenabicyclo[3.2.1]octa-3,6-diene, yields six volatile products. Semibullvalene, endo-6-ethynylbicyclo[3.1.0]hex-2-ene and 5-ethynyl-1,3-cyclohexadiene appear to arise from a singlet carbene. Mechanisms involving carbene to carbene rearrangements are proposed for the formation of endo-6-ethynylbicyclo[3.1.0]hex-2-ene and 5-ethynyl-1,3-cyclohexadiene. The triplet state of

2-carbenabicyclo[3.2.1]octa-3,6-diene is the suggested intermediate for the formation of bicyclo[3.2.1]octa-2,6-diene, tricyclo[3.2.1.0^{2,7}]oct-3-ene and tetracyclo[3.3.0^{2,8}.0^{4,6}]octane. The possibility of a diradical process for their formation is discussed.

In contrast to this triplet carbene chemistry, 2-carbenabicyclo[3.2.2]nona-3,6,8-triene gives only indene and 7-ethynyl-1,3,5-cycloheptatriene. These products are consistent with a singlet carbene. A mechanism involving a carbene to allene to carbene rearrangement is suggested for their formation, and a comparison to 2-carbenabicyclo[3.2.1]octa-3,6-diene is made. The two related carbenes, 2-carbena-6,7-benzobicyclo[3.2.2]nona-3,6,8-triene and 5-carbenatricyclo[6.1.0.0^{4,9}]nona-2,6-diene were also investigated. The products from these two carbenes and possible mechanisms for this product formation are discussed.

The chemistry of another unsaturated carbene, 4,4-diphenylcyclohexa-2,5-dienylidene, was also investigated. The major product from the pyrolysis of the lithium salt of 4,4-diphenyl-2,5-cyclohexadienone tosylhydrazone is 4,4-diphenyl-2,5-cyclohexadiene azine. Of the monomeric products, the major component is o-terphenyl. A deuterium labeling study including the preparation of deuterated o-terphenyl reference compounds was described. Carbon-13

nmr spectroscopy is used to assign the position of the deuterium label. Using these deuterium labeling studies, a mechanism for o-terphenyl formation is suggested.

Vinylcarbene Intermediates in Some Cyclic Systems

by

Karl Edward Swenson

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Doctor of Philosophy

Completed November 1979

Commencement June 1980

APPROVED:

Redacted for Privacy

Professor of Chemistry
in charge of major

Redacted for Privacy

Chairman of the Department of Chemistry

Redacted for Privacy

Dean of the Graduate School

Date thesis is presented Nov 26, 1979

Typed by Troi Tranter for Karl Edward Swenson

ACKNOWLEDGEMENTS

The author wishes to thank Dr. Peter K. Freeman for his guidance and patience, his fellow graduate students for their assistance and suggestions, and Liz Madden for her understanding and support.

TABLE OF CONTENTS

	<u>Page</u>
CHAPTER I. INTRODUCTION	1
CHAPTER II. SYNTHESIS OF CERTAIN α, β -UNSATURATED TOSYLHYDRAZONES	5
HISTORICAL BACKGROUND	5
DISCUSSION AND RESULTS	9
EXPERIMENTAL	11
CHAPTER III. CHEMISTRY OF 2-CARBENABICYCLO[3.2.1]OCTA-3,6-DIENE AND 2-CARBENABICYCLO[3.2.2]NONA-3,6,8-TRIENE	16
HISTORICAL BACKGROUND	16
DISCUSSION AND RESULTS	39
EXPERIMENTAL	79
CHAPTER IV. CHEMISTRY OF 4,4-DIPHENYL- CYCLOHEXA-2,5-DIENYLDIENE	119
HISTORICAL BACKGROUND	119
DISCUSSION AND RESULTS	130
EXPERIMENTAL	157
BIBLIOGRAPHY	175

LIST OF FIGURES

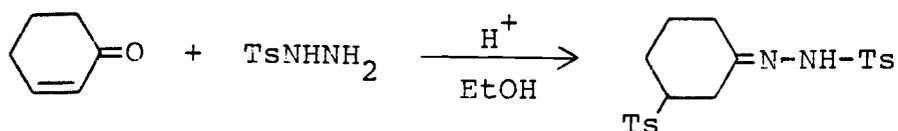
	<u>Page</u>
FIGURE I. CARBON-13 NMR SPECTRUM OF <u>o</u> -TERPHENYL146
FIGURE II. CARBON-13 NMR SPECTRUM OF 4'-DEUTERIO- <u>o</u> -TERPHENYL147
FIGURE III. CARBON-13 NMR SPECTRUM OF A MIXTURE OF <u>o</u> -TERPHENYL, 3'-DEUTERIO- <u>o</u> -TERPHENYL, AND 4'-DEUTERIO- <u>o</u> -TERPHENYL148

LIST OF TABLES

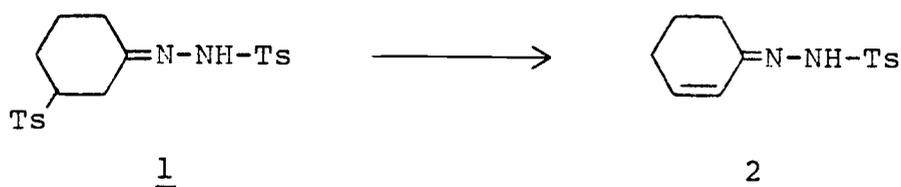
	<u>Page</u>
TALBE I. PERCENT COMPOSITION OF PRODUCTS FROM TOSYLHYDRAZONE <u>70</u>	44
TABLE II. PERCENT COMPOSITION OF PRODUCTS FROM TRICYCLIC BROMIDE <u>80</u>	51
TABLE III. PERCENTAGE OF C ₈ H ₁₀ PRODUCTS FROM <u>55</u>	53
TABLE IV. PERCENT COMPOSITION OF PRODUCTS FROM CARBENE <u>50</u>	133

aprotic decomposition of tosylhydrazone salts is one of the major methods of generating carbenes.

In most cases, tosylhydrazones can be easily prepared by reaction of the aldehyde or ketone with tosylhydrazine in ethanol or methanol. An acidic or basic catalyst such as hydrochloric acid or pyridine is often used.^{1,2} For certain α,β -unsaturated ketones, an attempt to form the tosylhydrazone yields a product in which a second tosyl group is added to the β -carbon atom.² The second chapter



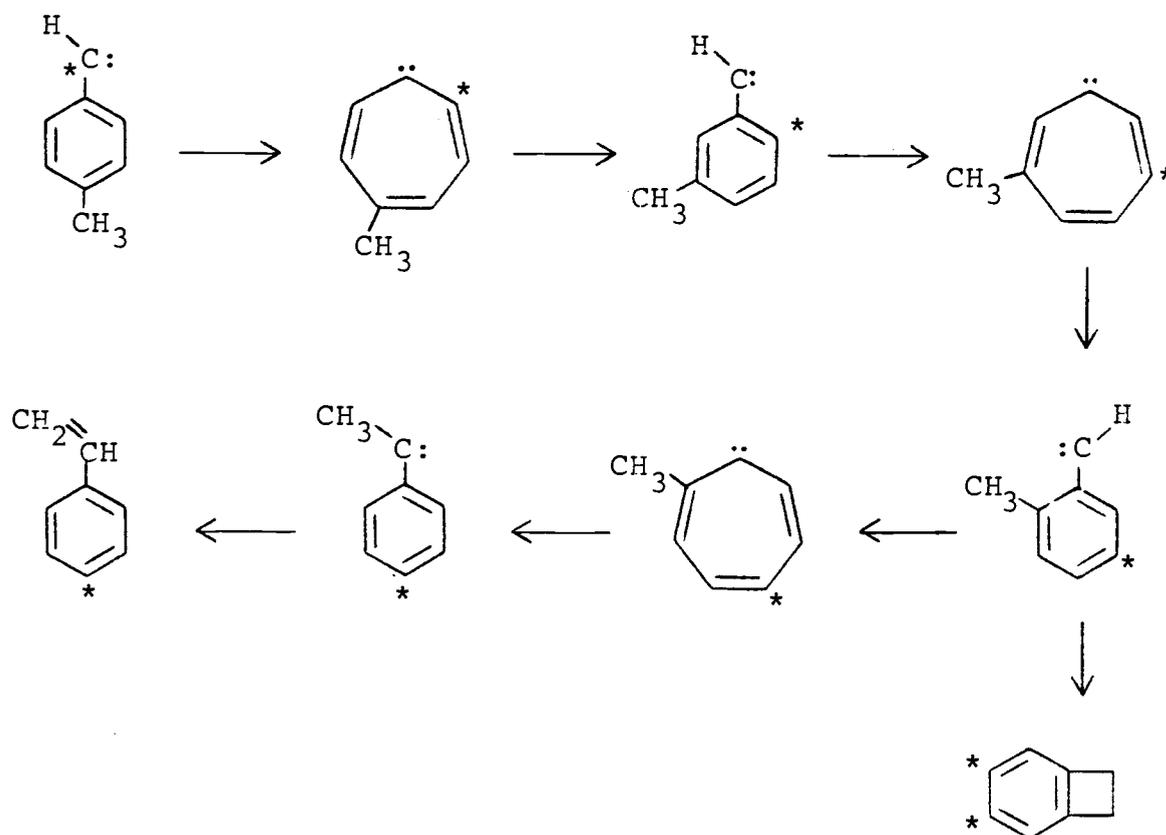
of this thesis describes a method to prepare α,β -unsaturated tosylhydrazones such as 2 from the 3-tosyl-2-tosylhydrazone 1 obtained from the reaction of the α,β -unsaturated ketone and tosylhydrazine.



Intramolecular carbene reactions are widely varied and extensively studied. Some of the more common processes

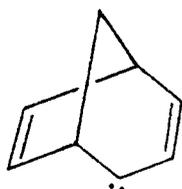
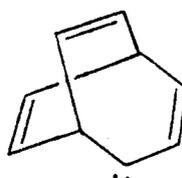
are insertion into a carbon-hydrogen bond or a carbon-carbon double bond, 1,2-hydride migration, or the initiation of a fragmentation reaction.

One of the more recent areas of intramolecular carbene reactions being studied involves carbene to carbene rearrangements. Most of the examples involve phenylcarbenes and have been reviewed recently by Jones.³ The

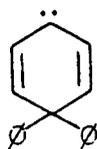
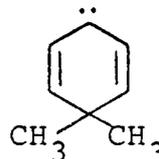


phenylcarbene can rearrange to a new carbene, cycloheptatrienyliidene, and continue to rearrange until the carbene is trapped.

An attempt to find some type of carbene to carbene rearrangement in unsaturated bicyclic systems such as 3 and 4 is discussed in chapter two. Both of these carbenes could be expected to have some type of aromatic stabilization which could influence the reactions they undergo.

34

The possibility of a carbene to carbene rearrangement of a different kind has prompted the study of carbene 5. Related systems of the type 6 have been studied^{4,5} and the

56

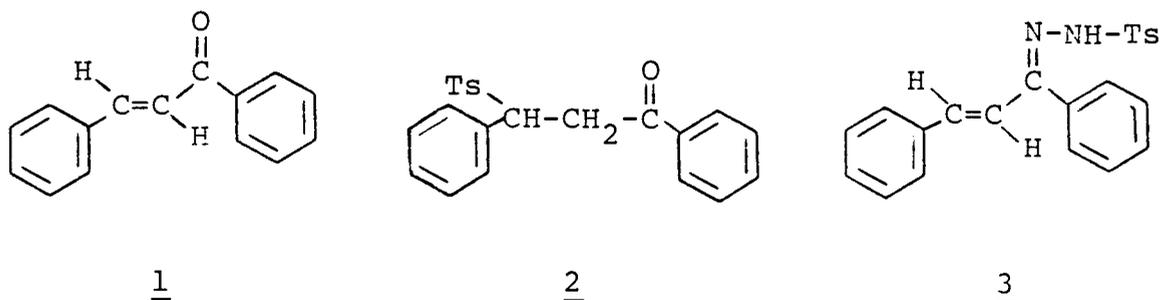
the chemistry of 5 will be compared to that of 6. This is discussed in chapter four.

CHAPTER II. THE SYNTHESIS OF SELECTED
 α,β -UNSATURATED TOSYLHYDRAZONES

HISTORICAL BACKGROUND

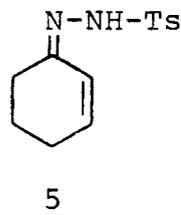
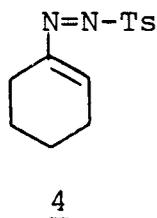
There are numerous references to tosylhydrazones of various α,β -unsaturated carbonyl compounds. Closs and co-workers⁶ investigated a series of simple α,β -unsaturated tosylhydrazones which were used to generate alkyl-substituted cyclopropenes. The monograph by Kirmse⁷ and review articles by Baron,⁸ Hartzler⁹ and Shapiro¹⁰ provide a multitude of further examples.

In most instances the α,β -unsaturated tosylhydrazones can be synthesized as simply as any other tosylhydrazone, but there are exceptions. Bartlett and Stevens¹¹ reported complications in the preparation of certain α,β -unsaturated tosylhydrazones. As one example, from chalcone 1 they obtained the ketosulfone 2. However both Durr¹² and Sato¹³ report that chalcone 1 gives the normal tosylhydrazone 3.



Since all three groups used similar reaction conditions, some subtle effect seems to be operative.

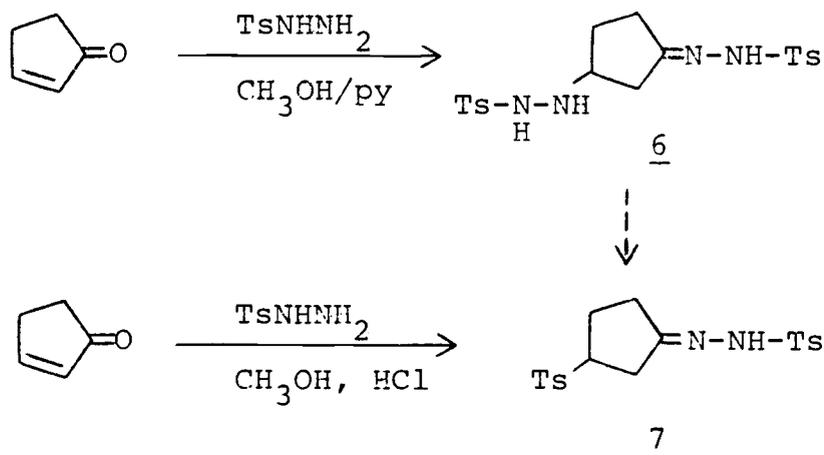
A closer examination of the literature will show that some obvious examples of unsaturated tosylhydrazones are absent. Two of the more striking are those from 2-cyclopentenone and methylvinyl ketone. The tosylhydrazone of 2-cyclohexenone has been prepared by an indirect method by Caglioti.¹⁴ In his study of azo-ene systems, the compound 4 was prepared in an aprotic solvent and tautomerized to 2-cyclohexenone tosylhydrazone 5. The existence of tosyl-



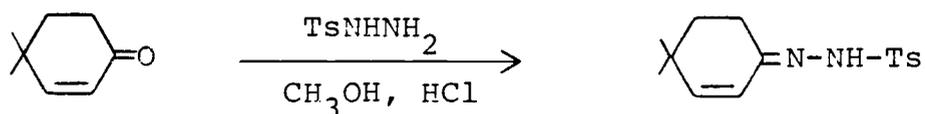
hydrazone 5 is implied in a paper by Paquette.¹⁵ A series of ketones was converted to a series of vinylsilanes by way of tosylhydrazone precursors. In this list was 2-cyclohexenone, but no comment was made about the formation of the tosylhydrazone.

Kirmse and Ruetz² examined the reaction of tosylhydrazine with 2-cyclopentenone and 2-cyclohexenone. In methanol with a pyridine catalyst, an adduct 6 was obtained in which a second molecule of tosylhydrazine had added to the double

bond. Additionally, the compound 6 could be converted to 7 simply by recrystallization. The addition of a second

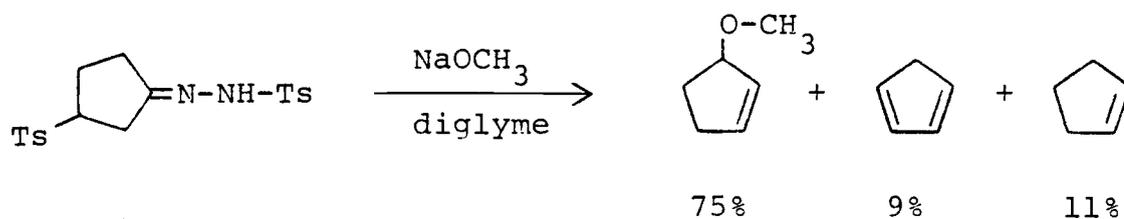


molecule of tosylhydrazine in a Michael fashion to the double bond can be prevented by steric means. In contrast to 2-cyclohexenone, 4,4-dimethyl-2-cyclohexenone gave only the normal tosylhydrazone. When 3-tosylcyclopentanone



tosylhydrazone 7 was thermally decomposed with sodium methoxide in diglyme, the tosyl residue was eliminated and

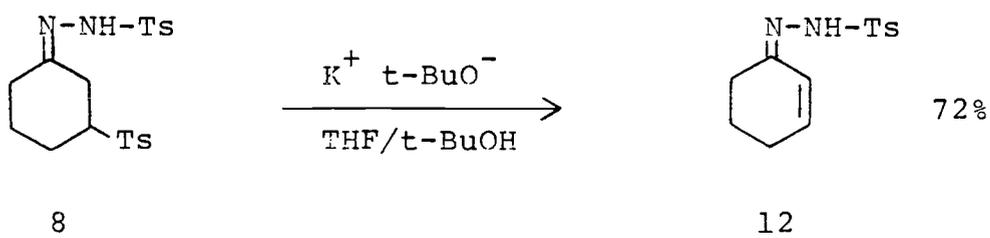
products corresponding to the intermediacy of 1-diazo-2-cyclopentene were obtained. The major product, the methyl ether, would be typical of a carbonium ion process, while the cyclopentadiene would be the expected carbene product. Similar results were obtained with 3-tosylcyclohexanone tosylhydrazone.

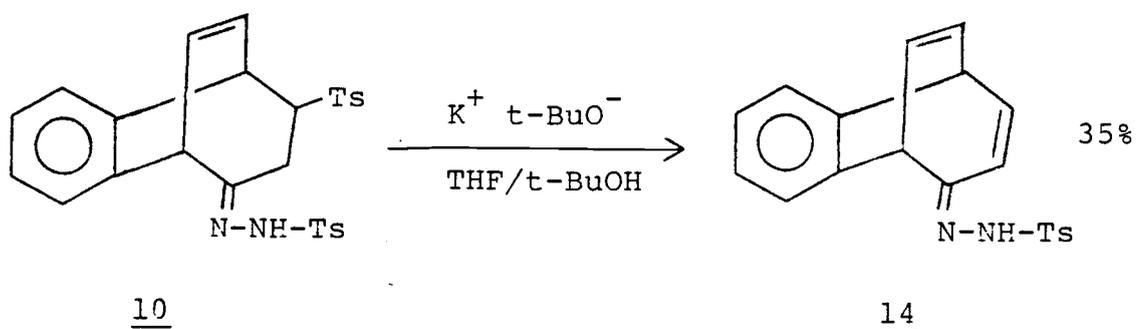
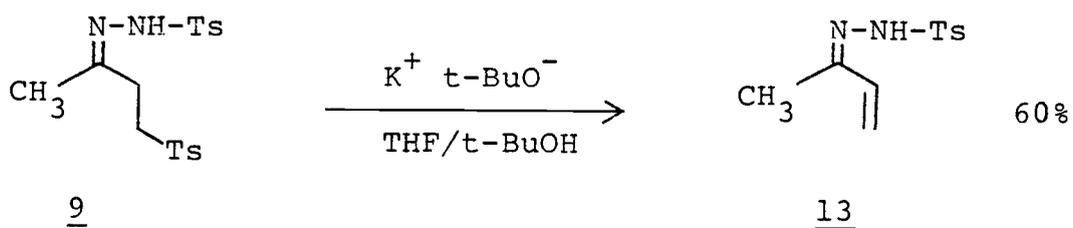
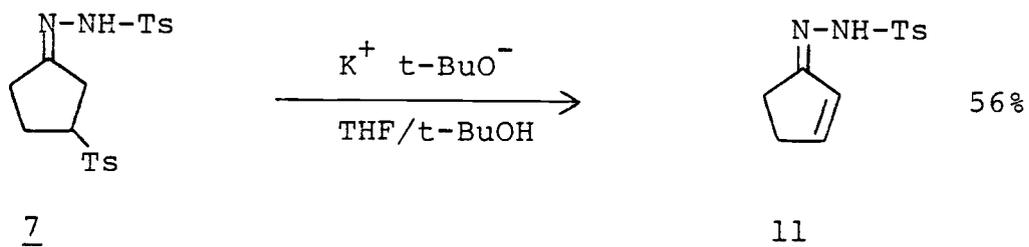


DISCUSSION AND RESULTS

At one point in the attempted preparation of several tosylhydrazones of α,β -unsaturated bicyclic ketones, it appeared that the 3-tosyltosylhydrazones of the type described by Kirmse² (e.g. structure 7) were the major product. A procedure was needed to prepare the "normal" tosylhydrazone or to convert the 3-tosyltosylhydrazone to the α,β -unsaturated tosylhydrazone. Since Kirmse had reported that 7 eliminated a tosyl group under basic decomposition conditions, an elimination reaction of this type was sought. After some experimentation with conditions, a tenfold excess of potassium tert-butoxide in a one to one mixture of tert-butyl alcohol and THF was chosen. This solvent mixture is used since both the tert-butoxide and the tosylhydrazone-sulfone dissolve in it. It is suggested that the described work up procedure, in which the salt of the newly formed α,β -unsaturated tosylhydrazone is isolated before acidification, should be followed as this method seems to give more satisfactory results.

The results of four cases are summarized below:





On the basis of these four examples, it would be expected that this method of converting 3-tosyltosylhydrazones to the α,β -unsaturated tosylhydrazone should turn out to be a very useful general method.

EXPERIMENTAL

General Experimental. Melting points were determined using a Büchi melting point apparatus and are uncorrected. All boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 727B infrared spectrophotometer. Proton nmr spectra were recorded on a Varian Associates EM-360 (60 MHz) or HA-100 (100 MHz) spectrometer. Carbon-13 nmr spectra were recorded on a Varian Associates FT-80A spectrometer. Mass spectra were obtained on a Varian-Matt Ch-7 mass spectrometer interfaced to a System 150 data system. High resolution mass spectra were carried out by the University of Oregon Chemistry department. Elemental analyses were performed by Chemalytics, Inc., 2330 S. Industrial Park Dr., Tempe, Arizona.

Preparation of 3-Tosylcyclohexanone Tosylhydrazone 8.

The title compound 8 was prepared by the acid catalyzed method of Kirmse.² The properties of the white, crystalline product agreed with those reported by Kirmse; mp 159-161° dec., lit 168-169°; nmr (100 MHz, CDCl₃), 8.24δ (broad s, 1H, N-H), 7.74(m, 4H, aromatic protons), 7.31(m, 4H, aromatic protons), 3.12(m, 1H, -CH-SO₂- proton), 2.84-1.14 (complex overlapping m, 8H, cyclohexyl protons), 2.45, 2.42 (two s, 3H each, aromatic methyls).

Preparation of 3-Tosylcyclopentanone Tosylhydrazone 7.

The compound was prepared by the acid catalyzed method of Kirmse.² The properties of the compound agreed with those reported; mp 141-143° dec., lit 153-154°; nmr (100 MHz, CDCl₃) δ7.89(m, 4H, aromatic protons), 7.33(broadened d, 4H, aromatic protons), 3.58(m, 1H, -CH-SO₂- proton), 2.86-1.90(m, 6H, cyclopentyl protons), 2.46(s, 6H, aromatic methyl superimposed over the cyclopentyl m).

Preparation of 1-Tosyl-3-butanone Tosylhydrazone 9.

The same method was employed as for 3-tosylcyclopentanone tosylhydrazone. The white solid had the following properties: mp 141-144° dec.; nmr (100 MHz, CDCl₃), δ7.78(m, 4H, aromatic protons), 7.65(broadened s, 1H, N-H proton), 7.34(m, 4H, aromatic protons), 3.32(m, 2H, H¹), 2.62(m, 2H, H²), 2.52, 2.49(two s, 3H each, aromatic methyl protons), 1.77(s, 3H, H⁴); ir (Nujol mull), 3230 cm⁻¹ (s), 1645 (w), 1602 (m), 1358 (s), 1312 (s), 1175 (s).

Anal. Calcd for C₁₈H₂₂N₂O₄S₂: C, 54.80; H, 5.62

Found: C, 54.57; H, 5.53.

Preparation of 2-Cyclohexen-1-one Tosylhydrazone 12.

A solution of potassium tert-butoxide in tert-butyl alcohol was prepared by dissolving 3.164 g of potassium (80.9 mmol) in 75 ml of tert-butyl alcohol in a 250 ml flask fitted with a reflux condenser, magnetic stirrer, gas inlet, and addition funnel. The addition funnel was charged with a solu-

tion of 3.40 g (8.09 mmol) of the 3-p-tosyl adduct of 2-cyclohexen-1-one tosylhydrazone dissolved in 75 ml of anhydrous THF. This tosylhydrazone solution was added to the potassium tert-butoxide over five minutes and the mixture heated at reflux for three hours, during which time a tan precipitate formed. After cooling, this tan salt (2.33 g, 7.69 mmol, 95%) was collected on a Buchner funnel and air dried. The salt was dissolved in 30 ml water, acidified with 3N HCl, and extracted three times with 25 ml of chloroform. The chloroform extracts were dried over magnesium sulfate and the chloroform removed on the rotary evaporator to yield 1.38 g (5.22 mmol, 72%) of the title tosylhydrazone. This was recrystallized from ethanol to yield mp 161-163°C dec., lit 164-165°C; nmr (100 MHz, CDCl₃), δ7.88(d, J=8 Hz, 2H, aromatic protons), 7.80 (broadened s, 1H, N-H proton), 7.34(d, J=8 Hz, 2H, aromatic protons), 6.44-6.05(m, 2H, vinyl protons), 2.47(s, 3H, aromatic methyl), 2.42-2.04(m, 4H, C⁴ and C⁶ cyclohexyl protons), 1.80(m, 2H, C⁵ cyclohexyl protons). This nmr spectrum agrees with that reported by Caglioti.¹⁴

Preparation of 2-Cyclopenten-1-one Tosylhydrazone 11.

The procedure described for 2 cyclohexen-1-one tosylhydrazone was followed. A solution of 1.828 g (4.50 mmol) of the 3-p-tosyl adduct of 2-cyclopenten-1-one tosylhydrazone in 50 ml of THF was treated with potassium tert-

butoxide (46.0 mmol) in 50 ml of tert-butyl alcohol. This yielded 0.629 g (2.52 mmol, 56%) of the title tosylhydrazone; mp 158-161°C dec.; nmr (100MHz, CDCl₃), δ7.90(d, J=8 Hz, 2H, aromatic protons), 7.34(d, J=8 Hz, 2H, aromatic protons), 6.70(m, 1H, vinyl proton), 6.28(m, 1H, vinyl proton), 2.60(m, 2H, cyclopentyl protons), 2.46(s, 3H, superimposed over m, 2H, aromatic methyl and cyclopentyl protons); ir (Nujol mull), 3200 cm⁻¹ (m), 1618 (w), 1596 (w), 1378 (m), 1324 (m), 1160 (s).

High resolution mass spectrum. Calculated for C₁₂H₁₄N₂O₂S: 250.078; Found: 250.077.

Preparation of 3-Buten-2-one Tosylhydrazone 13. The procedure described for 2-cyclohexen-1-one tosylhydrazone was followed. The elimination reaction was carried out with 2.20 g (5.58 mmol) of the 3-p-tosyl adduct of 3-buten-2-one tosylhydrazone using 55.6 mmol of potassium tert-butoxide. The title tosylhydrazone was obtained in 60% yield (0.793 g, 3.33 mmol); mp 121-130, nmr (100 MHz, CDCl₃), δ8.15(broadened s, 1H, N-H proton), 7.90(d, J=8 Hz, 2H, aromatic protons), 7.32(d, J=8 Hz, 2H, aromatic protons), 6.45(d of d, J=11, 18 Hz, 1H, H³ proton), 5.52(d, J=18 Hz, 1H, E-H⁴ proton), 5.42(d, J=11 Hz, 1H, Z-H⁴ proton), 2.43(s, 3H, aromatic methyl), 1.89(s, 3H, C¹ methyl); ir (Nujol mull), 3201 cm⁻¹ (s), 1601 (m), 1340 (s), 1171 (s).

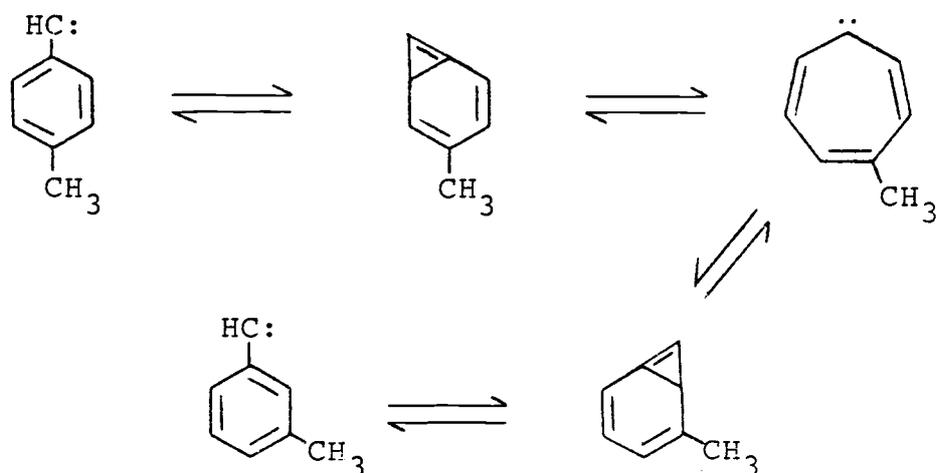
High resolution mass spectrum. Calculated for
 $C_{11}H_{14}N_2O_2S$: 238.078; Found: 238.078.

CHAPTER III. THE CHEMISTRY OF
2-CARBENABICYCLO[3.2.1]OCTA-3,6-DIENE AND
2-CARBENABICYCLO[3.2.2]NONA-3,6-8-TRIENE

HISTORICAL BACKGROUND

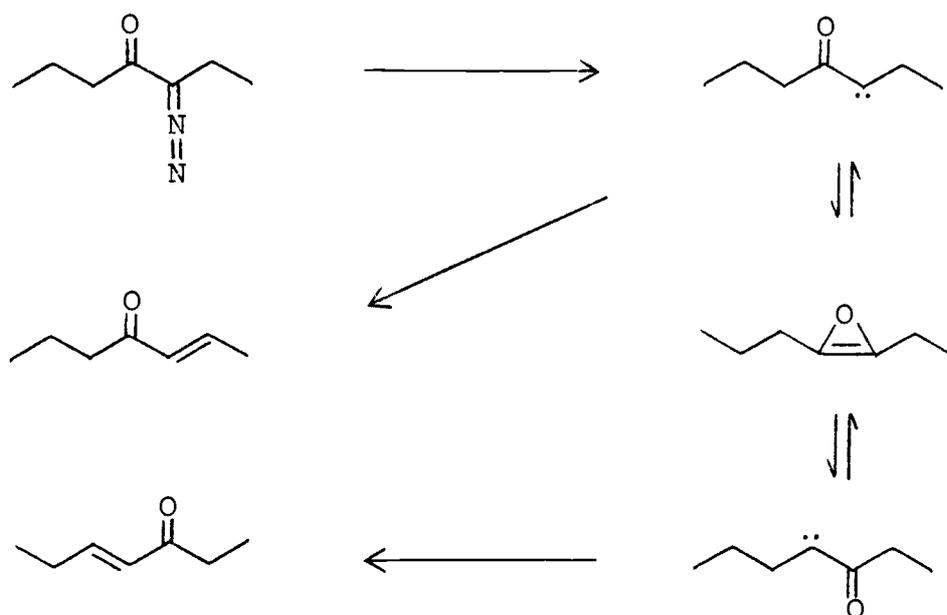
Carbene to carbene rearrangements have recently received considerable attention, particularly those of aryl carbenes. A phenyl carbene can rearrange to cycloheptatrienyliidene as in this example from Hedaya¹⁶ shown in Scheme I. A review article by Jones³ covers this type of reaction extensively.

SCHEME I

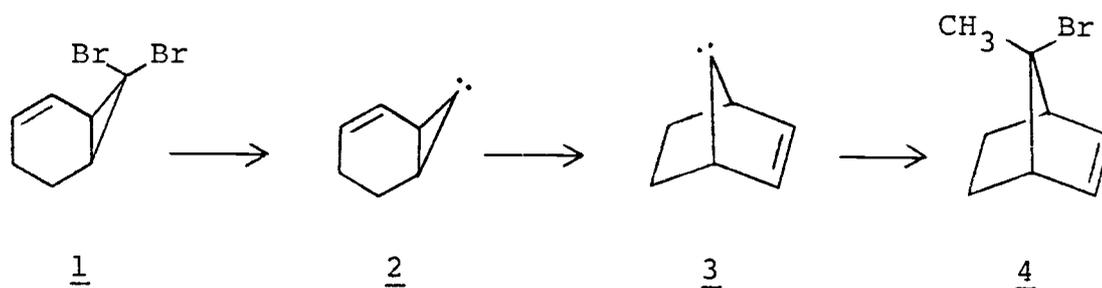


Another type of carbene to carbene rearrangement occurs with keto-carbenes. The carbene rearranges through

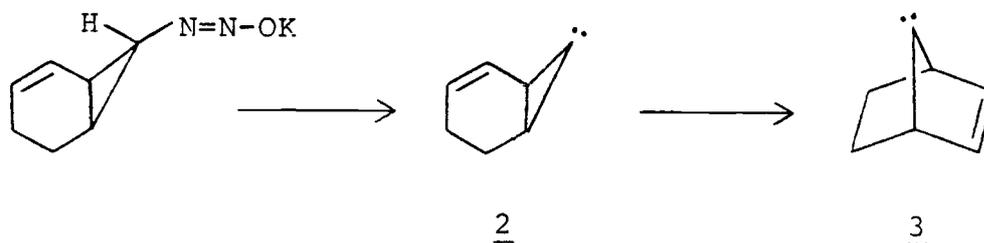
an oxirene to a second carbene. This example is from the work of Matlin and Sammes.¹⁷



A third type of reaction which has often been considered a carbene to carbene rearrangement is the conversion of vinylcyclopropylidene to cyclopentenylidene. Skattebol¹⁸ treated the bicyclic dibromide 1 with methyllithium and obtained 4. The two carbenes 2 and 3 were proposed as intermediates. The product 4 was obtained stereoselectively and none of the products obtained when carbene 3 was

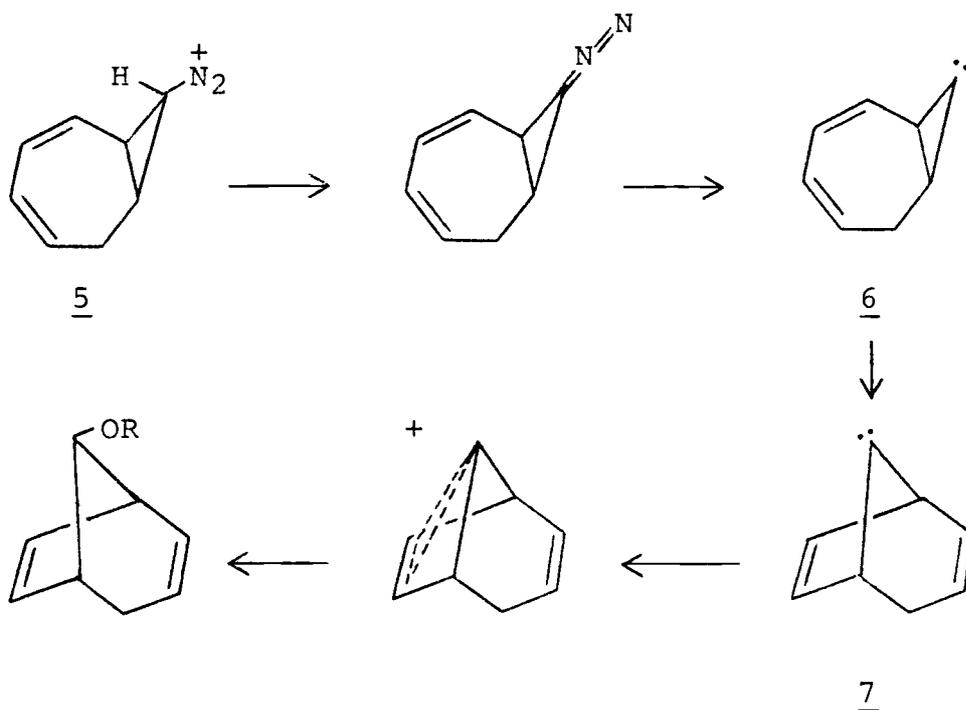


generated from the corresponding tosylhydrazone¹⁹ were found. Subsequently, Warner²⁰ has provided evidence that free carbenes are not present, but that bonding to lithium is necessary for the reaction to occur. The same carbene 2 has been generated from the corresponding diazotate²¹ and it rearranges to carbene 3; so in this case the vinyl-cyclopropylidene to cyclopentenylidene rearrangement may be



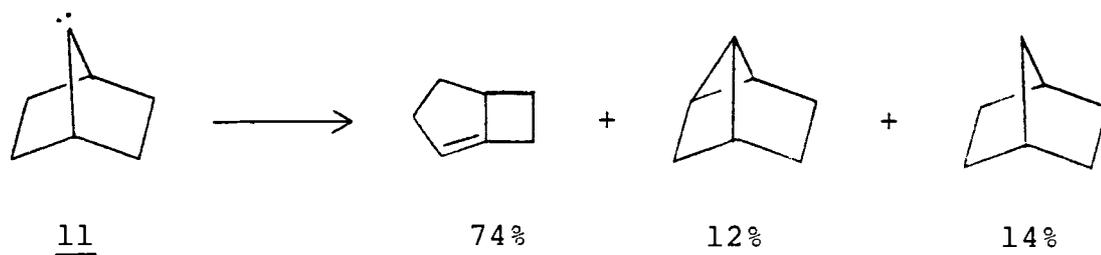
occurring. The same carbene to carbene rearrangement, 2 to 3, has been proposed by Kirmse²² to explain a product variation in his study of the 7-diazonium ion of bicyclo-[4.1.0]hep-2-ene. In a similar study of the ion 5, Kirmse²³ has proposed that the carbene 6 interconverts to carbene 7

which is then protonated and goes on to products. This particular rearrangement is receiving considerable attention at the present time. Jones²⁴ has discussed carbene to carbene rearrangements of this and other types in a recent review.



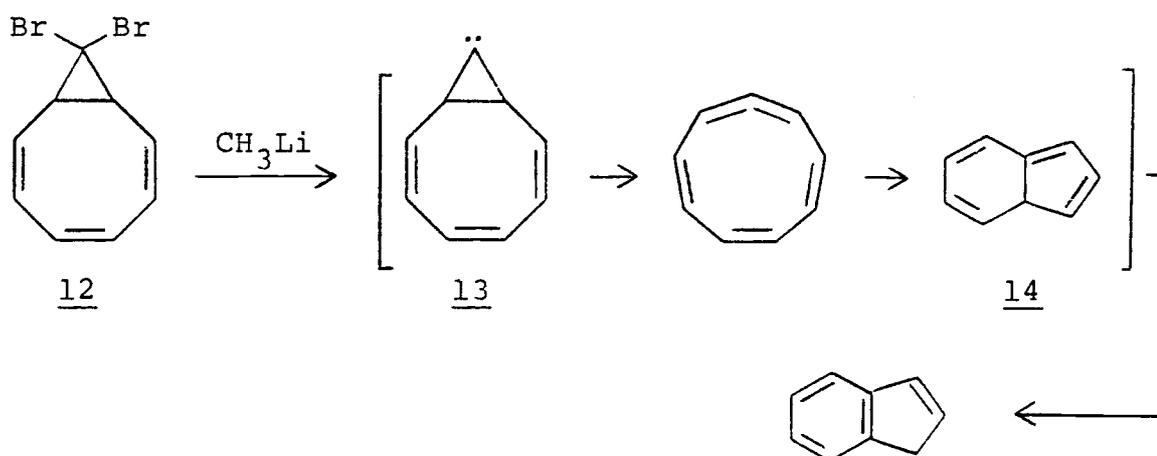
A different form of carbene to carbene rearrangement involving intermolecular proton transfer has been reported by Freeman and co-workers²⁵ (Scheme II). Carbene 8 was

presence of product 10. All of the deuterium at C-4 in 8 has been lost and 13% deuterium incorporation is found at C-8 of product 10. This points to an intermolecular process (path A) in which the deuterium at C-4 is lost to form a new carbene 9 which inserts into the C-H bond of C-6. This type of insertion in bicyclic systems is a well documented process.²⁶ Protonation of the anion of 9 at C-8 (the solvated D^+ which was lost at C-4 may be present as the counter ion) results in the product 10 with the small amount of deuterium incorporation. A similar scheme (path B) differs in the sequence of protonation-deprotonation steps. Considerable evidence points to extra stabilization for carbene 8 provided by the delocalized form 8b. A similar but unstabilized carbene, 11, undergoes 1,3 insertion and 1,2-alkyl migration. Neither of the analogous

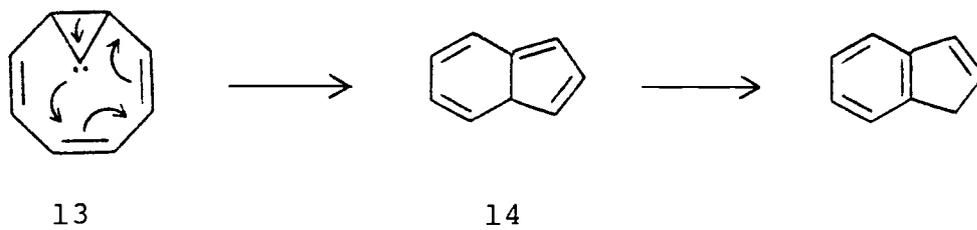


products are present in the case of 8. The fact that an intermolecular process takes place is consistent with extra stabilization. The longer lifetime of the stabilized carbene allows the proton transfer steps to occur, while in unstabilized cases intramolecular processes such as insertion or alkyl migration predominate.

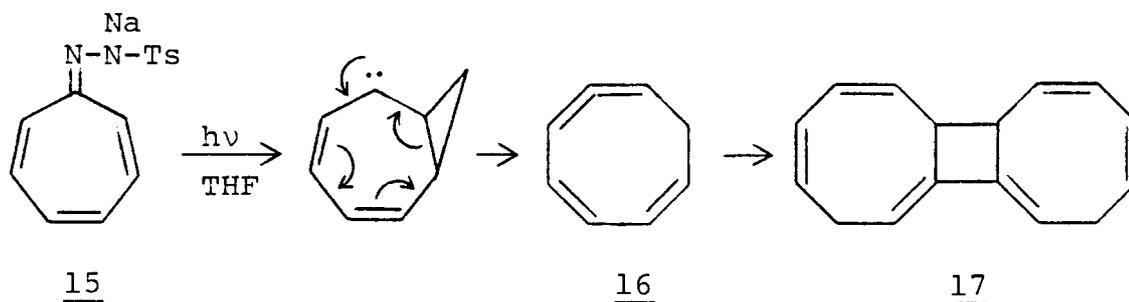
Strained cyclic allenes are another class of high energy intermediates in which rearrangements are numerous and often closely allied with carbenes. The smallest cyclic allene that has been isolated is 1,2-cyclononadiene.²⁸ Cyclic allenes with additional unsaturation have been the subject of a number of studies. Waali and Allison²⁹ treated dibromide 12 with methyllithium and obtained indene. The suggested mechanism involved formation



of the carbene or carbenoid, which rearranges to the cyclic allene followed by electrocyclic ring closure. A final 1,5 sigmatropic hydrogen shift afforded the product. While the mechanism including the cyclic allene was favored by the authors, conversion of the carbene 13 directly to 14 followed by a 1,5-sigmatropic shift of hydrogen was also considered.

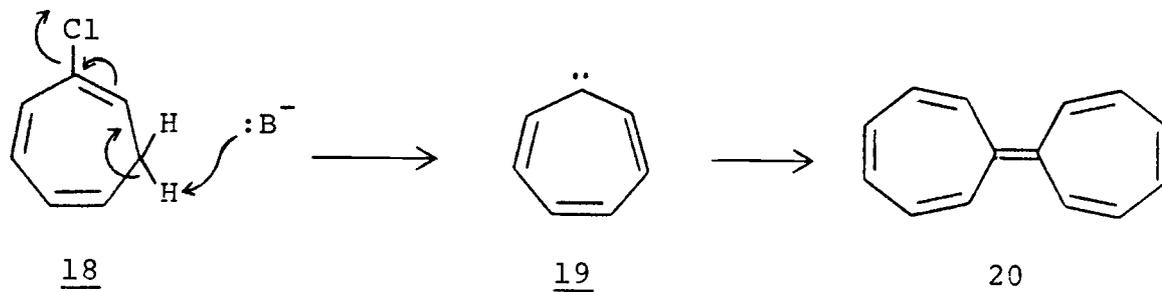


The tosylhydrazone salt 15 was photolyzed in tetrahydrofuran and the hydrocarbon 17 obtained.³⁰ It was

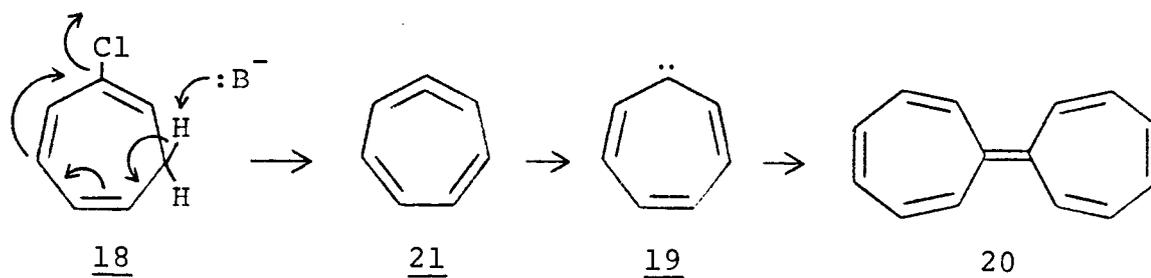


suggested that 17 was formed through the dimerization of the cyclic allene 16. Additionally, the allene 16 was trapped with diphenylisobenzofuran.

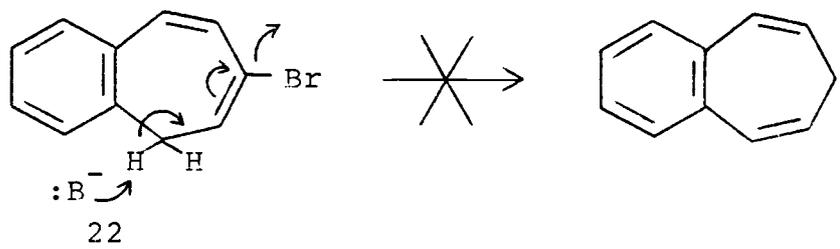
Mayor and Jones³¹ have provided evidence for an allene in a seven membered ring. The chloride 18 was treated with strong base and ultimately gave the dimer 20, which is the product of carbene 19 generated from the tosylhydrazone salt. Two possibilities for a mechanism exist. Vinylogous α -elimination directly to the carbene 19 could occur. Also to be considered was the possibility of vinylogous β -elimi-



nation to the allene 21, which is a valence tautomer of carbene 19. To investigate the two possibilities, the

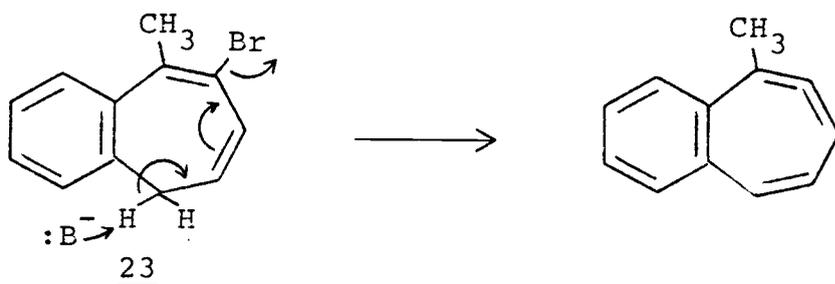


benzo analogs 22 and 23 were synthesized. Compound 22 would be expected to undergo an α -elimination process. The

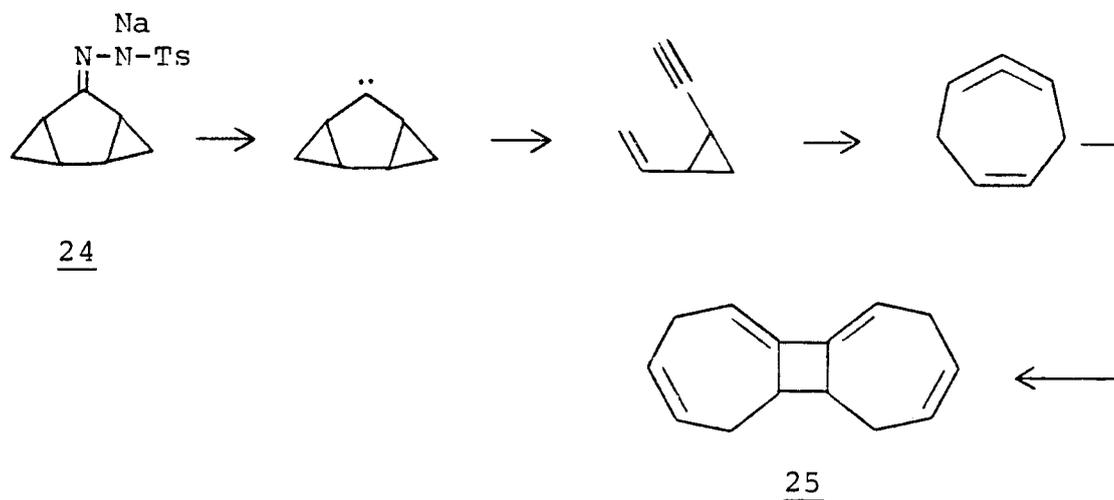


β -elimination should be retarded since the aromaticity of the benzene ring would have to be interrupted. Upon treatment with potassium tert-butoxide 22 was found to be inert to the reaction conditions. Compound 23, which would be

avored for the vinylogous β -elimination, went cleanly to the expected allene products. This showed that the allene actually was an intermediate in this type of reaction.

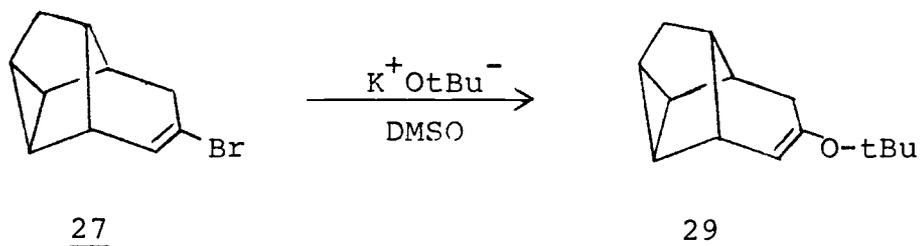
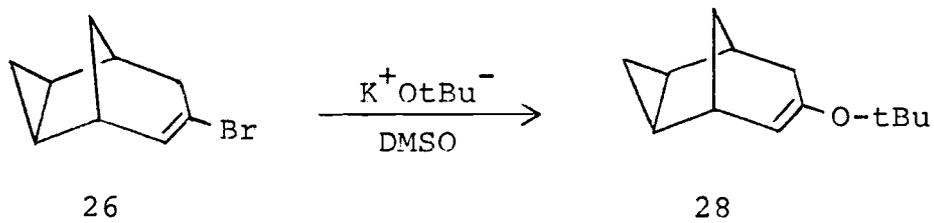


Another allene in a seven membered ring has been reported by Dolbier.³² The tosylhydrazone salt 24 was pyrolyzed under a variety of conditions and the dimer 25 was formed. Evidence is presented for the fragmentation

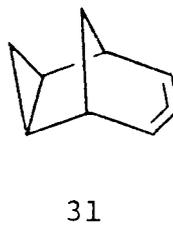
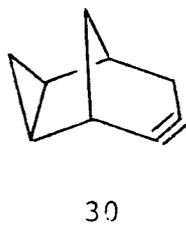


of the carbene to cis-1-ethynyl-2-vinylcyclopropane, which presumably undergoes a Cope rearrangement to 1,2,5-cycloheptatriene and then dimerizes.

Freeman and Hardy³³ investigated the behavior of vinyl bromides 26 and 27 upon reaction with potassium tert-butoxide in DMSO. Enol ethers 28 and 29 were formed

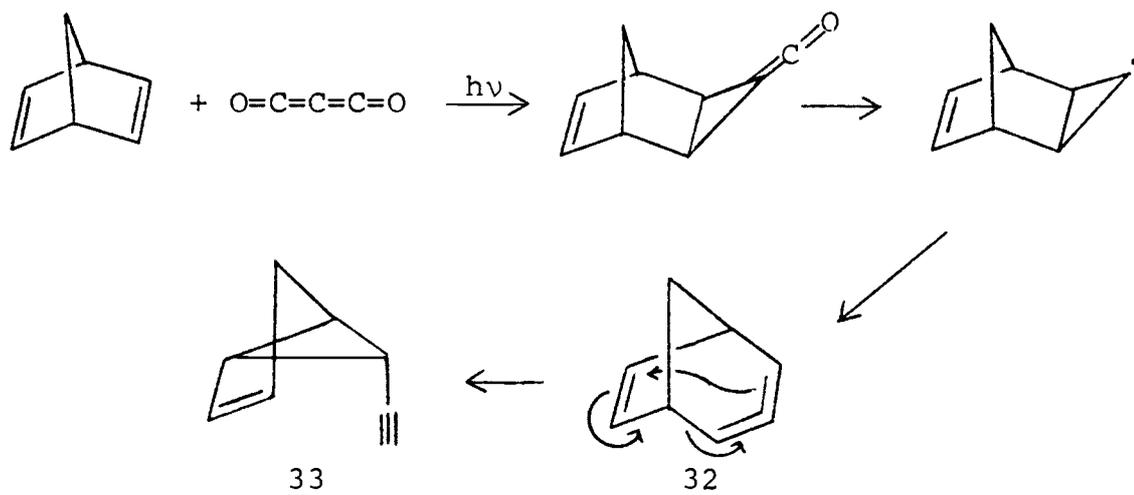


in each case. It was suggested that an acetylenic species such as 30 was the major product-determining intermediate, but a minor role for allenic intermediates such as 31 was considered.

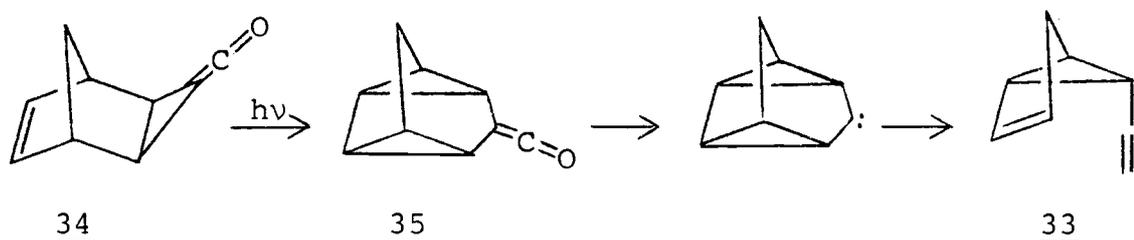


In a related study, a mixture of norbornadiene and carbon suboxide was photolyzed, producing a very low yield of endo-6-ethynylbicyclo[3.1.0]hex-2-ene 33.³⁴ One

mechanism suggested for the formation of 33 included the strained cyclic allene 32 as a possible intermediate. Also

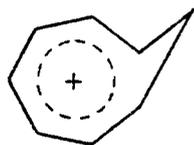
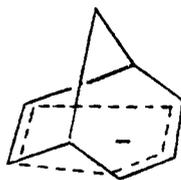
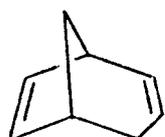
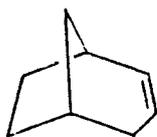
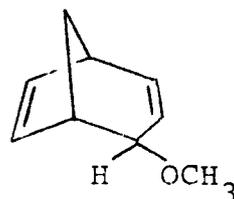


considered was the possibility that ketone 34 was converted to 35 photochemically before carbene generation had occurred.



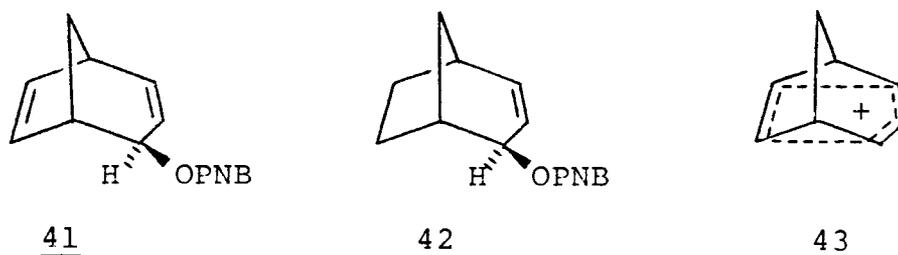
The search for extra stabilization for a carbene in the form of homoaromaticity or bicycloaromaticity will be one of the themes explored in this work. A number of examples of homoaromaticity exist both for carbonium ions and carbanions. The most often cited example of a homoaromatic carbonium ion is the homotropylium ion 36.³⁵ For

the carbanion case, an example of particular relevance to this work is 37. The diene 38 and the allylic analog 39

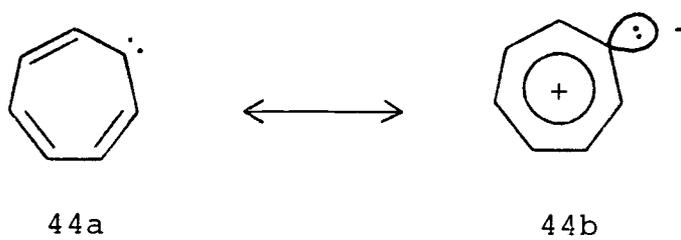
3637383940

were treated with base in a deuterated solvent and the exchange of rates of the allylic protons determined.³⁶ The diene 38 underwent isotope exchange 3×10^4 times faster than 39. The anion of 38 can be prepared by reaction of the ether 40 with sodium-potassium alloy. The nmr spectrum of the resulting anion is consistent with extensive delocalization as shown in 37.^{37,38}

An investigation of the solvolysis of the 2-para-nitrobenzoates 41 and 42 has been carried out.³⁹ The diene 41 solvolyzed about 100 times slower than 42. The second double bond is rate retarding, but the question of whether the 4- π electron antihomoaromatic cation 43 actually exists has not been conclusively determined.

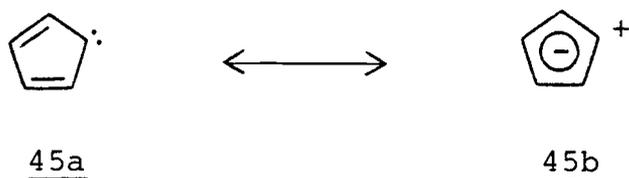


In the case of carbenes, several instances of stabilization deserve mention. Cycloheptatrienyliidene 44 might be



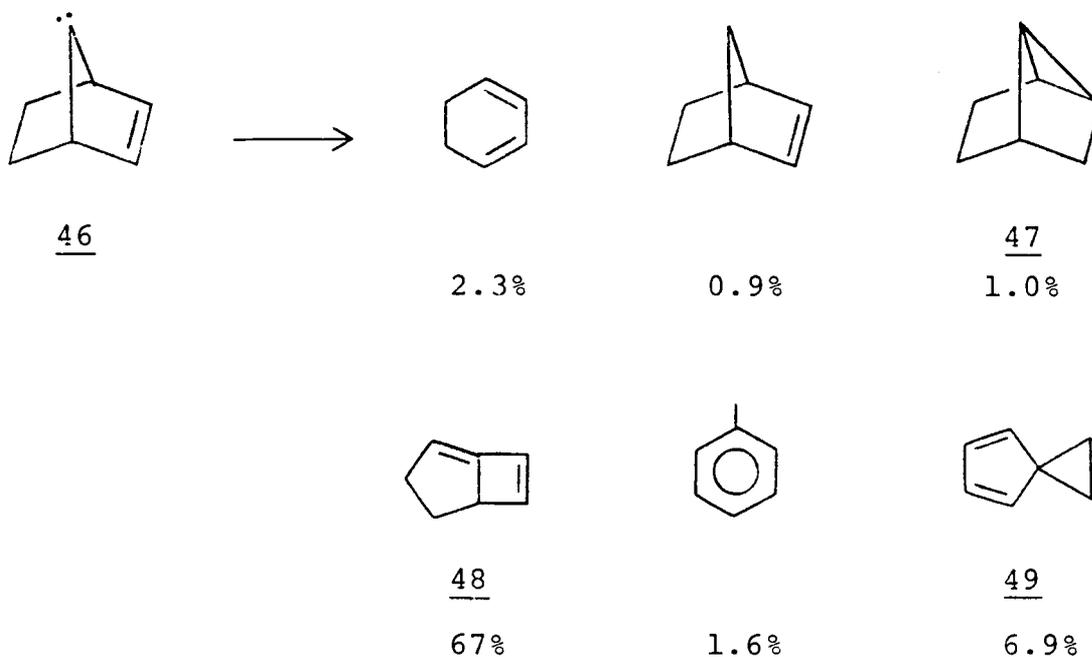
expected to show $6-\pi$ electron aromatic stabilization as do tropylium salts. The electrons of the carbene center are not involved in the aromatic delocalization, and the species might be expected to be particularly nucleophilic. A study in which 44 was added to a series of substituted styrenes⁴⁰ has been carried out, and a Hammett ρ value of +1.05 was obtained. This was the first positive ρ value for a carbene addition that has been found, and substantiates the strongly nucleophilic character of 44.

Cyclopentadienyliidene 45 could also show $6-\pi$ electron stabilization (45b) but the electrons of the carbene center would be included in the delocalized aromatic sextet. This

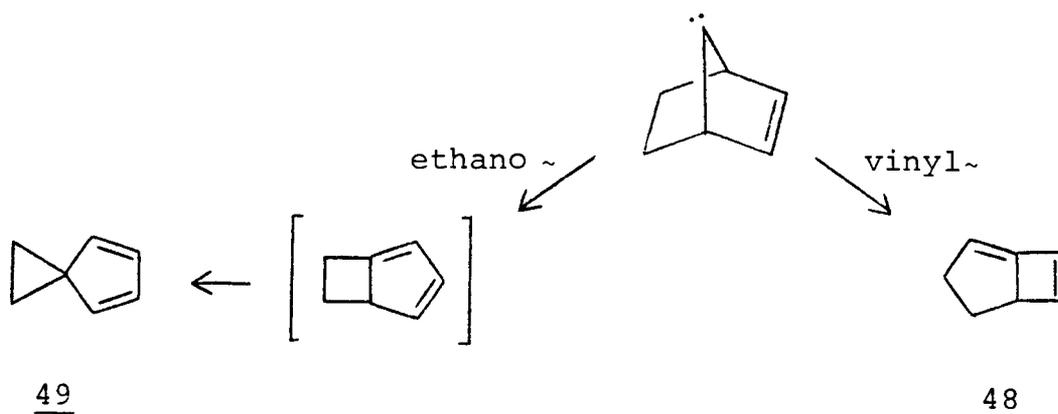


would impart a particular electrophilic character to 45, which is borne out in a Hammett ρ value of -0.76 (σ constants) or -0.46 (σ^+ constants).⁴¹

Homoallylic (bishomoaromatic) delocalization of a carbene was suggested as a possibility for 7-norbornenyli-
dene 46 by Moss.⁴² The products 48 and 49 were explained

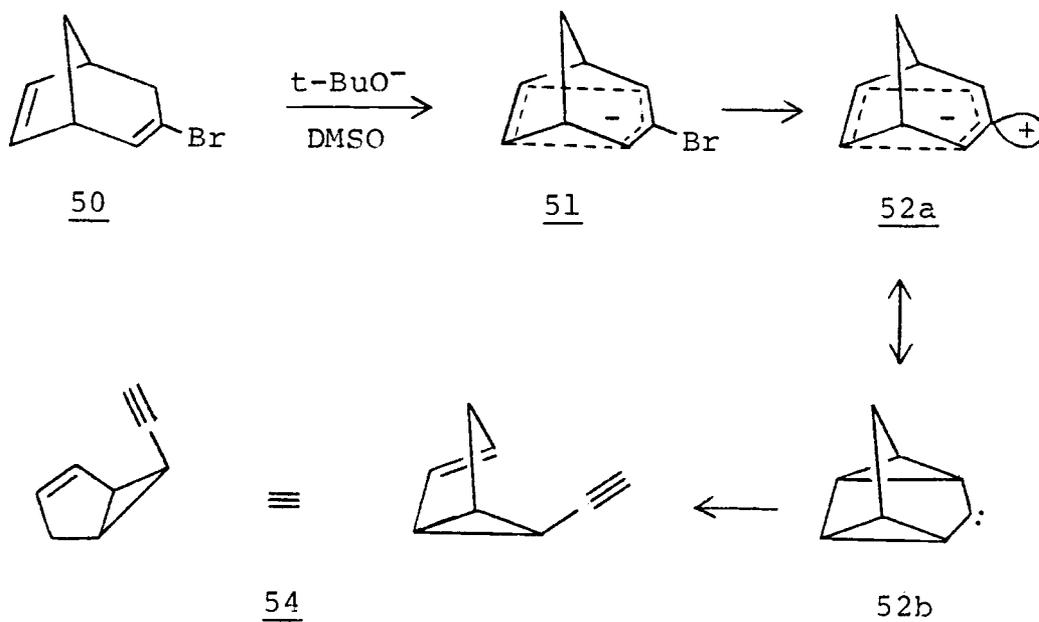


by either the ethano (49) or vinyl (48) bridge migration. The formation of 48 as the major product would point to

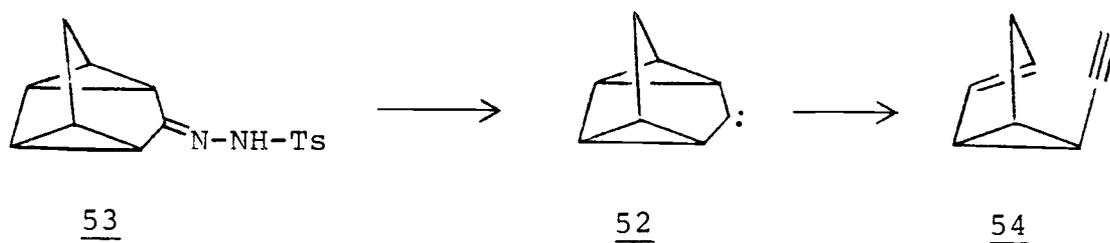


some influence of the π bond on the remote carbene center. The smaller amount of insertion product 47 as compared to that formed from 7-norbornanylidene 11 would also suggest some delocalization. In a subsequent study,⁴³ the nature of the vinyl migration was investigated, but the results were not overwhelmingly conclusive.

The most striking example of a homoconjugated carbene has been presented by Bergman.⁴⁴ The bromodiene 50 was treated with potassium tert-butoxide in DMSO and the product 54 obtained. The suggested mechanism involved formation of the homoaromatic bromoanion 51 followed by rate-determining loss of bromide ion to carbene 52. Carbene 52 is depicted as being delocalized, with the two electrons of the carbene

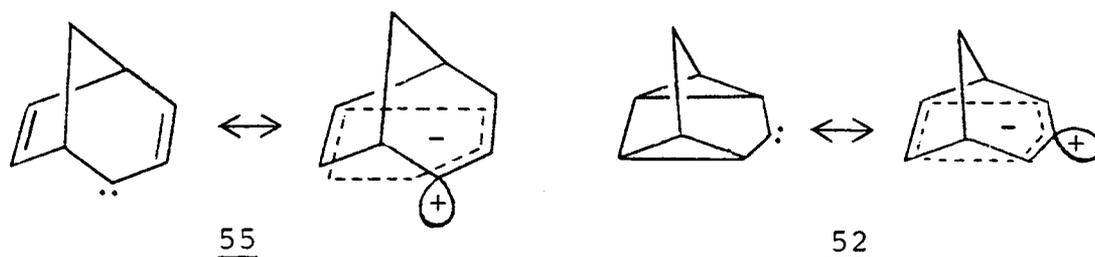


center included in the six-electron pseudo- π system. As further evidence for carbene 52, tosylhydrazone 53 was decomposed under aprotic conditions and compound 54 was obtained as the sole volatile product.

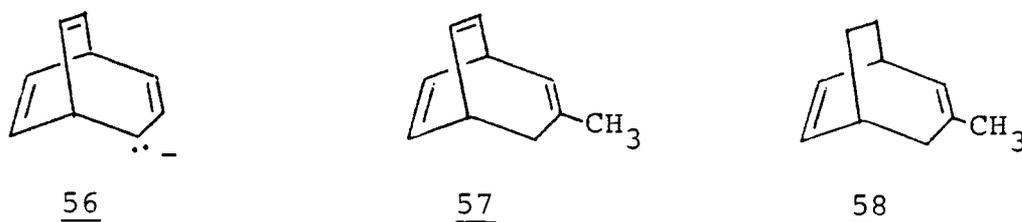


With this prospect of homoaromaticity, it was decided to investigate the chemistry of carbene 55. Since it is related to Bergman's carbene 52 by a 1,2-hydrogen shift,

these two carbenes may be part of the same intermediate manifold.



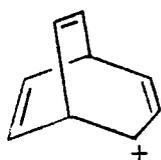
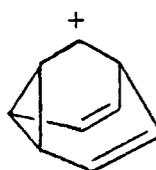
Another aspect of stabilization which has recently been described⁴⁵ is bicycloaromaticity. By consideration of the number of carbon atoms and the electron occupancy of each bridge, a prediction can be made on whether delocalization should exist. Using the nomenclature of Goldstein,⁴⁵ the anion 56 is called a $3^{-2}2^{\circ}$ system, where the numbers refer to the number of carbon atoms in each



bridge. The charge on that bridge is indicated in the superscript. Again from Goldstein's work, this $3^{-2}2^{\circ}$ system would be a stabilized bicycloaromatic system. Base-catalyzed deuterium exchange experiments have been carried out on the related system 57 by Staley⁴⁶ and it was found that exchange was 750 times greater than for the reference

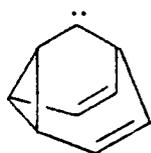
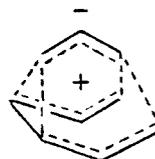
compound 58. Additionally, the nmr spectrum⁴⁷ of anion 56 shows extensive delocalization. Together, these results would tend to support the existence of bicycloaromatic stabilization.

The cation 59, a $3^+2^{\circ}2^{\circ}$ system, would be predicted to be destabilized. Solvolysis of the corresponding p-nitrobenzoate led only to the barbaralyl cation 60, and the desired ion 59 was probably never obtained.⁴⁷ No simple

5960

conclusions were drawn from this study about the possibility of bicycloaromatic destabilization. It was suggested that the homoaromatic nature of the ions was the major factor determining their behavior.

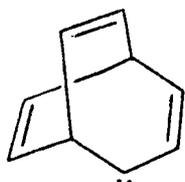
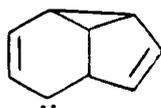
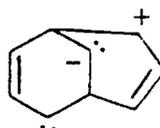
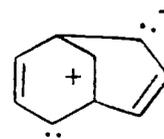
One example apparently exists of a carbene which is stabilized by bicycloaromaticity. The carbene 61, generated

6162

from the corresponding tosylhydrazone salt, did not add to electron-rich olefins such as cyclohexene and styrene. It did add to electron-deficient olefins such as dimethyl fumarate.⁴⁸ This particularly nucleophilic character was explained by suggesting that the carbene actually exists as the delocalized form 62, in which the pair of electrons at the carbene center is not included in the delocalization.

As example 62 implies, bicycloaromaticity can be applied to carbenes and used to speculate about their behavior. The pair of electrons in the carbene center can be included in the delocalization, in a p orbital, suggesting a particularly electrophilic carbene. For purposes of assigning nomenclature, this carbene will be isoelectronic with the anion. The pair of electrons can also be postulated to be excluded from the delocalized system, in an sp^2 orbital, leading to a nucleophilic carbene. For purposes of nomenclature this is isoelectronic with the cation.

If the electron pair of carbene 63 is included in the delocalization, a $3^-2^+2^0$ system, which is stabilized, is

636464a64b

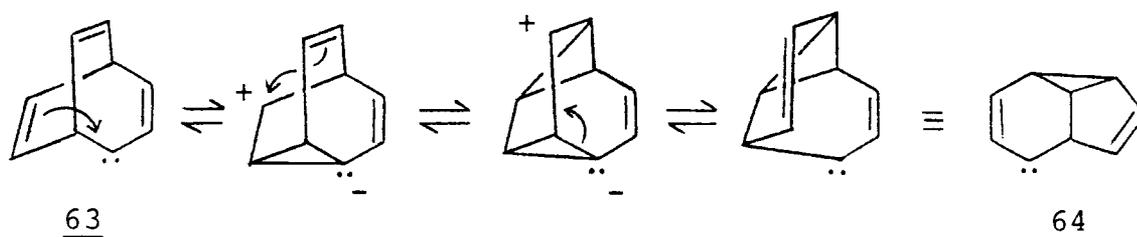
obtained. The alternate possibility, a $3^+2^{\circ}2^{\circ}$ system in which the electron pair is excluded from the delocalization, is destabilized. This suggests that carbene 63 should be stabilized and show electrophilic character.

Systems such as 64 can be treated in a collapsed form in which the cyclopropyl ring is cleaved and drawn as a dipole, as in 64a and 64b. The two possibilities for 64a are $3^+3^-1^-$, which includes the electron pair, and $3^+3^+1^-$, which excludes it. The $3^+3^-1^-$ system is stabilized while the $3^+3^+1^-$ system is not and the carbene would be predicted to be electrophilic. If the other dipolar form 64b is used, inclusion of the electron pair yields a $3^-3^-1^+$ system, while exclusion gives $3^-3^+1^+$. In this case the $3^-3^+1^+$ system would be stabilized, while the $3^-3^-1^+$ form would be destabilized. This leads to the conclusion that the form with the electron pair excluded would be favored and the carbene should be nucleophilic. From this discussion it can be seen that stabilization in carbene 64 can occur for either the nucleophilic or the electrophilic carbene, depending on how the cyclopropyl ring interacts with the remainder of the π system.

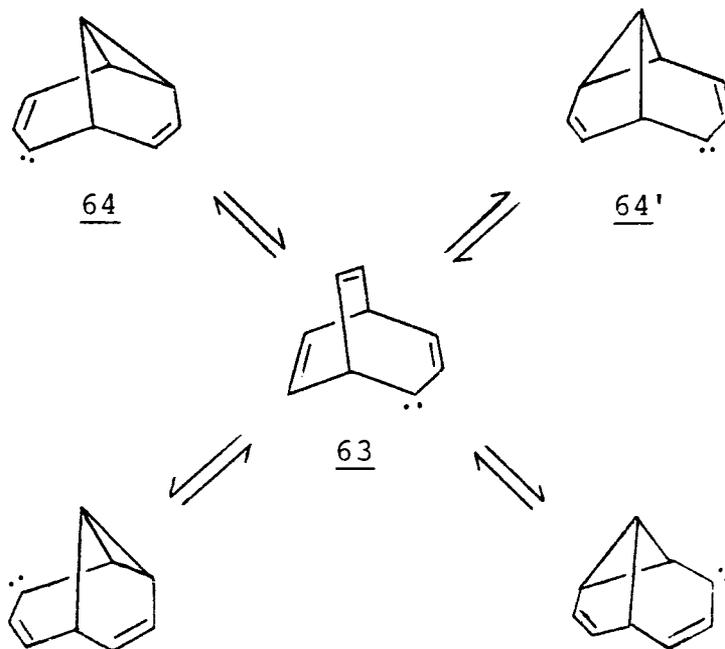
In addition to bicycloaromatic stabilization, carbene 63 could participate in a number of carbene to carbene rearrangements. One possibility involves the intercon-

version of carbenes 63 and 64 through a series of zwitterionic forms (Scheme III). Similar rearrangements of

SCHEME III

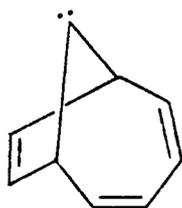
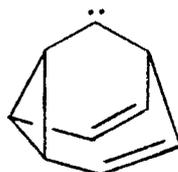


carbene 63 could lead to a number of different carbenes.



Of particular interest is the fact that two degenerate rearrangements such as 64 to 64' are possible.

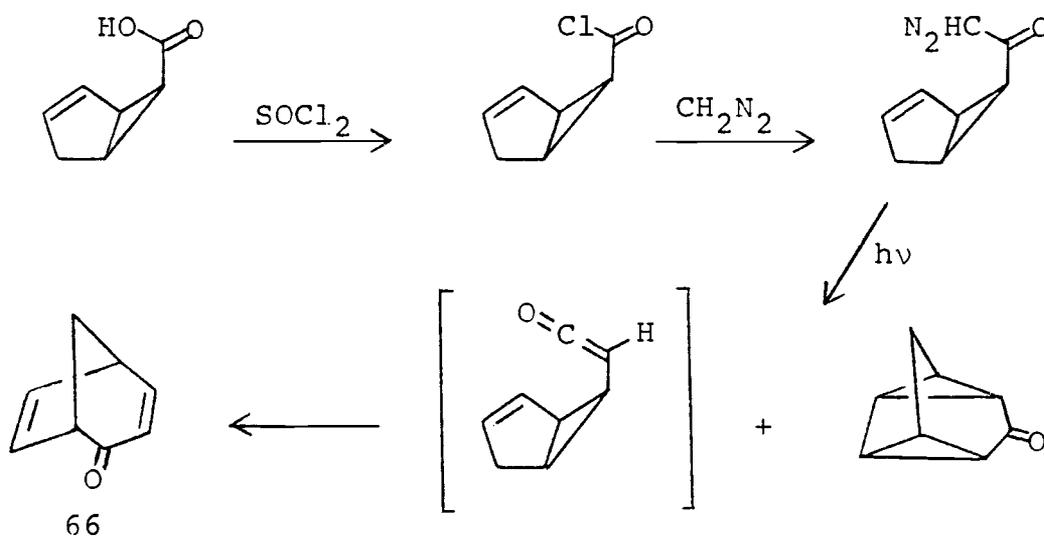
Shechter and co-workers^{49,50} have investigated the chemistry of 65, and Tsuruta⁴⁸ has studied 61. These two carbenes are isomeric to 63 and 64.

6561

The carbenes 63 and 64 have the possibility of bicycloaromatic stabilization and can be compared to related species of proven importance. Additionally, a myriad of intriguing rearrangements can be envisioned. With this range of fascinating possibilities, the study of carbenes 63 and 64 was begun.

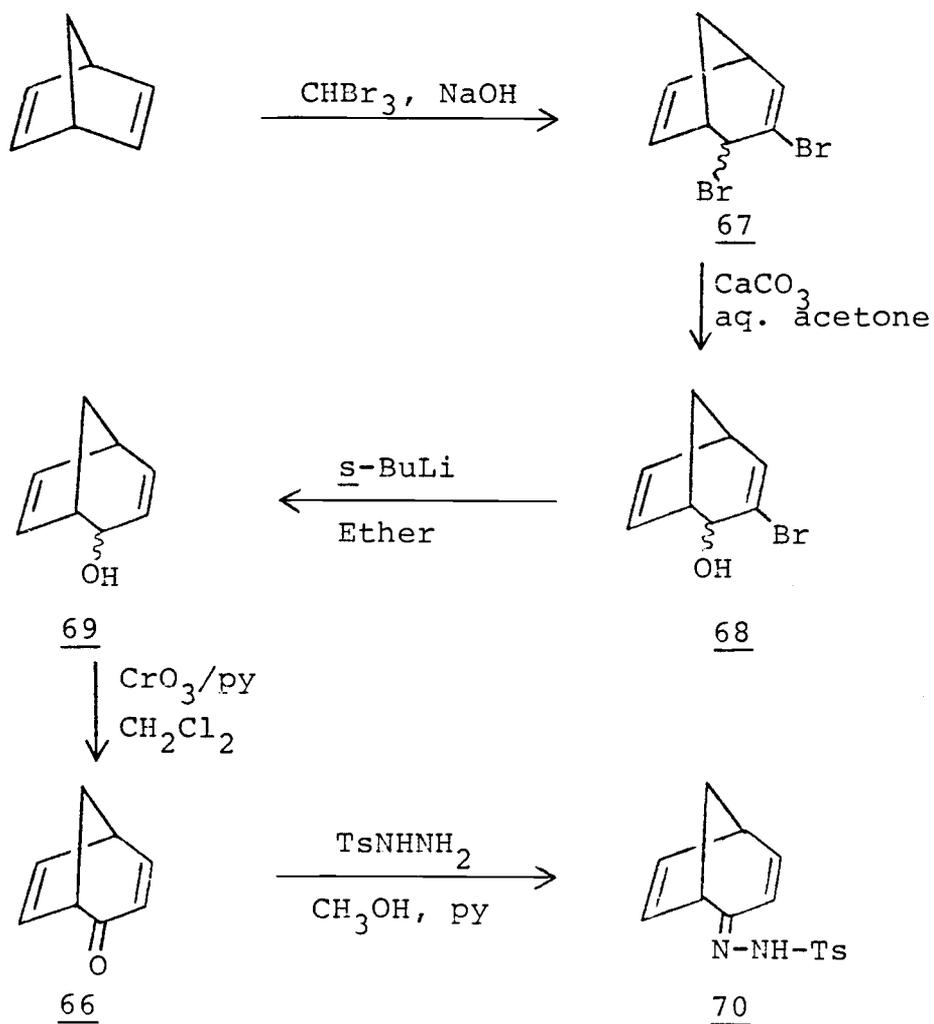
DISCUSSION AND RESULTS

Since decomposition of the alkali metal salt of a tosylhydrazone was the method chosen to generate the carbene, the first synthetic goal was the ketone corresponding to the desired carbene. Bicyclo[3.2.1]octa-3,6-dien-2-one 66 had been prepared previously by Freeman and Kuper⁵¹ using a Wolff rearrangement. Another synthesis



of 66 had been reported by Stothers and co-workers.⁵² Since 66 would be needed in relatively large quantities, implying large amounts of diazomethane, the general scheme of Stothers was adopted. A number of modifications to this scheme were made, so the synthesis is discussed in some detail. The synthesis is outlined in Scheme IV.

SCHEME IV



Dibromocarbene, generated from bromoform and sodium hydroxide in the presence of phase transfer catalyst, was added to norbornadiene to give the dibromide 67 in 39% yield. Hydrolysis was carried out either using silver nitrate or aqueous acetone and calcium carbonate. The latter procedure took about nine days for a large scale

(0.6 mol) reaction, but the bromoalcohol 68 was obtained in 75% yield.

Debromination of 68 was accomplished by Stothers using sodium-ammonia, but after some experimentation, alkyllithium reagents were chosen. In our hands, the sodium-ammonia led to excessive reduction of the carbon-carbon double bonds. The transformation of 68 to 69 was effected by *n*-butyllithium in 38% yield, while *sec*-butyllithium afforded a 45% yield of the epimeric alcohols 69.

Several oxidation procedures were tried. A modified Jones procedure⁵³ gave only 11% of the desired 66, so milder conditions were sought. Chromium trioxide-pyridine complex (Collins' reagent) prepared *in situ*⁵⁴ gave 34% yield. Pyridinium dichromate⁵⁵ in DMF at 0° yielded 36% of 66. All of these procedures afforded rather poor yields, but due to ease of use, the pyridinium dichromate would be the choice of the three.

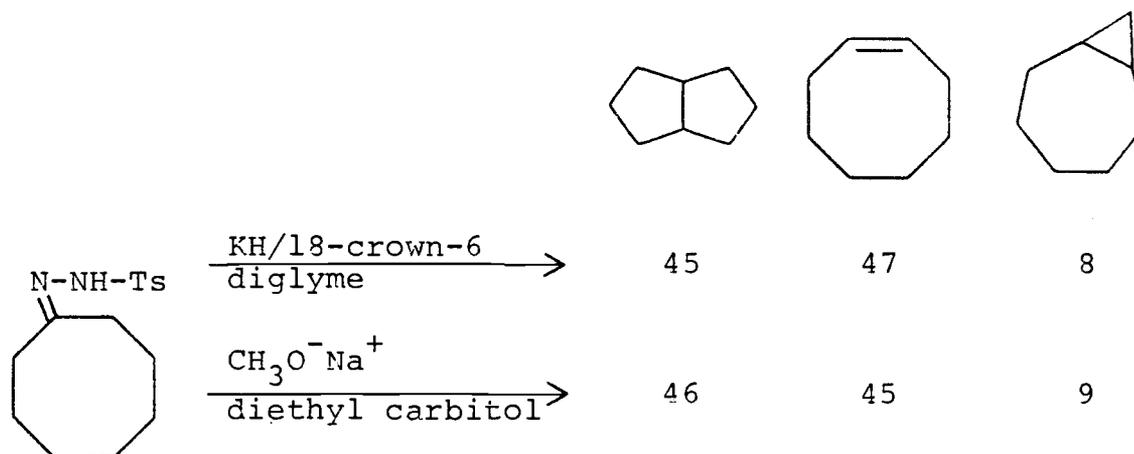
The tosylhydrazone 70 was prepared in 39% yield by treatment of 66 with one equivalent of tosylhydrazine in methanol at room temperature using pyridine as a catalyst. Attempts to use more vigorous conditions such as refluxing acidic ethanol led to varying amounts of an undesired side product, tentatively identified as the 3-tosyl adduct of 70.

With the tosylhydrazone in hand, the corresponding metal salts were made and decomposed under a variety of

conditions. The volatile products were separated by preparative vpc and identified by spectral means, usually by comparison to the spectra of authentic samples. A common method of carbene generation is pyrolysis of the dry lithium salt of a tosylhydrazone by heating in a flask under vacuum and then collecting the volatile products in traps maintained at Dry Ice temperature.⁴⁹ This has been called the static method by Dolbier.³² The dry salt was also decomposed by dropping it onto an already hot Pyrex surface. Drop static is Dolbier's term for pyrolysis of this form. The lithium salt was also photolyzed in anhydrous THF (0.0039 M). The irradiation was carried out through quartz at about 10° with a 450 watt Hanovia high pressure mercury lamp. Irradiation was discontinued when an equivalent amount of nitrogen had been collected. A fourth method of generating the carbene involved the thermal decomposition of the potassium salt of the tosylhydrazone in diglyme in the presence of 18-crown-6 ether. Complexation of the potassium ion with the crown ether was tried in an attempt to make the salt more soluble in diglyme, or possibly to lower the temperature needed to initiate diazo compound formation.

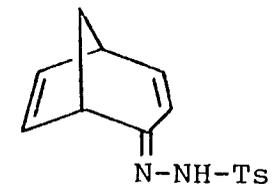
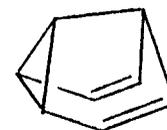
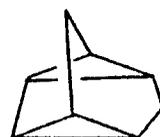
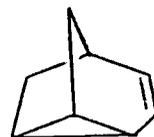
Since thermolysis of the salt of a tosylhydrazone using crown ether as a complexing agent is not commonly

used, a model system was investigated. Cyclooctanone tosylhydrazone was chosen since it is readily available and the chemistry of its carbene well documented. The results obtained agreed extremely well with those of Friedman and Shechter,⁵⁶ who had generated the carbene by treatment of the tosylhydrazone with 1.2 equivalents of sodium methoxide in diethyl carbitol. This appears to be good evidence that these complexed potassium ion conditions will provide the same results as more conventional methods of carbene generation.

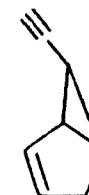
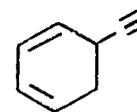


The results of the decomposition of tosylhydrazone 70 with the percent composition of products is shown in Table I. Compounds 38, 71, and 72 were identified by comparison of their nmr spectra with spectra of authentic samples available from previous work.^{57,58} Compounds 73 and 54

TABLE I.

PERCENT COMPOSITION OF PRODUCTS FROM TOSYLHYDRAZONE 70CONDITIONS

+



UNKNOWN

Dry salt (Li^+) pyrolysis (static)	44	7	10	24	9	6
Dry salt (Li^+) pyrolysis (static drop)	58	7	7	11	5	11
Photolysis (Li^+ salt) in THF	39	31	18	9	3	--
KH/18-crown-6 diglyme	19	12	10	13	17	28

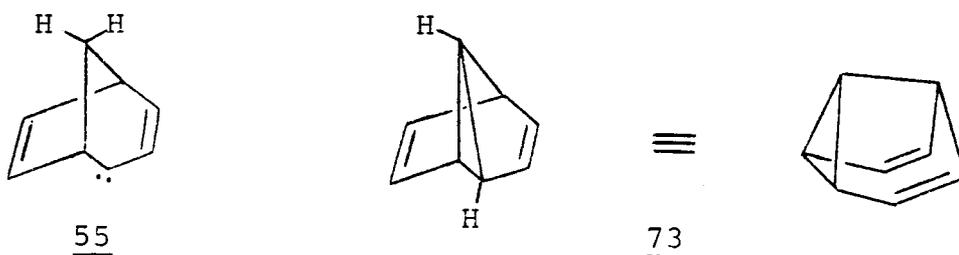
were identified by comparison of their nmr spectra with literature references of Zimmerman⁵⁹ and Bergman⁴⁴ respectively. Compound 74 was identified by comparison with an nmr spectrum of 74 obtained from Professor Murahashi.^{60,61} The products 73 and 74 are grouped together in Table I as they were not resolved under the vpc conditions used. An nmr spectrum of the two together was obtained from the dry salt pyrolysis (static). The nmr integrations indicate that compounds 74 and 73 are present in roughly a four to one ratio. One further compound was present in the amounts shown but was never identified. The nmr spectrum consisted solely of absorbances in the $\delta 1.5$ region.

The reason why the carbene was generated by a number of different methods is that in all cases, the yield of volatile products was extremely low, ranging from 1.5 to 3.0%. Unfortunately the alternate methods of tosylhydrazone salt decomposition did not improve the yield to any noticeable extent. In the lithium salt photolysis, some of the pentane insoluble residue was soluble in chloroform, and this was investigated. No unreacted tosylhydrazone was recovered, and the residue did not seem to have an appreciable amount of tosyl fragments in it (there were no aromatic or aromatic methyl absorbances in the nmr spectrum). The thoroughly nondescript nature of the nmr spectrum (two broad bands centered at about $\delta 3.8$ and $\delta 1.8$) and

mass spectrum, coupled with the small tlc Rf value (about 0.05), would make it seem unlikely that any low molecular weight discrete compound was present in any significant amount. This residue was dried and weighed and would account for essentially all of the remaining starting tosylhydrazone.

Examination of the products in Table I shows that they can be divided into two groups based on molecular formula. Products 73, 74 and 54 have the formula C_8H_8 which is the same as the parent carbene 55. The other compounds 38, 71 and 72 have the formula C_8H_{10} , indicating that two hydrogen atoms have been added to the carbene in some manner.

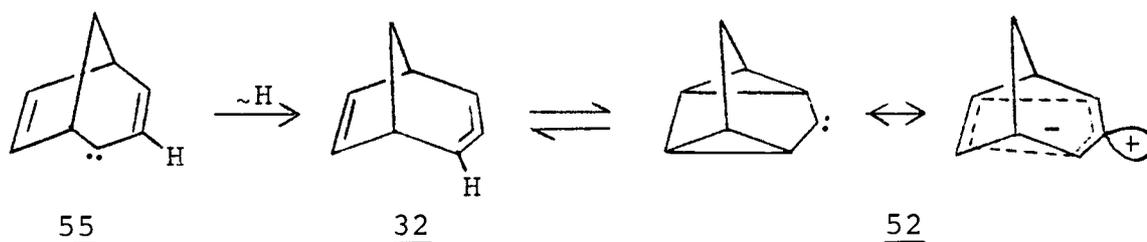
Of the C_8H_8 group, the formation of semibullvalene 73 can be explained by the insertion of the carbene into the carbon-hydrogen bond of the endo H-8 bridge proton. A



similar process occurs in 7-norbornylidene 11,²⁷ the carbene generated from norcamphortosylhydrazone,²⁶ and a number of less closely related examples.

The presence of endo-6-ethynylbicyclo[3.1.0]hex-2-ene 54 deserves more attention than the rather obvious 73.

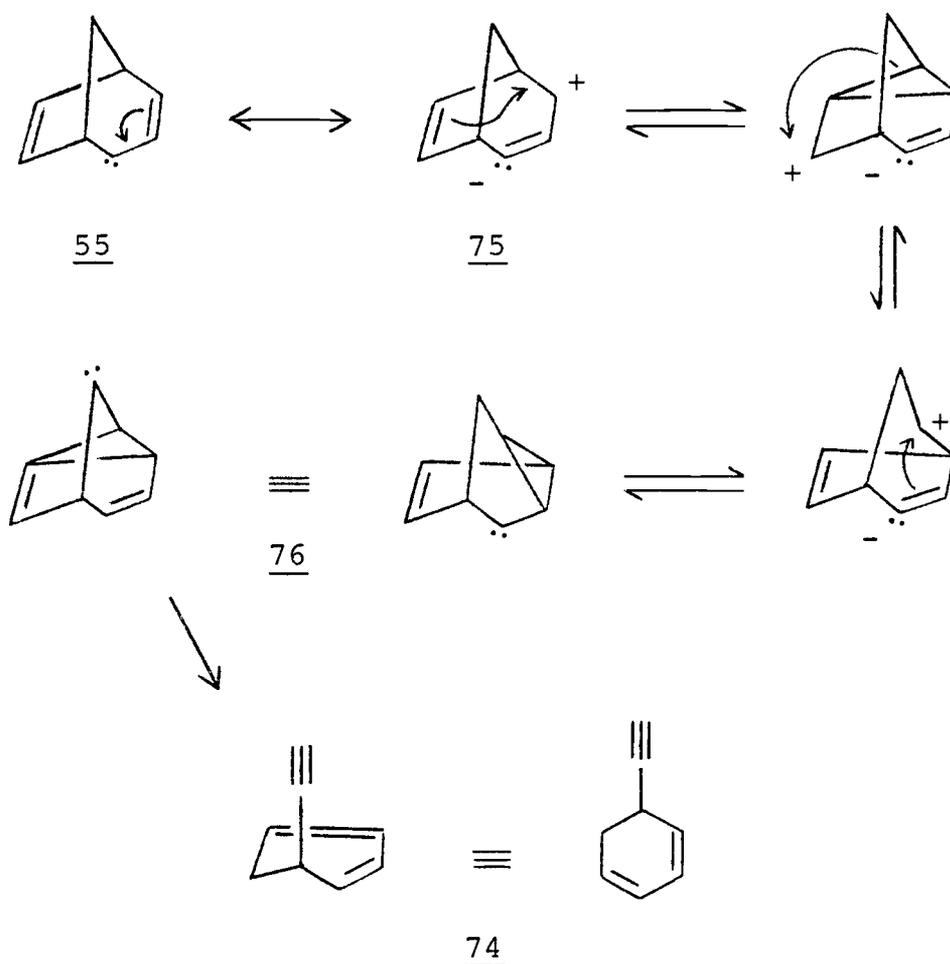
First, this is the same product that was obtained from bromide 50 and tosylhydrazone 53 by Bergman.⁴⁴ This would imply that it arises from the homoconjugated carbene 52. Carbene 52 could be formed from carbene 55 by a 1,2 hydride migration to the strained allene 32 which is a valence



isomer of 52. There is considerable literature precedent for the cyclic allene 32, including its proposal by Klumpp³⁴ and consideration of the similar species 31 by Freeman and Hardy.³³ This implies that carbene 55 has entered the same intermediate manifold as carbene 52. This conversion of 55 to 52 seems to be a reasonable explanation of the formation of 54.

The third C_8H_8 hydrocarbon obtained from carbene 55 has been identified as 5-ethynyl-1,3-cyclohexadiene 74. A possible mechanism for its formation is given in Scheme V. The carbene 55 can be shown as the resonance form 75, which can rearrange through a series of zwitterionic forms to the new carbene 76. This carbene would undergo a fragmentation reaction common to carbenes α to a cyclopropyl ring⁶² to give the observed product 74.

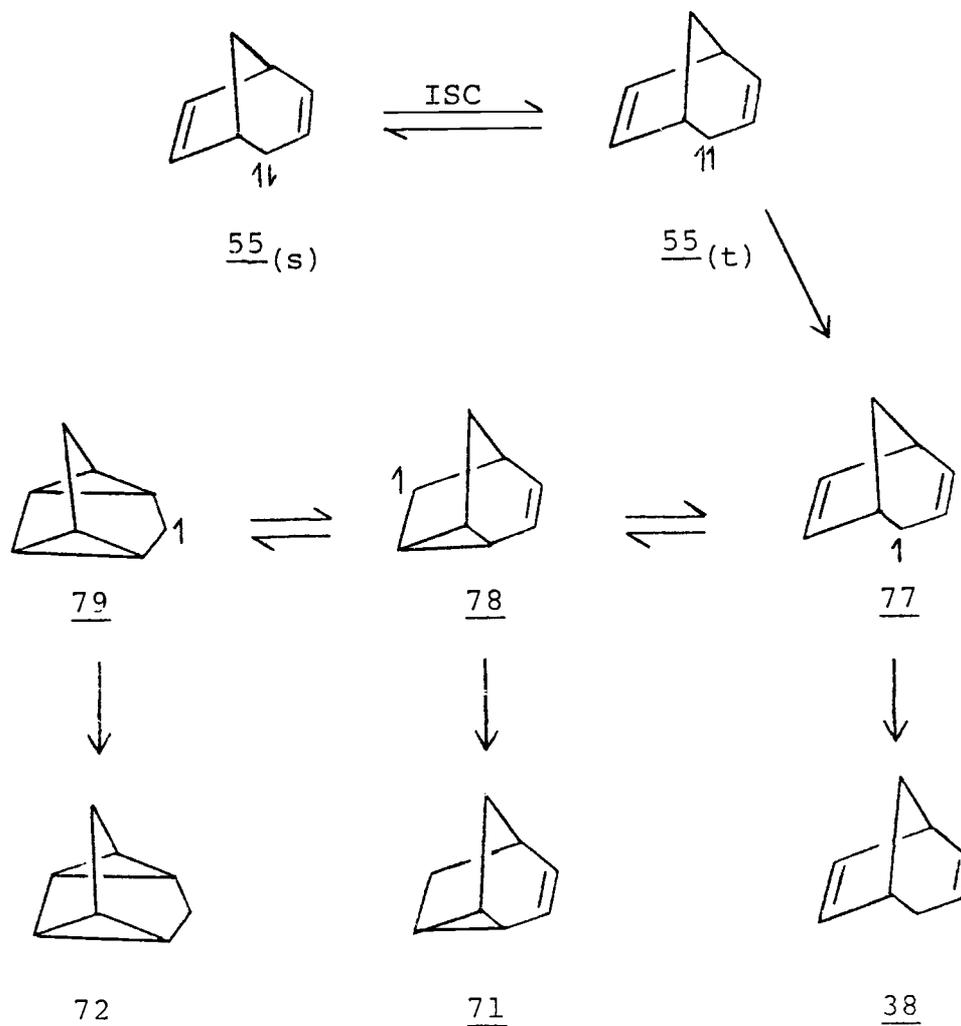
SCHEME V



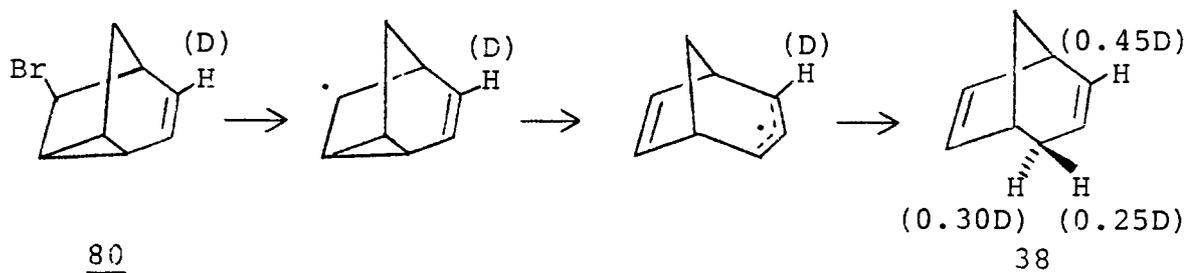
Compounds 38, 71 and 72, the other three products of carbene 55, have the formula C_8H_{10} , showing that two hydrogen atoms have been added to the parent carbene. Some type of radical hydrogen abstraction process is a reasonable first suggestion for a mechanism of their formation. Carbene 55, which would be generated as a singlet from the singlet diazo compound, might intersystem cross to the triplet which could abstract a hydrogen atom to form the radical 77. This radical could be in equilibrium with

radical species 78 and 79, each of which could abstract a second hydrogen atom leading to the observed products 38, 71 and 72 (Scheme VI).

SCHEME VI

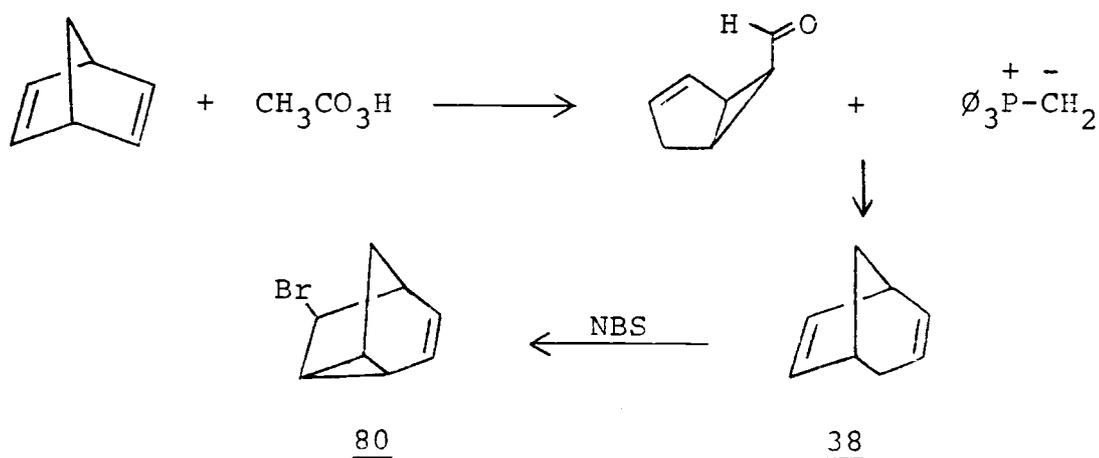


This radical system (77, 78, and 79) has been studied by Klumpp and co-workers⁶³ who treated tricyclic bromide 80 with tri-*n*-butyltin hydride or sodium in *tert*-butyl alcohol and THF, both free radical conditions, and obtained hydrocarbon product 38 with deuterium scrambling as would



be expected from an allylic radical. No comment was made as to the presence of possible minor hydrocarbon products 71 and 72.

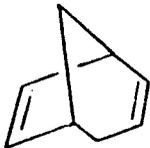
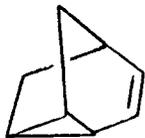
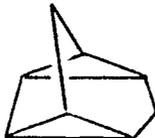
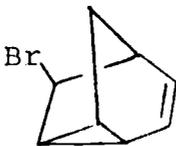
It was decided to repeat the above experiment and search for minor concentrations of 71 and 72. The tricyclic bromide was prepared by the series of reactions outlined below. Norbornadiene was treated with peracetic acid⁶⁴ to



give bicyclo[3.1.0]hex-2-en-6-endo-carboxaldehyde, which was allowed to react with the Wittig reagent, prepared from methyltriphenylphosphonium bromide and phenyllithium, to afford hydrocarbon 38.⁶⁵ Tricyclic bromide 80 was prepared

TABLE II.

PERCENT COMPOSITION OF PRODUCTS FROM TRICYCLIC BROMIDE 80

				
		<u>38</u>	<u>71</u>	<u>72</u>
	$(n\text{Bu})_3\text{SnH}$	98.7	1.3	<0.1
<u>80</u>	$\text{Na}/t\text{BuOH}$	97.5	2.5	<0.1

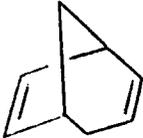
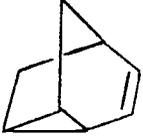
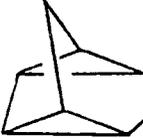
by reaction of 38 with N-bromosuccinimide.⁶³ The debromination of 80 was carried out using both tri-n-butyltin hydride and sodium in tert-butyl alcohol.⁶³ For the tri-n-butyltin hydride case, the hydrocarbon products were present in an overall yield of 19% with the percent composition shown in Table II. A similar product composition was obtained with sodium in tert-butyl alcohol with the yield of hydrocarbons found to be 29% (Table II).

A comparison of the product composition of this known radical process (Table II) with that obtained from the carbene shows noticeable differences. No tetracyclooctane 72 and only a very small amount (<3%) of the tricyclic octene 71 were found in the classical radical reaction. Table III shows the relative amounts of the three C₈H₁₀ hydrocarbons produced by the various methods of carbene generation.

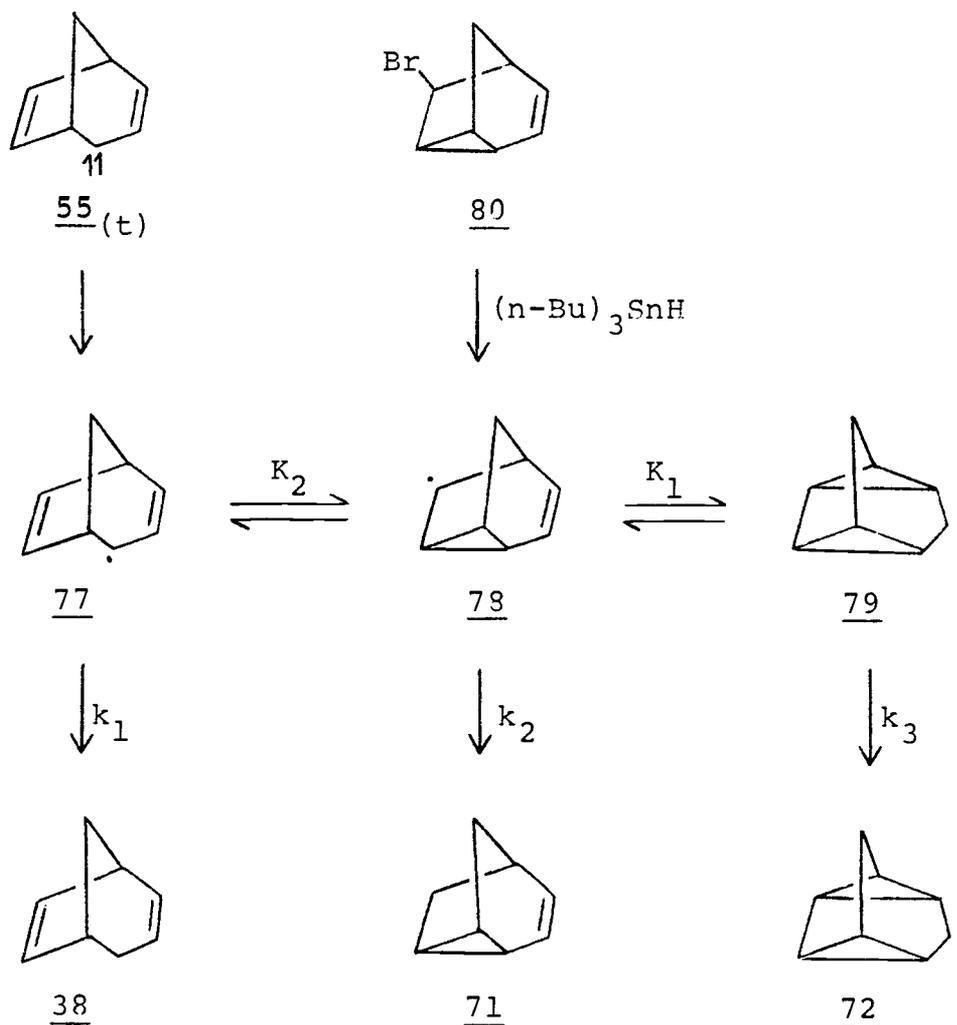
To compare the results of the radical reaction to those of the carbene process, some insight into the various individual processes occurring is needed. It might be expected that the radical 78 could be in equilibrium with the other two radical species 77 and 79 (Scheme VII). The ratios of 38 to 71 to 72 would depend upon the equilibria K₁ and K₂ and upon the rates k₁, k₂ and k₃ of the three hydrogen atom abstraction steps.

The norbornenyl-nortricyclyl radical equilibrium has been studied in detail and would seem to be a reasonable

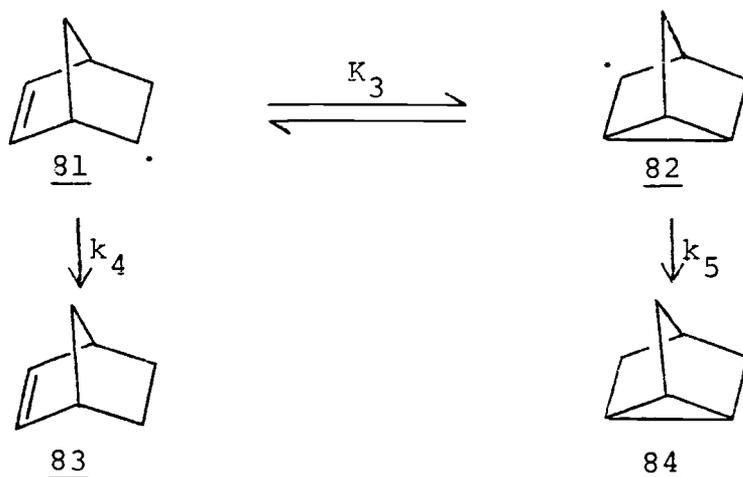
TABLE III.
 PERCENTAGE OF C₈H₁₀ PRODUCTS FROM 55

<u>CONDITIONS</u>				PERCENTAGE OF TOTAL VOLATILE PRODUCTS
	<u>38</u>	<u>71</u>	<u>72</u>	
Dry salt (Li ⁺) pyrolysis (static)	72	11	16	61
Dry salt (Li ⁺) pyrolysis (static drop)	81	10	10	72
Photolysis (Li ⁺ salt) in THF	44	35	20	88
KH/18-crown-6 diglyme	46	29	24	41

SCHEME VII



model. When the equilibrium is entered via the norbornenyl radical 81, a good chain transfer agent would favor 83, while product 84 is usually favored when the equilibrium K_3 is operative.⁶⁶ Little has been said about the rates k_4 and k_5 . Davies and co-workers⁶⁷ generated the radicals 81 and 82 in ether and suggested that hydrogen transfer from the solvent ether should be of a comparable rate



for both radicals since the radicals should be sterically similar. Kuivila⁶⁸ has provided evidence that the nortricyclene-norbornene ratio depends very little on the hydrogen donor, which may vary from organotin hydride to cumene to norborn-2-ene-5-carboxaldehyde.

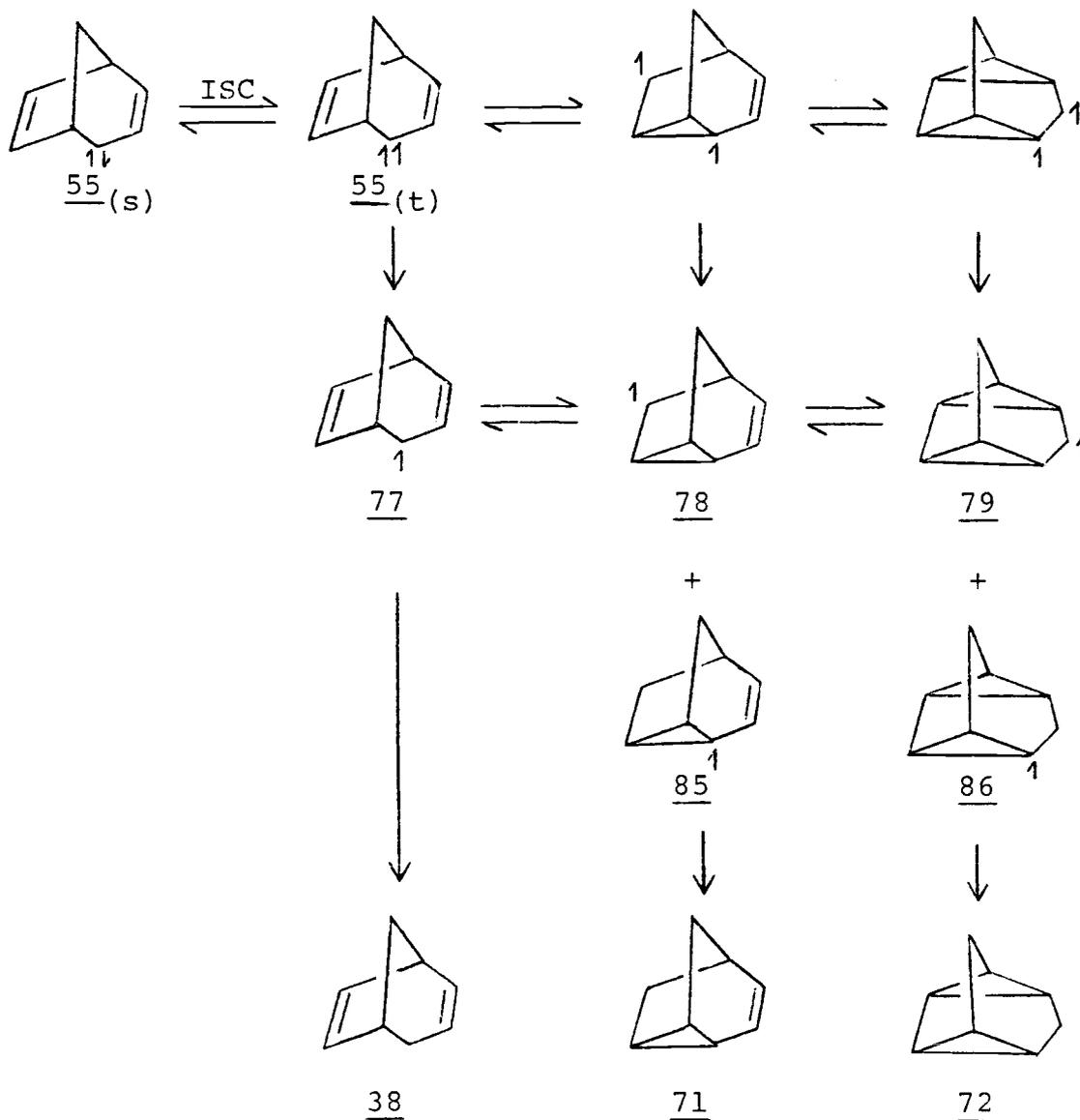
In comparing the radical 78, generated with tri-n-butyltin hydride, to a possible radical 77 from the triplet carbene, the equilibria K_1 and K_2 and the hydrogen abstraction steps k_1 , k_2 and k_3 need to be considered (Scheme VII). The working assumption will be made that the rates of hydrogen abstraction, k_1^{Sn} , k_2^{Sn} , and k_3^{Sn} , by the radical from tri-n-butyltin hydride are nearly equivalent. Similarly, the rates k_1^{THF} , k_2^{THF} , and k_3^{THF} , for hydrogen abstraction from THF by the proposed radical in the carbene case are also assumed to be nearly equivalent. In the free radical case, if equilibration of the three radical species is not complete, 71 would be formed from the parent radical in excess, so that 2.5% would be an upper limit to the

percentage of 71 to be expected from the carbene. If the radical species are present in equilibrium, the hydrocarbon ratio shown in Table II should also be that of the carbene.

For the carbene, if the equilibrium is operative, the percentage of products given in Table III would be representative. If the equilibrium is not obtained, an excess of 38 from the parent radical would be expected. Even so, from the carbene reaction, a significantly larger percentage of 71 and 72 was obtained than for the classical radical process. This would point to the possibility that the intermediates for the carbene process might be better represented by a set of intermediates other than the equilibrating radicals of Scheme VI.

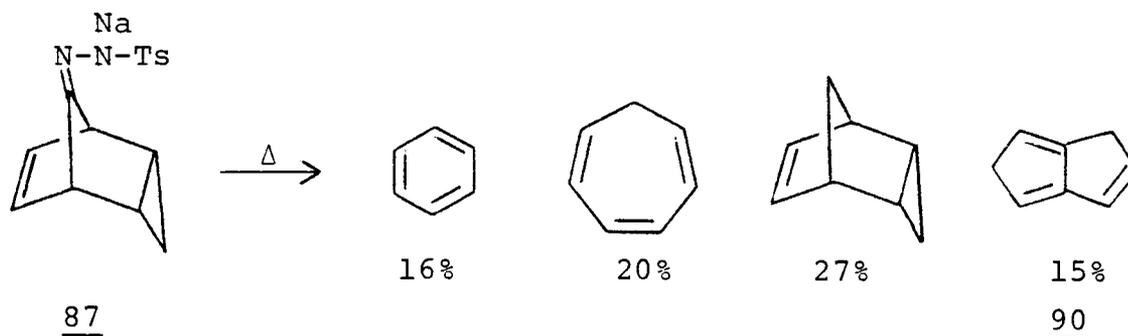
A logical alternative to the radical intermediate would be a diradical process (Scheme VIII). The singlet carbene 55(s) would intersystem cross to the triplet 55(t), which would be in equilibrium with two other diradical species. The triplet 55(t) and the two diradicals could abstract a hydrogen atom to give one of five radicals. The three radicals 77, 78 and 79 could be in equilibrium while radicals 85 and 86 cannot equilibrate and would have to go directly on to products 71 and 72 respectively. This mechanism would give larger amounts of products 71 and 72 than the classical radical process.

SCHEME VIII

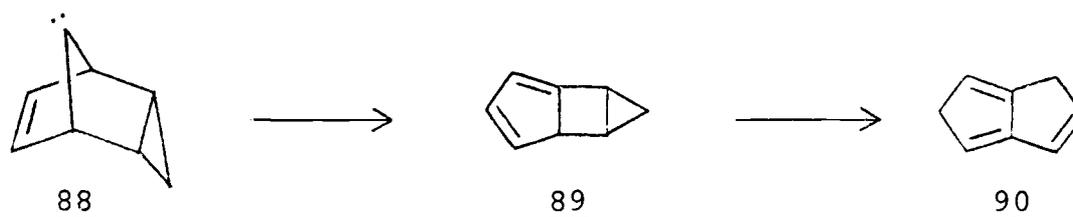


Since carbene 55 and carbene 52 seem to be part of the same intermediate manifold, comparison of other isomeric carbenes might prove of interest.

Two other C₈H₈ carbenes have been studied by Murahashi.⁶⁰ The tosylhydrazone salt 87 was decomposed to give four products. A mechanism was proposed for the forma-

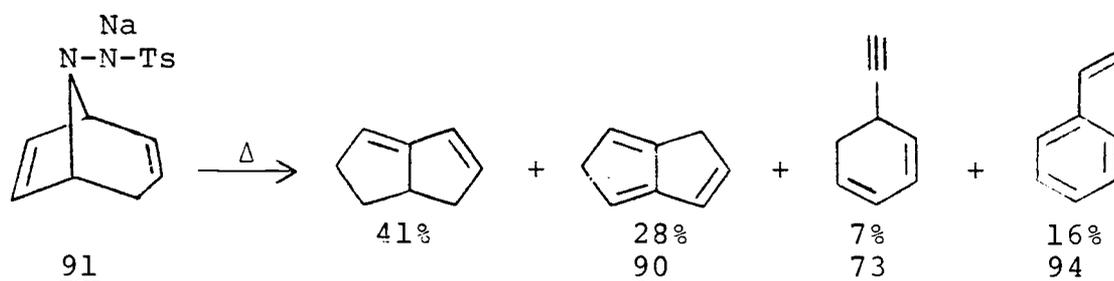


tion of 90 involving interaction of the p-orbital of carbene 88 and the cyclopropyl orbital to give intermediate 89. The



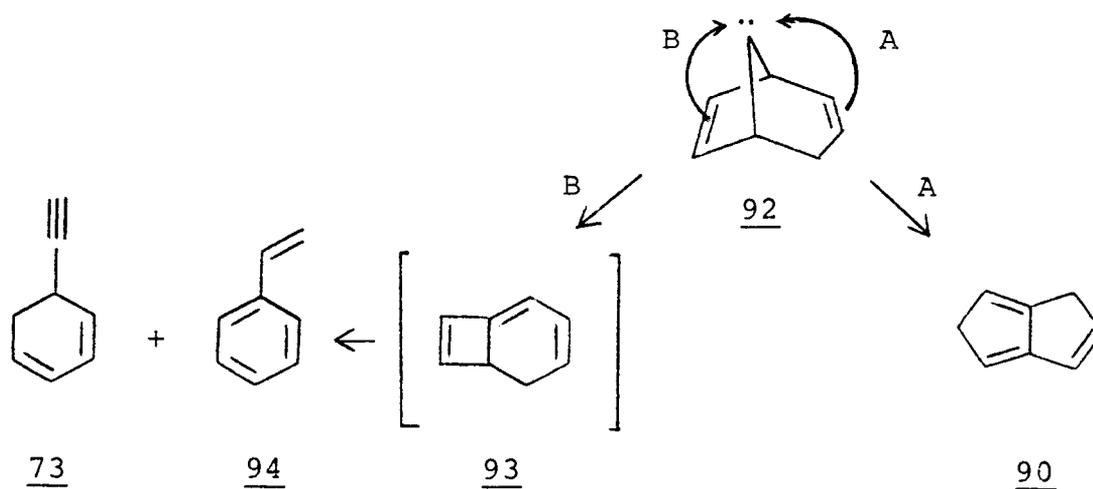
highly strained 89 could rearrange further to the observed pentalene 90.

Also studied by Murahashi⁶⁰ was the carbene derived from tosylhydrazone salt 91. Two pathways were proposed



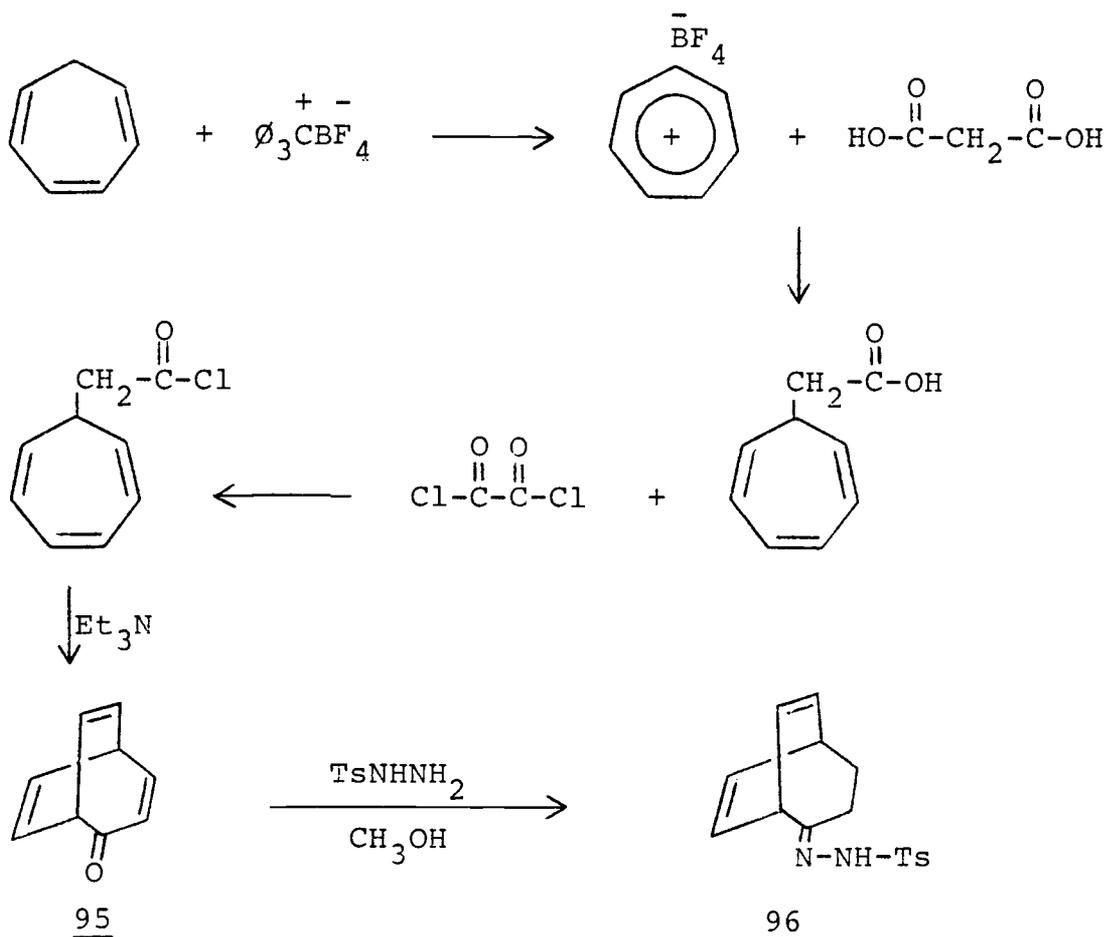
to explain the product formation. Interaction of the carbene center of 92 with the p orbital of the $\text{C}^2\text{-C}^3$ bond (path A) would lead to 90, while interaction with the p

orbital of the C⁶-C⁷ bond (path B) would lead to intermediate 93 and the two products 73 and 94.



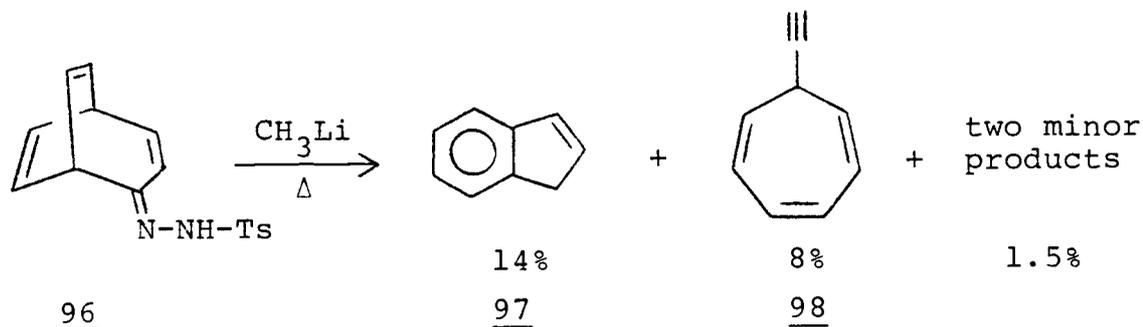
The main pathway for reaction for both carbenes 88 and 92 involves interaction of the carbene with an orbital from either a double bond or a cyclopropyl bond. Based on the product distribution, it would seem unlikely that either of these carbenes interconvert with carbene 55. The contrast between these carbenes and 55 shows some of the various intramolecular pathways available for a carbene to form stable products.

The second key intermediate in our study of bicycloaromatic carbenes with a potential for carbene to carbene rearrangements is the carbene 63 (Scheme IX), in which the methylene bridge of 55 is replaced with another π ribbon. The parent ketone was prepared according to the following synthetic scheme. Tropenium fluoroborate was prepared from



cycloheptatriene and trityl fluoroborate which had been prepared in situ.⁶⁹ The tropenium fluoroborate was treated with malonic acid to yield cycloheptatrienylacetic acid.⁷⁰ This acid was converted with oxalyl chloride to the acid chloride, which was treated with triethylamine in hexane to afford the bicyclic ketone **95**.⁴⁷ The tosylhydrazone **96** was prepared by treating the ketone with tosylhydrazine in methanol with a pyridine catalyst. As in the case of the [3.2.1] tosylhydrazone **70**, room temperature or lower reaction conditions produce the best results.

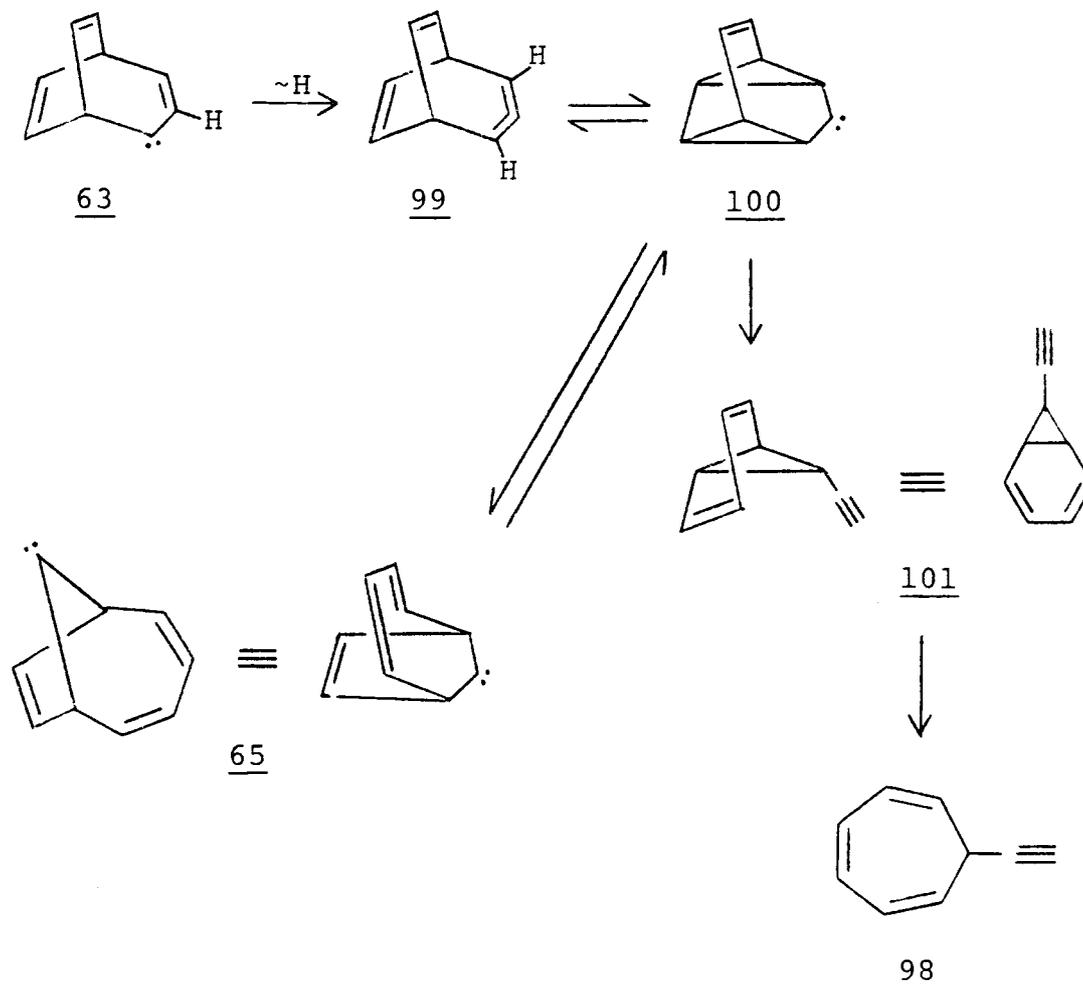
The tosylhydrazone 96 was converted to its lithium salt and the dry salt pyrolyzed by the static method.



Two major products were obtained. Indene 97 (14%) was identified by comparison of its nmr and ir spectra with that of an authentic sample. The 8% component was identified as 7-ethynyl-1,3,5-cycloheptatriene 98 by comparison of its nmr and ir spectra with those published.⁷¹ Two minor products were obtained in yields of 0.9% and 0.6%, but neither was identified.

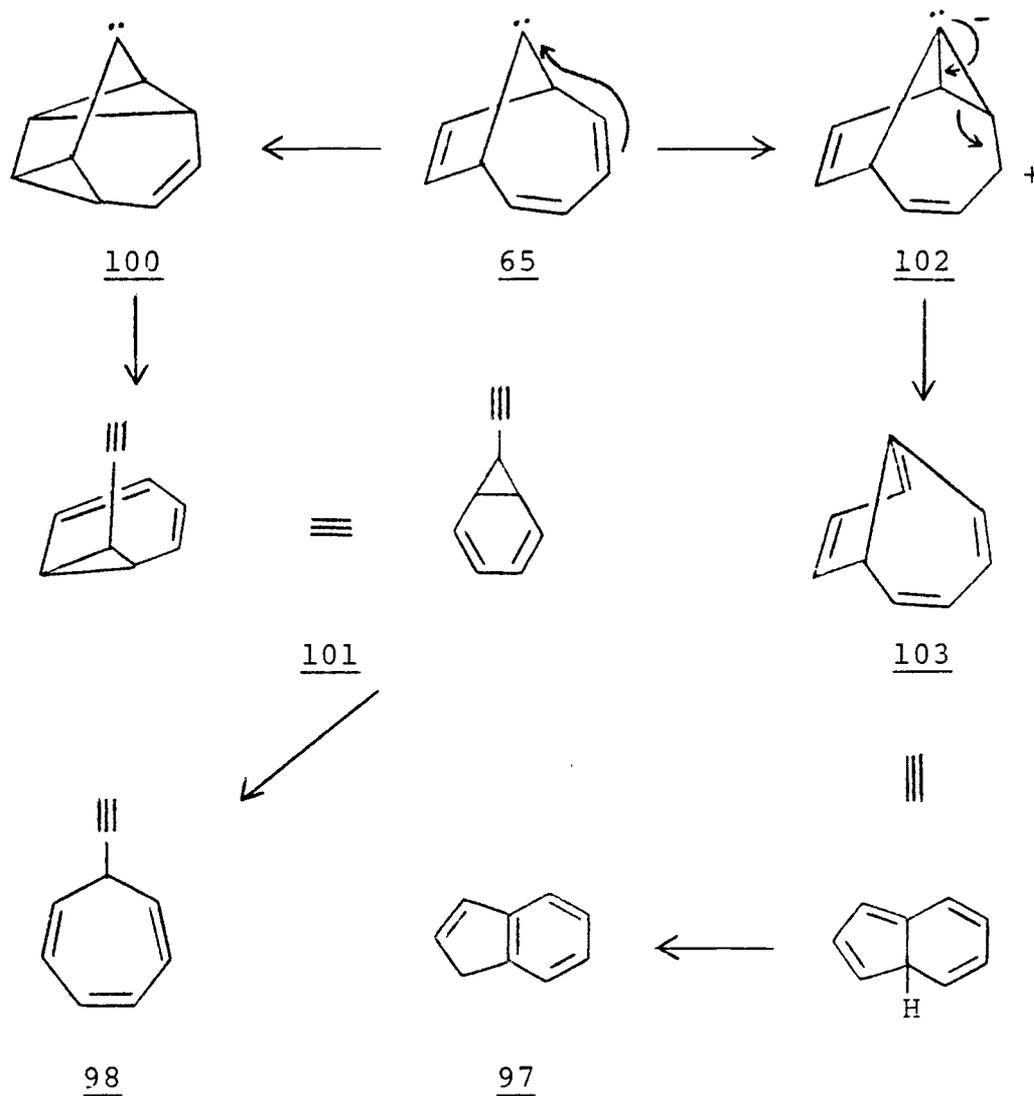
Both major compounds 97 and 98 have the same molecular formula, C_9H_8 , as the parent carbene. This is in contrast to the bicyclo[3.2.1] case 55, in which addition of two hydrogen atoms was a major process. A reasonable mechanism for the formation of indene 97 and ethynylcycloheptatriene 98 would begin in the same manner as the the rearrangement of carbene 55 (Scheme IX). The parent carbene 63 would undergo a 1,2-hydrogen migration to the strained allene 99, which is a valence tautomer of tetracyclic carbene 100. Two pathways are available for carbene 100. It could undergo the well documented fragmentation reaction⁶² to

SCHEME IX



afford bicyclohexadiene 101. This would undergo valence isomerization⁷² to the observed product 98. Alternatively, carbene 100 could undergo a thermally allowed $\sigma^2_s + \sigma^2_s + \pi^2_s$ cycloreversion reaction⁸³ to carbene 65.

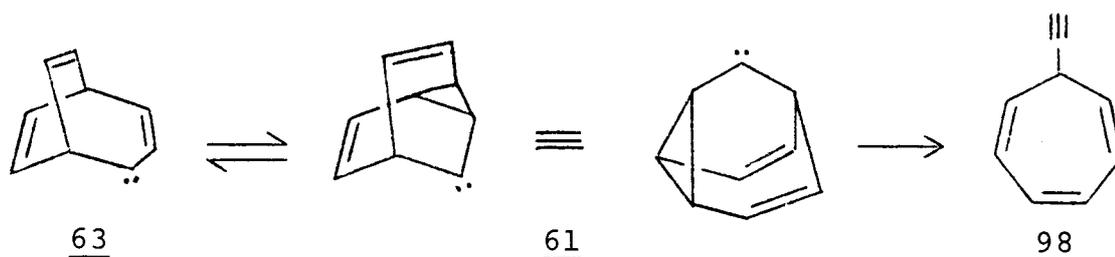
Carbene 65 has been generated from the corresponding tosylhydrazone by Shechter^{49,50}, who proposed the following scheme to explain its chemistry. The carbene 65 undergoes



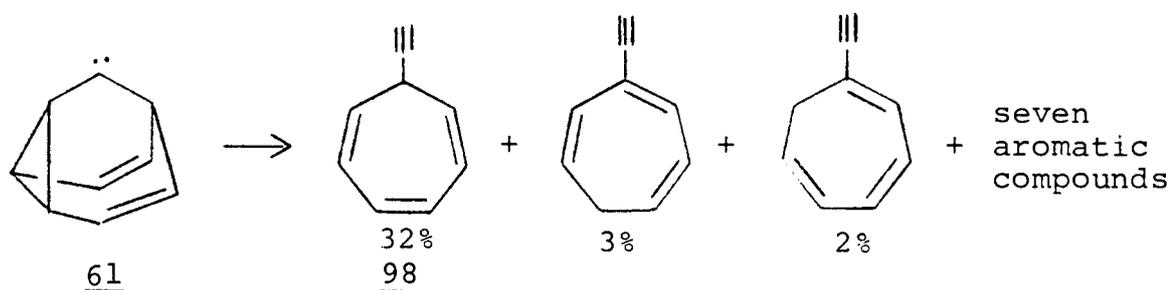
an internal cycloaddition reaction to form carbene 100, or it reacts through the zwitterionic form 102, which fragments to 103. A 1,5 hydrogen migration then yields the observed product indene 97. Carbene 100 fragments to 98 as discussed previously. The ratio of indene 97 to ethynylcyclohepta-

triene 98 from Shechter's carbene 65 is 95 to 5, while the ratio of 97 to 98 for carbene 63 is 64 to 36.

However an alternate pathway for the formation of 98 from carbene 63 should be mentioned. By analogy to Scheme V, 63 could rearrange through a series of zwitterions to carbene 61, which would fragment to ethynylcycloheptatriene



98. Barbaralylidene 61 has been generated from the corresponding tosylhydrazone salt.⁴⁸ The products obtained were the three ethynylcycloheptatrienes and seven aromatic

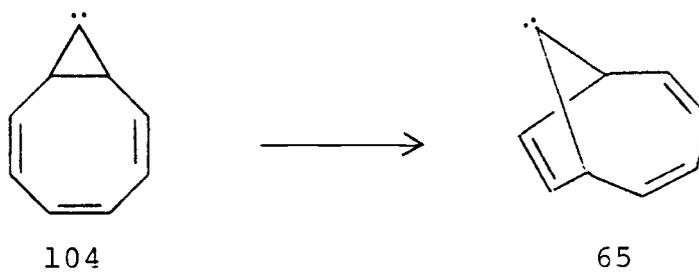


compounds. It was assumed that 98 was the product formed from the carbene, and the two minor ethynylcycloheptatrienes were derived from it by thermal 1,5 hydrogen shifts. No yields for the aromatic compounds were given, but it was stated that 98 was the major product. Of particular interest to the chemistry of 63 is the fact that indene

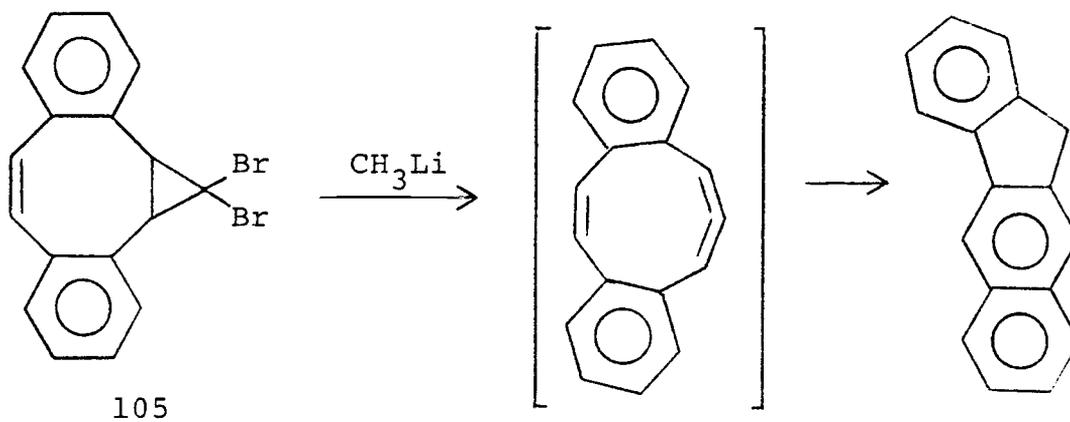
is not one of the aromatic compounds found. Since indene is the major product of carbene 63, and no aromatic other than indene is formed, the mechanism involving the strained allene 99, (Scheme IX) remains more attractive. This possibility of the interconversion of 63 and 61 is indicative of the complexity and scope of the possible interrelationships of the various C_9H_8 carbenes.

The chemistry of carbene 63 parallels that of carbene 65 rather closely, which is evidence for the common intermediate 100. 100 is in turn the valence isomer of the strained cyclic allene which is the key intermediate both here (99) and in the bicyclo[3.2.1] carbene (32).

Since carbenes 63 and 65 appear to share the common intermediate 100, other C_9H_8 species should be examined for the possibility of entering the same intermediate manifold. Carbene 104 has been studied by Waali.²⁹ The



possibility of the conversion of 104 to 65 was considered, but ruled unlikely on the basis of studies on the analogous system 105.



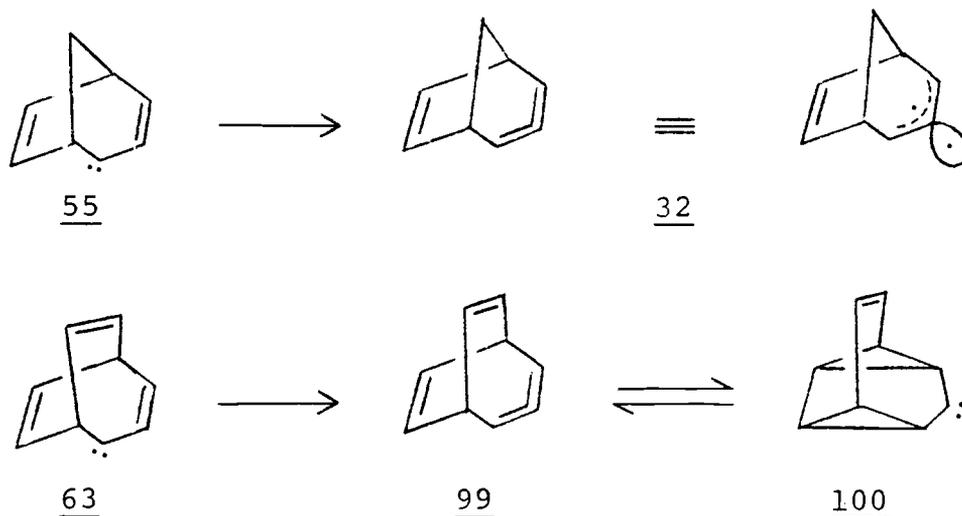
The most striking feature of a comparison of the [3.2.2] 63 and [3.2.1] 55 carbenes is that the major portion of the products from 55 appear to arise from a radical or diradical process. This implies that a triplet carbene 55(t) is readily formed. The alternative pathway involves the allene 32. In a similar manner, carbene 63 can react through the allene 99 (singlet process) or intersystem cross to the triplet 63(t). Allene 99 should be less strained than 32 because of its two carbon bridge as compared to the one carbon bridge of 32. The allene 99 is more easily formed and the singlet products deriving from it dominate. The more strained allene 32 is not readily formed and the alternative mechanism, intersystem crossing to the triplet, is the major product-determining pathway. This would be one possible explanation for the difference in product distribution between carbenes 55 and

63. An alternative discussion involves the fundamental structure of the cyclic allenes themselves.

The nature of strained allenic intermediates is not thoroughly understood. Possibilities include a strained but bonded allene, dipolar, or diradical species. Calculations by Dillon and Underwood⁷³ indicate that 1,2-cyclohexadiene 109 and smaller cyclic dienes may have triplet diradical ground states (110), while 1,2-cycloheptadiene and larger cyclic allenes would be singlets. This would

109110

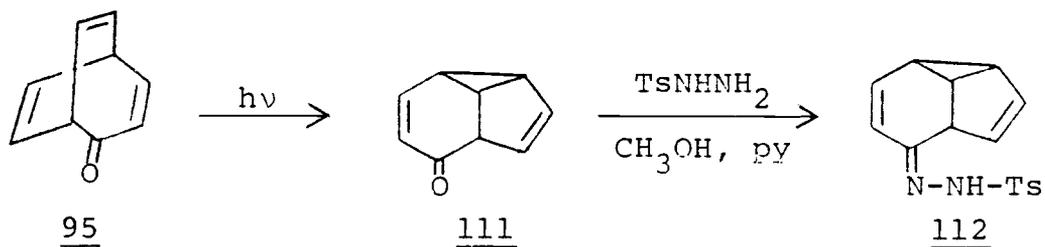
raise the fascinating possibility that the difference in chemistry of carbenes 55 and 63 is due to the different nature of the cyclic allenes 32 and 99. Allene 32 would be expected to be more strained because of its one-carbon bridge than 99 with its two-carbon bridge. The amount of strain difference is not known, but if it were significant, 32 could have one type of ground state, such as a triplet diradical, while 99 could have a different form such as the singlet. This hypothetical diradical allene would fit the observed chemistry of carbene 55, while a singlet 99 would be in equilibrium with the singlet carbene 100, whose chemistry is dominant for carbene 63.



In Scheme III, it was suggested that carbene 63 might rearrange to carbene 64. The ketone precursor of

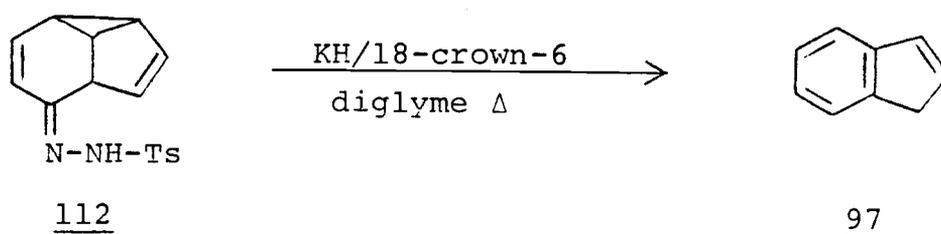


carbene 64 can be synthesized by a photochemical rearrangement of ketone 95.⁷⁴ This ketone 111 was contaminated with

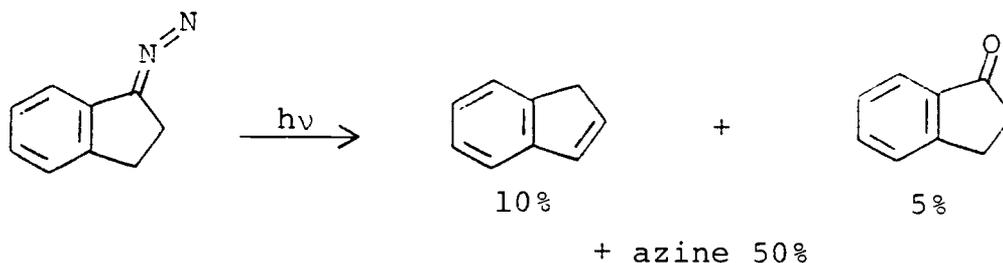


1-indanone, but could be purified to greater than 90% by distillation. The ketone 111 was converted to tosylhydra-

zone 112 by reaction with tosylhydrazine in methanol with a pyridine catalyst. The tosylhydrazone was decomposed by treatment with potassium hydride and 18-crown-6 in diglyme. The only volatile product obtained was indene 97 in 14% yield. (A vpc peak for an additional component present to an extent of 3% of the indene component would have been detected.) To rule out the possibility that the indene

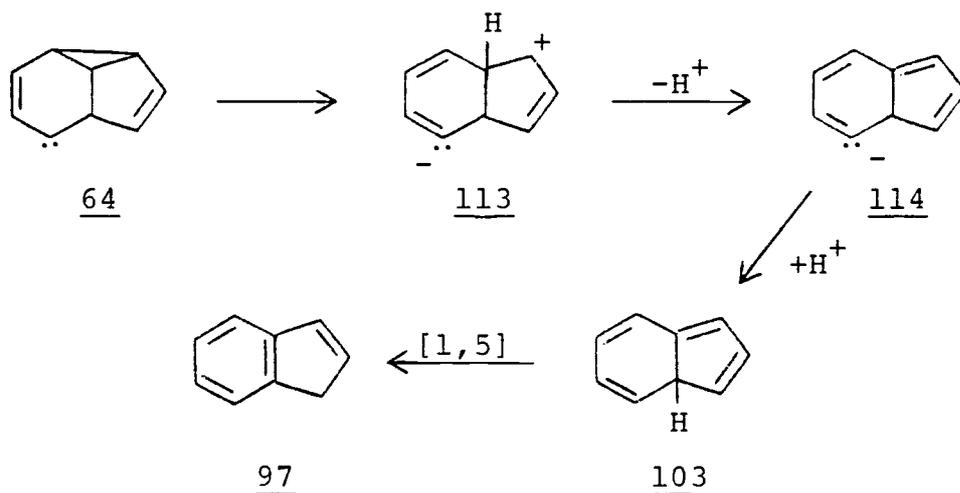


(or the majority of it) came from a possible indanone tosylhydrazone impurity in tosylhydrazone 112, indanone tosylhydrazone was prepared and decomposed under similar conditions. Two volatile compounds, indene 97 (6.9%) and an unknown (1.6%) were obtained. A reported photolysis of diazoindane agrees with these results. The products



obtained were indene (10%), indanone (5%) and 1-indanone azine (50%).⁷⁵ This low yield of indene from 1-indanylidene would offer good evidence that the indene obtained from the decomposition of 112 did not come from a possible 5% indanone tosylhydrazone impurity (none detectable by nmr, but 5% might have been present), but rather from 112 itself.

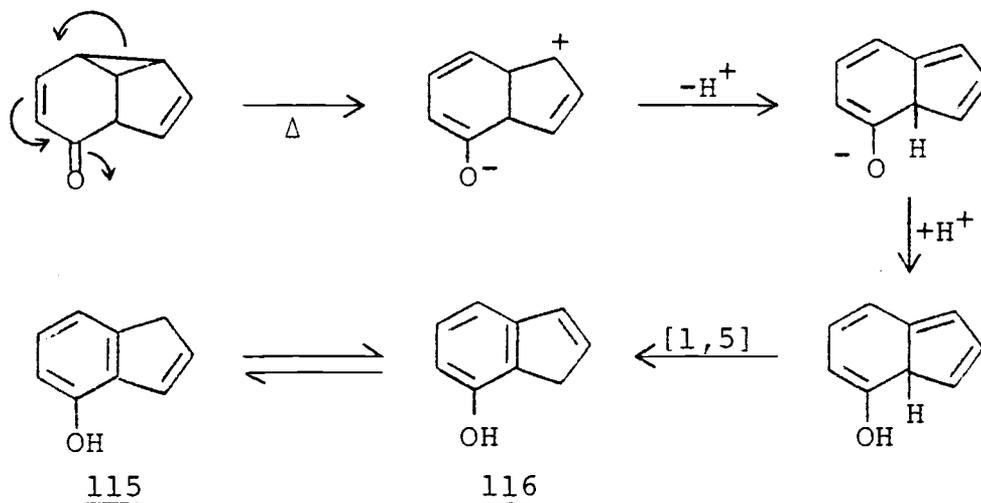
One possible mechanism for the formation of indene involves a zwitterion as shown. The cyclopropyl ring of



carbene 64 would cleave, leading to the zwitterion 113, which would lose a proton to give 114. The phenyl anion 114 would be protonated to 103. A thermal 1,5 hydrogen migration would afford the observed product indene 97.

The observation that the parent ketone 111 is thermally unstable might relate to the carbene mechanism. When an attempt was made to collect a sample of 111 by preparative vpc, the compound rearranged either on the column

or in the hot injector block. What was isolated was a mixture of 4-indenol 115 and 7-indenol 116.⁷⁶ A possible mechanism for their formation involves a zwitterion and is analogous to that postulated for the carbene. It has

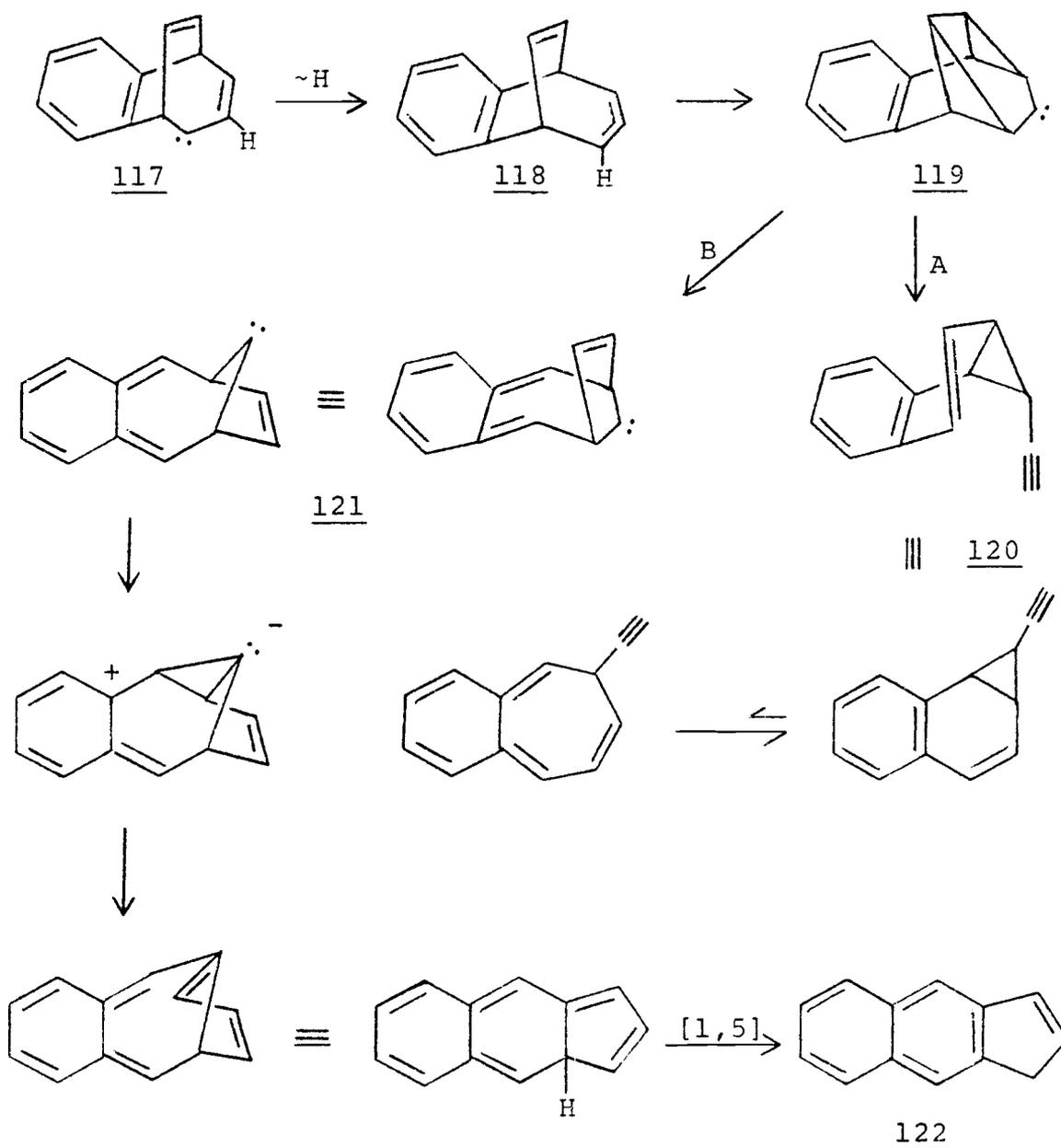


been shown that the two isomers 115 and 116 interconvert thermally⁷⁷ which would explain the presence of this mixture.

A question of prime importance is whether indene is the sole product. The bicyclic carbene 63 gave indene and ethynylcycloheptatriene in a 64 to 36 ratio. Since a product present in the amount of three percent of the observed indene would have been detected, and none was, it would seem unlikely that a carbene to carbene rearrangement of 64 to 63 is important. This would leave some less exciting possibility such as the zwitterionic pathway as a more likely mechanism of indene formation.

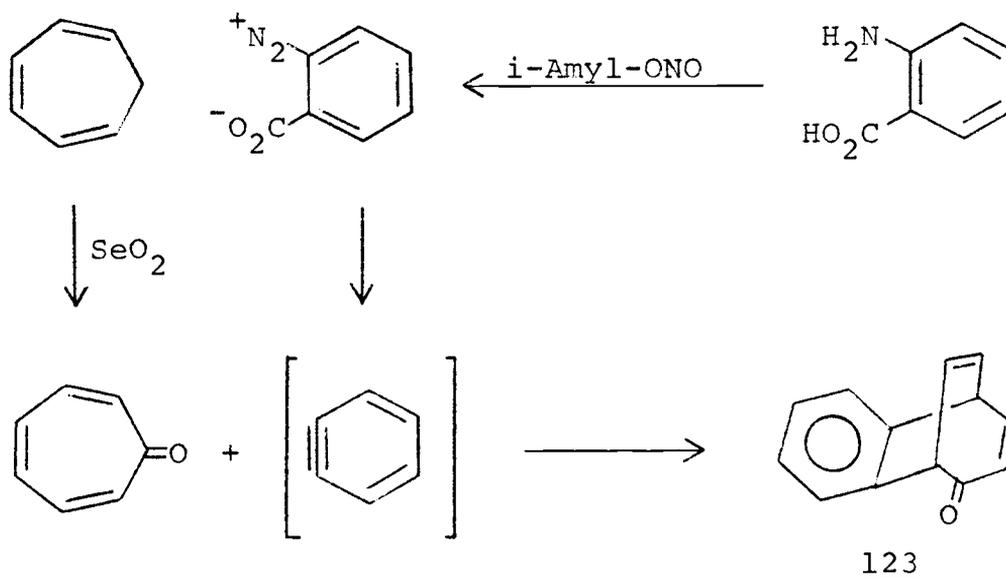
The benzannellated analog of carbene 63 could provide useful information about the chemistry of this species. A hypothetical mechanism which is analogous to that of carbene 63 is shown for carbene 117 (Scheme X). As in

SCHEME X

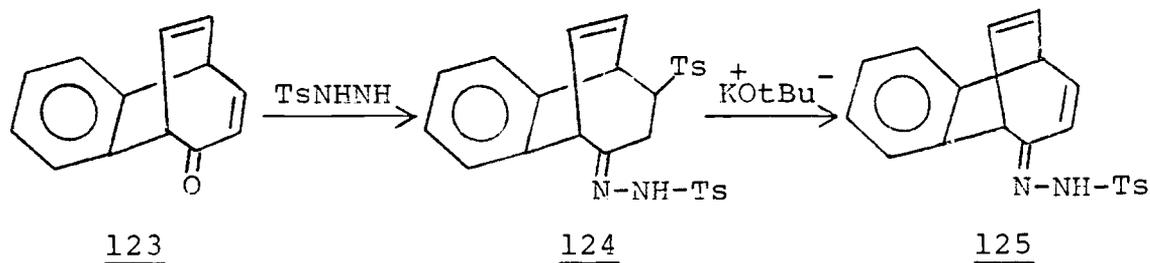


Scheme IX, the allene 118 would be formed by a 1,2-hydrogen migration. This allene is a valence isomer of the tetracyclic carbene 119, which could react further by pathways A or B. By pathway A a fragmentation would give 120, which would probably be the product isolated. The cycloreversion of pathway B would yield carbene 121, which would go on to the indene analog 122. Pathway B, however, involves disruption of the benzene aromaticity, which is not restored until the final product 122 is obtained. For this reason pathway A should be favored, and it would be predicted that the ethynyl compound 120 would dominate over the indene analog 122.

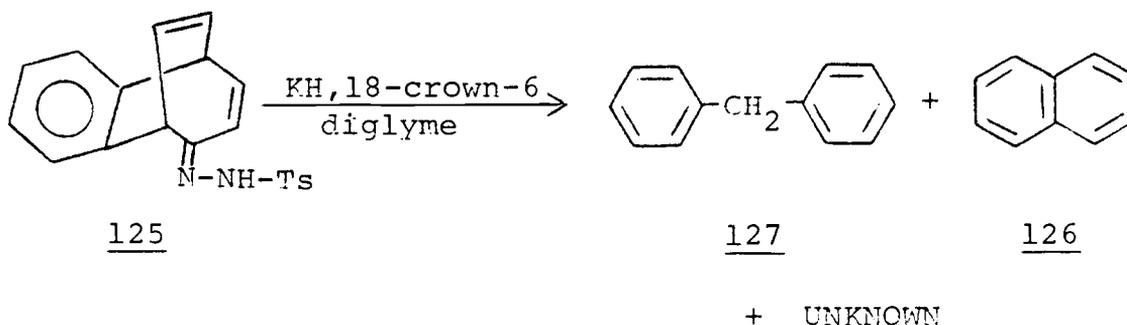
The ketone precursor of carbene 117 was synthesized by the following scheme. Tropone was prepared by selenium



dioxide oxidation of 1,3,5-cycloheptatriene.⁷⁸ Anthranilic acid was treated with iso-amylnitrite to give *o*-benzene-diazonium carboxylate, which was decomposed thermally in the presence of tropone to afford ketone 123.^{79,80} The ketone 123 was treated with tosylhydrazine in anhydrous ether. Rather than the desired tosylhydrazone, a product was obtained which was assigned the structure 124. This 3-tosyltosylhydrazone was treated with potassium tert-butoxide to give a product assigned the structure of the desired tosylhydrazone 125.

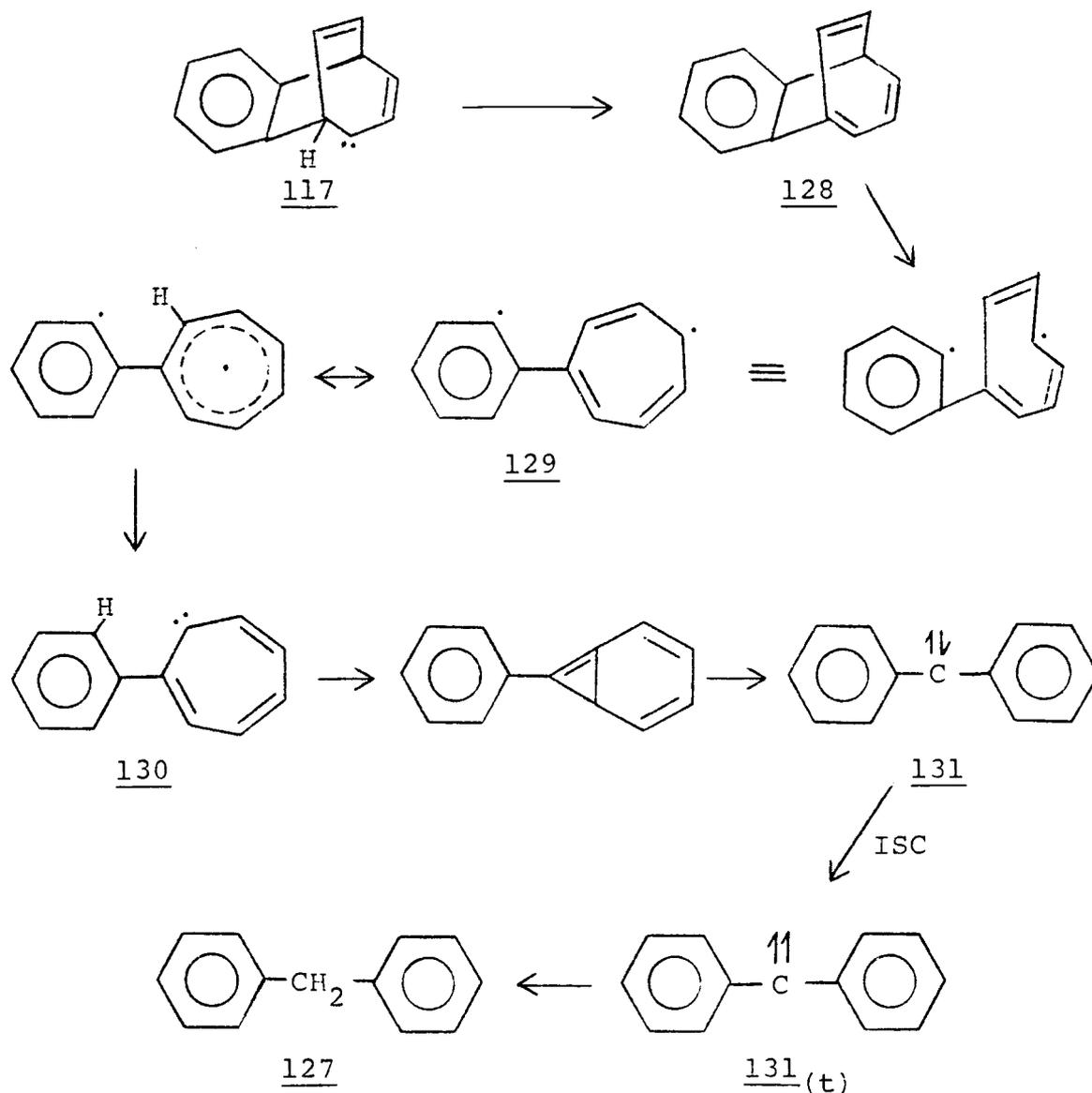


Tosylhydrazone 125 was decomposed by treatment with potassium hydride and 18-crown-6 in refluxing diglyme.

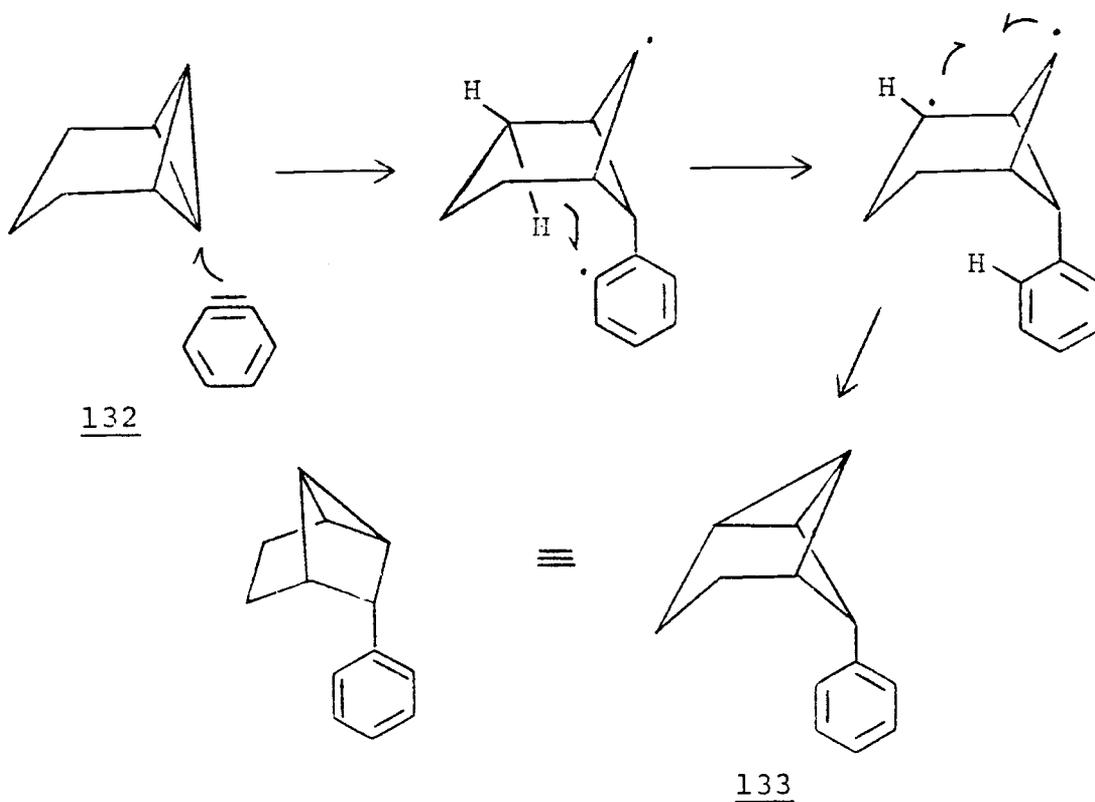


The products isolated were naphthalene 126 (67%), diphenylmethane 127 (29%) and an unknown (3.5%). The overall yield of these products was 3%.

An extensive rearrangement of the carbon skeleton of 125 is necessary to form diphenylmethane 127. A suggestion for the mechanism of this rearrangement involves a cycloheptatrienyliidene to phenylcarbene rearrangement of the

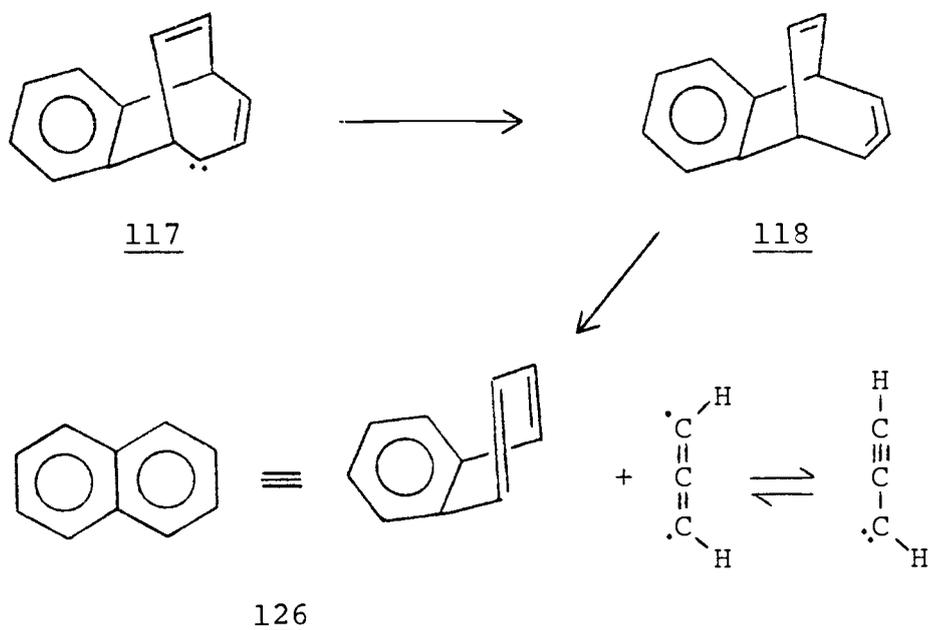


type discussed by Jones.³ A 1,2 hydrogen migration of the bridgehead hydrogen would form the strained cycloheptatriene 128. Bond cleavage could give a diradical 129. Hydrogen abstraction by the phenyl radical would afford carbene 130. The well documented rearrangement to 131 would follow. This carbene could intersystem cross to triplet 131(t), which would abstract two hydrogen atoms to afford the observed product 127. A somewhat similar example of intramolecular hydrogen abstraction by a phenyl radical moiety within a diradical has been presented by Gassman.⁸¹

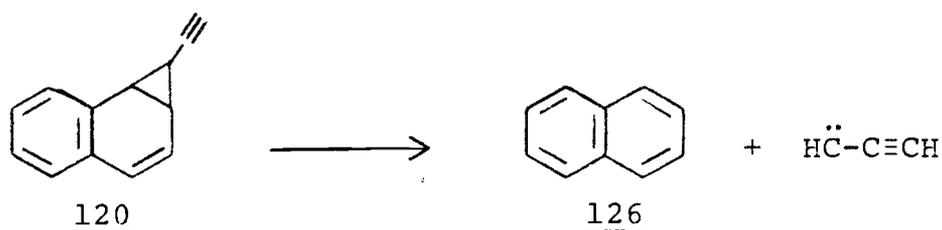


Benzyne was treated with tricyclo[4.1.0.0^{2.7}]heptane 132, to give product 133. The suggested mechanism involved formation of the diradical, followed by hydrogen abstraction by the phenyl radical through the favorable six-membered transition state. The diradical then closed to the observed product 133. In the case of 129 the transition state would be five-membered, but still should be favorable.

The major product from carbene 117 is naphthalene 126. A fragment with formula C₃H₂ must be lost from carbene 117 to give this product. Various mechanisms can be envisioned for this fragmentation. The simplest would involve a 1,2 hydrogen migration to the strained allene 118 followed by diradical cleavage to naphthalene. In Scheme X, it was



suggested that one of the expected products of the reaction would be 120. Another possible pathway to naphthalene would be a chelotropic reaction of 120. Since there is no



direct evidence and little literature precedent, these mechanisms are presented only as reasonable possibilities.

Since neither of the predicted products 120 or 122 was obtained, little analogy can be drawn to carbene 63. The lesson to be learned is that the carbene will undergo various rearrangements to yield aromatic products if at all possible. The importance of the ultimate formation of aromatic products is emphasized by the extensive reorganization of the carbon skeleton necessary to form these products.

EXPERIMENTAL

General experimental. The same general experimental procedures discussed in Chapter Two were followed. Vpc analyses were carried out on an Aerograph A-90-P2 chromatograph equipped with a thermal conductivity detector. The following columns were used:

- A. 19 ft x 0.25 in aluminum containing 15% Carbowax 20M on Chromosorb G, 60/80 mesh.
- B. 4 ft x 0.25 in aluminum containing 10% SE-30 on Chromosorb P, 60/80 mesh.
- C. 14 ft x 0.25 in aluminum containing 7% SE-30 on Chromosorb G, 60/80 mesh.
- D. 15 ft x 0.25 in aluminum containing 6% DC-200 on Anakrom AS, 60/80 mesh.
- E. 9 ft x 0.25 in aluminum containing 10% SE-30 on Chromosorb P, 60/80 mesh.
- F. 11 ft x 0.25 in aluminum containing 15% DC-710 on Chromosorb P, 60/80 mesh.
- G. 4 ft x 0.25 in aluminum containing 4% Carbowax 4000 on Chromosorb P, 60/80 mesh.
- H. 6 ft x 0.25 in aluminum containing 7% OV-17 on Chromosorb P, 60/80 mesh.
- I. 5 ft x 0.25 in aluminum containing 7% SE-30 on Chromosorb P, 60/80 mesh.

Product ratios and percentage yields calculated from chromatographic data are uncorrected for variations of thermal conductivity with molecular weight. Relative peak areas were measured with a Hewlett-Packard 3373B Integrator except for instances of extremely broadened peaks. The relative areas in these cases were determined by the average of a minimum of three weighings of the cut out peaks.

Diglyme and THF were dried by distillation from sodium benzophenone ketyl. Other commercial reagents were used as obtained unless otherwise noted. The dry salt pyrolysis of the tosylhydrazone salts was carried out at 0.1 torr in an all glass apparatus with the volatile products being collected in a series of two traps maintained at -78° .

Preparation of 3,4-Dibromobicyclo[3.2.1]octa-2,6-diene 67. Into a 250 ml flask equipped with a magnetic stirrer and reflux condenser was placed 100 ml (90.6 g, 0.98 mol) of freshly distilled norbornadiene and 17.2 ml (49.7 g, 0.197 mol) of bromoform. To this norbornadiene solution was added 132 ml of 50% sodium hydroxide prepared from 63 g (1.58 mol) of sodium hydroxide and 65 ml of water. Upon addition of 3 ml of Aliquat 336 (tridecylmethylammonium chloride) to the rapidly stirred mixture, the reaction darkened suddenly and became hot. It was

heated slowly and allowed to reflux for four hours. After cooling to room temperature, the dark brown reaction mixture was diluted with 200 ml of brine and extracted twice with 200 ml of ether. The combined ether extracts were washed three times with 250 ml of water and dried over magnesium sulfate. The ether and excess norbornadiene were removed on the rotary evaporator. The remaining black oil was distilled through a short path distillation apparatus (70-85°C, 0.14 mm; lit 77°C, 0.05 mm) to give 20.3 g (0.077 mol, 39%) of a colorless liquid. The nmr spectrum agrees extremely closely with that reported by Moore⁸² for an 83:11:6 mixture of exo and endo-3,4-dibromobicyclo[3.2.1]octa-2,6-diene and 3-exo-6-dibromotricyclo[3.2.1.0^{2,7}]oct-3-ene. The ratio obtained in this experiment (about 75:20:5) again is similar.

Silver Nitrate Assisted Hydrolysis of 3,4-Dibromobicyclo[3.2.1]octa-2,6-diene 67. A 100 ml flask fitted with a magnetic stirrer and reflux condenser was charged with 20.26 g (0.0767 mol) of dibromide 67 in 25 ml of acetone and 25 ml of water. To this solution, 12.9 g (0.076 mol) of silver nitrate was added, giving an immediate precipitate of silver bromide. The mixture was vigorously stirred and heated at reflux for one hour, during which time much silver bromide precipitated. After cooling, the silver bromide was removed by filtration and

the filtrate diluted with 200 ml of water. This diluted filtrate was extracted with three 75 ml portions of ether. The combined ether extracts were washed twice with 100 ml of 5% sodium bicarbonate and once with 100 ml water and dried over magnesium sulfate. The ether was removed on the rotary evaporator and the residue distilled through a short path distillation apparatus (58-82°C, 0.18 mm) to give 11.4 g (0.0570 mol) of a colorless liquid in 75% yield. Based on the nmr spectrum, this is a mixture of the exo and endo isomers of the desired 3-bromobicyclo[3.2.1]octa-3,6-dien-2-ol 68; nmr (60 MHz, CDCl₃), δ 6.99 (m, 2H, vinyl protons), 6.10 (m, 1H, vinyl proton), 4.43 (d, J=6 Hz, 1/3H, H² of endo-alcohol), 4.00 (d, J=2 Hz, 2/3H, H² of exo-alcohol), 3.00 (m, 2H, bridgehead H¹ and H⁵), 2.02 (m, 2H, bridge H⁸). The aliphatic region showed a somewhat higher than calculated integration, which is attributed to saturated impurities. Ir (neat, 0.1 mm), 3390 cm⁻¹ (s), 3052 (m), 2945 (s), 1655 (s), 1275 (s), 1038 (s), 845 (s), 725 (s).

Hydrolysis of 3,4-Dibromobicyclo[3.2.1]octa-2,6-diene 67 with Calcium Carbonate. A 2 L flask fitted with a magnetic stirrer and reflux condenser was charged with 164.62 g (0.6236 mol) of the title dibromide 67 in 600 ml acetone and 320 ml water (65% acetone/35% water). To this mixture, 76.4 g (0.764 mol) of calcium carbonate and 4 ml

of Aliquat 336 (tridecylmethylammonium chloride) were added. The resulting two phase slurry was heated to reflux and the course of the reaction followed by vpc (col B, 175°, 70 ml/min) monitoring the disappearance of starting dibromide. After nine days the reaction had essentially reached completion. The reaction mixture was cooled and the calcium carbonate removed by filtration on a Buchner funnel. This filtrate was diluted with 400 ml of brine and extracted twice with 350 ml of ether. The ether extracts were combined and washed twice with 300 ml of brine, twice with 400 ml of water, and dried over magnesium sulfate. The ether was removed on the rotary evaporator to leave a dark oil which was distilled through a short path distillation apparatus (66-77°C, 0.18 mm) to give 94.04 g (0.477 mol) of a colorless oil in 77% yield. The nmr spectrum of the bromoalcohol 68 is identical with that obtained from the silver nitrate assisted hydrolysis.

Debromination of 3-Bromobicyclo[3.2.1]octa-3,6-dien-2-ol 68 with n-Butyllithium. A 250 ml three-necked flask equipped with a reflux condenser, gas inlet, septum and magnetic stirrer was charged with 10.063 g (0.0500 mol) of the title bromoalcohol 68 dissolved in 75 ml of anhydrous ether. The flask was flushed with dry nitrogen and cooled to -78°C. To the cold, stirred solution was added 52.3 ml (0.119 mol) of 2.28 M n-butyllithium in hexane via syringe

over 20 minutes. A yellow color appeared and the solution was stirred at -78°C for 70 minutes. The solution was warmed to -12°C and stirred at this temperature for 25 minutes. Water was added dropwise to the rapidly stirred reaction mixture via syringe over a 20 minute period while the reaction warmed from -12°C to 5°C . After warming to room temperature, the solution was diluted with 150 ml brine and extracted twice with 75 ml of ether. The combined ether extracts were washed with 100 ml of brine and 150 ml of water and dried over magnesium sulfate. The ether was removed on the rotary evaporator to leave 7.74 g of a yellow oil as the crude product. This oil was distilled through a short path distillation apparatus ($63-70^{\circ}\text{C}$, 2.6 mm) to give 2.305 g (0.0189 mol) of a mixture of the desired exo- and endo-bicyclo[3.2.1]octa-3,6-dien-2-ol 69 in 38% yield; nmr (60 MHz, CCl_4), δ 6.30(d of d, $J=6, 3$ Hz, 1H, vinyl proton), 6.02(m, 1H, vinyl proton), 5.74(d of d, $J=6, 3$ Hz, 1H, vinyl proton), 5.12(m, 1H, vinyl proton), 3.76(broadened s, 2H, H^2 proton superimposed on $-\text{O}-\underline{\text{H}}$ proton), 2.54(m, 2H, H^1 and H^5 bridgehead protons), 1.82 (m, 2H, H^8 bridge protons). The aliphatic region showed a somewhat higher than expected integration indicating some saturated impurities. Ir (neat, 0.1 mm), 3350 cm^{-1} (s), 3050 (m), 3025 (m), 2940 (s), 1627 (w), 1055 (s).

Debromination of 3-Bromobicyclo[3.2.1]octa-3,6-dien-2-ol 68 with sec-Butyllithium. A 1 L three-necked flask fitted with a magnetic stirrer, reflux condenser, gas inlet and addition funnel was charged with 9.98 g (0.2380 mol) of sodium hydride (57.2% dispersion in mineral oil). The sodium hydride was washed with five 20 ml portions of dry hexane to remove the mineral oil. After removal of the last hexane wash, 200 ml of anhydrous ether was added to the sodium hydride, the flask thoroughly flushed with dry nitrogen and cooled to 0°C. A solution of 40.517 g (0.2015 mol) of the title bromoalcohol 68 in 110 ml anhydrous ether was placed in the addition funnel and added dropwise to the cold, stirred sodium hydride suspension over a period of 30 minutes. This mixture was stirred at 0°C for a further 45 minutes. Then the addition funnel was replaced with a septum and the reaction cooled to -78°. To this cold, stirred solution was added 242 ml (0.242 mol) of 1.0 M sec-butyllithium in cyclohexane via syringe over 30 minutes. The resulting brown solution was stirred at -78° for 2.75 hours and then warmed to 0°C for five minutes. Water was added dropwise, slowly via syringe to the rapidly stirred solution. This was stirred at 0°C for 20 minutes and then poured into 300 ml of brine and the layers separated. The aqueous layer was extracted with 400 ml of ether and the combined ether extracts washed

twice with 300 ml of brine and three times with 500 ml of water. After drying over magnesium sulfate, the ether was removed on the rotary evaporator to leave about 30 ml of a reddish oil. This oil was distilled (62-74°C, 4.0 mm) to give 10.975 g (0.0898 mol) of a colorless liquid for a yield of 45% of dienol 69, whose identity was verified by comparison of its nmr spectrum with that of 69 prepared previously.

Oxidation of Bicyclo[3.2.1]octa-3,6-dien-2-ol 69 with Chromium Trioxide and Sulfuric Acid. The general procedure of Monson⁵³ was followed. The 8.0 N chromic acid oxidizing reagent was prepared by dissolving 13.4 g of chromium trioxide in 25 ml of water. To this solution 12 ml of concentrated sulfuric acid was added. A 250 ml three-necked flask equipped with a magnetic stirrer, reflux condenser and addition funnel was charged with 6.0 g (0.0492 mol) of the title alcohol 69 dissolved in 150 ml of acetone and the reaction mixture cooled to 15°C. The addition funnel was charged with 6.15 ml (0.0492 equiv) of the chromic acid reagent, which was added to the alcohol solution at a rate such that the temperature remained below 20°C. When about 5 ml of chromic acid had been added, the reaction mixture had turned to the characteristic orange color of chromic acid and addition was stopped. The mixture was allowed to stir five minutes and then isopropyl alcohol was added to quench the excess oxidant. The

solution was decanted from the inorganic salts and these salts rinsed twice with 10 ml acetone. Solid sodium bicarbonate was added slowly to the solution with stirring until the solution was neutral. After filtration through a Buchner funnel, the acetone was removed on the rotary evaporator to leave a brown oil. This oil was diluted with 50 ml brine and extracted twice with 40 ml of ether. The combined ether extracts were washed with 50 ml of brine and three 50 ml portions of water, and then dried over magnesium sulfate. The ether was removed on the rotary evaporator to leave 2.873 g of yellow oil as the crude product. This oil was distilled (49-53°C, 1.9 mm) through a short path distillation apparatus to give 0.6250 g (5.2 mmol) of the desired bicyclo[3.2.1]octa-3,6-dien-2-one 66 in 11% yield. The identity of the product was confirmed by comparison of its nmr spectrum to a known spectrum on hand.⁵¹

Oxidation of Bicyclo[3.2.1]octa-3,6-dien-2-ol 69 with Chromium Trioxide-Pyridine Complex. The general procedure of Ratcliffe and Rodehorst⁵⁴ was followed. The oxidizing agent was prepared in a 500 ml flask by adding 14.9 g (0.149 mol) of chromium trioxide to a magnetically stirred solution of 23.9 ml (23.5 g, 0.298 mol) of pyridine in 350 ml of dichloromethane. The solution was protected with a Drierite drying tube and was allowed to

stir at room temperature for 15 minutes while the characteristic deep red color formed. A solution of 2.266 g (0.0186 mol) of the title alcohol 69 in 5 ml of dichloromethane was added to the oxidizing agent in one batch. A tarry black residue formed and the solution was allowed to stir at room temperature for 15 minutes. The red solution was decanted from the residue and diluted with 400 ml of ether. This ethereal solution was washed three times with 150 ml of 5% sodium hydroxide, once with 150 ml of 5% hydrochloric acid, once with 150 ml of 5% sodium bicarbonate and once with 150 ml of brine, and dried over magnesium sulfate. The ether was removed on the rotary evaporator and the residual oil distilled through a short path distillation apparatus (55-61°C, 3.0 mm) to give 0.764 g (6.37 mmol) of bicyclo[3.2.1]octa-3,6-dien-2-one 66 for a 34% yield. The nmr spectrum of the product ketone was identical to that of the ketone prepared previously by an alternate route.⁵¹

Oxidation of Bicyclo[3.2.1]octa-3,6-dien-2-ol 69 with Pyridinium Dichromate. The general procedure of Corey and Schmidt⁵⁵ was followed. A solution was prepared by dissolving 45.6 g (0.121 mol) of pyridinium dichromate in 70 ml DMF in a 250 ml flask equipped with a magnetic stirrer and Drierite drying tube. This was cooled to 0°C and a solution of 10.975 g (0.0898 mol) of the title

alcohol 69 in 30 ml of DMF was added to the cold, stirred oxidizing agent. The reaction was stirred at 0°C for five hours, poured into 1 L of water and extracted with five 200 ml portions of ether. The combined ether extracts were washed with three 500 ml portions of water and dried over magnesium sulfate. The ether was removed on the rotary evaporator to leave a yellow oil which was distilled (56-62°C, 4.2 mm) to yield 3.834 g (0.0319 mol, 36%) of the desired bicyclo[3.2.1]octa-3,6-dien-2-one 66 whose nmr spectrum was identical to that of an authentic sample.

Preparation of Bicyclo[3.2.1]octa-3,6-dien-2-one Tosylhydrazone 70. A solution of 0.625 g (5.21 mmol) of ketone 66 in 2 ml of methanol was added to 0.9638 g (5.18 mmol) of tosylhydrazine dissolved in 9 ml of methanol in a 25 ml flask equipped with a magnetic stirrer and a Drierite drying tube. Three drops of pyridine were added to the reaction and it was allowed to stir at room temperature. After about two hours a white precipitate started to form. The reaction was stirred for a total of eight hours at room temperature and then placed in a refrigerator overnight to complete precipitation. The white, powdery product was isolated on a Hirsch funnel and dried to give 0.569 g (1.97 mmol, 39%) of the desired tosylhydrazone; mp 149-152°C dec; nmr (100 MHz, CDCl₃), δ7.90 (d, J=9 Hz, 2H, aromatic protons), 7.35 (d, J=9 Hz, 2H, aromatic

protons), 6.80-6.35(m, 2H, vinyl protons), 5.92(m, 1H, vinyl proton), 5.68(d of d, J=9, 2 Hz, 1H, vinyl proton), 3.81-3.50(m, 1H, bridgehead proton), 3.04(m, 1H, bridgehead proton), 2.48(s, 3H, aromatic methyl), 2.18(m, 2H, bridge protons); ir (Nujol mull), 3210 cm^{-1} (m), 1602 (w), 1380 (s), 1340 (s), 1175 (s).

High resolution mass spectrum. Calculated for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$: 288.093; found: 288.094.

Dry Salt Pyrolysis of the Lithium Salt of Bicyclo-[3.2.1]octa-3,6-dien-2-one Tosylhydrazone 70. A 100 ml three-necked flask fitted with a magnetic stirrer, gas inlet and septum was charged with 0.7371 g (2.56 mmol) of the title tosylhydrazone 70 dissolved in 20 ml of anhydrous THF. To this tosylhydrazone solution at room temperature was added 1.71 ml (2.56 mmol) of 1.50 N methyllithium in ether. Hydrogen gas evolved and the solution was stirred at room temperature for 15 minutes. The THF was evaporated by blowing dry nitrogen over the stirred solution. When most of the THF had evaporated, the white lithium salt covered the inside of the flask. The standard all glass decomposition apparatus was set up and the salt heated to 198°C (oil bath temperature) under a vacuum of 0.1 mm while the volatile products were pumped over and collected in a trap maintained at -78°C. An estimate of the time nitrogen evolution begins and ceases can be made by watching the pressure of the

vacuum pump. Nitrogen evolution started at about 120°C and heating at 198°C was continued for ten minutes after nitrogen evolution had ceased. The volatile material in the traps was washed out with pentane and the pentane removed by distillation through a six-inch Vigreux column. The remaining yellow oil was analyzed by vpc (col A, 124°C, 75 ml/min). In addition to THF and benzene, six components A-F with retention times and percent composition as follows, were found; THF (6.3 min), benzene (8.5 min); A(14.1 min, 44%), B(18.2 min, 7.6%), C(20.8 min, 9.5%), D(26.8 min, 23.7%), E(34.4 min, 8.8%), F(37.6 min, 6.4%). Tridecane (39.8 min) internal standard was added and the total yield of volatile products was found to be 1.4%. These compounds were isolated by preparative vpc. Component A was identified as bicyclo-[3.2.1]octa-2,6-diene by comparison of its nmr spectrum with that of an authentic sample.⁵⁷ Component B was identified as tricyclo[3.2.1.0^{2,7}]oct-3-ene 71 by comparison of its nmr spectrum with that of an authentic sample.⁵⁸ Component C was identified as tetracyclo-[3.3.0^{2,8}.0^{4,6}]octane 72 by comparison of its nmr spectrum with that of an authentic sample.⁵⁷ Component D is a mixture of two products, one of which is semibullvalene 73, identified by comparison with its literature nmr.⁵⁹ The other product is 5-ethynyl-1,3-cyclohexadiene 74.⁶⁰

A 60 MHz nmr of 74 was kindly provided by Professor Murahashi⁶¹ and compared to our 100 MHz spectrum. Nmr integration shows the compounds 73 and 74 to be present in roughly a one to four ratio. Compound E remains unidentified; nmr (100 MHz, CDCl₃), δ 1.67 (singlet superimposed on m), 1.50 (broadened doublet, J=2 Hz). Component F has been identified as endo-6-ethynylbicyclo[3.1.0]-hex-2-ene 54 by comparison of its nmr spectrum with that published.⁴⁴

Decomposition of Bicyclo[3.2.1]octa-3,6-dien-2-one Tosylhydrazone 70 with Potassium Hydride and 18-crown-6- in Diglyme. A 100 ml flask equipped with a reflux condenser, gas inlet and magnetic stirrer was charged with 91.7 mg (0.504 mmol) of 22% potassium hydride in mineral oil. The potassium hydride was washed with six 5 ml portions of hexane to remove the mineral oil. After removal of the last hexane wash, 10 ml of anhydrous diglyme was added. Then 112.3 mg (0.390 mmol) of the title tosylhydrazone 70 was added with evolution of hydrogen. Upon addition of 110.3 mg (0.417 mmol) of 18-crown-6 a pink color appeared in the solution, but it faded after about five minutes of stirring. The reaction was heated to 140°C for two hours. After cooling, the reaction was diluted with 150 ml water and extracted with four 50 ml portions of pentane. The pentane extracts were

combined and washed with five 60 ml portions of water. After drying over sodium sulfate, the pentane was removed by distillation through a seven-inch Vigreux column. The residue was analyzed by vpc (col A, 125°C, 65 ml/min). The results were similar to those of the previous decompositions of this tosylhydrazone except that there were a number of new compounds present, probably residual mineral oil components. The six hydrocarbons found previously were present with percent composition as follows; bicyclo[3.2.1]octa-2,6-diene 38 (18.9%), tricyclo[3.2.1.0^{2,7}]oct-3-ene 71 (12.4%), tetracyclo[3.3.0^{2,8}.0^{4,6}]octane 72 (10.5%), the mixture of semibullvalene 73 and 5-ethynyl-1,3-cyclohexadiene 74 (13.0%), unknown E (28.4%) and endo-6-ethynylbicyclo[3.1.0]hex-2-ene 54 (16.8%). Tri-decane internal standard was added and the overall yield was found to be 1.5%.

Dry Salt Pyrolysis of the Lithium Salt of Bicyclo[3.2.1]octa-3,6-dien-2-one Tosylhydrazone 70 by Addition of the Salt to a Hot Surface. A solution of 196.2 mg (0.681 mmol) of the title tosylhydrazone 70 in 15 ml of dry THF was prepared in a 50 ml flask fitted with a septum, gas inlet and magnetic stirrer. To this tosylhydrazone solution was added 0.454 ml (0.681 mmol) of 1.50 M methyl lithium in ether. The THF was removed by blowing on the stirred solution with a stream of dry

nitrogen, and the salt dried further by pumping at 0.1 mm while warming the flask to about 40°C. The salt had coated the inside of the flask and had to be scraped off the glass with a spatula to transfer it to a curved test tube with a ground glass joint. The standard all glass decomposition apparatus was assembled and the curved test tube of salt fitted into the side neck of a three-necked flask. This flask was heated to 195°C in an oil bath while a pressure of 0.1 mm was maintained. The curved test tube was rotated and tapped, allowing small portions of the salt to drop into the hot flask where they decomposed immediately. The volatile products were collected in the two traps kept at -78°C. The traps were washed with pentane and the pentane removed by distillation through a seven-inch Vigreux column. The remaining oil was analyzed by vpc (col A, 123°C, 75 ml/min). The same six products found in the previous decompositions were obtained in the following percent composition; bicyclo[3.2.1]octa-2,6-diene 38 (58.3%), tricyclo-[3.2.1.0^{2,7}]oct-3-ene 71 (7.2%), tetracyclo[3.3.0^{2,8}.0^{4,6}]-octane 72 (7.3%), the mixture of semibullvalene 73 and 5-ethynyl-1,3-cyclohexadiene 74 (11.2%), unknown E (11.2%) and endo-6-ethynylbicyclo[3.1.0]hex-2-ene 54 (4.8%). Tridecane was added as an internal standard and the overall yield of volatile products was found to be 2.8%.

Irradiation of the Lithium Salt of Bicyclo[3.2.1]-octa-3,6-dien-2-one Tosylhydrazone 70. A 50 ml flask fitted with a magnetic stirrer, gas inlet and septum was charged with 0.2482 g (0.861 mmol) of the title tosylhydrazone 70 dissolved in 8 ml of anhydrous THF. The flask was purged with dry nitrogen and 0.52 ml (0.86 mmol) of 1.67 N methyllithium in ether was added with a syringe. Frothing and bubbling accompanied the gas evolution. The solution was stirred at room temperature for 15 minutes. The solution was diluted with anhydrous THF to a total volume of 220 ml (0.0039 M) and transferred to a vessel surrounding the quartz immersion well of a 450 watt Hanovia high pressure mercury lamp. The vessel was attached by latex tubing through a Drierite trap to a graduated cylinder inverted in a water bath so that nitrogen evolution could be monitored. The mercury lamp was fitted with a Vycor filter ($\lambda > 230$ nm) and the reaction vessel immersed in an ice bath. The tosylhydrazone salt solution was irradiated for 1.5 hours but no nitrogen was evolved and the solution did not darken perceptibly. The Vycor filter was removed and the solution irradiated directly through quartz as nitrogen slowly began to be generated. Irradiation was stopped when an equivalent amount of nitrogen had been collected (5.5 hours). The

solution was poured into 600 ml of water and extracted with three 75 ml portions of pentane. The pentane extracts were combined and washed four times with 100 ml portions of water. After drying over sodium sulfate, the pentane was removed by distillation through a seven-inch Vigreux column. The remaining oil was analyzed by vpc (col A, 111°C, 70 ml/min). Five of the six compounds obtained in the lithium salt pyrolysis were found with percent composition as follows; bicyclo[3.2.1]octa-2,6-diene 38 (39%), tricyclo[3.2.1.0^{2,7}]oct-3-ene 71 (31%), tetracyclo[3.3.0^{2,8}.0^{4,6}]octane 72 (18%), a mixture of semibullvalene 73 and 5-ethynyl-1,3-cyclohexadiene 74 (9%), and endo-6-ethynylbicyclo[3.1.0]hex-2-ene 54 (3%). Unknown E as reported for the thermal decompositions of 70 was absent. Tridecane internal standard was added and an overall yield of volatile products was found to be 2.7%.

The aqueous layer (with considerable particulate matter) from the pentane extraction was extracted further with 100 ml of chloroform and the chloroform layer dried over sodium sulfate. The aqueous layer was then acidified with 1 N HCl and extracted a final time with two 100 ml portions of chloroform. Again the combined chloroform extracts were dried over sodium sulfate. These two chloroform extracts were examined separately but in the

same manner. The chloroform was removed and nmr spectra taken. The first chloroform extract gave the following nmr; (60 MHz, CDCl_3), δ 4.4-3.3 (broad band), 2.7-1.0 (broad band). These undefined absorbances were present in a ratio of two to three. No aromatic, vinyl or aromatic methyl absorbances were present. The residue from the chloroform extracts of the acidified aqueous layer gave a very similar nmr. The two chloroform extracts were combined at this point. This residue showed a tlc Rf value of about 0.05 or less (CH_2Cl_2 , silica gel) under conditions where the starting tosylhydrazone and a known azine had large (about 0.6 or greater) Rf values. The ir spectrum was broadened; ir (film from CH_2Cl_2 solution), 3410 cm^{-1} (m), 2960 (s), 1722 (m), 1265 (s), 1050 (s), 800 (s). The mass spectrum showed no distinct molecular ion, but all molecular weights from 106 to 300 were represented in gradually decreasing intensity. This residual oil was dried by heating to 60°C at a vacuum of 0.05 torr for 24 hours. The residue weighed 0.2770 g, which is 112% (weight percent) yield. This discrepancy may be due to a small amount of non-volatile impurities from the solvent. This intractable residue seems to be the final product of the major portion of the reactant.

Preparation of Bicyclo[3.1.0]hex-2-en-6-endo-carboxaldehyde. The method of Meinwald and co-workers⁶⁴ was used. The aldehyde was purified by distillation, bp 74-82°C (70 mm). The nmr spectrum was identical with that reported.⁸⁵

Preparation of Bicyclo[3.2.1]octa-2,6-diene 38. The procedure of Brown and Occolowitz⁶⁵ was used to prepare the title compound in 27% yield. The nmr spectrum was identical to that of an authentic sample.

Preparation of *exo*-6-Bromotricyclo[3.2.1.0^{2,7}]oct-3-ene 80. The method of Klumpp and co-workers⁶³ was followed to prepare the title compound in 19% yield. The nmr spectrum was identical to that reported.

Debromination of *exo*-6-Bromotricyclo[3.2.1.0^{2,7}]oct-3-ene 80 with Tri-*n*-butyltin Hydride. Following the general procedure of Klumpp,⁶³ a 5 ml flask fitted with a magnetic stirrer, reflux condenser and gas inlet was charged with 207 mg (1.19 mmol) of the title bromide 80, 694 mg (2.39 mmol) of freshly prepared tri-*n*-butyltin hydride and 1.0 mg of azobisisobutyronitrile (AIBN). This solution was heated to 95°C under a nitrogen atmosphere for seven hours. After cooling, the volatile products were collected by distillation on an Aldrich Kugelrohr (65°C, 73 mm). The distilled product, 22.8 mg (0.21 mmol, 19% yield) of a colorless liquid was analyzed by vpc

(col A, 126°C, 70 ml/min). The three hydrocarbon products were identified by vpc retention times. Bicyclo[3.2.1]octa-2,6-diene 38, tricyclo[3.2.1.0^{2,7}]oct-3-ene 71 and tetracyclo[3.3.0^{2,8}.0^{4,6}]octane 72 were present in a ratio of 98.7 to 1.3 to 0 (less than 0.08) respectively.

Debromination of *exo*-6-Bromotricyclo[3.2.1.0^{2,7}]oct-3-ene 80 with Sodium in *tert*-Butyl Alcohol. The general procedure of Klumpp⁶³ was followed. A 25 ml flask fitted with a magnetic stirrer, reflux condenser and gas inlet was charged with 173 mg (0.94 mmol) of the title bromide 80 dissolved in 2.2 ml of dry tetrahydrofuran and 0.6 ml of dry *tert*-butyl alcohol. This solution was heated to 50° with rapid stirring in a nitrogen atmosphere. Then 171 mg (7.44 mmol) of sodium was added and the resulting mixture refluxed for 9.5 hours. After cooling, methanol was slowly added to destroy the excess sodium. The resulting solution was poured into 30 ml water and extracted with four 10 ml portions of pentane. The combined pentane extracts were washed with four 30 ml portions of water and dried over magnesium sulfate. The pentane was removed by distillation through a seven-inch Vigreux column to leave about 0.3 ml of a colorless liquid which was analyzed by vpc (col A, 120°C, 60 ml/min). The three hydrocarbons expected from the radical reaction were identified by vpc retention times. Bicyclo[3.2.1]octa-

2,6-diene 38, tricyclo[3.2.1.0^{2,7}]oct-3-ene 71 and tetracyclo[3.3.0^{2,8}.0^{4,6}]octane 72 were present in a ratio of 97.5 to 2.5 to 0 (less than 0.1) respectively. Tridecane internal standard was added and the yield of these three hydrocarbons was found to be 29%. An additional compound (possibly a dimer⁸⁴) was present at much longer vpc retention time, but it was not investigated.

Preparation of Tropenium Fluoroborate. Tropenium fluoroborate was prepared by the in situ technique of Dauben and co-workers⁶⁹ and used without further purification.

Preparation of Cycloheptatrienylacetic Acid. The general procedure of Jurch and Traylor⁷⁰ was followed to prepare cycloheptatrienylacetic acid from 59.0 g (0.322 mol) of tropenium fluoroborate and 59.9 g (0.576 mol) of malonic acid. The crude product was purified by distillation (105°C, 0.4 torr) to give 44.8 g (0.298 mol, 93%) of the desired product. Its identity was verified by mp 30.5-32.5 (lit. mp 30-33°C) and comparison of its nmr spectrum with that of an authentic sample.

Preparation of Bicyclo[3.2.2]nona-3,6,8-trien-2-one 95. The general procedure of Winstein and Grutzner⁴⁷ was followed. A 500 ml flask fitted with a drying tube and magnetic stirrer was charged with 37.0 g (0.2464 mol) of

cycloheptatrienylacetic acid dissolved in 250 ml of dry dichloromethane. Three drops of pyridine were added and then 33.8 ml (50.0 g, 0.3939 mol) of oxalyl chloride was added in one batch, causing much foaming and gas evolution. This was stirred at room temperature for three hours. The solvent was then removed under vacuum using first an aspirator and finally an oil pump. The remaining brown oil was dissolved in 450 ml of dry hexane. A 3 L flask equipped with a reflux condenser, magnetic stirrer, drying tube and 500 ml addition funnel was charged with 80 ml of dry triethylamine (distilled from barium oxide) dissolved in 1.6 L of dry hexane, and this solution was heated to reflux. The addition funnel was charged with the previously prepared acid chloride solution which was added slowly over three days. The reaction mixture had yellowed and copious amounts of triethylamine hydrochloride had precipitated. After cooling, the triethylamine hydrochloride was removed by filtration and the hexane removed on the rotary evaporator. The remaining brown oil was distilled carefully through a spinning band column. Two fractions were taken; (53-56° 0.30 torr) and (56-61°C, 0.20 torr). Analysis was performed by vpc (col C, 130°C, 60 ml/min). The crude reaction mixture showed two major products in roughly a one to one ratio. It was subsequently shown that the product

with the longer retention time was 1-indanone, while the shorter retention time component was the desired bicyclic ketone 95. The lower boiling distillation fraction was shown by vpc to be the bicyclic ketone with less than 1% contamination by 1-indanone. This fraction crystallized upon standing. Its identity was verified by comparison of its nmr spectrum to that published.¹⁰⁶ This fraction gave 2.306 g (0.0174 mol) for a yield of 7% based on cycloheptatrienylacetic acid. The higher boiling distillation fraction was shown by vpc to be an 85:15 mixture of 1-indanone and the bicyclic ketone.

Preparation of Bicyclo[3.2.2]nona-3,6,8-trien-2-one Tosylhydrazone 96. A 100 ml flask fitted with a magnetic stirrer and a drying tube was charged with 2.990 g of (22.7 mmol) of the title ketone dissolved in 20 ml methanol. To this ketone solution was added 4.210 g (22.7 mmol) of tosylhydrazone dissolved in 40 ml methanol. After the addition of 1 ml pyridine, the reaction was allowed to stir at room temperature overnight. The solution, which had yellowed slightly, was concentrated on the rotary evaporator to about one half of its original volume and stored in a freezer. This yielded 5.60 g (18.7 mmol, 82%) of the tosylhydrazone 96. Recrystallization from ethanol yielded tosylhydrazone 96 with a mp 191-193°C dec. and an nmr spectrum that suggests that

the tosylhydrazone exists as a mixture of its syn and anti isomers; nmr (100 MHz, CDCl_3), δ 7.87(d, $J=8$ Hz, 2H, aromatic protons), 7.32(d, $J=8$ Hz, 2H, aromatic protons), 6.68(broadened t, $J=8$ Hz, 1H, vinyl proton), 6.51-6.05(m, 4H, vinyl protons), 5.61(d of d, $J=11, 2$ Hz, 0.5H, vinyl H^3 proton), 5.38(d of d, $J=11, 2$ Hz, 0.5H, vinyl H^3 proton), 4.52(m, 0.5H, H^1 bridgehead proton), 4.00(m, 0.5H, H^1 bridgehead proton), 3.63(m, 1H, H^5 bridgehead proton), 2.46(broadened s, 3H, aromatic methyl protons); ir (Nujol mull), 3230 cm^{-1} (m), 1618 (w), 1600 (w), 1340 (s), 1175 (s).

High resolution mass spectra. Calculated for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$: 300.093; found: 300.093.

Dry Salt Pyrolysis of the Lithium Salt of Bicyclo-[3.2.2]nona-3,6,8-trien-2-one Tosylhydrazone 96. A 50 ml flask fitted with a magnetic stirrer, septum and N_2 inlet was charged with 0.1264 g (0.421 mmol) of the title tosylhydrazone 96 dissolved in 10 ml anhydrous THF. To this solution was added via syringe 0.29 ml (0.42 mmol) of 1.47 M methyllithium in ether. Gas was evolved and the solution was stirred at room temperature for 15 minutes. The THF was removed by blowing dry nitrogen over the stirred solution. When most of the THF had been removed, the standard decomposition apparatus was set up and the salt dried further by pumping at 0.1 torr

while warming to 40°C. The salt was decomposed by heating the flask to 185°C and the volatile products collected in two traps maintained at -78°C. Nitrogen evolution began at about 130°C and heating at 185°C was continued for 15 minutes after nitrogen evolution had ceased. The volatile material in the traps was washed out with pentane and the pentane removed by distillation through a seven-inch Vigreux column. The remaining oil was analyzed by vpc (col D, 115°C, 70 ml/min). Four products, G, H, I and J, were found, with the following retention times and percent composition; G(6.5 min, 3.6%), H(8.8 min, 34.6%), I(11.5 min, 2.5%), J(14.8 min, 59.3%). Compounds H, I and J were collected by preparative vpc (col D, 115°C, 70 ml/min). Compound H was identified as 7-ethynyl-1,3,5-cycloheptatriene 98 by comparison of its nmr and ir spectra with those published.⁷¹ Compound I remains unknown; nmr (100 MHz, CDCl₃), δ7.30-6.87(m, 1H), 6.18(m, 1H), 5.47(m, 1H), 2.31(m, 2H). Compound J was identified as indene 97 by comparison of its nmr and ir spectra with those of an authentic sample. Undecane internal standard was added and the yields determined as follows; G(0.9%), 7-ethynyl-1,3,5-cycloheptatriene 98 (8.3%), I (0.6%), and indene 97 (14.2%).

Preparation of Tricyclo[6.1.0.0^{4,9}]nona-2,6-dien-

5-one 111. The general procedure of Paquette and Broadhurst⁷⁴ was followed. A 500 ml Pyrex flask was charged with 0.4269 g (3.23 mmol) of bicyclo[3.2.2]octa-3,6,8-dien-2-one 95 and 0.2095 g (0.781 mmol) of Michler's ketone (4,4'-bis-(dimethylamino)-benzophenone) dissolved in 400 ml of anhydrous benzene. This solution was deoxygenated with bubbling nitrogen for 45 minutes and irradiated through Pyrex with a 450 watt Hanovia high pressure mercury lamp. The reaction was followed by vpc (col E, 150°C, 70 ml/min) monitoring the disappearance of starting material. After 85 min the reaction had gone to completion. The benzene was removed on the rotary evaporator, and replaced with 100 ml of pentane-ether (1:1). This caused the Michler's ketone to precipitate and it was removed by filtration. The filtrate was washed with three 50 ml portions of water and dried over sodium sulfate. Four more batches similar to this were run, using a total of 2.1100 g (0.0160 mol) of bicyclic ketone 95. These five batches were combined and the ether removed on the rotary evaporator to leave a yellow oil, which was distilled (0.08 torr, 45-47°C) through a short path to yield 0.6237 g (4.720 mmol) of the title ketone 111 for a 30% yield. This ketone was slightly contaminated (about 10%) with another ketone identified as 1-indanone by comparison

of its nmr spectrum with that of an authentic sample.

The title ketone 111 has the following nmr (100 MHz, CDCl_3); δ 6.53(d of d, $J=10, 5$ Hz, 1H, H^1), 6.00(d, $J=10$ Hz, 1H, H^6), 5.84(d of d of d of d, $J=5, 2, 2, 1$ Hz, 1H, H^3), 5.54(d of d of d, $J=5, 2, 1$ Hz, 1H, H^2), 3.38(d of d, $J=8, 2$ Hz, 1H, H^4), 2.90(d of t, $J=8, 2$ Hz, 1H, H^1), 2.61(d of q, $J=8, 1$ Hz, 1H, H^9), 2.03(d of t, $J=8, 5$ Hz, 1H, H^8).

Preparation of Tricyclo[6.1.0.0^{4,9}]nona-2,6-dien-5-one Tosylhydrazone 112. A 10 ml flask was charged with 0.399 g (3.02 mmol) of tricyclo[6.1.0.0^{4,9}]nona-2,6-dien-5-one 111 and 0.562 g (3.02 mmol) of tosylhydrazine dissolved in 6 ml of methanol. To this solution was added two drops of pyridine and the solution stirred at room temperature. The reaction was monitored by tlc (silica gel, chloroform). After five hours, the starting ketone had reacted and the reaction solution was placed in the freezer to induce crystallization. No crystallization had occurred after 24 hours. The methanol was removed on the rotary evaporator and the resulting brown oil dissolved in warm ethanol. This was cooled in the freezer overnight to yield 0.0878 g (0.292 mmol, 10%) of tosylhydrazone mp 141-143°C dec.; nmr (100 MHz, CDCl_3), δ 7.86 (d, $J=8$ Hz, 2H, aromatic protons), 7.60(broadened s, 1H, N-H proton), 7.32(d, $J=8$ Hz, 2H, aromatic protons), 6.38

(d, $J=9$ Hz, 1H, H^6 proton), 6.12(m, 1H, H^7), 5.77(m, 1H, vinyl proton), 5.47(d of d, $J=7, 2$ Hz, 0.5H, vinyl proton), 5.27(d of d, $J=7, 2$ Hz, 0.5H, vinyl proton), 4.20-3.50(m, 1H, H^4), 2.46(s superimposed on m, 4H, aromatic methyl and cyclopropyl protons), 2.22(m, 1H, cyclopropyl proton), 1.74(m, 1H, cyclopropyl proton). The product appears uncontaminated by 1-indanone tosyl-hydrazone indicated by the absence of 1-indanone tosyl-hydrozone absorptions at $\delta 2.70$ and 3.04 . Ir (Nujol mull), 3205 cm^{-1} (m), 1642 (w), 1600 (m), 1350 (s), 1175 (s).

High resolution mass spectrum. Calculated for $C_{16}H_{16}N_2O_2S$: 300.093; found: 300.093.

Attempted Preparative Vpc Isolation of Tricyclo-[6.1.0.0^{4,9}]nona-2,6-dien-5-one 111. A sample of the crude title ketone 111 was subjected to preparative vpc (col E, 155°C , 60 ml/min). Two unresolved peaks at 16 min were collected as one and the following nmr obtained; $\delta 6.98$ (m, 3H, aromatic protons), 6.53 (m, 2H, vinyl protons), 4.80 (broadened s, 1H, phenolic proton), 3.35 (broadened s), 3.28 (t, $J=1$ Hz). The two signals at 3.35 and 3.28 together integrate to two protons (indene allylic). These two compounds appear to be a mixture of 4-indenol 115 and 7-indenol 116 based on comparison to the literature spectra.⁷⁶

Decomposition of Tricyclo[6.1.0.0^{4,9}]nona-2,6-dien-5-one Tosylhydrazone 112 with Potassium Hydride and 18-crown-6 in Diglyme. A 100 ml flask fitted with a magnetic stirrer and gas inlet was charged with 62.7 mg (0.345 mmol) of 22% potassium hydride in mineral oil. The potassium hydride was washed with five 5 ml portions of dry hexane. After removal of the last hexane wash, 10 ml of anhydrous diglyme was added and the flask thoroughly flushed with nitrogen. A solution of 75.6 mg (0.252 mmol) of the title tosylhydrazone 112 in 5 ml of diglyme was added to the stirred potassium hydride suspension. After the gas evolution had subsided, 67.3 mg (0.255 mmol) of 18-crown-6 in 3 ml of diglyme was added. The flask was fitted with a reflux condenser and the reaction heated to 140°C for 2.5 hours. Upon cooling it was poured into 200 ml of cold water and extracted three times with 60 ml of pentane. The pentane extracts were combined and washed five times with 100 ml of water and dried over sodium sulfate. The pentane was removed by distillation through a seven-inch Vigreux column to leave about 0.5 ml of yellow oil which was analyzed by vpc (col F, 131°C, 70 ml/min). Two compounds were present; the first at 12 minutes was identified as residual diglyme by vpc retention time and comparison of the nmr spectrum of the sample collected by preparative vpc with the spectrum

of an authentic sample. The second compound at 18.5 minutes was identified as indene 97 by vpc retention time and comparison of the nmr spectrum of the isolated compound (preparative vpc) with that of an authentic sample. No other compounds (less than 3% of indene) were present by vpc. Tridecane internal standard was added and the yield of indene was found to be 14%.

Decomposition of 1-Indanone Tosylhydrazone with Potassium Hydride in Tetrahydrofuran/Diglyme. A 100 ml flask fitted with a magnetic stirrer, reflux condenser and gas inlet was charged with 97.5 mg (0.536 mmol) of 22% potassium hydride in mineral oil. The potassium hydride was washed five times with 10 ml of dry hexane, and after removal of the last hexane wash 10 ml of anhydrous THF was added. To the stirred potassium hydride suspension was added 130.5 mg (0.435 mmol) of 1-indanone tosylhydrazone in 5 ml of THF. After the gas evolution had subsided, 111.6 mg (0.422 mmol) of 18-crown-6 in 5 ml of THF was added and the reaction heated at reflux (65°C) for 20 minutes. No nitrogen seemed to be evolved, so 22 ml of anhydrous diglyme was added, which raised the reflux temperature to 95°C. The solution turned a deep blue-green color and was heated at reflux at this temperature for 80 minutes. After cooling, the reaction was poured into 150 ml of water, which resulted in the imme-

diate loss of the blue-green color. This aqueous solution was extracted with four 40 ml portions of pentane. The combined pentane extracts were washed with five 100 ml portions of water and dried over sodium sulfate. The pentane was removed by distillation through a seven-inch Vigreux column to leave a small amount of yellow oil which was analyzed by vpc (col D, 125°C, 65 ml/min). In addition to diglyme (9 min) two other products were found. An unidentified compound appeared at 11 min, and a compound identified as indene 97 by comparison of its retention time at 14.8 min. The indene 97 identification was verified by comparison of the nmr spectrum of the vpc collected compound with that of an authentic sample. Dodecane internal standard was added and the yield of indene was found to be 6.9% and of the unknown 1.6%.

Preparation of Cyclooctanone Tosylhydrazone. A 100 ml flask fitted with a reflux condenser and magnetic stirrer was charged with 4.0681 g (32.2 mmol) of cyclooctanone and 6.218 g (33.4 mmol) of tosylhydrazine in 40 ml of 95% ethanol. Three drops of hydrochloric acid were added and the solution heated at reflux for 45 minutes, during which time a white precipitate formed. After cooling to room temperature the reaction was placed in the freezer to complete precipitation. The product was separated by filtration using a Buchner funnel and

dried to give 7.963 g (27.1 mmol, 84%) of tosylhydrazone whose nmr spectrum was consistent with the desired product; nmr (100 MHz, CDCl_3), δ 7.83(d, J=8 Hz, 2H, aromatic protons superimposed over broadened s, 1H, N-H proton), 7.23(d, J=8 Hz, 2H, aromatic protons), 2.38(s, 3H, aromatic methyl), 2.27(m, 4H, cyclooctyl protons), 1.88-0.95(m, 10H, cyclooctyl protons), mp 132-135°C, lit 140-141°C.

Decomposition of Cyclooctanone Tosylhydrazone with Potassium Hydride and 18-Crown-6 in Diglyme. A 50 ml flask fitted with a magnetic stirrer, reflux condenser and gas inlet was charged with 0.1435 g (0.789 mmol) of 22% potassium hydride in mineral oil. The potassium hydride was washed with five 10 ml portions of dry hexane. After removal of the last hexane wash, 10 ml of anhydrous diglyme was added. The flask was thoroughly flushed with dry nitrogen and a solution of 0.1912 g (0.650 mmol) of cyclooctanone tosylhydrazone in 7 ml of dry diglyme was added to the potassium hydride suspension. After the gas evolution had subsided, a solution of 0.1711 g (0.647 mmol) of 18-crown-6 in 3 ml of diglyme was added and the solution heated at 145°C for two hours. After cooling, the reaction was poured into 150 ml of water and extracted four times with 50 ml portions of pentane. The combined pentane extracts were washed five times with 60 ml of

water and dried over sodium sulfate. The pentane was removed by distillation through a seven-inch Vigreux column to leave about 0.5 ml of yellow oil which was analyzed by vpc (col F, 100°C, 65 ml/min). Three products with the following percent composition and retention times were found; A(12.3 min, 45%), B(14.5 min, 8%), C(16.1 min, 47%). These products were isolated by preparative vpc and nmr spectra obtained. Compound A was identified as cis-bicyclo[3.3.0]octane by comparison of its nmr spectrum to that reported.¹⁰⁷ Compound B is bicyclo[5.1.0]octane as reported for this reaction by Friedman and Shechter.⁵⁵ Its nmr spectrum is consistent with this assignment; nmr (100 MHz, benzene/carbon tetrachloride), δ 2.15(m, 2H), 1.86-1.10(two overlapping m, 4H), 0.80(m, 4H), 0.18(m, 2H). Compound C was identified as cyclooctene by comparison of its nmr spectrum with a published spectrum.^{108a}

Preparation of Tropone. The general procedure of Radlick⁷⁸ was followed. The identity of the product was confirmed by comparison of its nmr^{109a} and ir¹¹⁰ spectra with those published.

Preparation of 6,7-Benzobicyclo[3.2.2]nona-3,6,8-trien-2-one 123. The procedures of Kende⁷⁹ and Grutzner⁸⁰ were generally followed. The o-benzenediazoniumcarboxylate was prepared in a 600 ml beaker fitted with a magnetic stirrer and thermometer. In this beaker, 33.10 g (0.2414

mol) of anthranilic acid was dissolved in 250 ml anhydrous THF and the solution cooled in an ice bath to 5°C. To this solution was added a solution of 0.3 g of trichloroacetic acid in 10 ml THF followed by 43 ml (37.96 g, 0.324 mol) of freshly prepared isoamyl nitrite¹¹¹ over five minutes. The mixture was warmed to 18-23°C for one hour while the tan precipitate of o-benzenediazonium-carboxylate formed. This salt was isolated on greased filter paper in a taped Buchner funnel. At no time was the salt allowed to dry! The still moist salt was transferred to a 500 ml flask fitted with a reflux condenser and gas inlet. To this salt was added 21.45 g (0.2022 mol) of tropone. The flask containing this mixture was immersed in a 37°C oil bath and warmed at this temperature without stirring under a nitrogen atmosphere. Gas bubbles slowly evolved, but after two hours, for no apparent reason, the reaction suddenly generated enough heat to cause the THF to reflux rapidly. The oil bath was removed and the flask cooled in ice. Once the reaction had slowed down, it was again warmed at 37°C for a total of eight hours. After cooling, the crude product, a black oil, was concentrated on the rotary evaporator and then poured over 200 ml of alumina in a 350 ml fritted funnel and washed with 1400 ml of ether. The ether washes were dried over magnesium sulfate and the ether removed on the rotary

evaporator to yield about 30 ml of a black oil. This oil was distilled through a short path distillation apparatus with fractions collected at 56-96°C (0.34 torr) and 96-111°C (0.34 torr). The first fraction was identified by its nmr spectrum as unreacted tropone (8.975 g, 84.6 mmol, 42%). The second fraction (6.1182 g, 33.6 mmol, 17%) was the desired ketone, which was crystallized from hexane to give 4.005 g (0.0220 mol, 11%) of 6,7-benzobicyclo[3.2.2]nona-3,6,8-trienone 123 with an nmr identical to that reported by Kende.⁷⁹

Reaction of 6,7-Benzobicyclo[3.2.2]nona-3,6,8-trien-2-one 123 with Tosylhydrazone. A 50 ml flask fitted with a magnetic stirrer and drying tube was charged with 0.8294 g (4.557 mmol) of the title ketone 123 and 1.666 g (8.943 mol) of tosylhydrazone in 35 ml dry ether and was stirred at room temperature overnight. A white precipitate had formed and precipitation was completed by placing the reaction in the freezer overnight. The product was isolated to yield 1.6536 g (3.273 mmol, 72%) of white crystals. The product has been assigned the structure of the 3-tosyl adduct 124 of the desired tosylhydrazone based on the nmr spectrum; nmr (100 Hz, CDCl₃/d₆-DMSO), δ7.78(d, J=8 Hz, 4H, p-tolyl aromatic protons), 7.42-7.08 (two superimposed d and broadened s, 8H, p-tolyl and aromatic protons), 6.29(m, 2H, vinyl protons), 4.18(m, 1H,

proton α to sulfone), 3.88-3.42(m, 2H, bridgehead protons), 3.08(m, 2H, methylene α to C=N), 2.47, 2.45(s, 6H, aromatic methyl protons); mp 142-144°C dec.; ir (Nujol mull), 3200 cm^{-1} (w), 1640 (w), 1605 (m), 1345 (m), 1170 (s).

Preparation of 6,7-Benzobicyclo[3.2.2]nona-3,6,8-trien-2-one Tosylhydrazone 125. A 250 ml flask fitted with a reflux condenser, magnetic stirrer, gas inlet and addition funnel was charged with 40 ml tert-butyl alcohol to which was added 1.33 g (34.1 mmol) of potassium. The reaction was stirred under a nitrogen atmosphere until all the potassium dissolved. The addition funnel was charged with a solution of 1.566 g (3.10 mmol) of 124 dissolved in 30 ml of anhydrous THF. This was added to the potassium tert-butoxide solution over ten minutes. The reaction mixture yellowed and was heated to 45°C for 75 minutes. After cooling the orange precipitate was isolated on a Buchner funnel. This salt was dissolved in 50 ml water and acidified with 1 N hydrochloric acid. This solution was extracted with three 50 ml portions of chloroform. The chloroform extracts were dried over sodium sulfate and the chloroform removed on the rotary evaporator to yield 1.050 g (3.00 mmol, 96%) crude product. This was recrystallized from ethanol/water to give 0.3796 g (1.08 mmol, 35%) of the desired tosylhydrazone; mp 126-

129°C dec.; nmr (100 MHz, CDCl_3), δ 8.20(broadened s, 1H, -NH proton), 7.83(d, $J=8$ Hz, 2H, p-tolyl aromatic protons), 7.25(m, 8H, aromatic and vinyl protons), 6.92-6.28(m, 2H, vinyl protons), 4.53-4.23(m, 1H, H-1 bridgehead proton), 3.80-3.70(m, 1H, H-5 bridgehead proton), 2.48(broadened s, 4H, aromatic methyl protons). The spectrum was broadened, and these integrations reported may well be inaccurate. The low values for the vinyl protons are disturbing. Ir (Nujol mull), 3210 cm^{-1} (m), 1705 (m), 1600 (m), 1170 (s).

Decomposition of 6,7-Benzobicyclo[3.2.2]nona-3,6,8-trien-2-one Tosylhydrazone 125 with Potassium Hydride and 18-Crown-6 in Diglyme. A 50 ml flask fitted with a gas inlet, reflux condenser and magnetic stirrer was charged with 0.499 g (2.74 mmol) of 22% potassium hydride in mineral oil. The potassium hydride was washed with six 5 ml portions of dry hexane. After removal of the last hexane wash, 20 ml of anhydrous diglyme was added to the potassium hydride and the reaction flask thoroughly flushed with dry nitrogen. To this suspension was added 0.6199 g (2.348 mmol) of 18-crown-6 and 0.6018 g (1.719 mmol) of the title tosylhydrazone 125. The mixture turned pink to red to purple and eventually went black. The mixture was heated at reflux for two hours. After cooling, it was poured into 150 ml of water and extracted

three times with 70 ml of pentane. The combined pentane extracts were washed five times with 100 ml of water and dried over sodium sulfate. The pentane was removed on the rotary evaporator to leave about 0.5 ml of yellow oil which was analyzed by vpc (col G, 122°C, 70 ml/min). The aqueous layer from the pentane extractions was further extracted three times with 70 ml of chloroform. The combined chloroform extracts were washed six times with 100 ml of water and dried over magnesium sulfate. The chloroform was removed on the rotary evaporator to leave 15 ml of a dark liquid which was primarily diglyme based on vpc analysis. This liquid was taken up in 150 ml hexane and washed with six 100 ml portions of water. The hexane solution was dried over magnesium sulfate and concentrated on the rotary evaporator to leave about 0.5 ml of brown oil which was analyzed by vpc. Since this residue and that from the pentane extracts were similar, they were combined and analyzed by vpc (col G, 122°C, 70 ml/min). Three compounds were found with the following retention times and percent composition; A(5.1 min, 67%), B(16.1 min, 29%), C(18.3 min, 3.5%). Compounds A and B were collected by preparative vpc. Compound A was identified as naphthalene 126 by comparison of its nmr spectrum with that of an authentic sample. Compound B was identified as diphenylmethane 127 by comparison of its nmr^{108b}

and ir¹¹² spectra to those published. An internal standard of 2-methylnaphthalene was added and the yield of volatile products was found to be 3.0%.

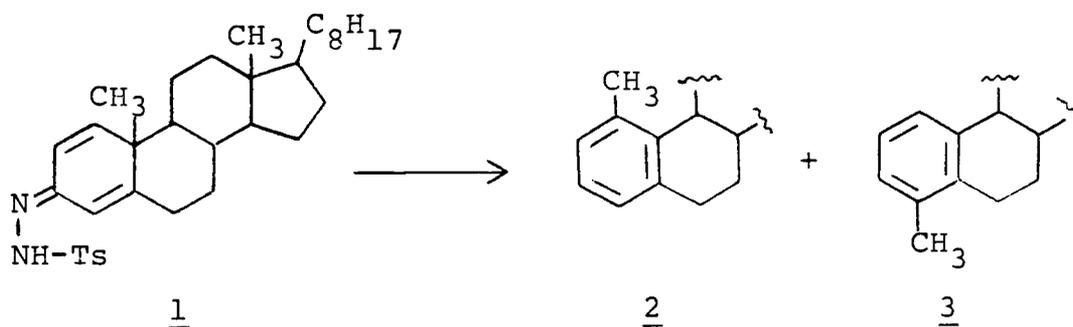
CHAPTER IV. THE CHEMISTRY OF
4,4-DIPHENYLCYCLOHEXA-2,5-DIENYLIDENE

HISTORICAL BACKGROUND

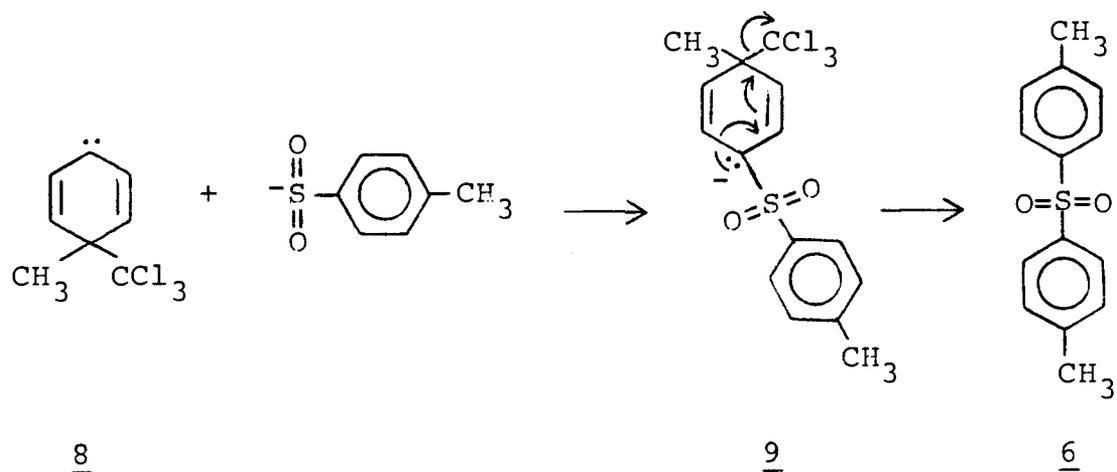
Cyclohexadienones have been extensively studied due to the number of rearrangements they can undergo. These rearrangements can be thermal, acid catalyzed⁸⁶ or photochemical.⁸⁷ In a similar manner cyclohexadienylidenes could also undergo a variety of reactions, and several examples have been examined.

An example of a cyclohexadienylidene from a steroidal system is known.⁸⁸ Tosylhydrazone 1 when decomposed with a strong base in diglyme gave the two aromatized products 2 and 3 (Scheme I).

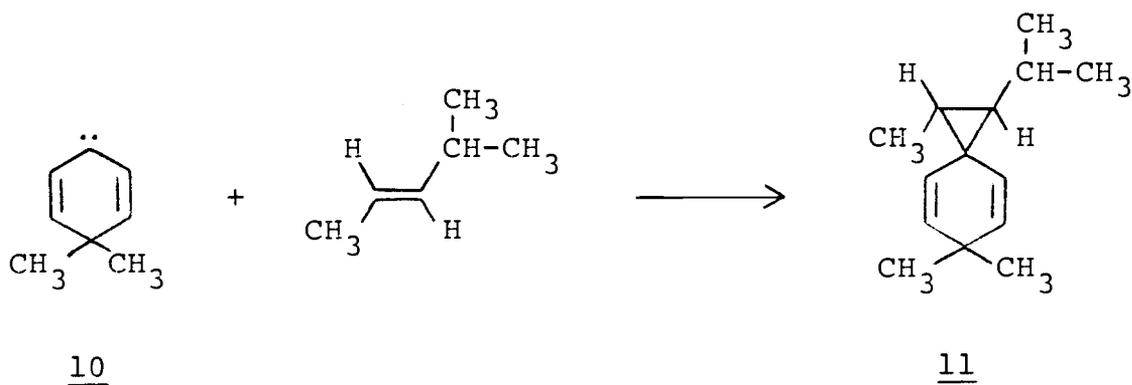
SCHEME I



The tosylhydrazone salt 4 gave products 5 and 6 when decomposed in refluxing diglyme.⁸⁹ It was suggested

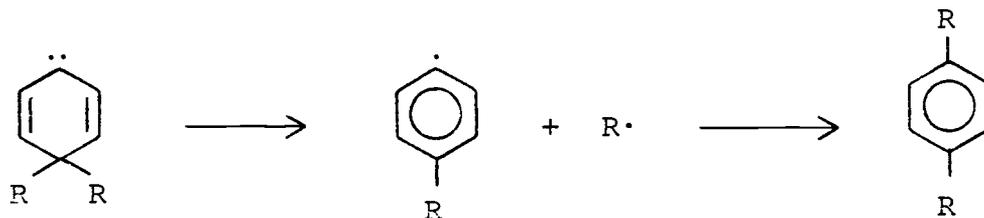


The addition reaction of carbene 10 to olefins has been studied by Jones and co-workers.⁹⁰ Photolysis of

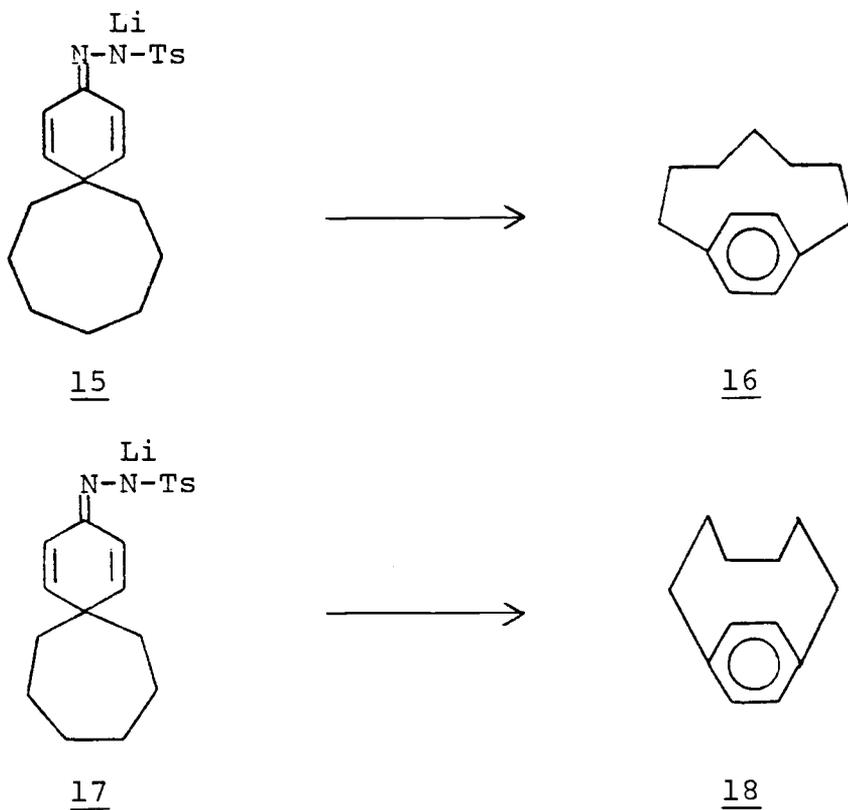


the corresponding diazo compound generated the carbene. The carbene added stereospecifically to the olefin to yield products of the type 11.

SCHEME II

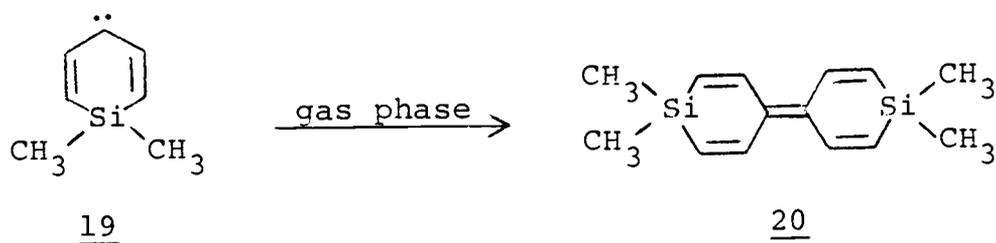


The observation that 10 yields p-xylene 12 led Jones to exploit this reaction in the synthesis of paracyclophanes. Pyrolysis of the tosylhydrazone salt 15 gave [7]paracyclophane 16,⁹² while 17 yielded the analog 18 in which the benzene ring is deformed.⁹³ A radical

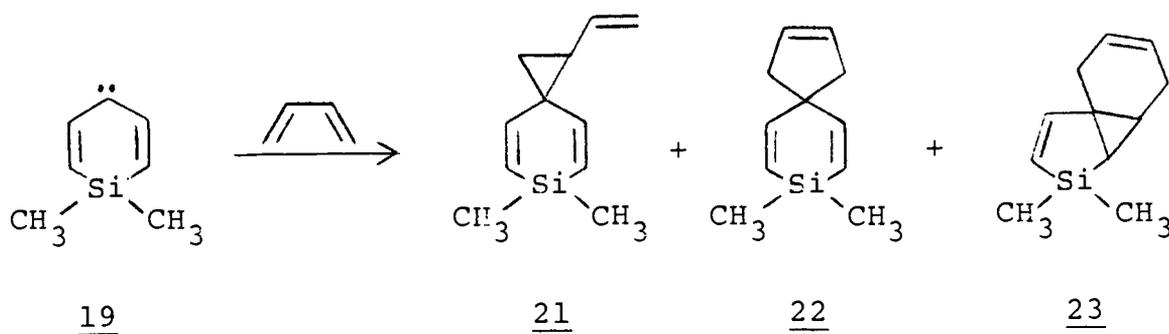


mechanism as in Scheme II was suggested. These and other gas phase carbene reactions have been reviewed by Jones.⁹⁴

Recently, work on the silicaon analog of 10 has been reported. Gas phase decomposition of the diazo compound to form 19 leads only to the dimer 20.⁹⁵ In contrast,

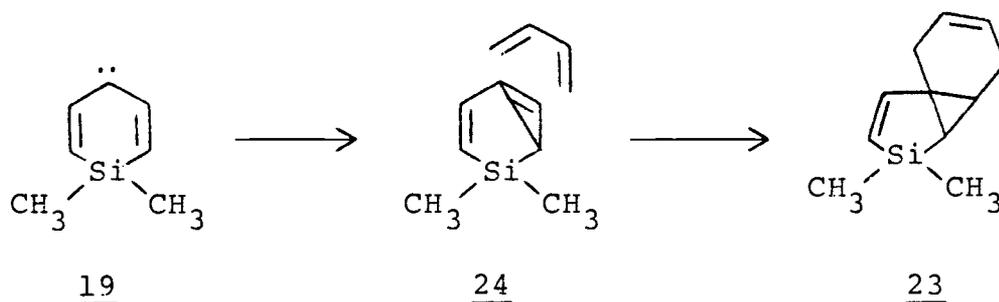


generation of 19 photolytically in solution in butadiene gave three products, 21, 22, and 23.⁹⁶ Of particular

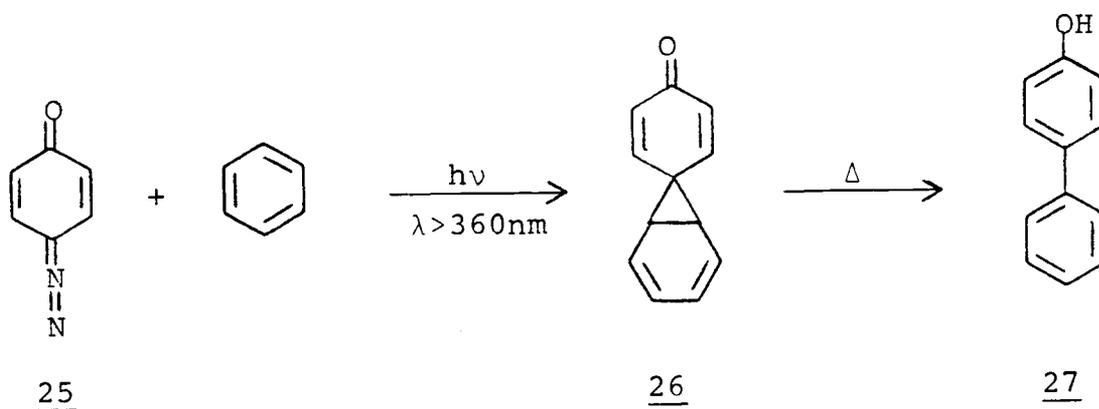


importance is 23. The suggested mechanism for its formation involves the intermediate cyclopropene 24, which is trapped as the Diels-Alder product 23. None of the

Diels-Alder product 23. None of the analogous product was found from a similar reaction of 10 with butadiene.



Cyclohexadienone carbenes are also known and have been studied. As one example, diazo compound 25 was photolyzed in benzene.⁹⁷ The product obtained was phenol

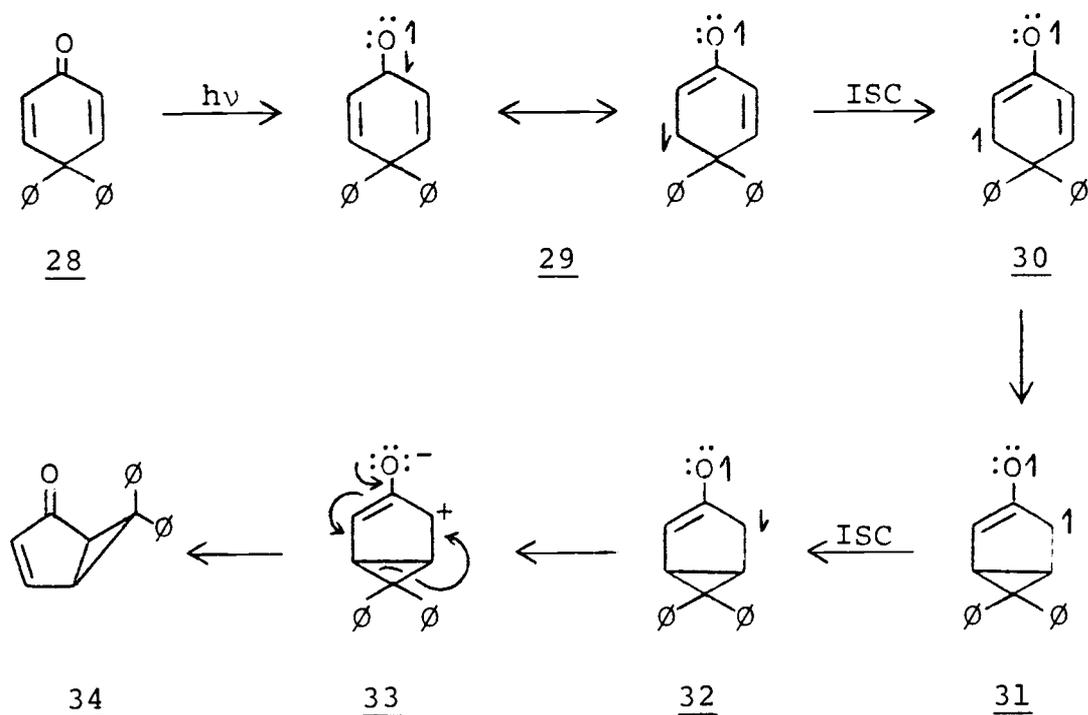


27. It was suggested that the spiro compound 26 was an intermediate in the reaction and rearranged thermally to the observed product 27. A number of other cyclohexadienone carbenes undergo analogous addition reactions.

These addition reactions and the electronic structure of cyclohexadienone carbenes are discussed in a review article by Ershov and Nikiforov.⁹⁸

One of the most intensively studied photochemical reactions of cyclohexadienones is that of 4,4-diphenylcyclohexadienone 28. The product of prime importance from this reaction is ketone 34. Zimmerman and co-workers^{99,100} proposed a mechanism (Scheme III) in which

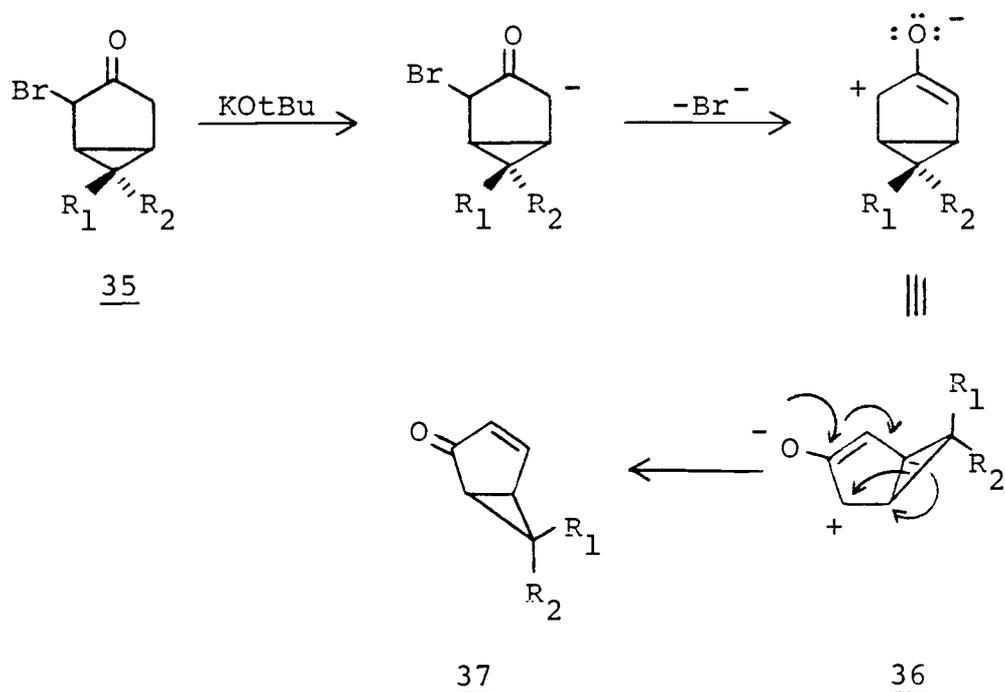
SCHEME III



the ketone 28 is excited to the singlet 29 which inter-system crosses to the triplet 30. This undergoes electronic reorganization (called bond alteration by Zimmerman) to 31. This new triplet 31 undergoes inter-system crossing to the singlet 32. Electron demotion of 32 gives the zwitterion 33. A [1,4]-sigmatropic shift to the electron deficient center completes the transformation to 34.

An analog to zwitterion 33 has been generated independently (Scheme IV). In compound 35, the two aryl

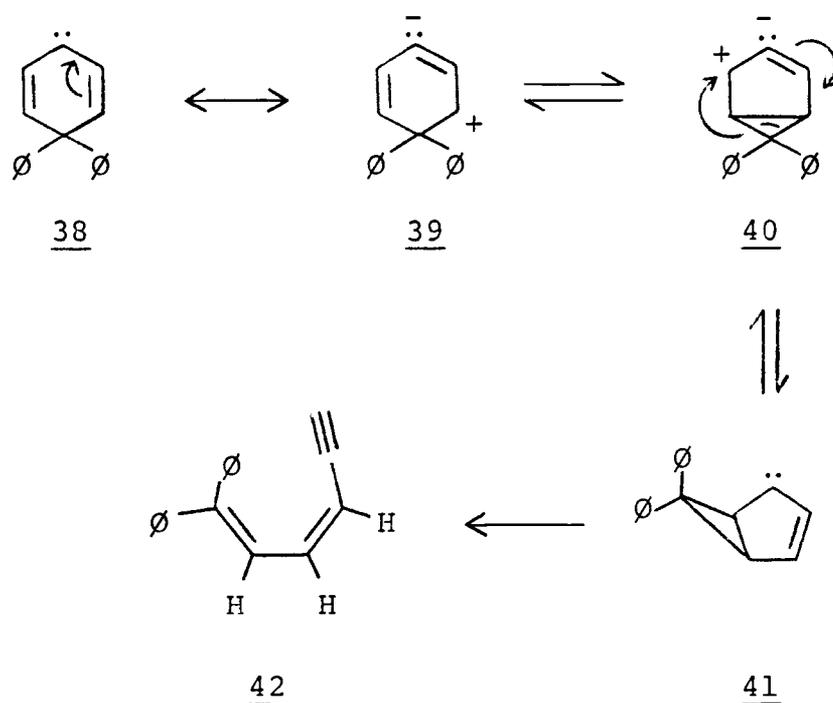
SCHEME IV



groups are different. Upon treatment with potassium tert-butoxide, zwitterion 36 was formed. This zwitterion is analogous to 33 and underwent a similar rearrangement to 37, providing evidence for the presence of this intermediate in the photoreaction (Scheme III). Additionally, aryl group R_1 is endo in both the reactant 35 and the product 37. Zimmerman¹⁰¹ discusses this in terms of a "slither mechanism" as shown by the arrows in 36. Another way of viewing the observed stereochemistry is to note that the configuration has been inverted at C-4. This may be classified as a [1,4]-sigmatropic shift and would be predicted by orbital symmetry considerations to proceed with inversion.¹⁰² This cyclohexadienone photochemistry has been summarized in a review by Zimmerman.¹⁰³

In many instances, carbenes can be viewed as though they were zwitterions. These zwitterionic forms of carbenes were extensively utilized in discussing rearrangement mechanisms in Chapter Three of this thesis. A carbene analogy can be drawn to Zimmerman's photochemical zwitterionic intermediate 33 (Scheme V). The carbene 38 could be represented as a resonance hybrid of 38 and 39, which could be in equilibrium with 40. Intermediate 40 is the analog of 33 and could be predicted to undergo a rearrangement similar to that observed in 33. The result of this rearrangement is the new carbene 41. Carbene 38,

SCHEME V



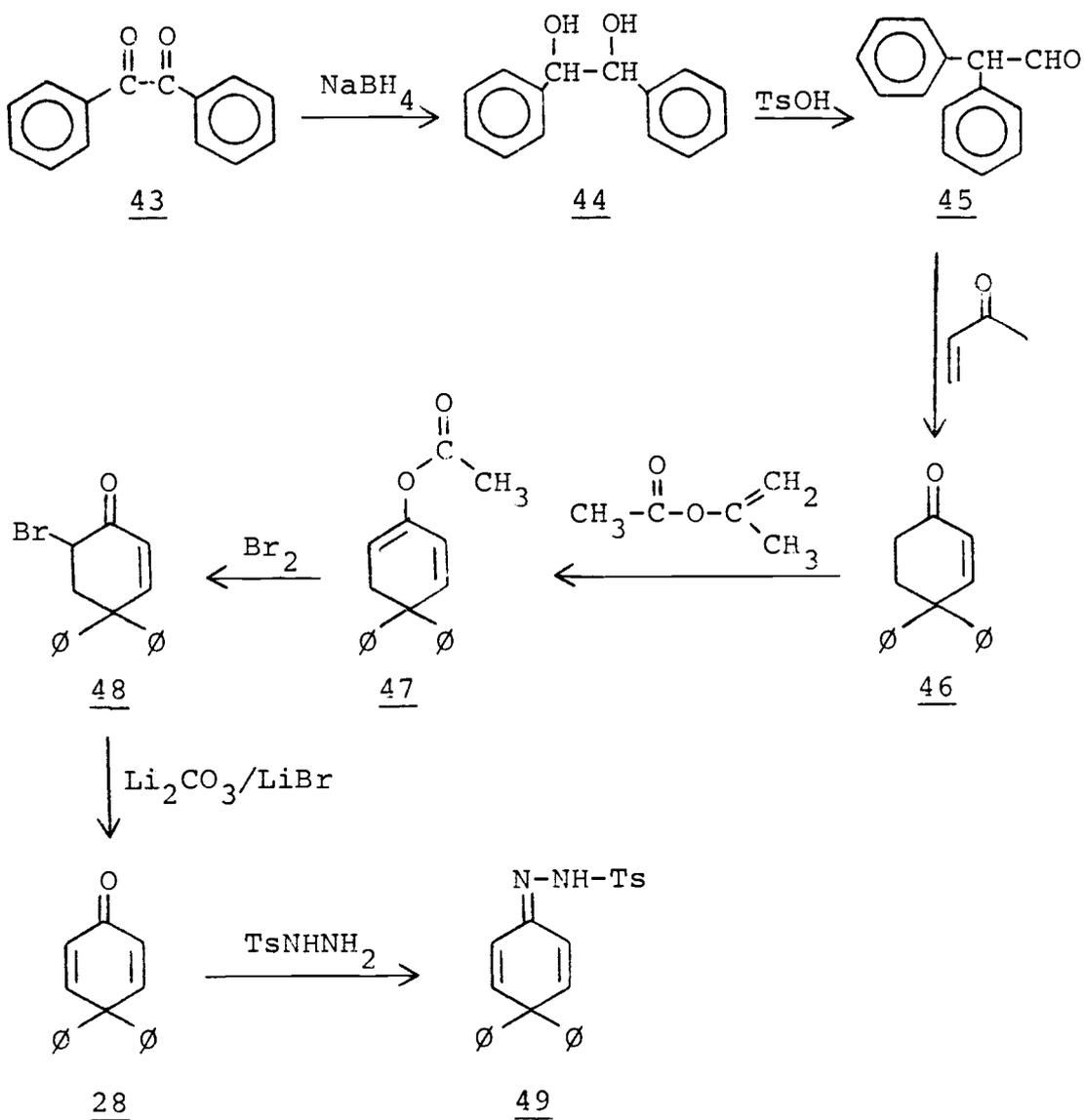
then, could possibly undergo a carbene to carbene rearrangement. The new carbene would react further to yield stable products. An obvious suggestion would be a fragmentation reaction to 42.

The possibility of a carbene to carbene rearrangement of 38 to 41 and the opportunity to compare 4,4-diphenylcyclohexadienylidene 38 to the previously explored dimethyl analog 10 prompted the study of carbene 38.

DISCUSSION AND RESULTS

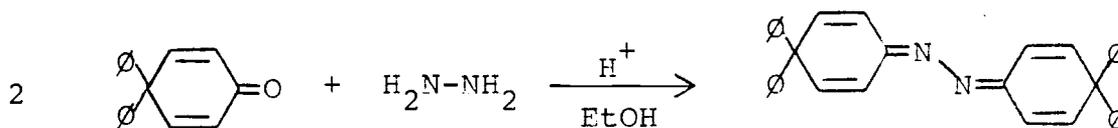
The synthesis of ketone 28 (Scheme VI) has been developed by Zimmerman and co-workers and was followed with little modification. Benzil 43 was reduced with

SCHEME VI



sodium borohydride to dihydrobenzoin 44. Acid catalyzed rearrangement of 44 gave diphenylacetaldehyde 45.⁹⁹ Condensation of 45 with methyl vinyl ketone produced 4,4-diphenylcyclohex-2-en-1-one 46. Reaction of 46 with isopropenyl acetate gave the enol-acetate 47. Bromination of 47 produced bromo-enone 48. Dehydrobromination of 48 with lithium carbonate-lithium bromide in DMF gave the desired ketone 28.¹⁰⁵ Conversion of 28 to the tosylhydrazone 49 was performed with tosylhydrazine in refluxing methanol with no complications.

The tosylhydrazone was converted to its lithium salt with methyllithium and decomposed thermally. Separation on a silica gel column monitored by tlc gave an early eluting fraction which was analyzed by vpc. The major product (51%) of the reaction, eluting second from the silica gel column, was a yellow solid identified as 4,4-diphenyl-2,5-cyclohexadienone azine 51. An authentic sample of the azine 51 was prepared by reaction of the ketone 28 with hydrazine. The azine had nmr and mass spectra identical to the compound isolated from the pyrolysis of the lithium salt of 49.

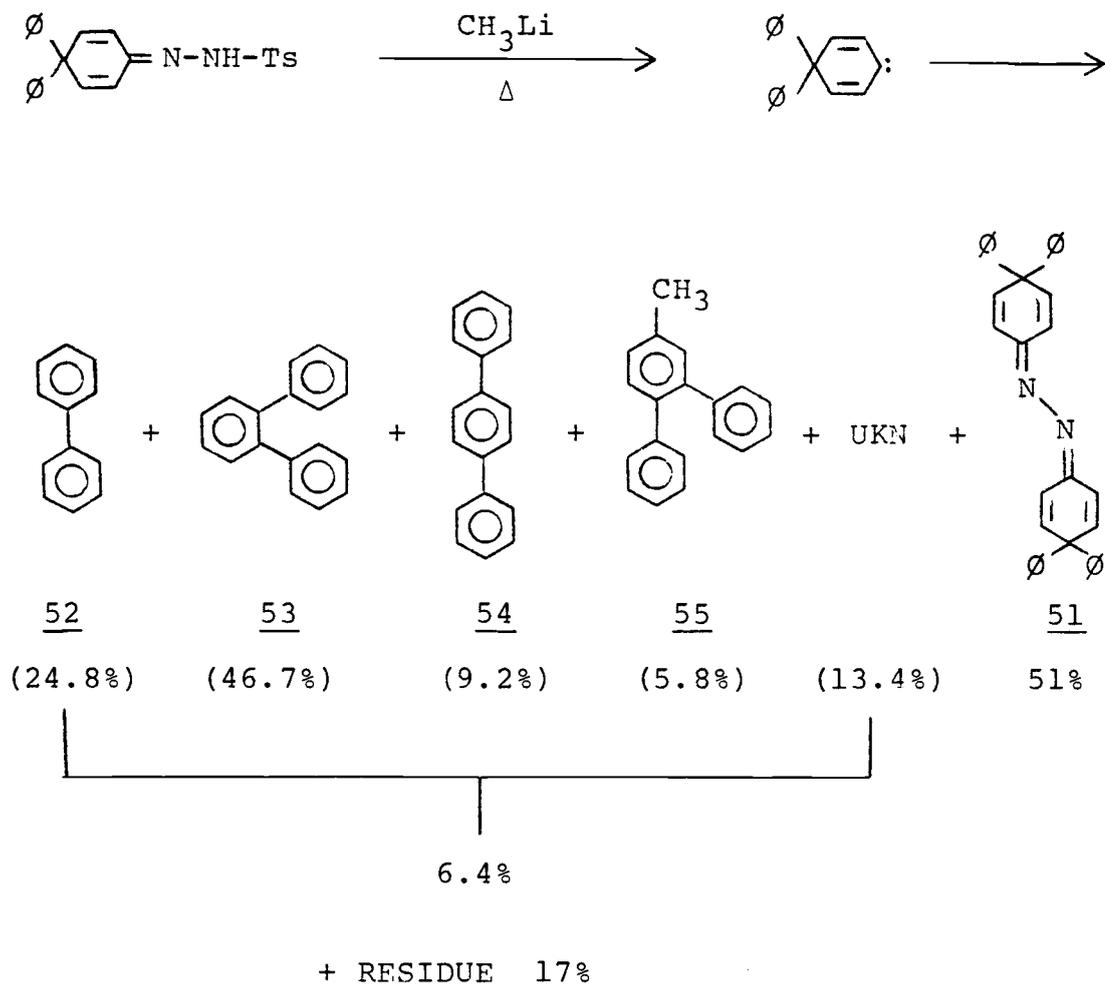
51

Analysis by vpc of the early eluting fraction of the silica gel column gave five major components. Biphenyl 52, o-terphenyl 53, and p-terphenyl 54 were identified by comparison of their vpc retention times, nmr spectra, and mass spectra with authentic samples. Another compound gives nmr and mass spectra consistent with its being a methyl substituted terphenyl 55. One other component remains unidentified. The total yield for the vpc volatile components was 6.4%.

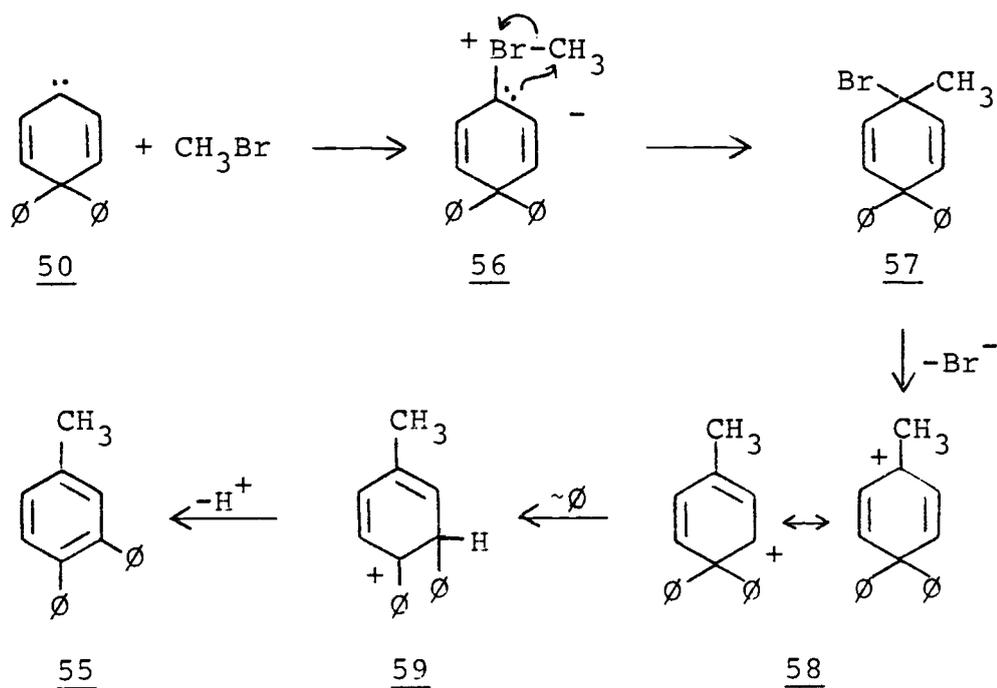
Finally, a non-volatile residue was isolated from the silica gel column which accounted for a further 17% of the reactant. The products obtained from carbene 50 are summarized in Table IV. The percent composition of the vpc volatile compounds is given in parentheses.

Azines are commonly found products of the reaction of a carbene with a diazo compound.¹¹³ A number of possible pathways for their formation exist. No attempt was made to study the compound 51 beyond its identification. Biphenyl 52 and p-terphenyl 54 may arise by a radical pathway such as that illustrated in Scheme II. A cleavage product such as 52, as well as 54, is suggestive of a radical mechanism. The substituted terphenyl 55 was only tentatively identified.¹¹⁴ The methyl group presumably came from methyllithium in some form. When the tosylhydrazone 49 was converted to its sodium salt

TABLE IV

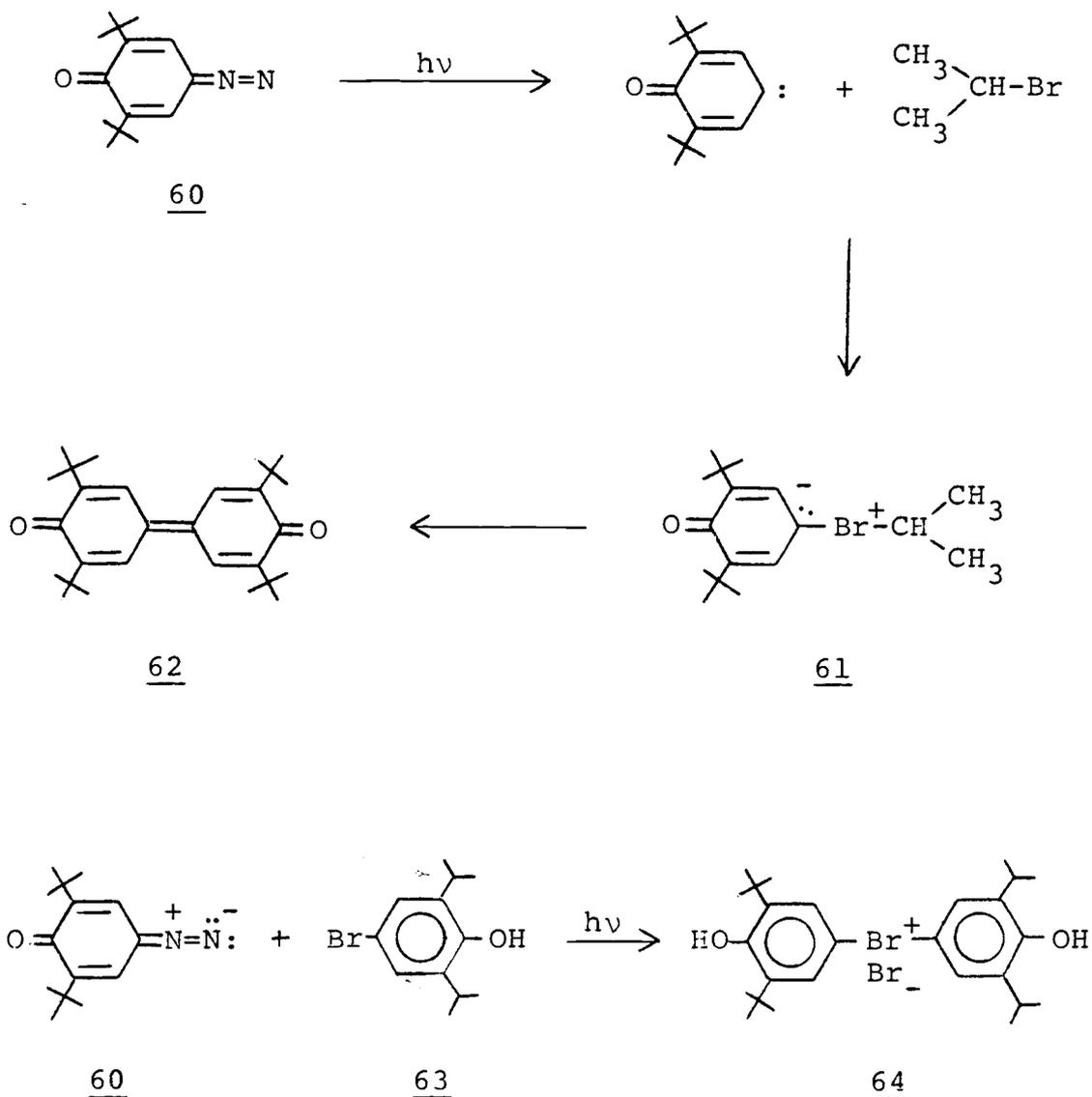


with sodium hydride and photolyzed, no 55 was found. Since commercial methyllithium is stabilized as a complex with lithium bromide, a small amount of bromomethane may



be present. The carbene 50 would react with bromomethane to form the ylid 56. Rearrangement of 56 would give the alkyl bromide 57, which could ionize to the carbonium ion 58. Phenyl migration followed by proton loss affords the product 55.

Instances of ylid formation by reaction of a carbene with an alkyl or aryl halide are known. Diazo compound 60 was photolyzed in the presence of isopropyl bromide. The product obtained was the diphenoquinone 62.^{115,116} An intermediate ylid, 61, was proposed. Additional evidence for the ylid was obtained by using halide 63. The salt 64 was isolated and could be converted further to a diphenoquinone.



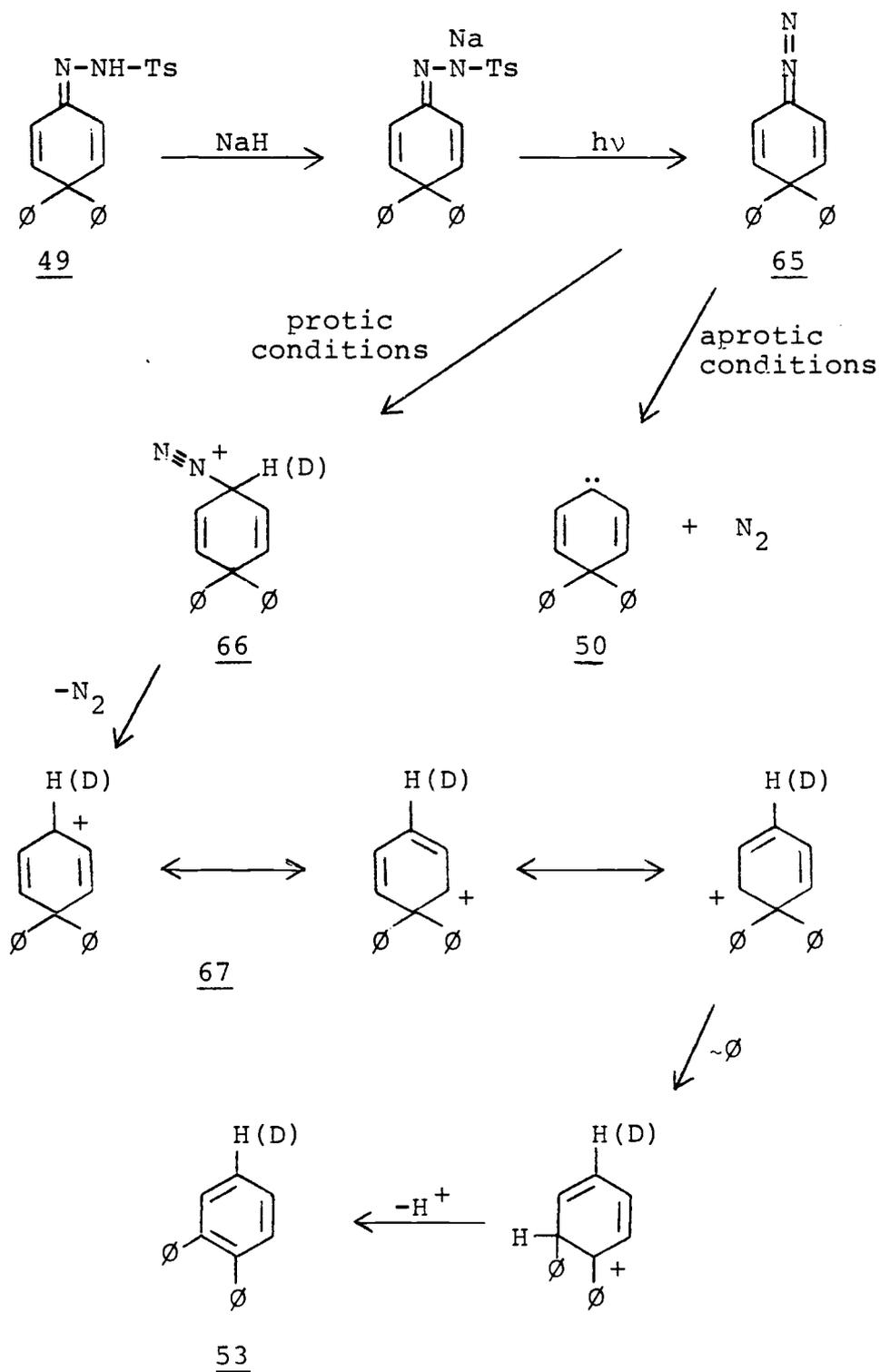
The major monomeric product of carbene 50 is o-terphenyl 53. Its presence is of considerable interest in that no ortho products were isolated from the analogous carbenes 10 or 14. Since 53 would be the expected product of a carbonium ion process, establishment of 53 as a

bona fide carbene product is necessary. The carbonium ion arises as shown in Scheme VII. The tosylhydrazone 49 is converted to its salt and decomposed to give the intermediate diazo compound 65. Under aprotic conditions, 65 loses nitrogen to give the carbene 50. In the presence of a proton source, 65 is converted to the diazonium ion 66 which can lose nitrogen to form the carbonium ion 67. A phenyl migration followed by proton loss would yield o-terphenyl 53 as the product.

To test whether the carbonium ion process was operative, tosylhydrazone 49 was converted to its sodium salt with sodium hydride. This salt was photolyzed in THF in the presence of one equivalent of deuterium oxide which would act as a proton source and be incorporated in 53 if the carbonium ion pathway were followed. After isolation by preparative vpc, 53 was analyzed by low voltage mass spectrometry. Within experimental error, no deuterium was found incorporated in the product. This provides good evidence that 53 was formed from a carbene and not as the result of trace amounts of protic impurities.

At least three reasonable mechanisms, all involving carbene to carbene rearrangements, can be proposed for a pathway from carbene 50 to o-terphenyl 53. Deuterium labeling studies could provide evidence as to which route

SCHEME VII

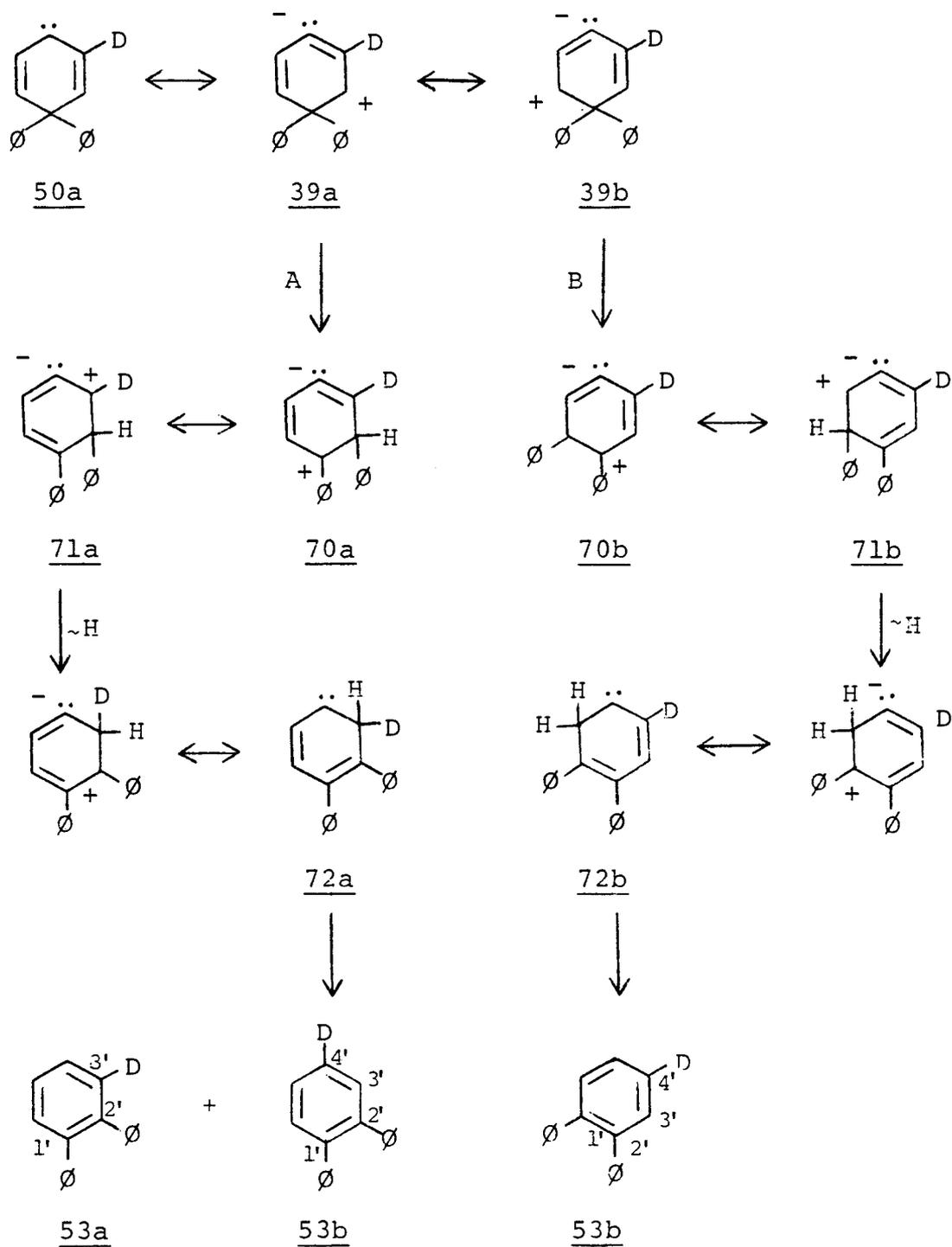


is operative. In the following schemes, the monodeuterated carbene 50a will be used to show the labeling pattern.

The first mechanism and possibly the most straightforward is shown in Scheme VIII. The carbene 50a is shown with its zwitterionic resonance forms 39. A phenyl migration to the positive center of 39 gives a new zwitterion 70. Using the resonance form 71, a hydride migration yields the new carbene 72. Finally, a 1,2 hydride migration affords the observed o-terphenyl 53. In following the deuterium label, pathway B leads only to 53b, with the deuterium label in the 4' position. Pathway A would lead to a mixture of 53a and 53b. The ratio of 53a and 53b derived from 72a would depend on the deuterium isotope effect for the 1,2 hydride migration (72a to 53). Deuterium isotope effects for olefin formation from carbenes have been studied by Kirmse.¹¹⁸ The k_H/k_D value for 1,2 carbon-hydrogen insertion for a series of simple alkyl carbenes ranged from 1.1 to 1.4. Applying a k_H/k_D range of 1.0 to 1.5 to the o-terphenyl derived from 72a, the overall ratio of 53a to 53b for Scheme VIII would fall in the range of 75-80% of 53b to 20-25% of 53a.

The second possibly mechanism for conversion of carbene 50a to o-terphenyl 53 (Scheme IX) involves the bicyclic zwitterion 40 suggested in Scheme V. The carbene

SCHEME VIII

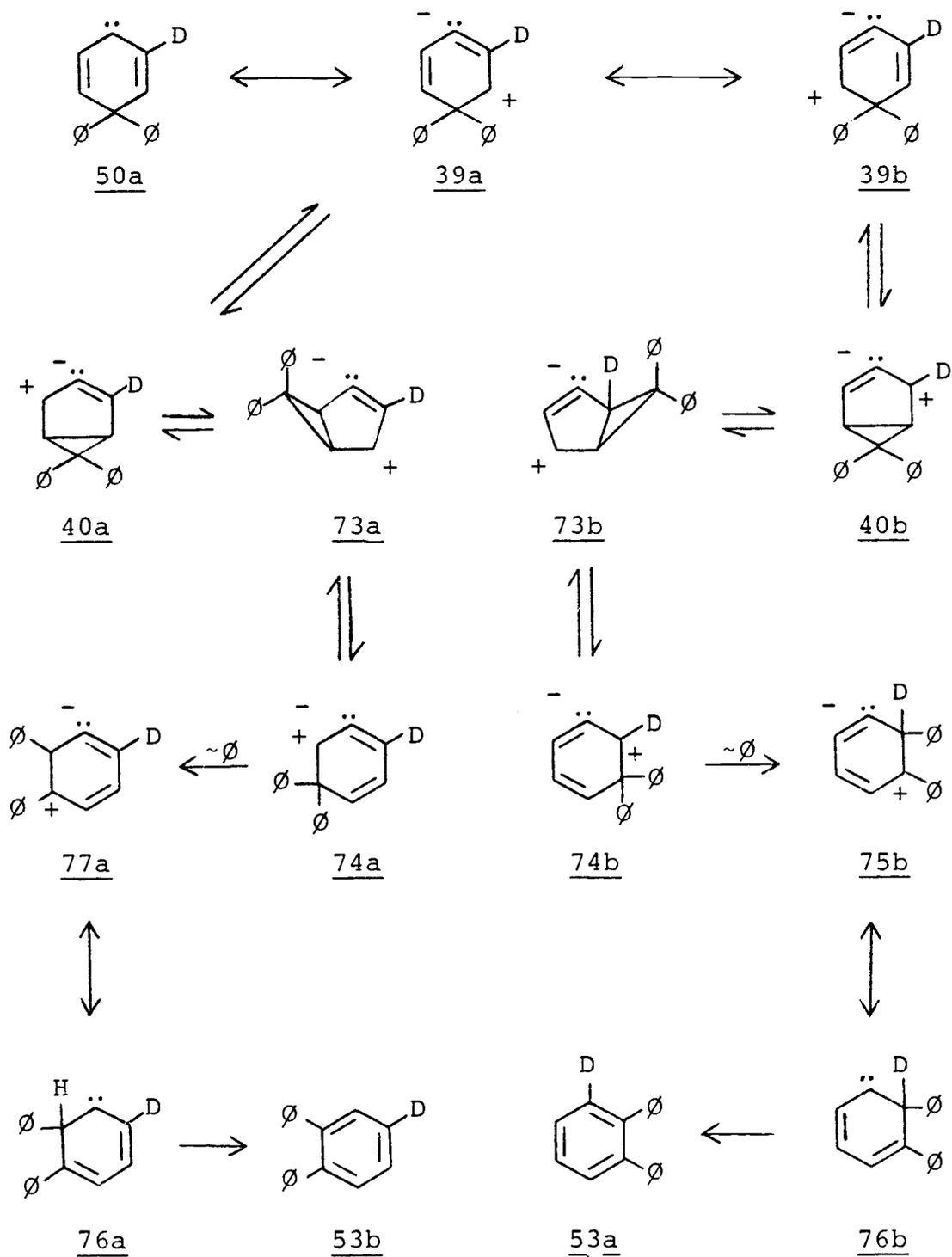


50a, again represented with its zwitterionic resonance form 39, could be in equilibrium with a second zwitterion 40. This zwitterion 40 could undergo a 1,4 alkyl shift to the electron deficient center to form the new zwitterion 73. Cleavage of the cyclopropyl bond of 73 leads to 74. A phenyl migration gives a new zwitterion 75, which is a resonance form of carbene 76. Again this is a carbene to carbene rearrangement. A 1,2 hydride migration in carbene 76 gives the product o-terphenyl 53. Examination of the deuterium label shows that a 50:50 mixture of 53a and 53b would be formed.

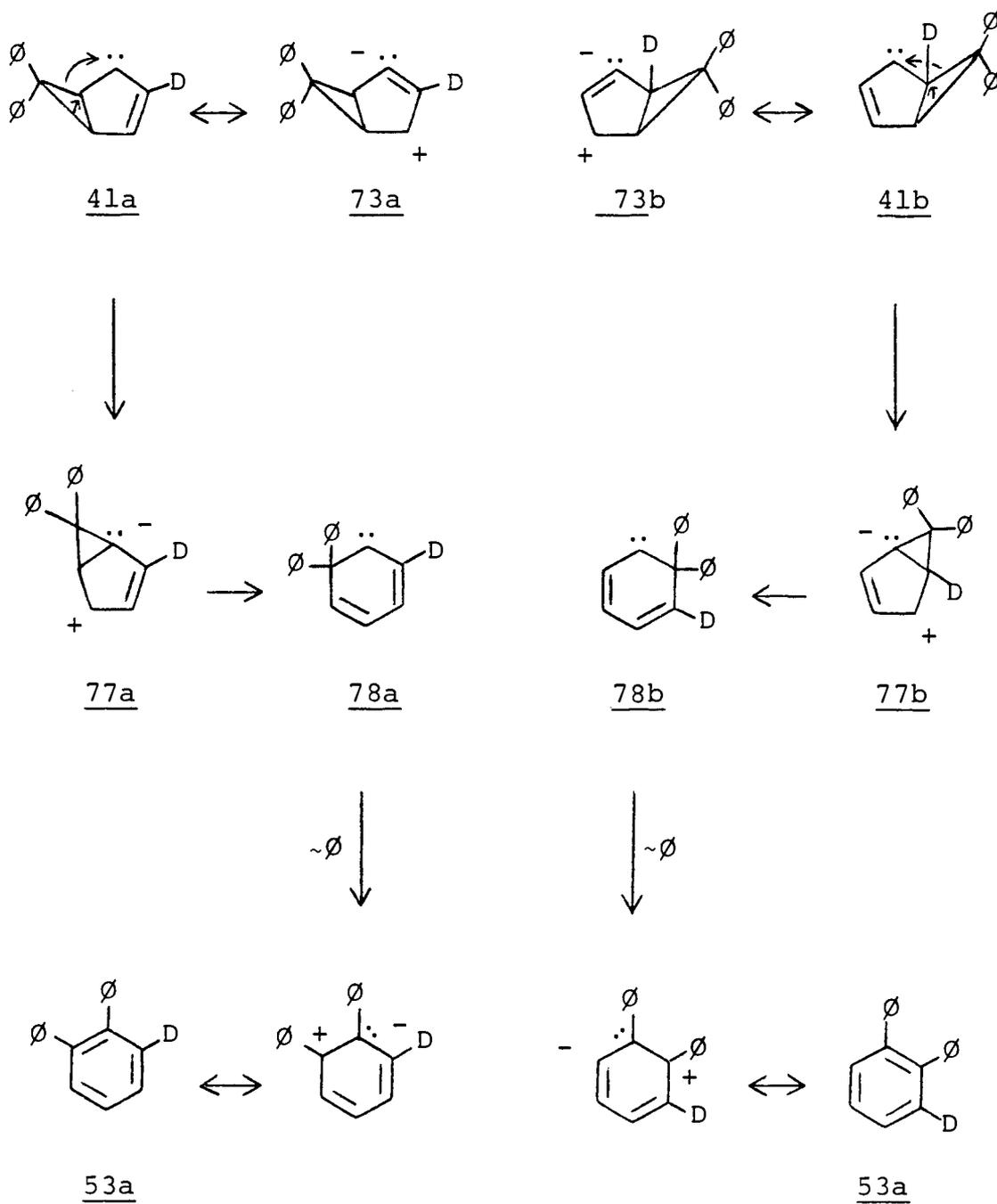
The third possible mechanism (Scheme X) for o-terphenyl formation again involves the zwitterion 73. Conversion of 50a to 73 would be the same as in Scheme IX. The zwitterion 73 is a resonance form of carbene 41. Two sequential 1,2 alkyl migrations (the slither mechanism) would give 77. Rearrangement of 77 gives the new carbene 78. Migration of phenyl to the carbene center would give o-terphenyl 53. The deuterium labeled carbene 50a would produce only 53a by this mechanism.

The mechanism of Scheme X features both 1,2 alkyl migrations (41 to 77) and a 1,2 phenyl migration (78 to 53) to the carbene center. Both migrations are known. An example from Wilt¹¹⁹ examines the competition between these two reactions. The tosylhydrazone 79 was decomposed

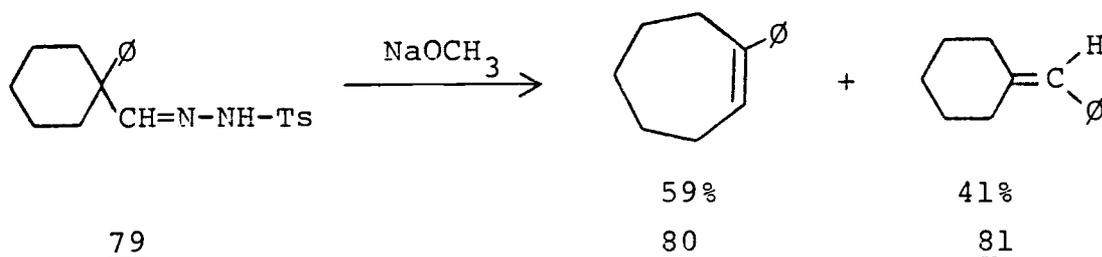
SCHEME IX



SCHEME X



with sodium methoxide to generate the carbene, which went on to two alkene products 80 and 81. A 1,2 alkyl migra-

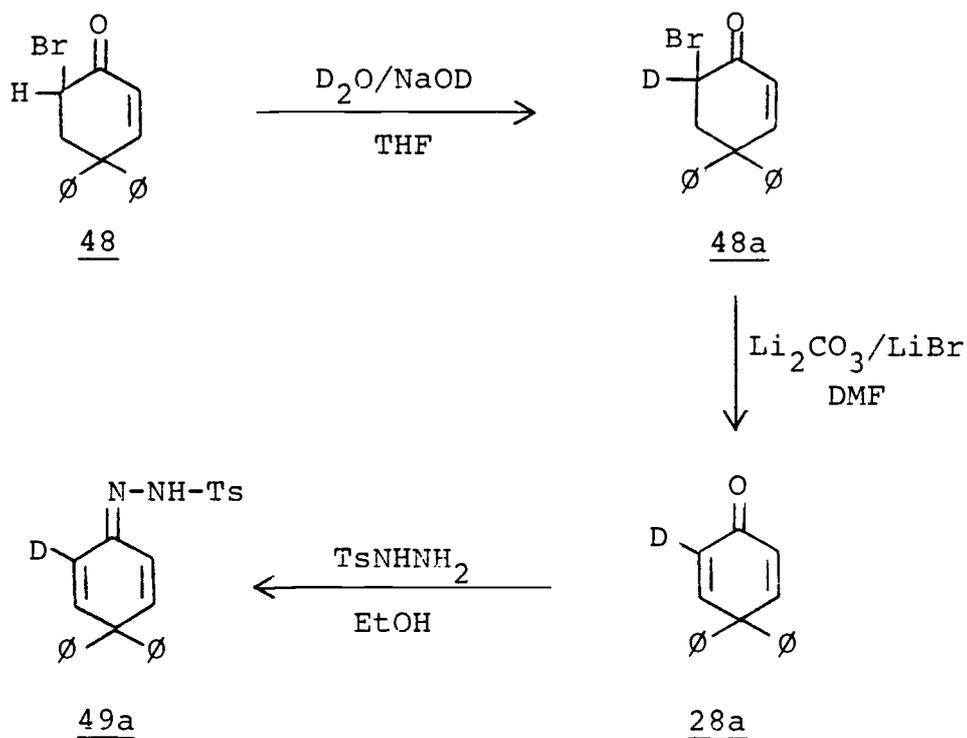


tion affords compound 80, while 81 is the result of the 1,2 phenyl migration. A series of tosylhydrazones of various ring sizes were examined and the competition between the phenyl and alkyl migrations discussed.

In order to investigate the mechanism of o-terphenyl formation from carbene 50, the deuterium labeled carbene 50a was needed. Scheme XI outlines the synthesis of tosylhydrazone 49a. Bromoenone 48 was treated with $\text{D}_2\text{O}/\text{NaOD}$ in THF to give the deuterated bromoenone 48a. Reaction of 48a with lithium carbonate-lithium bromide gave 28a, which was converted to the tosylhydrazone 49a with tosylhydrazine in ethanol. The position of deuterium incorporated in 48a was verified by nmr and the amount of deuterium incorporation in 28a was determined by low voltage mass spectrometry.

The tosylhydrazone 49a was converted to its lithium salt and pyrolyzed as the dry salt. The product distri-

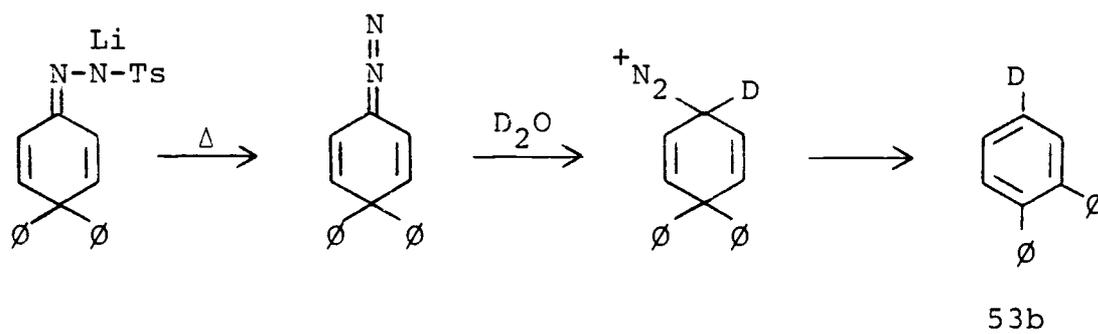
SCHEME XI



bution was similar to that obtained for the undeuterated case (Table IV). The o-terphenyl was isolated and deuterium incorporation determined by low voltage mass spectrometry. The most promising approach for determination of deuterium distribution involved ^{13}C nmr. Figure I shows the ^{13}C nmr spectrum of undeuterated o-terphenyl. All seven different carbon atoms are resolved. The assignments were made using the method of Levy¹²⁰ and were

verified by preparation of o-terphenyl with deuterium at known positions.

Under protic conditions, the salt of tosylhydrazone 49 is converted to the diazo compound, which is protonated and finally yields o-terphenyl 53 (Scheme VII). If the proton source is D_2O , the specifically labeled 4'-deuterio-o-terphenyl 53b can be prepared. The ^{13}C nmr

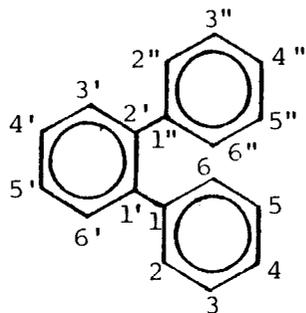


spectrum of this compound is shown in Figure II. In a similar manner, the deuterated tosylhydrazone salt, upon treatment with water, yields a 50:50 mixture of 3'-deuterio-o-terphenyl 53a and 4'-deuterio-o-terphenyl 53b. The ^{13}C nmr spectrum of this mixture is shown in Figure III.

Comparison of the ^{13}C nmr spectra of undeuterated o-terphenyl 53 (Figure I) and 4'-deuterio-o-terphenyl 53b (Figure II) shows two striking differences. Upon incorporation of deuterium at the 4' position, the carbon

FIGURE I

Carbon-13 NMR Spectrum of *o*-Terphenyl



53

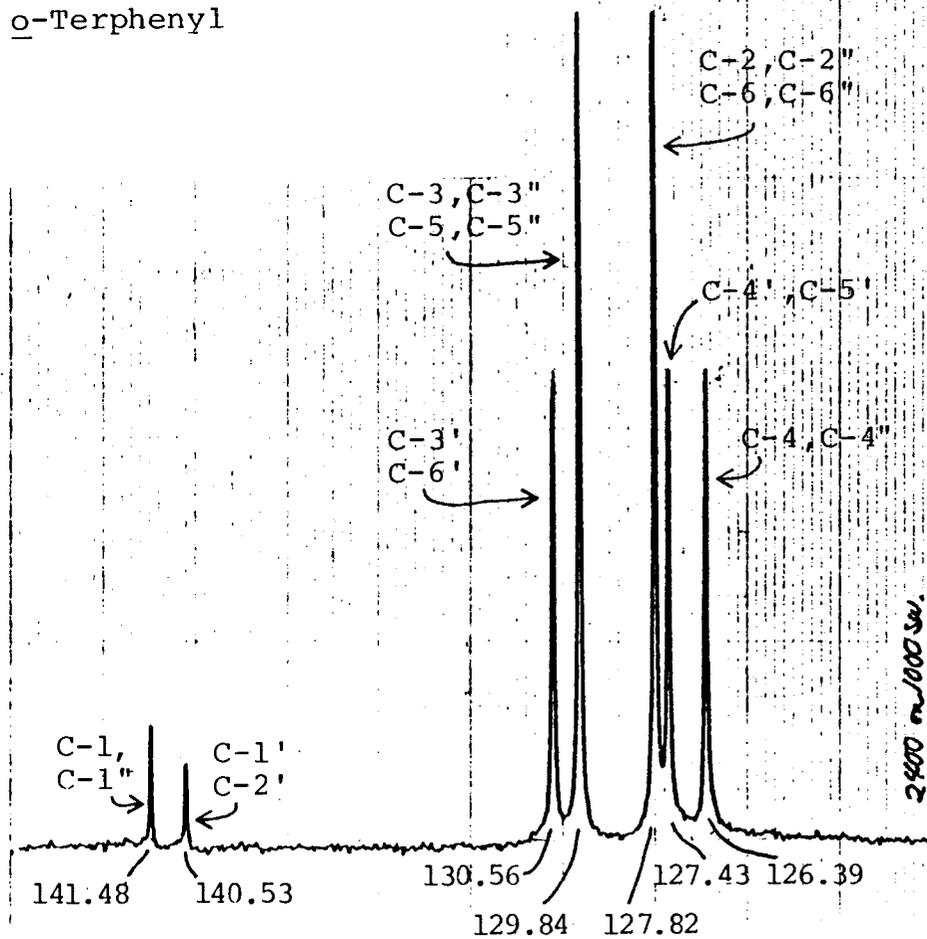
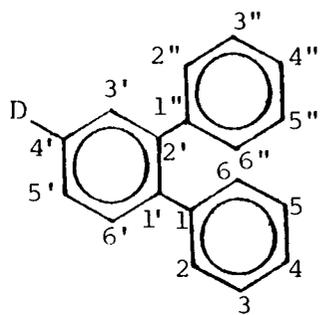


FIGURE II

Carbon-13 NMR Spectrum of
4'-Deuterio-o-terphenyl



53b

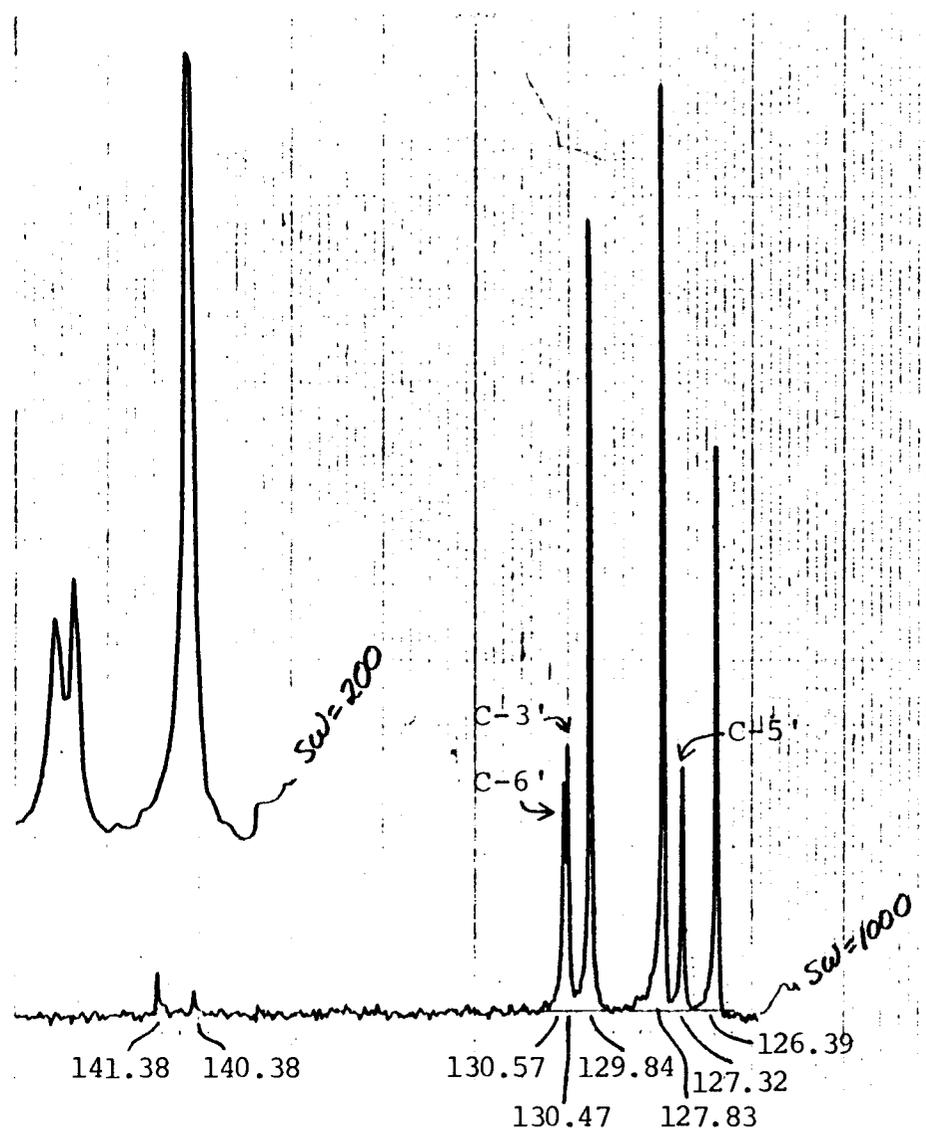
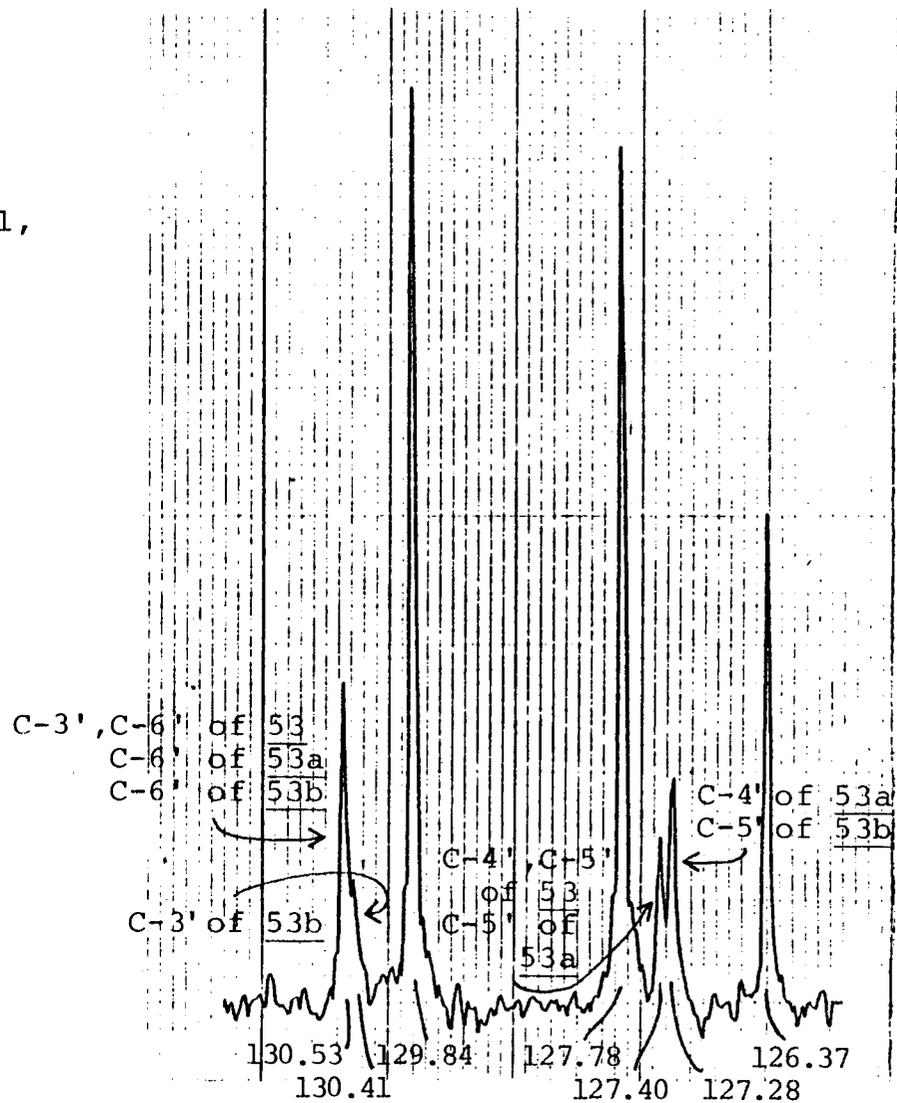
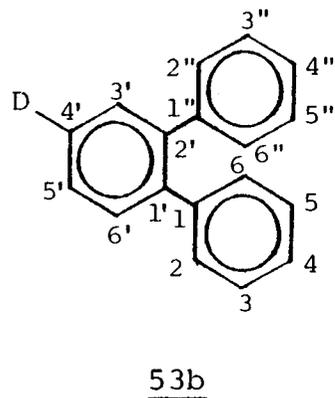
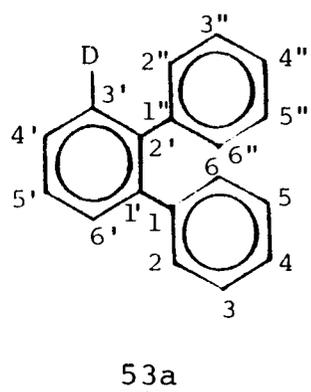
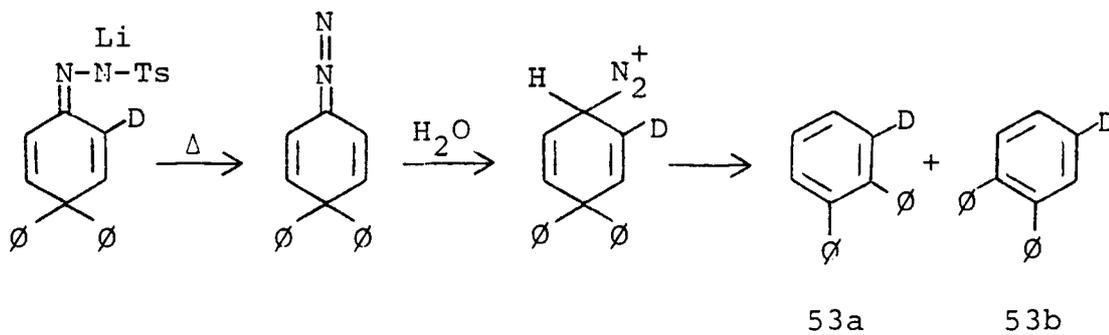


FIGURE III

Carbon-13 NMR Spectrum of a Mixture
of o-Terphenyl, 3'-Deuterio-o-terphenyl,
and 4'-Deuterio-o-terphenyl



absorbance for C-3',6' is split into two peaks and the absorbance for C-4',5' has decreased to about one half of its original intensity. Spiesscke and Schneider¹²¹



noted that the ^{13}C nmr signal for the carbon atom bonded directly to a deuterium atom is often not observed. Since the sample of 53b used to obtain Figure II is mono-deuterated (>98%), the carbon atom at 4' does not give rise to a ^{13}C nmr signal. What is observed is the carbon atom 5', and the intensity of this nmr signal is one half that of the undeuterated *o*-terphenyl, where both 4' and 5' are observed as the one absorbance.

A deuterium isotope effect on ^{13}C chemical shifts in a series of substituted benzenes has been observed.¹²² The geminal carbons (^{13}CCD) are shifted upfield an average of 0.1 ppm. The signal, assigned to C-5' in 53b is 0.11 ppm upfield from the C-4',5' signal of undeuterated

o-terphenyl, in agreement with the predicted geminal isotope effect.

This deuterium isotope effect also explains the two signals for C-3' and C-6'. The downfield absorbance (130.57 ppm) is assigned to C-6' as it has the same chemical shift as the C-3', 6' signal of undeuterated o-terphenyl. The peak shifted upfield by 0.10 ppm is C-3' as would be expected from the presence of the geminal deuterium atom.

Further verification of these assignments is given by the mixture of 53a and 53b (Figure III). The absorbance at 130.53 is from four carbon atoms, C-3' and C-6' of undeuterated 53, C-6' of 53a, and C-6' of 53b. The signal shifted upfield 0.12 ppm to 130.41 ppm by the geminal deuterium isotope effect is C-3' of 53b. The signal at 127.40 ppm is from C-4' and C-5' of 53 and C-5' of 53a. The signal shifted upfield to 127.28 ppm is from C-4' of 53a and C-5' of 53b.

With all the carbon absorbances assigned for these three o-terphenyl samples, an attempt to obtain quantitative data for the amount of deuterium incorporation at each position was made. Stothers¹²³ states that ¹³C nmr signals from an undeuterated carbon atom in a sample can be used as an internal calibration to determine the amount of deuterium incorporation. The peak chosen as

a reference was the C-4, C-4" signal at 126.37 ppm. Since deuterium incorporation at a carbon atom causes a "disappearance" of the ^{13}C nmr signal, the amount of decrease from the reference atom is indicative of deuterium incorporation.

The deuterated o-terphenyl from the carbene reaction was isolated by preparative vpc. The ^{13}C nmr spectrum of this sample was obtained and was superficially quite similar to that of Figure III. Specifically, there were twin signals at 130.5-130.4 ppm and 127.4-127.3 ppm, showing that deuterium was present at both C-3' and C-4'. The complete signal at 130.5-130.4 ppm was carefully integrated, as was the reference signal (129.37 ppm). In addition, the total deuterium incorporation is known from low ionization voltage mass spectrometry. This information allows the relative amounts of 53a (C-3' deuterated) and 53b (C-4' deuterated) to be determined).

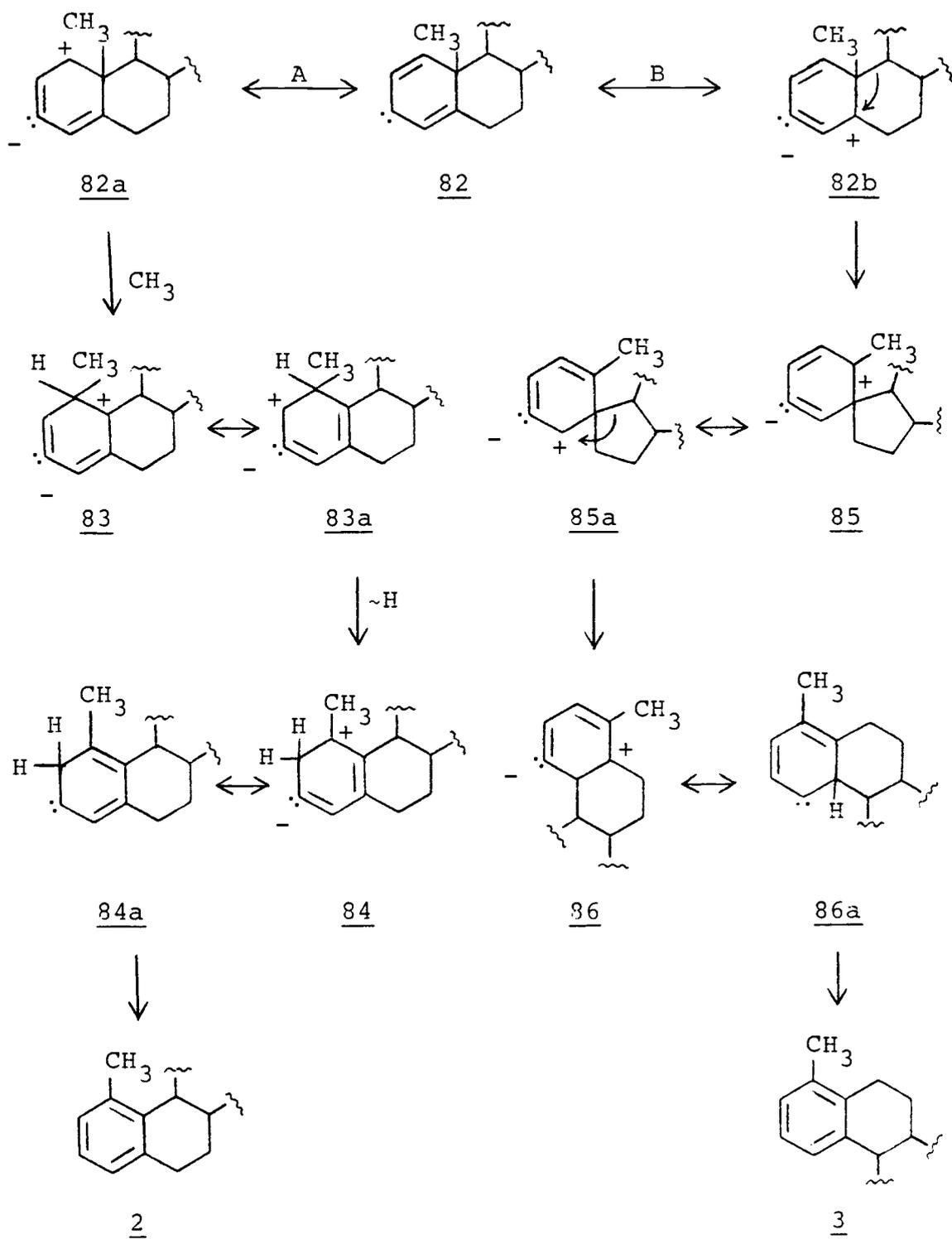
The deuterium incorporation was found to be $69 \pm 8.8\%$ 53a to $31 \pm 8.8\%$ 53b. This does not fit the predicted deuterium labeling pattern of any of the three mechanisms outlined in Schemes VIII, IX, and X. If this deuterium ratio is accepted explicitly, a combination of the mechanisms is suggested. The mechanism of Scheme X would be implicated since it predicts all 53a and 53a is the dominant product. Since Schemes IX and X share the same

intermediate 73, and since Scheme IX predicts a 50:50 mixture of 53a and 53b, a contribution from the mechanism of Scheme IX to account for the 31% of 53b observed would seem reasonable. The mechanistically more straightforward Scheme VIII should not, however, be ruled out as a minor contributor and source of 53b.

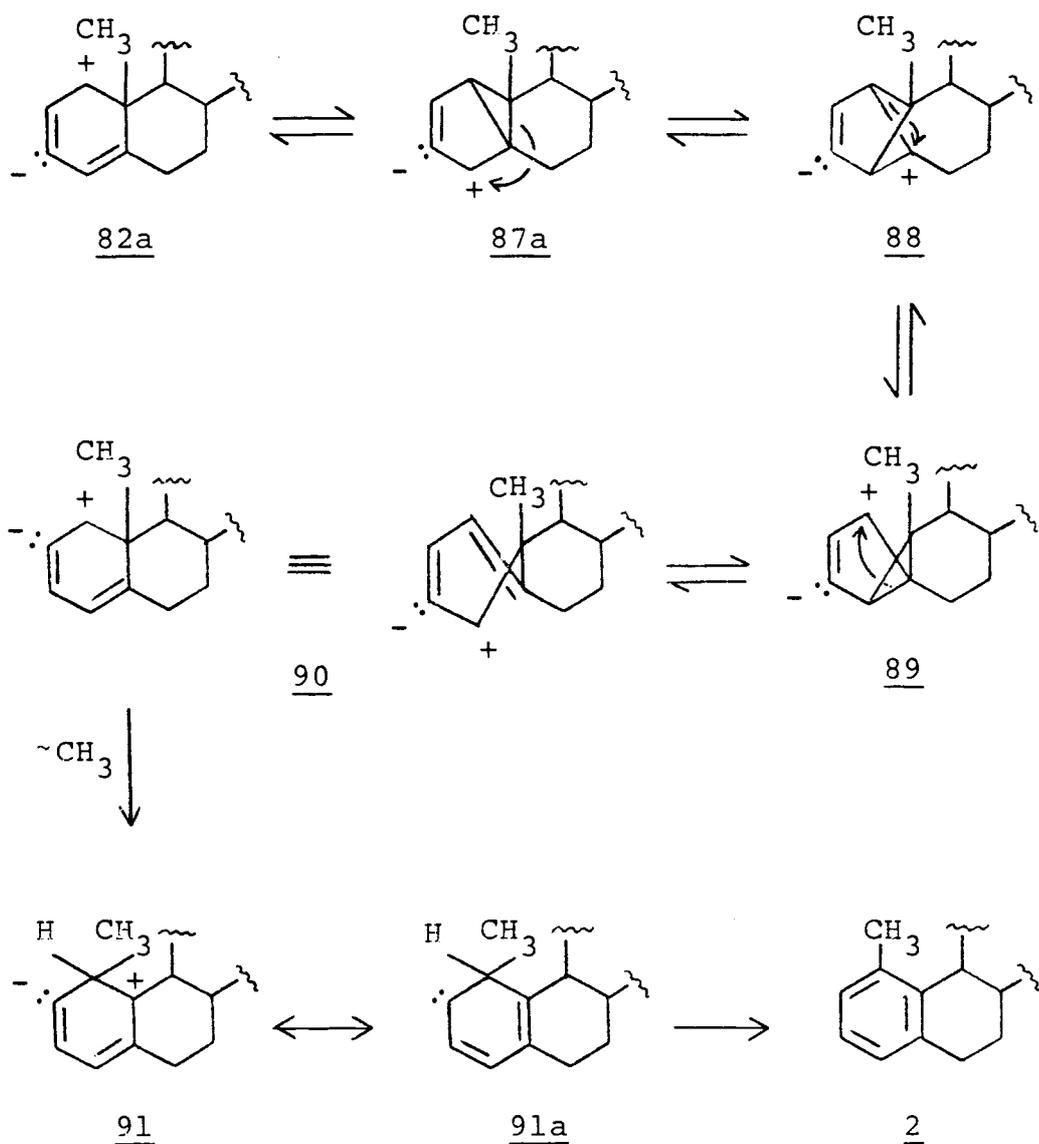
Further insight into these mechanistic possibilities can be found from the work of Dannenberg and Gross⁸⁸ (Scheme I). Their suggested mechanism for the formation of 2 and 3 (Scheme XII) most closely resembles the mechanism of Scheme VIII. The carbene 82 can be shown as the zwitterionic resonance forms 82a and 82b. In pathway A, methyl migration yields the new zwitterion 83 and its resonance form 83a. Hydride migration in 83a forms 84, which is a resonance form of carbene 84a. A final 1,2-hydride migration affords the observed product 2. In the alternate pathway B, alkyl migration in 82b gives the spiro compound 85. A further alkyl migration in 85a yields the zwitterion 86, which is a resonance form of the carbene 86a. Again a final 1,2-hydride migration gives the product 3. Some variation of the steps of Scheme XII can also lead to the observed products 2 and 3.

The mechanism of Scheme IX can also be applied to this steroid case (Scheme XIII). The zwitterion 82a could

SCHEME XII



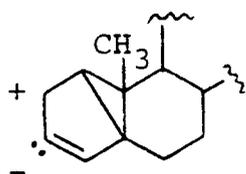
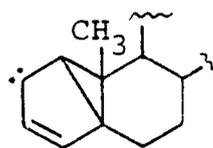
SCHEME XIII



be in equilibrium with the new zwitterion 87a. An alkyl shift gives 88 and another alkyl shift leads to 89. These two sequential 1,2-alkyl migrations constitute the "slither mechanism". Cleavage of the cyclopropyl ring

produces 90. A methyl migration gives 91, which is a resonance form of the carbene 91a. A final 1,2-hydride migration would give the observed product.

Other attempts to find mechanisms relating to those of Schemes IX and X can be made by using the intermediates 87b and the carbene 89a (analogous to Scheme X). No

87b89a

obvious straightforward pathway from either of these intermediates seems to be available to form either 2 or 3. The mechanisms of Scheme XII or a closely related mechanism remains the choice for the conversion of carbene 82 to products 2 and 3.

The mechanism of Scheme XII is closely related to that of Scheme VIII. This would imply that Scheme VIII may be the mechanism of choice for the conversion of carbene 50 to o-terphenyl 53. However the deuterium labeling data suggest that a combination of the mechanisms outlined in Schemes VIII, IX, and X are acting simultaneously. Several questions concerning the deuterium labeling experiment should be raised. One is the low

(42%) deuterium incorporation of the experimental sample. Another point is that if the mechanism of Scheme X is operative, carbene 41 should be present as an intermediate. Carbene 41 would be predicted to fragment to 42, but no 42 was found as a product. Finally, it must be considered whether the integration of the ^{13}C nmr signals reflect the deuterium incorporation precisely enough to measure the small differences needed to decide among the three mechanisms. Because of these concerns, the deuterium labeling study should be considered an attempt to find a method to differentiate between the mechanisms of Schemes VIII, IX, and X, rather than the absolute mechanistic answer itself.

EXPERIMENTAL

General Experimental. The equipment and procedures of the general experimental sections of chapters two and three were used. ^{13}C nmr integrations were made by averaging the weight of a minimum of five cut out peaks from the expanded spectra.

Preparation of Hydrobenzoin 44. Hydrobenzoin 44 (36.6 g, 0.171 mol, 72%) was prepared by the method of Zimmerman and Schuster⁹⁹ using the sodium borohydride (6.30 g, 0.158 mol) reduction of benzil 43 (50.0 g 0.238 mol). The product crystallized as white lustrous plates and was characterized by its nmr spectrum; nmr (60 MHz, CDCl_3), δ 7.38(s, 10H, aromatic protons), 4.89 (broadened s, 2H, $-\text{CH}-\text{OH}$ protons), 2.26(broadened s, 2H, $-\text{OH}$ protons). This is identical to that reported in the literature.^{109b}

Preparation of Diphenylacetaldehyde 45. Diphenylacetaldehyde 45 (7.23 g, 36.9 mmol, 47%) was prepared by the acid catalyzed rearrangement of hydrobenzoin 44 (16.80 g, 78.4 mmol) using the method of Zimmerman and Schuster.⁹⁹ The product was purified by distillation (111-118°C, 0.1 torr, lit. 143-155°C, 0.65 torr). The nmr spectrum is consistent with the assigned product; nmr (60 MHz, CCl_4), δ 9.82(d, $J=3$ Hz, 1H, aldehydic

proton, 7.28(s, 10H, aromatic protons), 4.76(d, J=3 Hz, 1H, benzylic proton).

Preparation of 4,4-Diphenylcyclohex-2-en-1-one 46.

The procedure of Zimmerman¹⁰⁴ was followed. The condensation of 182.6 g (0.932 mol) of diphenylacetaldehyde 45 and 71.4 g (1.016 mol) of methyl vinyl ketone yielded 178.5 g (0.7198 mol, 77%) of the title ketone 46 after recrystallization from ethanol. The nmr spectrum was consistent with the structure assigned; nmr (60 MHz, CCl₄), δ 7.19(s superimposed over d, 11H, aromatic and one vinyl proton), 6.00(d, J=10 Hz, 1H, vinyl proton), 2.80-2.05(symmetrical m, 4H, cyclohexyl protons).

Preparation of 5,5-Diphenyl-2-acetoxy-1,3-cyclohexa-

diene 47. The procedure of Zimmerman and co-workers was followed.¹⁰⁵ The reaction of 178.5 g (0.7198 mol) of 4,4-diphenylcyclohex-2-en-1-one 46 with excess isopropenyl acetate (as solvent) afforded the desired product 47 in 82% yield (173.2 g, 0.5891 mol) after crystallization from ethanol. The nmr spectrum was identical to that reported by Zimmerman¹⁰⁵; nmr (CCl₄) δ 7.10(s, 10H, aromatic protons), 6.14(d of d, J=10, 0.6 Hz, 1H, vinyl proton), 5.74(d of d, J=10, 1 Hz, 1H, vinyl proton), 5.35(t of d of d, J=4.5, 1.0, 0.6 Hz, 1H, vinyl proton), 2.93(d, J=4.5 Hz, 2H, allylic protons), 1.97(s, 3H, acetyl protons).

Preparation of 6-Bromo-4,4-diphenylcyclohex-2-enone

48. Again the procedure of Zimmerman was followed.¹⁰⁵ A suspension of 79.0 g (0.2724 mol) of 5,5-diphenyl-2-acetoxy-1,3-cyclohexadiene 47 in carbon tetrachloride was brominated with 13.7 ml (42.7 g, 0.2685 mol) of bromine. The crude product was recrystallized from ethanol to yield 59.4 g (0.1817 mol, 67%) of the title bromide 48. The nmr spectrum agreed with that reported by Zimmerman¹⁰⁵; nmr (CCl₄), δ 7.40-7.00(m, 11H, aromatic and C=CHCO), 6.17 (d, J=11 Hz, 1H, vinyl proton), 4.55(d, of d, J=12, 6 Hz, 1H, CHBrCO), 3.08(m, 2H, cyclohexyl protons).

Preparation of 4,4-Diphenyl-2,5-cyclohexadienone 28.

The procedure of Zimmerman¹⁰⁵ was followed. The dehydrobromination of 59.4 g (0.1817 mol) of 6-bromo-4,4-diphenylcyclohex-2-enone 48 was carried out in DMF using 45.7 g (0.612 mol) of lithium carbonate and 52.2 g (0.601 mol) of lithium bromide. After recrystallization from ethanol, 28.9 g (0.1173 mol, 65%) of the title dienone 28 was obtained. Its nmr spectrum is consistent with its structure; nmr (100 MHz, CDCl₃), δ 7.21(m, 12H, aromatic protons superimposed over vinyl protons), 6.28(d, J=10 Hz, 2H, vinyl protons); mp 117.5-119.5°C; lit. 123-124.5°C.⁹⁹

Preparation of 4,4-Diphenyl-2,5-cyclohexadienone

Tosylhydrazone 49. A solution of 5.037 g (20.5 mmol) of 4,4-diphenyl-2,5-cyclohexadienone 28 in 50 ml of methanol was prepared in a 100 ml flask fitted with a magnetic stirrer and reflux condenser. It was necessary to warm the mixture to 50°C to dissolve all of the dienone. A solution of 3.812 g (20.5 mmol) of tosylhydrazine in 10 ml of methanol (also warmed to 50°C) was added to the dienone solution and this solution heated to 60°C for four hours. Upon cooling, an off-white precipitate formed and precipitation was completed by placing the reaction in the refrigerator overnight. The crude product was recrystallized from methanol to afford 4.701 g (11.3 mmol, 55%) of the desired tosylhydrazone 49; mp 140-141°C dec.; nmr (100 MHz, CDCl₃), δ7.90(d, J=8 Hz, 2H, tosyl aromatic protons), 7.22(m, 12H, aromatic and tosyl aromatic protons), 6.80(broadened s, 2H, vinyl protons), 6.32(d, J=4 Hz, 2H, vinyl protons), 2.39(s, 3H, aromatic methyl protons); ir (Nujol mull), 3260 cm⁻¹ (m), 1650 (w), 1595 (m), 1345 (s), 1160 (s). Chemical ionization mass spectrum. Calculated for C₂₅H₂₂N₂O₂S: 414; positive ion 415, negative ion 413.

Dry Salt Pyrolysis of the Lithium Salt of 4,4-Di-phenyl-2,5-cyclohexadienone Tosylhydrazone 49. A 100 ml flask fitted with a magnetic stirrer, gas inlet, and septum was charged with 0.9386 g (2.265 mmol) of the title tosylhydrazone 49 dissolved in 20 ml of anhydrous THF. The flask was thoroughly flushed with dry nitrogen and 1.30 ml (2.28 mmol) of 1.75 M methyllithium was added via a syringe. Then an additional 0.3 ml (0.53 mmol) of methyllithium was added, just enough to produce a distinctive deep gold color presumed to be the dianion. A heavy white precipitate formed and this suspension was stirred under nitrogen at room temperature for 45 min. The THF was removed by blowing on the stirred suspension with a stream of dry nitrogen. When most of the THF had evaporated, the remainder was removed by pumping at 0.3 torr for one hour. The usual all glass decomposition apparatus was set up and the salt decomposed by heating to 185°C. Nitrogen evolution began at 118°C and heating was continued for ten minutes after nitrogen evolution had ceased. The volatile products which had been collected at -78°C were washed from the traps with benzene. The residue in the decomposition flask was dissolved in 50 ml of benzene and combined with the benzene washes of the traps. The combined benzene

extracts were washed six times with 75 ml of water and dried over magnesium sulfate. The benzene was removed on the rotary evaporator to leave a reddish-yellow oil. This oil was chromatographed on a 1.8 x 30 cm silica gel column (E. M. Reagents Silica Gel 60, 70/230 mesh) eluting with 200 ml of 90/10 hexane-dichloromethane, 100 ml of 70/30 hexane-dichloromethane, 100 ml of 60/40 hexane-dichloromethane, and finally 100 ml of methanol to remove the polar residue. The column fractions were analyzed by tlc (silica gel, dichloromethane) and combined into three fractions. The fraction with the largest R_f value was further analyzed by vpc (col H, 210°C, 70 m./min) after removal of the solvent on the rotary evaporator. Five major volatile components with the following retention times and percent composition were obtained; A(1.3 min, 24.8%), B(9.0 min, 46.7%), C(12.6 min, 5.8%), D(29.2 min, 9.2%), and E(41.0 min, 13.4%). Comparison of vpc retention times, nmr spectra, and mass spectra to commercially available authentic samples was used to identify A as biphenyl 52, B as o-terphenyl 53, and D as p-terphenyl 54. Compound C has m/e 244 and nmr (80 MHz, CDCl₃), δ7.38(s, 2H, aromatic protons), 7.20, 7.11(s at 7.20 and two almost merged singlets at 7.11, total area 12H, aromatic protons),

2.40(s, 2H, aromatic methyl). This has been tentatively identified as a methyl substituted terphenyl. Compound E, m/e 244, nmr (80 MHz, CDCl_3), δ 7.63-7.00 (three complex overlapping m in the aromatic region) remains unidentified. Anthracene was added as an internal standard and the yield of volatile product from this column fraction was found to be 6.4%. The second fraction (intermediate R_f) from the column chromatography was evaporated on the rotary evaporator to give 0.2791 g (0.572 mmol, 51%) of yellow-brown solid identified as 4,4-diphenyl-2,5-cyclohexadiene azine 51 by comparison of its nmr and mass spectra with those of an authentic compound. The third column fraction (R_f about 0.05) was evaporated and weighed to give 0.0887 g (estimated as MW 230 for 0.385 mmol, 17%). The nmr spectrum of this fraction and its R_f value of 0.05 would lead to its being termed "uncharacterizable high molecular weight residue".

Synthesis of 4,4-Diphenyl-2,5-cyclohexadiene Azine

51. A 10 ml flask fitted with a magnetic stirrer was charged with 0.2296 g (0.933 mmol) of 4,4-diphenyl-2,5-cyclohexadienone 28 and 26.8 μl (27.5 mg, 0.4666 mmol) of 85% hydrazine hydrate in 10 ml of 95% ethanol. After the addition of one drop of concentrated hydrochloric acid, the reaction was allowed to stir for seven days.

A brilliant yellow precipitate formed, which was isolated to yield 0.1371 g (0.281 mmol, 60%) of azine 51 identified by its nmr and mass spectra; mp 231-233°C dec.; nmr (100 MHz, $\text{CDCl}_3/\text{CCl}_4$), δ 7.28(s, 24H, aromatic and vinyl protons), 6.73, 6.66(two d, $J=1$ Hz, total of 4H, vinyl protons); ir (Nujol mull), 1665 cm^{-1} (s), 1600 (m), 1555 (m), 1038 (s), 830 (s), 760 (s), 705 (s).

High resolution mass spectrum. Calculated for $\text{C}_{36}\text{H}_{28}\text{N}_2$: 488.225; found: 488.222.

Photolysis of the Sodium Salt of 4,4-Diphenyl-2,5-cyclohexadienone Tosylhydrazone 49 in THF in the Presence of Deuterium Oxide. A 50 ml flask fitted with a magnetic stirrer and gas inlet was charged with 69.2 g (1.65 mmol) of a 57.2% sodium hydride dispersion in mineral oil. The sodium hydride was washed with three 15 ml portions of hexane. After the removal of the last hexane wash, 25 ml of anhydrous THF was added and the flask thoroughly purged with dry nitrogen. A solution of 0.507 g (1.22 mmol) of the title tosylhydrazone 49 dissolved in 10 ml of THF was added to the sodium hydride suspension. Gas was evolved and a white precipitate formed. This was stirred for 15 minutes at room temperature and then the salt was collected on a Hirsch funnel and dried in a vacuum desiccator overnight. This salt was placed in

30 ml of anhydrous THF in a pyrex flask to form a suspension and deoxygenated with bubbling nitrogen for 30 minutes. To this suspension was added 0.022 ml (24.3 mg, 1.21 mmol, 1.0 equivalent) of 99.8% deuterium oxide. The suspension was irradiated with a 450 watt Hanovia high pressure mercury lamp for six hours. The now yellow mixture was diluted with 150 ml of water and extracted twice with 200 ml of chloroform. The combined chloroform extracts were washed three times with 200 ml of water and dried over sodium sulfate. The chloroform was removed on the rotary evaporator and the residue analyzed by vpc (col I, 190°C, 60 ml/min). An internal standard of 4,4'-di-tert-butylbiphenyl was added and the yield of o-terphenyl 53 was determined to be 7.1%; an 11% yield of other vpc volatile products was found, in addition to a 13.3% yield of the 4,4-diphenyl-2,5-cyclohexadiene azine 51. The o-terphenyl was collected by preparative vpc and subjected to 12.6 eV mass spectral analysis to determine deuterium incorporation if any. This was compared with undeuterated o-terphenyl. Undeuterated o-terphenyl gives m/e 230. The m+1 peak (231) for 13 runs was 0.1956 ± 0.0076 of the m peak. For 11 runs of the experimental sample, m+1 was 0.1940 ± 0.0068 of the m peak. This would give -0.0016 ± 0.0144 d₁ in

the experimental sample. Using an error propagation formula¹¹⁷ $\sigma_{\theta} = [(0.0076)^2 + (0.0068)^2]^{1/2} = 0.0102$.

This shows that there is $-0.16 \pm 1\%$ d_1 , or no detectable deuterium in the experimental sample.

Preparation of 6-Bromo-6-deuterio-4,4-diphenylcyclohex-2-enone 48a. A solution of 3.6380 g (11.1 mmol) of 6-bromo-4,4-diphenylcyclohex-2-enone 48 was prepared in 14 ml of anhydrous THF in a 25 ml flask fitted with a magnetic stirrer and reflux condenser. The flask was thoroughly flushed with dry nitrogen and 1.55 ml (77.5 mmol) of 99.8% D_2O was added. Then 3 mg of sodium was added and gas evolved as the sodium dissolved. After stirring at room temperature under nitrogen overnight, 15 ml of anhydrous benzene was added and the cloudy benzene solution dried over magnesium sulfate. The benzene was removed on the rotary evaporator to yield a brown oil whose nmr spectrum differed from that of 6-bromo-4,4-diphenylcyclohex-2-enone 48 in that the d of d at $\delta 4.55$ ($CHBrCO$) was absent (greater than 90%) and the m at $\delta 3.08$ had collapsed to a simpler pattern. No attempt was made to purify this product. It was used as is in the preparation of 2-deuterio-4,4-diphenyl-2,5-cyclohexadienone 28a.

Preparation of 2-Deuterio-4,4-diphenyl-2,5-cyclohexadienone 28a. The procedure of Zimmerman¹⁰⁵ used previously in the preparation of the undeuterated compound was followed. The crude 6-bromo-6-deuterio-4,4-diphenylcyclohex-2-enone 48a (assumed to be 11.1 mmol) was dehydrohalogenated using 2.79 g (37.8 mmol) of lithium carbonate and 3.19 g (36.7 mmol) of lithium bromide. The crude product was recrystallized from ethanol to yield 1.486 g (6.02 mmol, 54%) of the deuterated dienone 28a. The yield is calculated for the two steps from 6-bromo-6-deuterio-4,4-diphenylcyclohex-2-enone 48a. Mass spectral analysis at 12.6 eV indicated the dienone to consist of $29.9 \pm 1.2\%$ d_0 , $68.8 \pm 1.7\%$ d_1 , and $1.3 \pm 1.1\%$ d_2 . A second batch was run, which consisted of $53.7 \pm 1.1\%$ d_0 , $43.3 \pm 1.0\%$ d_1 , and $3.1 \pm 0.1\%$ d_2 .

Preparation of 2-Deuterio-4,4-diphenyl-2,5-cyclohexadienone Tosylhydrazone 49a. The same procedure used to prepare the undeuterated compound was followed. The reaction was carried out with 1.403 g (5.68 mmol) of the deuterated dienone and 1.062 g (5.70 mmol) of tosylhydrazine to yield 1.726 g (4.151 mmol, 73%) of the title tosylhydrazone 49a.

Decomposition of the Lithium Salt of 4,4-Diphenyl-2,5-cyclohexadienone Tosylhydrazone 49 in Diglyme and Deuterium Oxide. A 25 ml flask fitted with a magnetic stirrer, septum, reflux condenser, and gas inlet was charged with 0.643 g (1.55 mmol) of the title tosylhydrazone 49 dissolved in 6 ml of anhydrous diglyme. To this stirred solution at room temperature was added 0.88 ml (1.54 mmol) of 1.75 M methyllithium in ether and then an additional 0.12 ml (0.21 mmol) of methyllithium was added to induce formation of the deep gold color of the dianion. This solution was stirred at room temperature for 30 minutes and then 1.20 ml (1.20 g, 60.0 mmol) of 99.8% deuterium oxide was added. The first drop caused the gold color to disappear. The septum was replaced with a stopper and this now cloudy solution was heated to reflux for two hours, during which time a yellow solid formed on the inside of the reaction flask. After cooling, the reaction was diluted with 75 ml of water and extracted with 40 ml of chloroform. The chloroform extract was washed with three 50 ml portions of water and dried over magnesium sulfate. The chloroform was removed on the rotary evaporator and the crude product purified by chromatography through a 0.5 x 10 in silica gel column eluting with dichloromethane. The

chromatography was monitored by tlc (silica gel, dichloromethane). The fractions containing o-terphenyl were combined and the solvent removed on the rotary evaporator. An attempt was made to crystallize the resulting oil from methanol, but it was unsuccessful. The o-terphenyl was then isolated by preparative vpc (col H, 210°C, 70 ml/min, 9.5 min). No attempt was made to determine the yield. Mass spectral analysis at 16 eV indicated the o-terphenyl 53b consisted of $2.48 \pm 0.29\%$ d_0 , $98.07 \pm 0.83\%$ d_1 , and $-0.55 \pm 0.71\%$ d_2 . The ^{13}C nmr spectrum of commercially available undeuterated o-terphenyl 53 was obtained (Figure I) and assigned using the method of Levy.¹²⁰ ^{13}C nmr (20 MHz, CDCl_3), 141.48 ppm (C-1, C-1"), 140.53 (C-1', C-2'), 130.56 (C-3', C-6'), 129.84 (C-3, C-3", C-5, C-5"), 127.82 (C-2, C-2", C-6, C-6"), 127.43 (C-4', C-5'), 126.39 (C-4, C-4"). The ^{13}C nmr spectrum of the experimentally derived 4-deuterio-o-terphenyl 53b (Figure II) was assigned as follows; ^{13}C nmr (20 MHz, CDCl_3), 141.38 ppm (C-1, C-1"), 140.38 (C-1', C-2'), 130.57 (C-6'), 130.47 (C-3'), 129.84 (C-3, C-3", C-5, C-5"), 127.83 (C-2, C-2", C-6, C-6"), 127.32 (C-5'), 126.39 (C-4, C-4"). Since essentially complete deuterium incorporation was achieved, no signal for C-4' (expected at 127.43) is observed.¹²¹ Additionally, the signal for C-5' is at 127.32, shifted 0.11 ppm upfield by the

deuterium isotope effect. The deuterium isotope effect also explains the 0.10 ppm upfield shift of C-3' from C-6'.

Decomposition of the Lithium Salt of 2-Deuterio-4,4-diphenyl-2,5-cyclohexadienone Tosylhydrazone 49a in Diglyme and Water. A 25 ml flask fitted with a magnetic stirrer, gas inlet, and septum was charged with 0.4059 g (0.975 mmol) of the title tosylhydrazone 49a (29.9 \pm 1.2% d_0 , 68.8 \pm 1.7% d_1 , and 1.3 \pm 1.1% d_2 , determined from the ketone 28a) dissolved in 5 ml of dry diglyme. The flask was thoroughly flushed with dry nitrogen and 0.56 ml (0.98 mmol) of 1.75 M methyllithium in ether was added. Then an additional 0.17 ml (0.30 mmol) of methyllithium was added to induce the formation of a deep gold "end-point". This was stirred at room temperature for 45 minutes while the gold color faded. The 1.00 ml (55.6 mmol) of distilled water was added, which caused the solution to become cloudy. The septum was replaced with a reflux condenser and the solution was heated at reflux for 90 minutes under a nitrogen atmosphere. After cooling, the reaction was diluted with 75 ml of water and extracted with 40 ml of benzene. The benzene extract was washed with six 75 ml portions of water to remove the diglyme and dried over magnesium sulfate. The benzene

was removed on the rotary evaporator and the deuterated o-terphenyl was isolated by preparative vpc (col H, 210°C, 75 ml/min, 9.5 min). Mass spectral analysis at 16 eV indicated that the o-terphenyl consisted of $27.8 \pm 0.8\%$ d_0 , $72.6 \pm 0.8\%$ d_1 , and $-0.37 \pm 0.34\%$ d_2 . The ^{13}C nmr spectrum (Figure III) of this mixture of undeuterated o-terphenyl 53 (27.4%), 3'-deuterio-o-terphenyl 53a (36.3%), and 4'-deuterio-o-terphenyl 53b (36.3%) was assigned as follows; ^{13}C nmr (20 MHz, CDCl_3), 130.53 ppm (C-3' and C-6' of 53, C-6' of 53a, and C-6' of 53b), 130.41 (C-3' of 53b), 129.84 (C-3, C-3", C-5, C-5" of 53, 53a, and 53b), 127.78 (C-2, C-2", C-6, C-6" of 53, 53a, and 53b), 127.40 (C-4' and C-5' of 53, and C-5' of 53a), 127.28 (C-4' of 53a and C-5' of 53b), 126.37 (C-4, C-4" of 53, 53a, and 53b).

Dry Salt Pyrolysis of the Lithium Salt of 2-Deuterio-4,4-diphenyl-2,5-cyclohexadienone Tosylhydrazone 49a.

The procedure for the undeuterated case was followed, using 0.6415 g (1.544 mmol, $53.7 \pm 1.1\%$ d_0 , $43.3 \pm 1.0\%$ d_1 , and $3.1 \pm 0.1\%$ d_2 , determined from the ketone 28a) of 49a and titrating 1.75 M methyllithium until the gold "endpoint". The column chromatography yielded three main fractions, as before. The first column fraction was analyzed by vpc (col H, 210°C, 60 ml/min) to give the

following components and percent compositions; biphenyl 52 (32.3%), o-terphenyl 53 (34.3%), compound C from the undeuterated case 55 (11.0%), p-terphenyl 54 (10.2%), compound E (12.2%), and several other minor components. Anthracene was added as an internal standard and the yield of vpc volatile components was found to be 2.9%. The second column chromatography fraction yielded 0.2200 g (0.450 mmol, 58.3%) of azine 51, while the third yielded 0.0789 g (estimated MW of 230 for 0.343 mmol, 22%) of "residue". The o-terphenyl was isolated by preparative vpc and low voltage mass spectrometry showed that the product consisted of $58.18 \pm 1.12\%$ d_0 , $41.32 \pm 1.53\%$ d_1 , and $0.50 \pm 0.50\%$ d_2 . The ^{13}C nmr spectrum was qualitatively very similar to the mixture of 53, 53a, and 53b of Figure III, and was assigned in an identical manner; ^{13}C nmr (20 MHz, CDCl_3), 130.53 ppm (C-3' and C-6' of 53, C-6' of 53a, and C-6' of 53b), 130.41 (C-3' of 53b), 129.84 (C-3, C-3", C-5, C-5" of 53, 53a, and 53b), 127.78 (C-2, C-2", C-6, C-6" of 53, 53a, and 53b), 127.40 (C-4' and C-5' of 53, and C-5' of 53a), 127.28 (C-4' of 53a and C-5' of 53b), 126.37 (C-4, C-4" of 53, 53a, and 53b).

Incorporation of deuterium on a carbon atom causes the loss of that ^{13}C nmr signal¹²¹ and this decrease in signal intensity as compared to an undeuterated reference carbon atom can give the amount of deuterium incor-

poration.¹²³ The double signal at 130.53-130.41 ppm was chosen to examine for deuterium incorporation while the 126.37 signal was chosen to be the reference. These peaks were integrated by cutting and weighing to give means and standard deviations of 0.0245 ± 0.0004 g (eight samples) for the 130.53-130.41 peak and 0.0286 ± 0.0005 g (eight samples) for the 126.37 reference peak.

In the region of 130.53-130.41, ^{13}C nmr signals for C-3' and C-6' of 53 and 53b are present, but only the C-6' signal is present for 53a. This decrease in signal intensity was used to find the deuterium incorporation in the following manner:

Let x = mole fraction of 53 (d_0)

y = mole fraction of 53b (d at C-4')

z = mole fraction of 53a (d at C-3')

c = detector response X moles of sample

From the assignments of the signals at 130.53-130.41 and 126.37,

$$(2x + 2y + z)c = \text{area at } 130.53-130.41 = 0.0245$$

$$2(x + y + z)c = \text{area at } 126.37 = 0.0286$$

These two equations may be solved for c and combined to give

$$\frac{2x + 2y + z}{2x + 2y + 2z} = \frac{0.0245}{0.0286}$$

It is also true that

$$x + y + z = 1$$

From the mass spectral data, $x = 0.5818$ moles. The solution to the above equations is then $y = 0.1315$ moles and $z = 0.2867$ moles. The percentages of y and z are 31.4% y (53b) to 68.5% z (53a). The standard deviation is 8.8% using an error propagation formula.^{117a} This is assuming that the detector response is identical for the reference and experimental signals.

BIBLIOGRAPHY

- (1) Bamford, W. R.; Stevens, T. S. J. Chem. Soc. 1952, 4735.
- (2) Kirmse, W.; Ruetz, L. Justus. Liebigs. Ann. Chem. 1969, 726, 30.
- (3) Jones, W. M. Acc. Chem. Res. 1977, 10, 353.
- (4) Berdick, T. E.; Levin, R. H.; Wolf, A. D.; Jones, Jr., M. J. Am. Chem. Soc. 1973, 95, 5087.
- (5) Jones, Jr., M.; Harrison, A. M.; Rettig, K. R. J. Am. Chem. Soc. 1969, 91, 7462.
- (6) Closs, G. L.; Closs, L. E.; Böll, W. A. J. Am. Chem. Soc. 1963, 85, 3796.
- (7) Kirmse, W. "Carbene Chemistry"; Second Ed.; Academic Press: New York, N. Y., 1971.
- (8) Baron, W. J.; et al. "Carbenes from Diazo Compounds", in "Carbenes", Vol. I: Eds., Moss, R. A.; Jones, Jr., M.; John Wiley and Sons: New York, N. Y., 1961; p 1.
- (9) Hartzler, H. D. "Unsaturated Carbenes", in "Carbenes", Vol. II: Eds., Moss, R. A.; Jones, Jr., M.; John Wiley and Sons: New York, N. Y., 1961; p 43.
- (10) Shapiro, R. H. "Alkenes from Tosylhydrazones", in "Organic Reactions", Vol. 23: Ed., Dauben W. G.; John Wiley and Sons: New York, N. Y., 1976; p 405.
- (11) Bartlett, R. K.; Stevens, T. S. J. Chem. Soc. C 1967, 1964.
- (12) Durr, H. Chem. Ber. 1970, 103, 369.
- (13) Sato, T.; Homma, I. Bull. Chem. Soc. Jpn. 1971, 44, 1885.
- (14) Caglioti, L.; Dondoni, A.; Rosini, G. Chim. Ind. (Milan) 1968, 50, 122.

- (15) Taylor, R. T.; Degenhardt, C. R.; Melega, W. P.; Paquette, L. A. Tetrahedron Lett. 1977, 159.
- (16) Hedaya, E.; Kent, M. E. J. Am. Chem. Soc. 1971, 93, 3283.
- (17) Matlin, S. A.; Sammes, P. G. Chem. Commun. 1972, 11.
- (18) Skattebl, L. Tetrahedron 1967, 23, 1107.
- (19) Moss, R. A.; Dolling, U-H.; Whittle, J. R. Tetrahedron Lett. 1971, 931.
- (20) Warner, P.; Chang, S-C. Tetrahedron Lett. 1978, 3981.
- (21) Holm, K. H.; Skattebl, L. J. Am. Chem. Soc. 1977, 99, 5480.
- (22) Kirmse, W.; Jendralla, H. Chem. Ber. 1978, 111, 1873.
- (23) Kirmse, W.; Richarz, U. Chem. Ber. 1978, 111, 1895.
- (24) Jones, W. M.; Brinker, U. H. "Some Pericyclic Reactions of Carbenes", in "Pericyclic Reactions", Vol. I: Eds., Marchand, A. P.; Lehr, R. E.; Academic Press: New York, N. Y., 1977; p 109.
- (25) Freeman, P. K.; Hardy, T. A.; Raghavan, R. S.; Kuper, D. G. J. Org. Chem. 1977, 42, 3882.
- (26) Nickon, A.; Werstiuk, N. H. J. Am. Chem. Soc. 1966, 88, 4543.
- (27) Moss, R. A.; Whittle, J. R. Chem. Commun. 1969, 341.
- (28) Skattebol, L. Acta. Chem. Scand. 1963, 17, 1683.
- (29) Waali, E. E.; Allison, N. T. J. Org. Chem. 1979, 44, 3266.
- (30) Oda, M.; Itō, Y.; Kitahara, Y. Tetrahedron Lett. 1975, 2587.
- (31) Mayor, C.; Jones, W. M. Tetrahedron Lett. 1977, 3855.

- (32) Dolbier, Jr., W. R.; Garza, O. T.; Al-Sader, B. H. J. Am. Chem. Soc. 1975, 97, 5083.
- (33) Freeman, P. K.; Hardy, T. A. Tetrahedron Lett. 1973, 3317.
- (34) Klumpp, G. W.; Van Dijk, P. M. Recl. Trav. Chim. Pays-Bas 1971, 90, 381.
- (35) von Rosenberg, J. L.; Mahler, J. E., Pettit, R. J. Am. Chem. Soc. 1962, 84, 2842.
- (36) Brown, J. M.; Occolowitz, J. L. Chem. Commun. 1965, 376.
- (37) Brown, J. M. Chem. Commun. 1967, 638.
- (38) Winstein, S.; Ogliaruso, M.; Sakai, M.; Nicholson, J. M. J. Am. Chem. Soc. 1967, 89, 3656.
- (39) Diaz, A. F.; Sakai, M.; Winstein, S. J. Am. Chem. Soc. 1970, 92, 7477.
- (40) Christensen, L. W.; Waali, E. E.; Jones, W. M. J. Am. Chem. Soc. 1972, 94, 2118.
- (41) Durr, H.; Werndorf, F. Angew. Chem. Int. Ed. Eng. 1974, 13, 483.
- (42) Moss, R. A.; Dolling, U-H.; Whittle, J. R. Tetrahedron Lett. 1971, 931.
- (43) Moss, R. A.; Ho, C-T. Tetrahedron Lett. 1976, 3397.
- (44) Bergman, R. G.; Rajadhyaksha, V. J. J. Am. Chem. Soc. 1970, 92, 2163.
- (45) Goldstein, M. J.; Hoffman, R. J. Am. Chem. Soc. 1971, 93, 6193.
- (46) Staley, S. W.; Reichard, D. W. J. Am. Chem. Soc. 1969, 91, 3998.
- (47) Grutzner, J. B.; Winstein, S. J. Am. Chem. Soc. 1972, 94, 2200.
- (48) Tsuruta, H.; Mori, S.; Nishizawa, Y.; Mukai, T.; Murahashi, S.; Hino, K.; Bansho, K.; Moritani, I. Chem. Lett. 1974, 1497.

- (49) Antkowiak, T. A.; Sanders, D. C.; Trimitsis, G. B.; Press, J. B.; Shechter, H. J. Am. Chem. Soc. 1972, 94, 5366.
- (50) Babu, T. V. R.; Schechter, H. J. Am. Chem. Soc. 1976, 98, 8261.
- (51) Freeman, P. K.; Kuper, D. G. Chem. Ind. 1965, 424.
- (52) Stothers, J. B.; Swenson, J. R.; Tan, C. T. Can. J. Chem. 1975, 53, 581.
- (53) Monson, R. S. "Advanced Organic Synthesis"; Academic Press: New York, N. Y., 1971; pp 3-4.
- (54) Ratcliffe, R.; Rodehorst, R. J. Org. Chem. 1970, 35, 4000.
- (55) Corey, E. J.; Schmidt, G. Tetrahedron Lett. 1979, 399.
- (56) Friedman, L.; Shechter, H. J. Am. Chem. Soc. 1961, 83, 3159.
- (57) Freeman, P. K.; Kinnel, R. unpublished results.
- (58) Rao, V. N. M. Ph.D. Thesis, University of Idaho, 1965.
- (59) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Grunewald, G. L.; Sherwin, M. A. J. Am. Chem. Soc. 1969, 91, 3317.
- (60) Okumura, K.; Murahashi, S.-I. Tetrahedron Lett. 1977, 3281.
- (61) Murahashi, S.-I. private communication.
- (62) Freeman, P. K.; Kuper, D. G. J. Org. Chem. 1965, 30, 1047.
- (63) Japenga, J.; Klumpp, G. W.; Stapersma, J. Tetrahedron 1977, 33, 2847.
- (64) Meinwald, J.; Labana, S. S.; Chadha, M. S. J. Am. Chem. Soc. 1963, 85, 582.

- (65) Brown, J. M.; Occolowitz, J. L. J. Chem. Soc. B 1968, 411.
- (66) Cristol, S. J.; Davies, D. I.; J. Org. Chem. 1964, 29, 1282.
- (67) Davies, D. I.; Done, J. N.; Hey, D. H. Chem. Commun. 1966, 725.
- (68) Warner, C. R.; Strunk, R. J.; Kuivila, H. G. J. Org. Chem. 1966, 31, 3381.
- (69) Dauben, Jr., H. J.; Honnen, L. R.; Harman, K. M. J. Org. Chem. 1960, 25, 1442.
- (70) Jurch, G. R.; Traylor, T. G. J. Am. Chem. Soc. 1966, 88, 5228.
- (71) Hoskinson, R. M. Aust. J. Chem. 1970, 23, 399.
- (72) Maier, G. Angew. Chem. Int. Ed. Eng. 1967, 6, 402.
- (73) Dillon, P. W.; Underwood, G. R. J. Am. Chem. Soc. 1974, 96, 779.
- (74) Paquette, L. A.; Broadhurst, M. J. J. Org. Chem. 1973, 38, 1893.
- (75) Moss, R. A.; Funk, J. D. J. Chem. Soc. C 1967, 2026.
- (76) Retcofsky, H. L.; Queiser, J. A.; Friedel, R. A. Chem. Ind. 1966, 340.
- (77) Friedman, S. Kaufman, M. L.; Blaustein, B. D.; Dean, R. E.; Wender, I. Tetrahedron 1965, 21, 485.
- (78) Radlick, P. J. Org. Chem. 1964, 29, 960.
- (79) Ciabattoni, J.; Crowley, J. E.; Kende, A. S. J. Am. Chem. Soc. 1967, 89, 2778.
- (80) Carlsen, R. O.; Grutzner, J. B. J. Org. Chem. 1977, 42, 2183.
- (81) Gassman, P. G.; Richmond, G. D. J. Am. Chem. Soc. 1970, 92, 2090.

- (82) Moore, W. R.; Moser, W. R.; La Prade, J. E. J. Org. Chem. 1963, 28, 2200.
- (83) Woodward, R. B.; Hoffman, R. "The Conservation of Orbital Symmetry"; Academic Press, Inc.: New York, N. Y., 1970.
- (84) Sakai, M. Tetrahedron Lett. 1973, 339.
- (85) Rey, M.; Dreiding, A. S. Helv. Chim. Acta 1965, 48, 1985.
- (86) Miller, B. Acc. Chem. Res. 1975, 8, 245.
- (87) Zimmerman, H. E. "A New Approach to Mechanistic Organic Photochemistry" in "Advances in Photochemistry", Vol. I: Eds., Noyes, Jr., W. A.; Hammond, G. S.; Pitts, Jr., J. N.; Wiley-Interscience: New York, N. Y., 1963; p 183.
- (88) Dannenberg, H.; Gross, H. J. Tetrahedron 1965, 21, 1611.
- (89) Fry, A. J. J. Am. Chem. Soc. 1965, 87, 1816.
- (90) Jones, Jr., M.; Harrison, A. M.; Rettig, K. R. J. Am. Chem. Soc. 1969, 91, 7462.
- (91) Berdick, T. E.; Levin, R. H.; Wolf, A. D.; Jones, Jr., M. J. Am. Chem. Soc. 1973, 95, 5087.
- (92) Wolf, A. D.; Kane, V. V.; Levin, R. H.; Jones, Jr., M. J. Am. Chem. Soc. 1973, 95, 1680.
- (93) Kane, V. V.; Wolf, A. D.; Jones, Jr., M. J. Am. Chem. Soc. 1974, 96, 2643.
- (94) Jones, Jr., M. Acc. Chem. Res. 1974, 7, 415.
- (95) Barton, T. J.; Banasiak, D. S. J. Organometal. Chem. 1978, 157, 255.
- (96) Coleman, B.; Jones, Jr., M. J. Organometal. Chem. 1979, 168, 393.
- (97) Durr, H.; Kober, H. Tetrahedron Lett. 1972, 1259.

- (98) Ershov, V. V.; Nikiforov, G. A. Russian Chemical Reviews 1975, 44, 816.
- (99) Zimmerman, H. E.; Schuster, D. I. J. Am. Chem. Soc. 1962, 84, 4527.
- (100) Zimmerman, H. E.; Swenton, J. S. J. Am. Chem. Soc. 1964, 86, 1436.
- (101) Zimmerman, H. E.; Crumrine, D. S. J. Am. Chem. Soc. 1968, 90, 5612.
- (102) Brennan, T. M.; Hill, R. K. J. Am. Chem. Soc. 1968, 90, 5614.
- (103) Zimmerman, H. E. Angew. Chem Int. Ed. Eng. 1969, 8, 1.
- (104) Zimmerman, H. E.; Hancock, K. G.; Licke, G. C. J. Am. Chem. Soc. 1968, 90, 4892.
- (105) Zimmerman, H. E.; Hackett, P.; Juers, D. F.; McCall, J.; Schröder, B. J. Am. Chem. Soc. 1971, 93, 3653.
- (106) Goldstein, M. J.; Odell, B. G. J. Am. Chem. Soc. 1967, 89, 6356.
- (107) Moniz, W. B.; Dixon, J. A. J. Am. Chem. Soc. 1961, 83, 1674.
- (108) Pouchert, C. J.; Campbell, J. R. "The Aldrich Library Library of NMR Spectra:", Vol. I; The Aldrich Chemical Company: Milwaukee, Wis., 1974; a, no. 38D; b, 47A.
- (109) "Sadtler Standard NMR Spectra", Research Laboratories, Inc.: Philadelphia, Pa. 1974: a, Vol 14, no. 9264; b, Vol 10, no. 6303.
- (110) Doering, W. von E.; Detert, F. J. Am. Chem. Soc. 1951, 73, 877.
- (111) Noyes, W. A. "Organic Syntheses", collective Vol. II, A. H. Blatt, ed.; John Wiley and Sons: New York, N. Y., 1943; pp 108-109.
- (112) Pouchert, C. J. "The Aldrich Library of Infrared Spectra", Second Ed.; The Aldrich Chemical Company: Milwaukee, Wis., 1975; no. 2, 5016.

- (113) Kirmse, W. "Carbene Chemistry"; Second Ed.; Academic Press: New York, N. Y., 1971; pp 415-417.
- (114) Zimmerman, H. E.; Juers, D. F.; McCall, J. M.; Schröder, B. J. Am. Chem. Soc. 1971, 93, 3662.
- (115) Pirkle, W. H.; Koser, G. F. Tetrahedron Lett. 1968, 3959.
- (116) Pirkle, W. H.; Koser, G. F. J. Am. Chem. Soc. 1968, 90, 3598.
- (117) Overman, R. T.; Clark, H. M. "Radioisotope Techniques"; McGraw-Hill: New York, N. Y., 1960; p 108: a, p 109.
- (118) Kirmse, W.; von Scholtz, H.-D.; Arnold, H. Justus. Liebigs. Ann. Chem. 1968, 711, 22.
- (119) Wilt, J. W.; Kosturik, J. M.; Orłowski, R. C. J. Org. Chem. 1965, 30, 1052.
- (120) Levy, G. C.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists"; Wiley-Interscience: New York, N. Y., 1972; pp 80-81.
- (121) Spiesecke, H.; Schneider, W. G. J. Chem. Phys. 1961, 35, 731.
- (122) Bell, R. A.; Chan, C. L.; Sayer, B. G. Chem. Commun. 1972, 67.
- (123) Stothers, J. B. "¹³C Nmr Studies of Reaction Mechanisms and Reactive Intermediates", in "Topics in Carbon-13 Nmr Spectroscopy", Vol. I: Ed. Levy, G. C.; John Wiley and Sons: New York, N. Y., 1974; p 237.