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Shakespeare, William Calvin, Ph.D.

University of New Hampshire, 1993

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I. ASYMMETRIC PHOTOCHEMISTRY. II. EXPLORATORY AND MECHANISTIC STUDIES ON THE TRIPLET SENSITIZED VAPOR PHASE PHOTOCHEMISTRY OF ALLENES. III. DEVELOPMENTS IN THE SYNTHESIS OF STRAINED CYCLIC CUMULENES.

BY

William C. Shakespeare
B. A. Gettysburg College, 1985

DISSERTATION

Submitted to the University of New Hampshire
in Partial Fulfillment of
the Requirements for the Degree of

Doctor of Philosophy
in
Chemistry

May, 1993

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This dissertation has been examined and approved.

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of Chemistry

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May 1, 1993
Date

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DEDICATION

This work is dedicated to my loving parents, William and Anne Shakespeare. Their love and support throughout my often unpredictable youth was unabating. I remember well the myriad projects that my mother assisted me with, the one involving Ham Hocks and Hush Puppies being up near the top! I remember my fathers attendance at all of my swim meets as a child (his swims in the pool at half-time perhaps being the highlight!), and how pleased it made me feel. I could want nothing more than to give to my children as much love as my parents have given to me. Thanks you two.

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If I were to acknowledge each and every individual who in some way affected my soujourn at the University of New Hampshire, this portion of my thesis would probably be the longest. However, there are several individuals who warrant special comment.

The first is my loving wife Betina. Her support and dedication to excellence has had a profound affect on my life, both as a scientist and as a husband. Indeed, I owe a great del to her. She has not, however, succeded in curbing my unquenchable desire to procrastonate, perhaps no one will.

I would also like to acknowledge my advisor Dr. Richard Johnson for his guidance and support throughout the years. He was an excellent mentor with a richly diversified background who taught us all a great deal.

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ABSTRACT

I. ASYMMETRIC PHOTOCHEMISTRY.
II. EXPLORATORY AND MECHANISTIC STUDIES ON THE TRIPLET SENSITIZED VAPOR PHASE PHOTOCHEMISTRY OF ALLENES.
III. DEVELOPMENTS IN THE SYNTHESIS OF STRAINED CYCLIC CUMULENES.

by

William C. Shakespeare

University of New Hampshire, May, 1993

The development and implementation of a new chiral triplet sensitizer derived from 1,1'-binaphthol is described. Irradiation of 1,3-diphenylallene (**16**) in the presence of 4,5,6,7-tetrahydro-dinaphtho[2,1-*g*:1',2'-*i*][1,6]dioxecine (**10**) resulted in 0.66% optical induction. Irradiation of 1,3-cyclooctadiene (**17**) in the presence of **10** resulted in 11.3% optical induction. The singlet state of **10** could be effectively quenched by higher diene concentration, substantially reducing the optical yield. Irradiation of *trans*-1,2-diphenyl-cyclopropane (**1**) in the presence of **10** resulted in very low optical yields.

The mechanism by which triplet excited state allenes react in the vapor phase is investigated through both theory and experiment. Benzene sensitized vapor phase irradiation of cyclohexylallene (**63**) yields *cis* and *trans*-1,3,8-nonatriene (**82**) as the primary products. Triene **82** undergoes triplet sensitized [4 + 2] cycloaddition reactions yielding bicyclic alkenes **45** and **83**. Additionally, **82** undergoes a series of triplet sensitized [2 + 2] cycloadditions,

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yielding bicyclic alkenes **84-86**. The absence of any observed tricyclics argues for the intermediacy of planar triplet allene **89**, instead of triplet cyclopropylidene **88**. Benzene sensitized vapor phase irradiation of vinylidenecycloheptane (**64**) yielded only starting material. Models indicated that neither intermediate, triplet cyclopropylidene **99** or planar triplet allene **100**, was particularly well suited for hydrogen abstraction to occur. Benzene sensitized solution phase irradiation of either **63** or **64** yielded only starting material.

Ab initio calculations at the UMP3/6-31G*//UHF/3-21G level are reported for hydrogen abstraction from methane by triplet cyclopropylidene (**52**), and planar triplet allene (**61**). The calculations predict E_a = 16.7 and 18.8 kcal/mol for hydrogen abstraction by **52** and **61**, respectively.

The synthesis and trapping of 1-phenyl-1,2-cyclohexadiene (**137**) is described. Several pathways directed toward the synthesis of 1,2-cyclopentadiene (**131**) are also described. Additionally, the development of a new, and presumably general route to cyclic allenes is presented.

The syntheses and trapping of 1,2,3-cyclohexatriene (**199**) and cyclohexen-3-yne (**240**) are described. Both are prepared by introduction of the strained π bond through fluoride induced elimination of vicinal trimethylsilyl, and triflate or halide groups. Both syntheses are general and should be applicable to different ring sizes.

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GENERAL INTRODUCTION

Because of the diverse nature of material that comprised this dissertation, it has been divided into the following three chapters: 1) Asymmetric organic photochemistry, 2) The photochemistry of allenes, 3) Synthesis and trapping of strained cumulenes. Each chapter is self-contained, complete with its own introduction, statement of the goals, results and discussion, and conclusions.

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CHAPTER I

ASYMMETRIC ORGANIC PHOTOCHEMISTRY: A NEW CHIRAL TRIPLET SENSITIZER

Introduction

Optically active molecules are abundant in nature and play a pivotal role in the existence of all living systems. Indeed, most biochemical reactions result from interactions involving one specific enantiomer. As a consequence, chemists have long been interested in optical activity and ways in which optically active compounds can be generated. Although asymmetric ground state reactions have now become commonplace, many aspects of asymmetric photochemistry remain poorly understood. Among the least explored questions is asymmetric induction with a chiral triplet or singlet sensitizer. This chapter reviews briefly the area of asymmetric organic photochemistry, and describes the results obtained from the use of a new chiral triplet sensitizer.

Photochemical asymmetric induction as a means of producing enantiomerically pure or enriched compounds has received increasing attention during the last two decades. Conceptually, this approach has been known for some time, but actual experimentation has yielded few cases demonstrating substantial optical induction.

The most common and most successful approach to asymmetric photochemistry has been the use of chiral prosthetic groups. Optical induction *via* these groups results from diastereofacial differentiation in the transition state. These chiral auxiliaries, which may be attached to either reactant, are often conveniently

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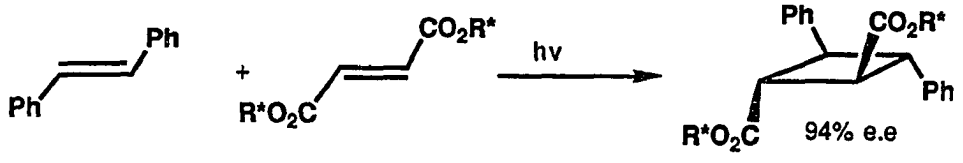
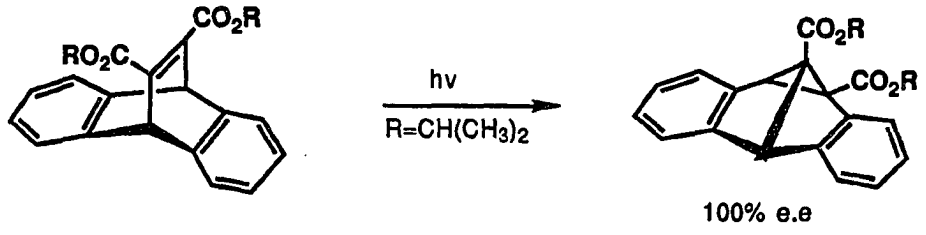
removed after the photochemical step, yielding products with high enantiomeric excesses (e.e.). One example, by Tolbert and Ali,[1] describes the addition of *trans*-stilbene to an optically active fumarate ester (Scheme 1). To explain their result, the authors invoke extensive π stacking, resulting in a rigid transition state. This approach to asymmetric photochemical synthesis is the subject of a recent review.[2]



Scheme 1

A second method employed in asymmetric induction is the use of a chiral environment. Scheffer and co-workers recently reported the synthesis of a diester with 100% enantiomeric excess (e.e.) from irradiation of a chiral single crystal (Scheme 2).[3] While there are relatively few examples of this extraordinary reaction, it clearly demonstrates the enormous impact a chiral environment may have, and holds considerable promise for the future.



Scheme 2

Another method used in chiral discrimination has been circularly polarized light (CPL). CPL has associated with it inherent

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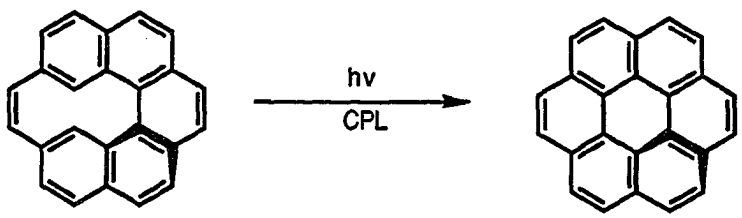
helicity: which may be either right- or left-handed. When solutions containing a mixture of enantiomers are irradiated with a given helicity of CPL, light is absorbed differentially by the individual enantiomers. This is the phenomenon of circular dichroism. For reactions which interconvert enantiomers, accumulation of one over another may be observed. Asymmetric synthesis of helicenes has also been described; these experiments, however, have not provided more than 0.2% optical yield (Scheme 3).[4]



Scheme 3

Asymmetric Induction by Energy Transfer

Singlet energy transfer is believed to occur over long distances; however, triplet transfer and single electron transfer (SET) generally involve bimolecular collisions. To achieve asymmetric induction, it is essential to have a chiral sensitizer which recognizes handedness, and interacts differentially with individual enantiomers. The difference in interaction can be rationalized according to the principles of diastereomerism. Because the sensitizer is chiral, it reacts with individual enantiomers forming two discrete complexes. The transition states are therefore diastereomeric; depending on the reaction type, this can lead to the formation of optically active products. The idea is pictorially displayed in Scheme 4 (S = sensitizer, A = acceptor).

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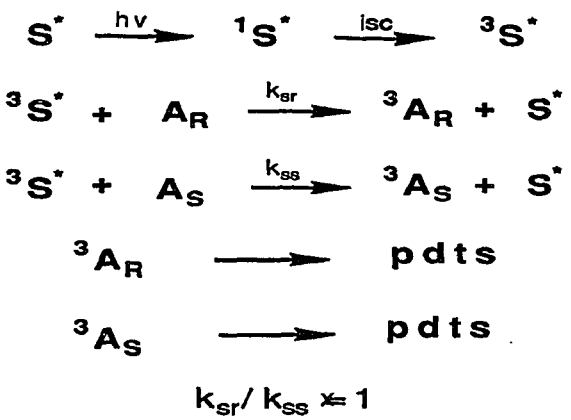

Scheme 4

The anticipated mechanism responsible for photochemical asymmetric induction by energy transfer, still a subject of some speculation, may depend upon the specific type of reaction. In general, energy transfer is described according to two types of mechanisms: The Forster mechanism,[5] which involves long-range coupling of transition moments, dominant in singlet-singlet processes, or the Dexter mechanism,[6] involving short-range coupling by orbital overlap, most prominent in triplet-triplet processes. To achieve chiral recognition, it follows that the Dexter mechanism should be operative in order to facilitate chiral discrimination. Additionally, reactions should occur at rates below diffusion control; otherwise, every collision would result in energy transfer, thus providing no discrimination between enantiomers.[4]

This phenomenon was first demonstrated by Hammond and Cole, who irradiated racemic, *trans*-1,2-diphenylcyclopropane (**1**) in the presence of optically active amide **2**.[7] They reported a modest 7% optical induction after separation from the sensitizer. The reaction involves *cis-trans* isomerization which interconverts enantiomers through the *cis* structure **3** (Scheme 5). At the photostationary state,

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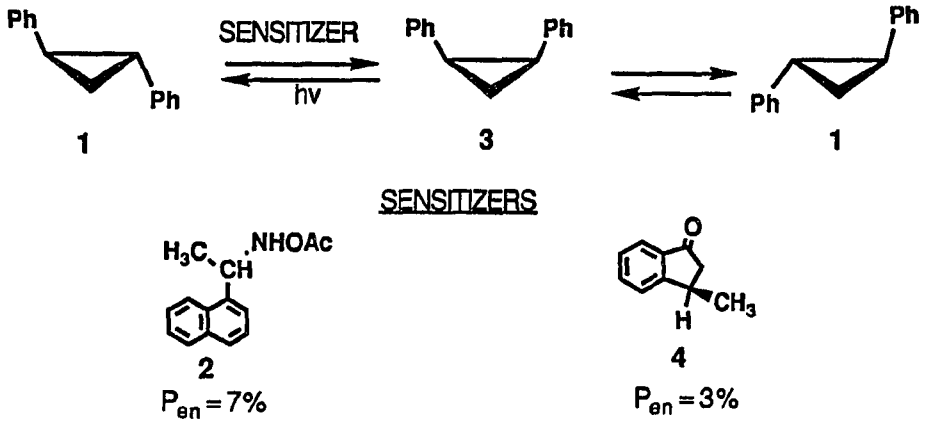
an excess of one enantiomer over another was observed. The authors first suggested that the reaction took place from the triplet state but later established it was a singlet process.[8] Kagan *et al.* employed the same sensitizer for energy transfer to a chiral sulfoxide, and observed a 2.5% e.e.[9]



Scheme 5

Ouannes *et al.* demonstrated that asymmetric induction could be achieved during the transfer of triplet energy.[10] Using (R)-(-)-3-methyl-1-indanone (**4**) as the sensitizer, they obtained 3% e.e. of *trans* **1** (Scheme 5). The authors suggested, based on reaction conditions, that the rate of reaction was diffusion controlled. It is not surprising then that their measured e.e. is somewhat smaller than that observed by Hammond and Cole.[8] If the reaction was indeed diffusion controlled, then every collision resulted in energy transfer, allowing for little discrimination between enantiomers.

The only attempt to resolve allenes by this method was reported by Weiss *et al.*, who in 1973 irradiated 2,3-pentadiene in the presence of a chiral sensitizer, 21,22-dihydroneoergosterol.[11] As with previous results, only slight optical induction (3.4%) was

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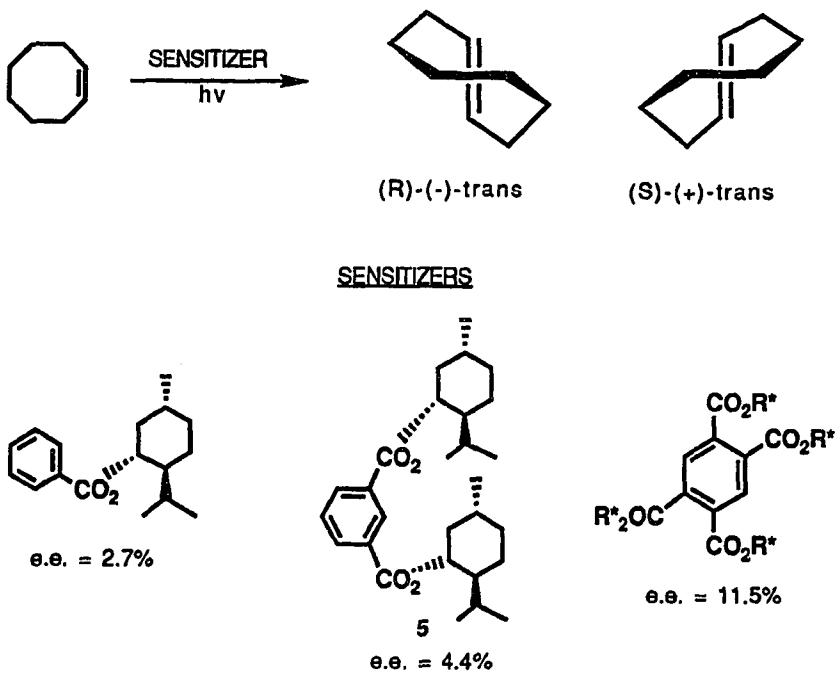
observed. The authors noted that models indicated a slight preference for energy transfer to the (R) isomer, based on steric arguments.

Some years later, Inoue and co-workers observed asymmetric *cis-trans* photoisomerization of cyclooctene sensitized by chiral aromatic esters.[12a] Depending on the ester employed, they observed optical inductions anywhere from 0.3% to 11% (Scheme 6). They suggested that *cis-trans* isomerization took place *via* an exciplex of



Scheme 6

the excited singlet ester and cyclooctene. Once isomerization to the *trans* isomer was complete, two diastereomeric exciplexes existed; relaxation back to the ground state at different rates, then, led to modest optical induction. They later found the degree of optical induction to be dependent on temperature; with two of the esters they observed an interesting phenomenon.[12b] Upon irradiation with

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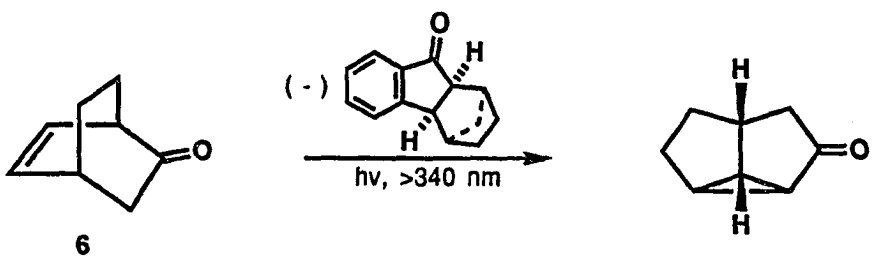
tetra-(-)-bornyl pyromellitate (**5**) at temperatures below -190 C, photosensitization afforded the (S)-(+)-*trans* isomer, and the optical yield increased to 11% at -800 C. Conversely, as the temperature rose above -190 C, the (R)-(-)-*trans* isomer predominated, the optical yield increasing as the irradiation temperature increased to a theoretical yield of 12-63% at infinite temperature. This implied that one exciplex, that yielding the (S)-(+)-*trans*, predominated at lower temperatures while another prevailed at higher temperatures, yielding the (R)-(-)-*trans*.

Two papers describing sensitized asymmetric photo-rearrangements have been reported.

In the course of investigating potential building blocks for the synthesis of polycyclopentanoid terpenes and prostacyclin analogs, Demuth and co-workers[13] studied the triplet sensitized oxadi-π-methane rearrangement of **6** with a chiral ketone (Scheme 7). Irradiation at -780 C resulted in enhancement of the 1R,5S-isomer (10% e.e.), but the optical yields were far too low to be of practical application.



6
racemic

(1S, 5R)

Scheme 7

Hoshi *et al.* described a two step photochemical transformation of lactone **7** to bicyclic **8** in the presence of several different

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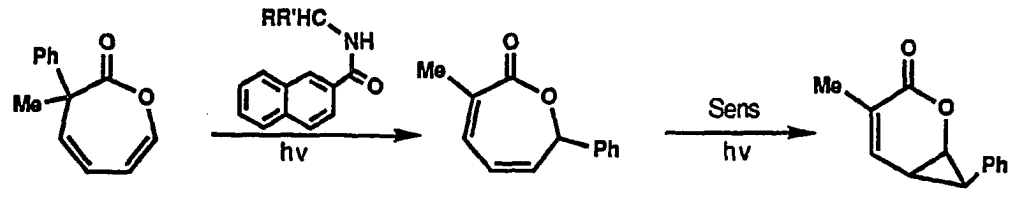
optically active amides and esters (Scheme 8).[14] The recovery of optically active starting material led the authors to postulate that differentiation was occurring in the first step, that which involves a 1,5-phenyl shift. They reported 1% optical induction.



7 8

P_{en} = 1%

Scheme 8

Results and Discussion

As described above, only limited success has been obtained, to date, with chiral triplet sensitizers. The limitations may arise because sensitizers were based on inherently symmetric, disymmetrically perturbed chromophores. In principle, an inherently disymmetric chromophore may be more effective. For example, in the sensitizers employed by Inoue *et al.*, (Scheme 6) chirality was imposed through attachment of a chiral prosthetic group to an aromatic ring. This group is considerably removed from the actual site of energy transfer. The diastereomeric effect of the two exciplexes is therefore weakened, because the full effect of this chiral auxillary is not realized. The result is very little optical induction in the products. We believed the solution to this problem was the development of a sensitizer whose chirality was also the center for energy transfer. An obvious candidate for this was a binaphthyl chromophore whose inherent chirality allows both of the necessary properties to be in close proximity. The remainder of this

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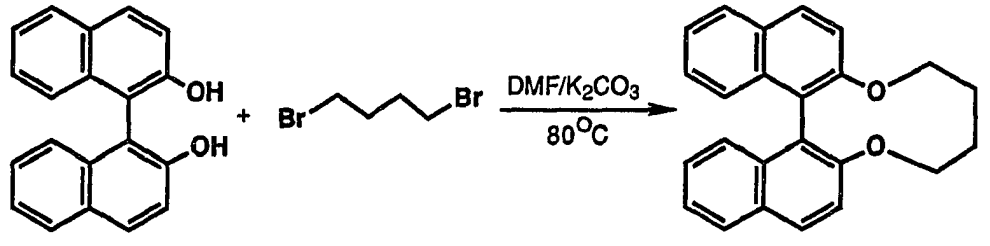
chapter describes a new chiral triplet sensitizer, derived from 1,1'-binaphthol, and some exploratory results obtained from its irradiation in the presence of several substrates.

The sensitizer chosen for the study was the substituted binaphthol 4,5,6,7-tetrahydrodinaphtho[2,1-*g*:1',2'-*i*][1,6]dioxecine (**10**), shown in Scheme 9. The molecule is inherently dissymmetric, thus enhancing the potential for optical induction through localization of the two characteristics discussed above. The following were also instrumental in the choice of **10**: (a) The molecule may be selectively excited. (b) Photoracemization does not occur (this was shown to be true by Lavalette *et al.*[16]). (c) The compound may be conveniently removed during workup procedures and recovered for further use.



9
(R)-(+)

10
$[\alpha]_D$ = -218.9
$\varepsilon = 6.789 \cdot 10^3$

Scheme 9

The synthesis of racemic **10** was first reported by Daub *et al.* in 1973.[15] This same method permits the convenient synthesis of optically pure **10** in 89% yield, from the commercially available diol **9**.[149] The specific rotation of **10** was -218.9°, and the extinction coefficient, measured at 331 nm, was $6.789 \cdot 10^3$. As mentioned previously, this allows for specific excitation of the sensitizer. The

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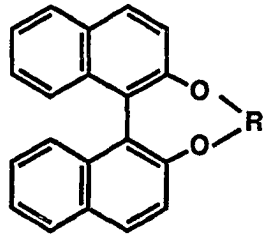
choice of the (R)-(+) isomer of **10** was purely arbitrary; it is clear the (S)-(-) isomer could be used with equal success, however, one would expect the products, after irradiation, to have an equal but opposite sign.

Some time after Daub reported his initial synthesis, Lavalette and Caberet reported on the enantiomeric stability of a series of bridged binaphthols in their triplet state.[16] Among the derivatives studied (Figure 1), only compound **11** suffered a complete loss of optical activity after irradiation. Conversely, compounds **10** and **12-14** showed no signs of photoracemization, even after prolonged periods of excitation. Through interpretation of fluorescence and phosphorescence spectra, they determined the triplet energy (57.2 kcal/mol), and the singlet lifetime (8.4 ns) for compound **10.** The low triplet energy demands that energy transfer be somewhat endothermic, allowing for greater chiral discrimination in the transition state. Additionally, knowledge of the triplet lifetime allows distinction between singlet and triplet processes through the use of Stern-Volmer kinetics.



11 R = CH_2
12 R = $(CH_2)_2$
13 R = $(CH_2)_3$
10 R = $(CH_2)_4$
14 R = POOH

Figure 1. Derivatives of Optically Active Binaphthols

Photoresolution of 1,3-Diphenylallene (16)

The first substrate we investigated was 1,3-diphenylallene (**16**). The molecule is chiral, and triplet sensitization should result in

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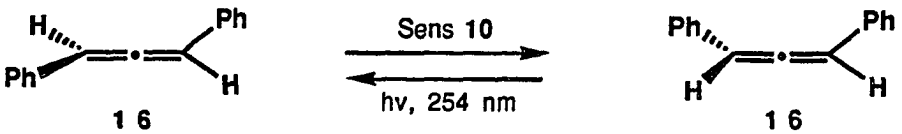
rapid interconversion of enantiomers. Optically active **16** was first synthesized by Jacobs and Danker in 1957, albeit with low optical yields.[17a] The optical purity was greatly increased by Jones *et al.*, who isolated the allene with a large rotation, $[\alpha]^{20}_D$ +1020°.[17b] The absolute configuration was determined to be (S) by Mason and Vane from electronic absorption and circular dichroism spectra.[17c] Soon thereafter, Rossi and Diversi, succeeded in synthesizing the (R) isomer with $[\alpha]^{20}_D$ -1137°, after asymmetric hydroboration and successive recrystallizations.[17d]

Irradiation of 1,3-diphenylallene (**16**) and sensitizer **10** was conducted in degassed solutions of hexane, using a Rayonet apparatus equipped with 350 nm lamps. Extended irradiation of the solution was required in order to observe a measurable rotation. After ten hours of irradiation, no optical rotation could be observed. After 42.5 hours of irradiation, however, a small, yet measurable rotation, $[\alpha]^{20}_D$ +7.43, was obtained (Scheme 10). This corresponds to an e.e. = 0.66%. Attempts to increase this number by lowering the temperature (-40° C), were unsuccessful.



16 **16**

P_{en} = 0.66%

Scheme 10

Photoresolution of 1,3-Cyclooctadiene (17)

cis,trans-1,3-Cyclooctadiene (**17**) has been known for some time;[18] it is also chiral. In spite of its long existence, no resolution of the enantiomers had been reported until 1985, when Sandstrom *et*

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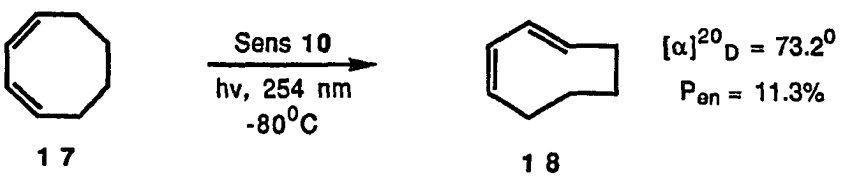
al. achieved separation using chromatography on microcrystalline triacetylcellulose.[19] About the same time, Inoue *et al.* reported the photochemical interconversion of the *cis-cis* and *cis-trans* isomers at a variety of different wavelengths.[20] This led us to believe that energy transfer to **17** with chiral sensitizer **10** could possibly result in formation of optically active **18**. Additionally, the low triplet energy of **17** should allow for efficient energy transfer.

Indeed, irradiation of diene **17** and sensitizer **10** in a thoroughly degassed solution of pentane, led to optically active **18**, with $[\alpha]^{20}_{D}$ +6.18° (Scheme 11). Based on the data from Sandstrom *et al.*, this represented a 0.95% e.e.[19] In this case, however, as the temperature of the medium was lowered, the rotation increased substantially. At -45° C the optical rotation was $[\alpha]^{20}_{D}$ +22.32°, and at -80° C it was $[\alpha]^{20}_{D}$ +73.2°. This represents 11.3% e.e., and suggests that at even lower temperatures, higher optical induction may be achieved.



17 18

Scheme 11

In order to investigate the reaction further, the concentration of starting diene was increased to where 80% of the singlet state of sensitizer **10** was quenched. In theory, the measured rotation of diene **18** should decrease. Indeed, irradiation at -60° C results in a significantly smaller rotation, $[\alpha]^{20}_{D}$ +6.86°. It is well known that singlet energy transfer occurs over much longer distances; this

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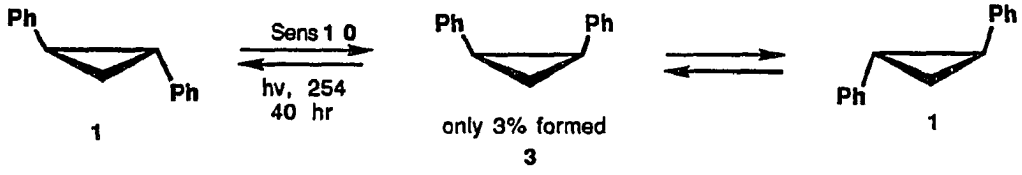
would imply less discrimination, and lower optical yields. While this result then, is not surprising, it is unprecedented.

As previously mentioned, optical induction presumably occurs in the diastereomeric transition state for energy transfer. Once the initial exciplex is formed, rotation about one double bond of the diene unit brings about two diastereomeric exciplexes, since rotation induces chirality in the twisted diene. Collapse of the exciplex then, and decay back to the ground state of the diene unit, yields optically active material. The lower the temperature, the more discrimination is observed in the transition state, and hence, the higher the optical yield.

Photoresolution of *trans*-1,2-Diphenylcyclopropane (1)

The results obtained from irradiation of *trans*-1,2-diphenylcyclopropane (**1**) and sensitizer **10** were puzzling. Irradiation for periods up to 40 hours with a variety of light sources produced no measurable rotations beyond experimental error (Scheme 12). In fact, at the longest periods, only 3% of the *cis* isomer (through which enantiomers are interconverted) was produced! This low yield implies that energy transfer is vastly inefficient. The result is unfortunate in view of the archetypal disposition of **1**.



Scheme 12

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Conclusion

The initial goals of this project were the development of a new chiral triplet sensitizer and its application to the area of asymmetric organic photochemistry. The project was exploratory in nature and is by no means complete. It is clear that a great many more reactions warrant investigation to explore fully the potential of this sensitizer. While the results surrounding 1,2-cyclooctadiene (**17**) were impressive, those concerning allene **16** and cyclopropane **1** were obviously disappointing and warrant further investigation.

It is not immediately clear why reactions of the sensitizer **10**, with both allene **16**, and cyclopropane **1**, failed to achieve higher degrees of optical induction. In the case of allene **16**, it is certainly possible that energy transfer may have been too endothermic to permit efficient interconversion of enantiomers. It is also possible that the system required much longer periods of irradiation (e.g. 200 hours and up). *trans*-1,2-Diphenylcyclopropane **1**, however, has an unusually low energy radical-like triplet at approximately 53 kcal/mol.[21] Energy transfer from the sensitizer (57 kcal/mol) should be modestly exothermic; it was surprising then, to observe such a low yield of the *cis* isomer, through which enantiomers are interconverted. Again, considerably longer irradiation times may be required.

Scheme 13 provides a list of some additional substrates that should be investigated to understand more fully the process of triplet sensitization by **10**. Currently, alkene **19** is being studied, but to date has only resulted in small optical induction.[22]

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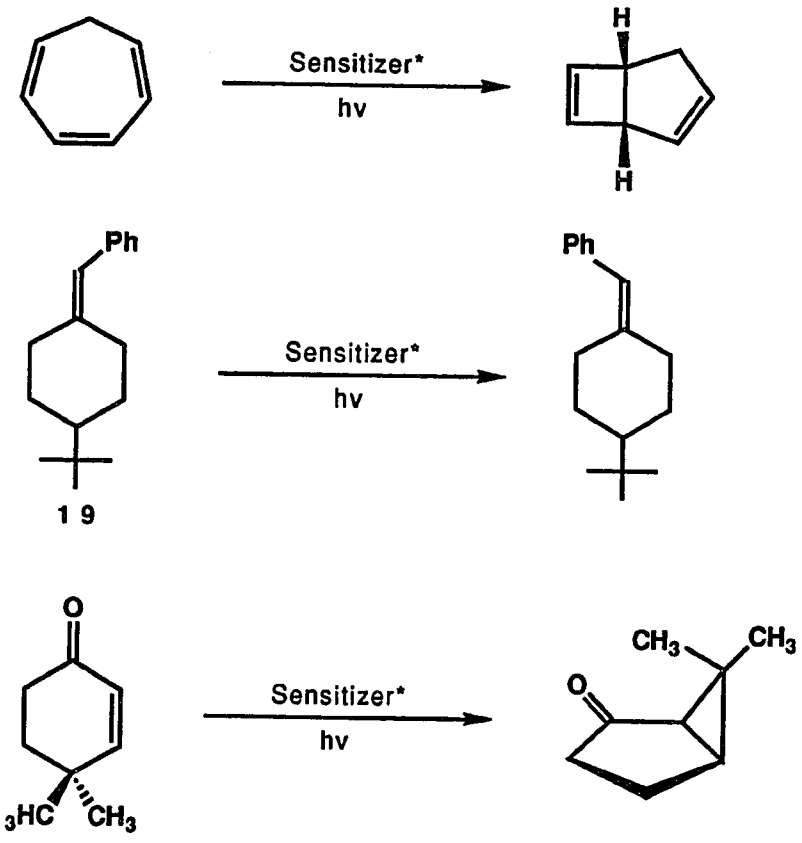

Scheme 13

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CHAPTER 2

THE PHOTOCHEMISTRY OF ALLENES

Introduction

Allenes constitute the class of hydrocarbons which are characterized by a 1,2-diene unit. The last 30 years have yielded an impressive array of experimental investigations on the physical and chemical properties of the allene functional group. Because of their unusual electronic structure and diverse reactivity, allenes have held the focus of both theoreticians and experimentalists. The ground state chemistry of allenes is well understood, and their embracement by the synthetic community is amply documented.[23] Surprisingly, not until the past two decades have the photochemical properties of this functional group been studied with any great detail.

Many aspects of allene photochemistry now appear to be well characterized; this is in part due to the efforts of our own research group. Considerable emphasis, devoted to characterization and mechanistic interpretation of both singlet and triplet processes, has led to an increased understanding of this functional group. It is clear, however, the observed reactions vary greatly, depending both on structural modifications of the allene, and reaction conditions.

The purpose of this chapter is to present the results of both experimental and theoretical studies focused on the mechanism by which triplet excited state allenes react in the vapor phase. No attempt is made to review fully the field of allene photochemistry;

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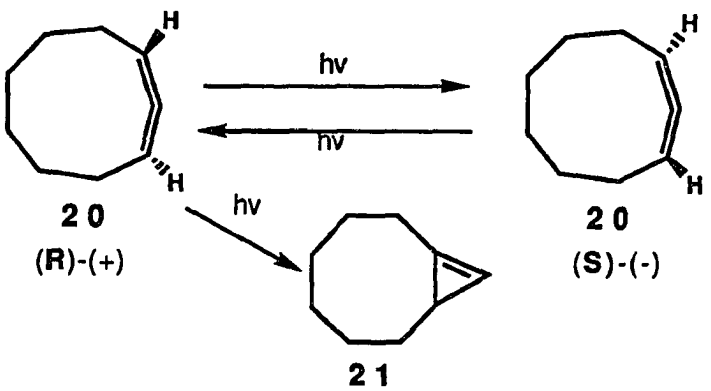
rather, literature of direct significance is described. For a more complete survey, the reader is referred to a recent review.[24]

Allene Singlet Photochemistry

The most efficient process in allene photochemistry is π bond rotation. This reaction is analogous to *cis-trans* isomerization in simple alkenes. If the allene is 1,3-disubstituted, and thus chiral, facile interconversion of enantiomers can be observed. Stierman and Johnson studied the photoracemization of optically active 1,2-cyclononadiene (**20**). Direct and sensitized irradiation of **20** resulted in rapid decay of optical activity. In the direct irradiation experiment, competitive rearrangement to cyclopropene **21** enabled them to establish k_{rac}/k_{rearr} = 70, based on irradiations to partial conversion (Scheme 14).[25]



$k_{racemization}/k_{rearrangement}$ = 70

Scheme 14

Aside from π bond rotation, 1,2-hydrogen migration is the dominant process in the singlet photochemistry of allenes. In 1975, Chapman reported on irradiation of allene (**22**) in a matrix at 8 K. He observed the formation of cyclopropene (**23**) and propyne (**24**). Although Chapman initially considered cyclopropylidene (**25**) to be

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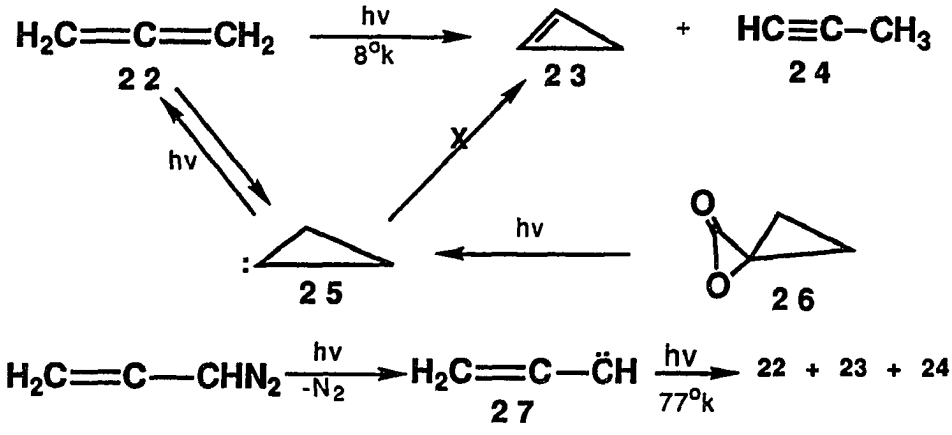
the intermediate, its independent generation from spirolactone **26** produced only allene (**22**). Upon irradiation of matrix-isolated vinylcarbene (**27**), however, allene (**22**), cyclopropene (**23**), and propyne (**24**) were all produced.[26] This result implicates vinylcarbene (**27**) as a common intermediate (Scheme 15).



Scheme 15

Some years later, Johnson and Stierman investigated both solution and vapor phase singlet photoreactions of 1,2-cyclononadiene (**20**, Scheme 16).[25] Direct irradiation of **20** in pentane produced cyclopropene **21**, cyclononyne (**28**), and tricyclic **29** (ratio 94:3:3). The authors concluded the reaction may have proceeded by a [σ2a + π2a] concerted process. This conclusion was based on the independent generation of potential vinylcarbene intermediates, which yielded, in addition to cyclopropene **21**, a variety of other isomers. The concerted process involves both simultaneous migration of hydrogen (or carbon) and C_1-C_3 bond formation. Deuterium labeling studies yielded k_H/k_D = 1.3 which provided argument for the migration of hydrogen. 1,3-Hydrogen migration to cyclononyne (**28**) is also observed as a minor process.

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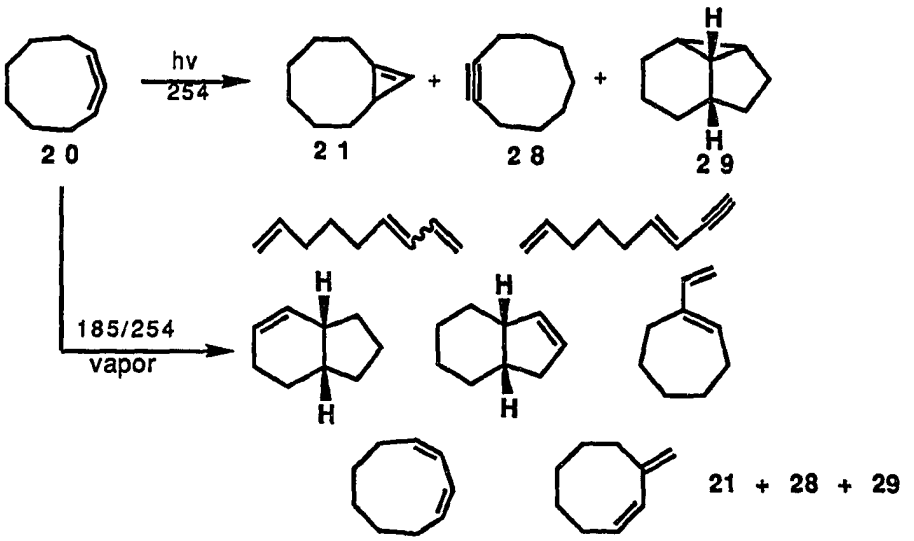
The vapor phase chemistry of **20** was considerably more complex than that observed in solution. Irradiation at shorter wavelengths (185/254 nm) furnished a host of new structures in addition to those observed in solution (Scheme 16). Presumably, some products may result from the population of higher energy states produced by the shorter wavelength lamps.



Scheme 16

Carbon migration has also been observed in the singlet photochemistry of allenes. Steinmetz and co-workers reported on the photochemistry of various exocyclic allenes.[27] In all cases, cyclopropene and propyne derivatives were formed; however, several products, **30** and **31**, were best described as resulting from 1,2-carbon migration (Scheme 17). Perhaps the most interesting result, however, is the formation of **32**, which requires extrusion of a carbon atom.

In summary then, the singlet manifold of allenes is marked principally by 1,2-hydrogen migration, and simple π bond rotation.

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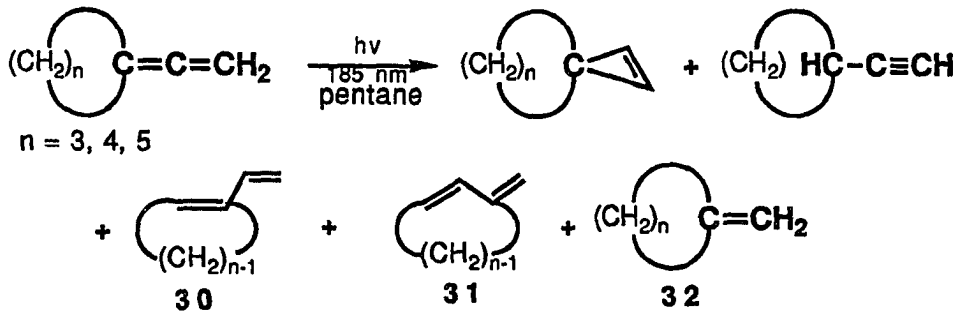
Additional mechanisms are also operative and appear to be both highly substrate and reaction dependent.



Scheme 17

Allene Triplet Photochemistry

The earliest detailed investigation of allene triplet photoreactions was reported by Ward and Karafiath in the late 1960s.[28] They conducted benzene sensitized vapor phase photolyses on several allenic hydrocarbons, including 1,2-hexadiene (**33**), 1,2,6-heptatriene (**34**), 1,2,6-cyclononatriene (**35**), and 1,2-cyclononadiene (**20**).

Benzene sensitized photolysis of 1,2-hexadiene (**33**) led to the formation of **36**, **37**, **38**, and **39** as primary photoproducts.[28a] Biradical **40** was proposed to be the intermediate in the formation of **37**, **38** (fragmentation) and **36** (ring closure). The lack of cyclohexene in the photolysate, however, led the authors to consider a concerted mechanism as well. The formation of bicyclo[3.1.0]hexane (**39**) was suggested to proceed through intermediate cyclopropylidene **41**, followed by insertion into a C-H bond (Scheme 18).

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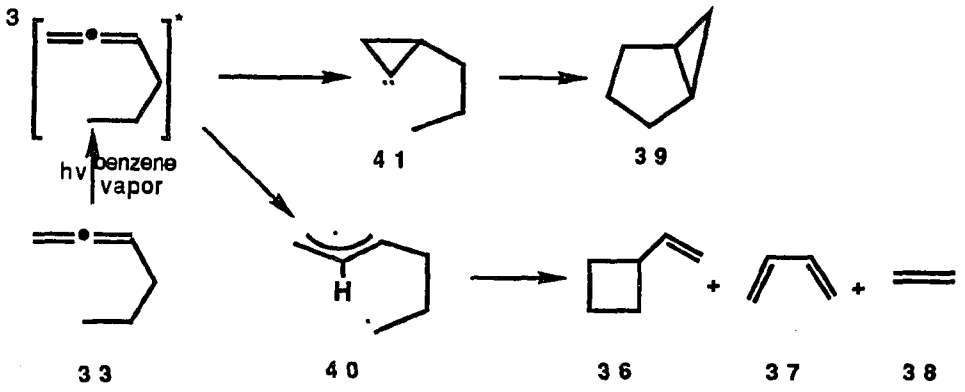
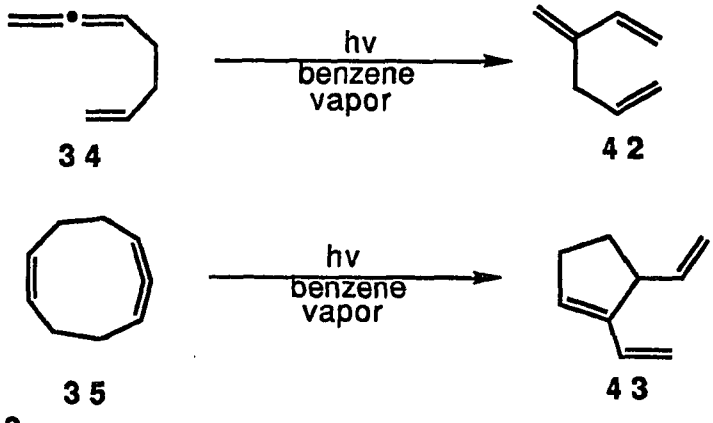


Scheme 18

Vapor phase benzene photolysis of 1,2,6-heptatriene (**34**) and 1,2,6-cycloheptatriene (**35**) led to the sole formation of trienes **42** and **43**, respectively. In both cases, no evidence for the formation of triplet cyclopropylidene was observed. While the authors argued for a photo-Cope rearrangement, under conditions of triplet sensitization, a stepwise mechanism involving a planar biradical seems more likely (Scheme 19).[28a,b]



Scheme 19

One of the more interesting results reported by Ward and Karafiath was the smooth conversion of 1,2-cyclononadiene (**20**) into tricyclo[4.3.0.0.^{2,9}]nonane (**29**). The authors suggested

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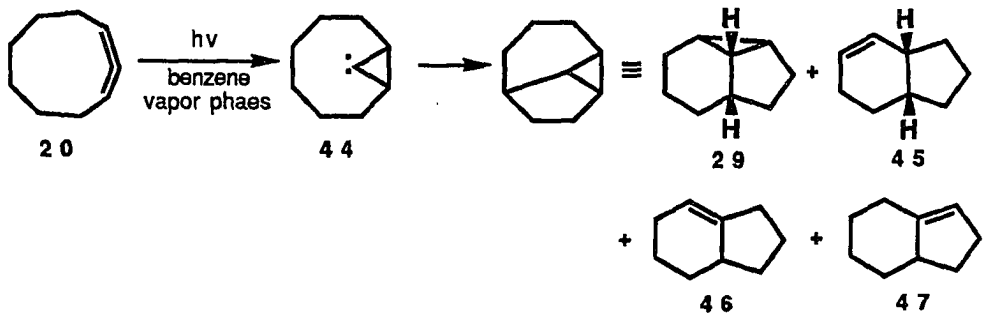
cyclopropylidene **44** as a potential intermediate. Hydrogen abstraction by **44**, followed by intersystem crossing and subsequent insertion, provided the most economical route to **29** (Scheme 20).[28a,c]



Scheme 20

Nearly fifteen years later, Johnson and Stierman provided a more detailed analysis of the mixture from the vapor phase benzene sensitized photolysis of **20**.[25] In addition to reported tricyclic **29**, three minor isomers were isolated and characterized as **45**, **46**, and **47**. Two potential intermediates were considered to be accessible from the triplet excited state of **20** (the energetics of triplet energy transfer permit the formation of either): planar triplet allene **48**, and triplet cycylopropylidene **44**. Reaction pathways leading directly to products may be drawn from either intermediate (Scheme 21); the only difference being the timing for formation of the three-membered ring.

The authors envisioned biradical **49** as the logical progenitor to alkenes **46** and **47**. Convincing evidence for the existence of this species came from its independent generation by flow vacuum thermolysis. Passage of tricyclic **29** through a quartz tube resulted in the isolation of both alkenes in a near-statistical ratio. Either

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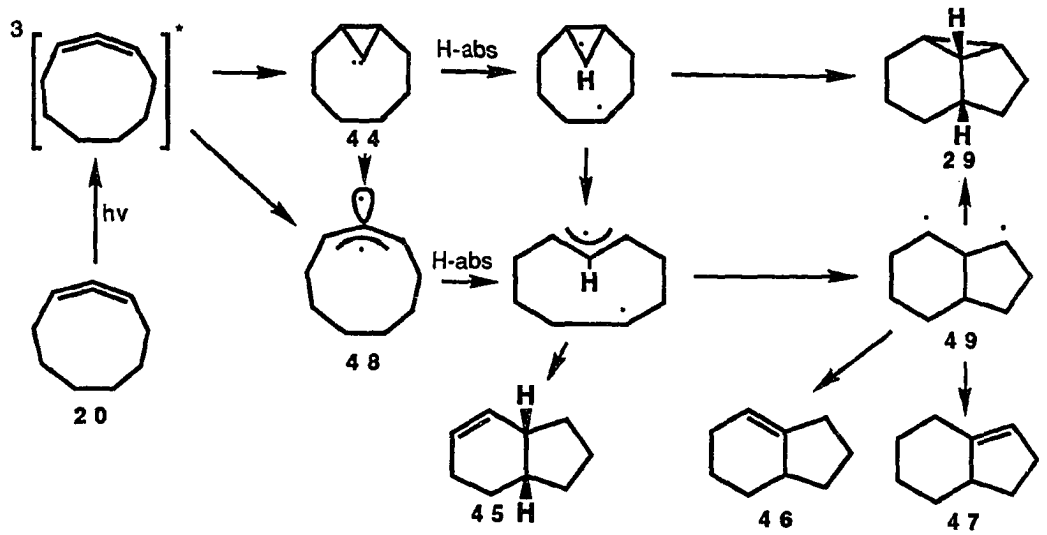

Scheme 21

mechanism, however, may explain the formation of biradical **49**. The authors concluded, "the most straightforward interpretation is that a duality of mechanisms exists."

Strong evidence for the intermediacy of triplet cyclopropylidenes in the vapor phase comes from the remarkable collection of tricyclics observed upon triplet sensitization of 1,2-cyclodecadiene (**50**, Scheme 22). These strained isomers almost certainly arise from both *cis* and *trans* isomers of **51**; however, small amounts (< 2% each) of alkenes were isolated as well.[29] What is most interesting about this reaction is its low selectivity, which implies minimal geometric requirements in the transition state. A more detailed discussion of this observation will be presented in a forthcoming section. Theoretical studies (*vide* infra) on hydrogen abstraction by triplet C_3H_4 intermediates, suggest cyclopropylidene (**52**) is remarkably insensitive to approach angle for hydrogen abstraction.

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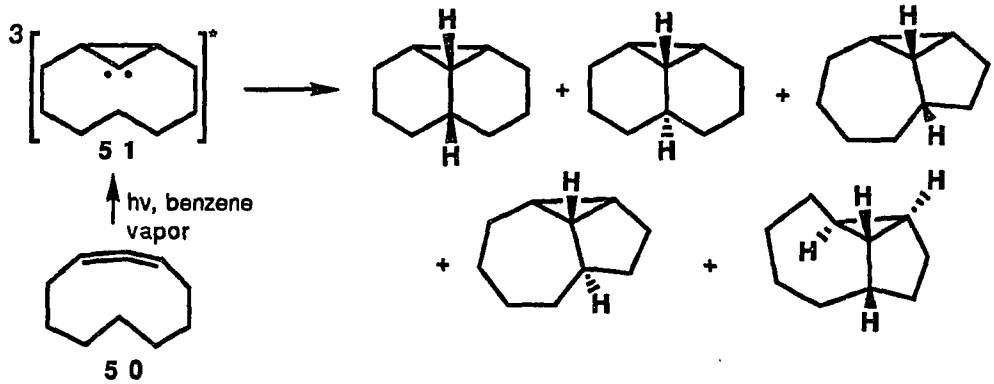
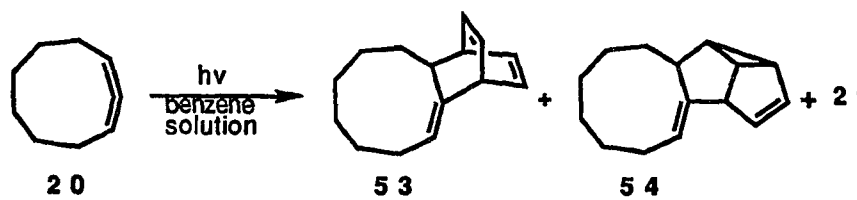


Scheme 22

Several investigations of solution phase triplet allene photoreactions have also appeared; these demonstrate the surprising phase dependence of triplet reactions. While the vapor phase reaction of 1,2-cyclononadiene (**20**) produces tricyclic **29** in high yield, Gilbert *et al.* reported that solution phase reactions produce exclusively cycloadducts **53** and **54** (Scheme 23).[30] Upon more careful examination, however, Johnson and Stierman observed small quantities of **29** as well as 2% of an unidentified isomer.[25] Through studies with optically active **20**, they determined k_{rac}/k_{rearr} = 60; thus as in direct irradiation, π bond rotation is the most facile triplet process in solution.



Scheme 23

Johnson and Price reported on the solution phase irradiation of

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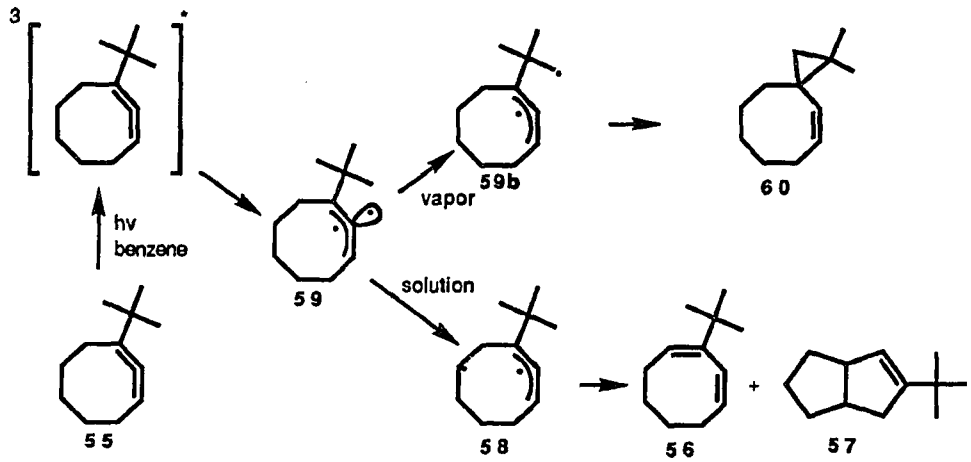
1-*tert*-butyl-1,2-cyclooctadiene (**55**).[31] In contrast to the above result, the reaction is remarkably efficient, yielding diene **56** and bicyclic **57** in 79% overall yield (Scheme 24). The reaction proceeds through diradical **58** which results from abstraction of a hydrogen



Scheme 24

at C-7 by the planar triplet species **59**. The vapor phase chemistry of **55** presumably involves the same intermediate **59**; however abstraction at tert-butyl, followed by insertion, yields **60**. The authors proposed that the low pressure vapor phase reaction involved a vibrationally "hot" triplet species, and thus follows a higher energy pathway (abstraction to give the least stable diradical **59b**), while in solution, a vibrationally "cold" triplet is more selective.

In an attempt to further understand the triplet reactions of allenes, Johnson and Stierman established state correlations for planar allene and cyclopropylidene.[25] Along C_2 pathways, T_1 of allene correlates with a planar C_{2v} minimum, while T_2 correlates with triplet cyclopropylidene. Since vertical T_1 and T_2 allene are not

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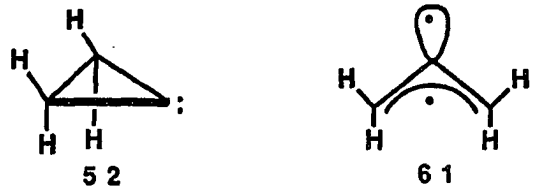
accessible *via* energy transfer with benzene ($^3B_{2u}$, 3.66 eV), they suggest a short lived exciplex is responsible for nonvertical energy transfer to either planar allene ($^3A_2$, 2.22 eV), or cyclopropylidene ($^3B_1$, 3.4 eV). Furthermore, they expect the more exothermic process to dominate in solution ($^3B_{2u}$-> $^3A_2$); this results principally in π bond rotation. The observed cycloaddition chemistry presumably arises from interaction of excited state benzene with allene.

In summary, the vapor phase reactions of triplet excited state allenes, appear to be governed principally by hydrogen abstraction. Depending on the substrate, arguments can be made for the intermediacy of either triplet cyclopropylidene (**52**) or planar triplet allene (**61**). The solution phase triplet photochemistry of allenes results predominantly in cycloaddition chemistry, and π bond rotation.

One goal of this project was to probe more thoroughly the mechanism by which triplet allenes react in the vapor phase. Both theory and experiment were called upon to achieve this goal. We first investigated hydrogen abstraction in two allenes in which potential geometries for hydrogen abstraction were well defined. Through characterization of the products, we hoped to understand more completely the role that cyclopropylidene (**52**) and bent planar allene (**61**) play in the triplet chemistry of allenes (Fiqure 2).



52 61

Figure 2. Cyclopropylidene (52) and planar triplet allene (61)

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Additionally, we conducted an ab initio study of hydrogen abstraction by both triplet cyclopropylidene (**52**) and planar triplet allene (**61**) to estimate the activation energies, and investigate geometric factors for these processes.

Another goal of this project was the implementation of natural abundance deuterium NMR in studying the kinetic isotope effect for the photorearrangemt (**20**) to (**29**). The project was partly exploratory in nature, designed to ascertain the usefulness of the technique itself, while providing further insight into the triplet sensitized vapor phase photochemistry of allenes. Additionally, we hoped to synthesize *cis*-6,7-dideutero-1,2-cyclononadiene (**62**) as a further mechanistic probe.

Triplet Vapor Phase Photochemistry of 1,2-Cyclohexylallene (63) and Vinylidenecycloheptane (64)

Exploratory Triplet Photochemistry

In the present study, two C_9H_{14} isomers, **63** and **64**, were chosen for the investigation of triplet reactions; these are shown in Scheme 25. These allenes can presumably react *via* either cyclopropylidene or planar triplet intermediates. Exclusive reaction through one or the other should result in isolation of very different products. Hydrogen abstraction by cyclopropylidene intermediates should result in a preponderance of tricyclic structures (Scheme 25). By contrast, reaction through either planar triplet biradical is expected to yield principally bicyclics. Analysis of the products should thus distinguish effectively between these two potential pathways.

Synthesis of the two starting allenes **63** and **64** by the classic

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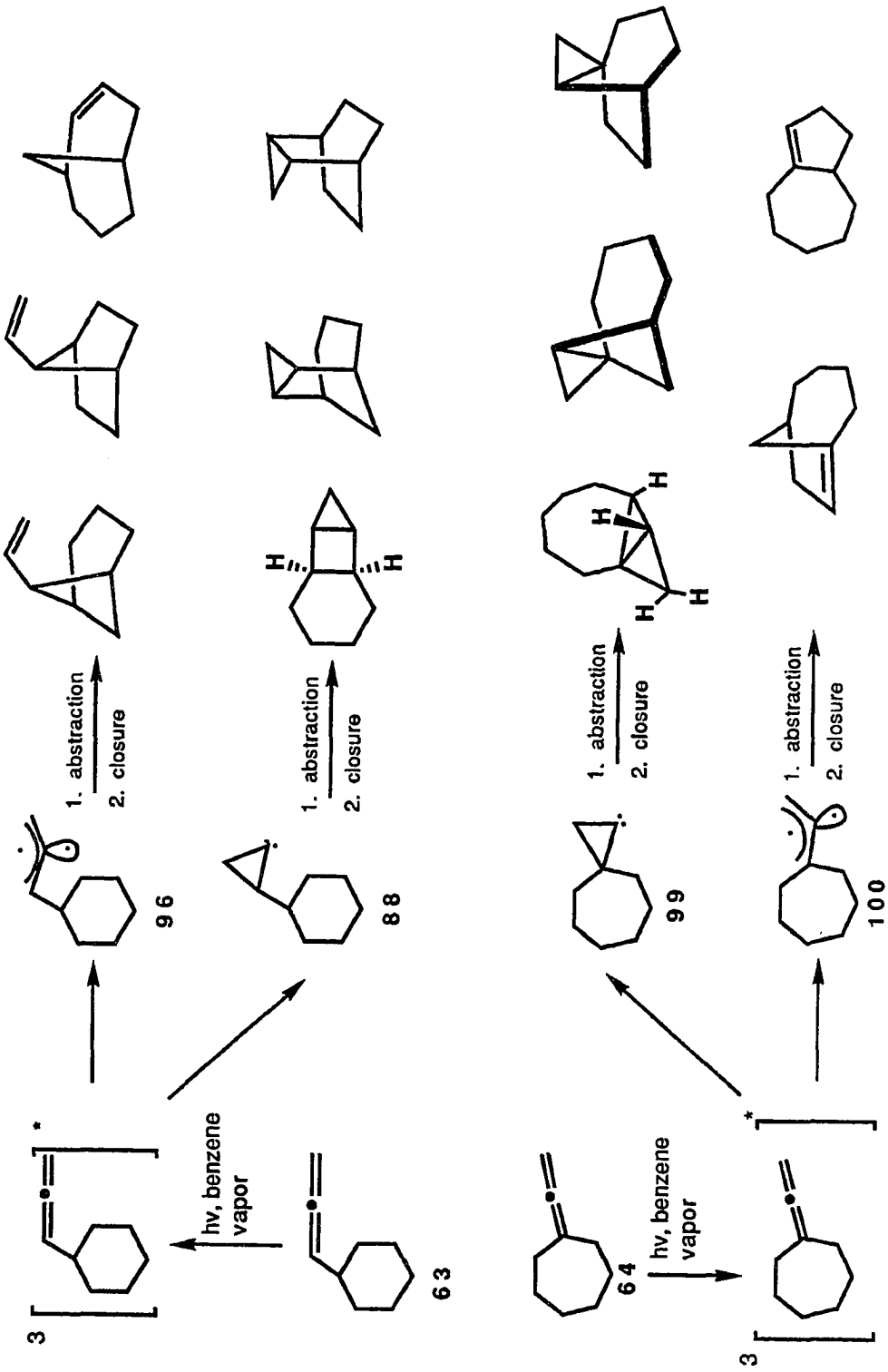

Scheme 25

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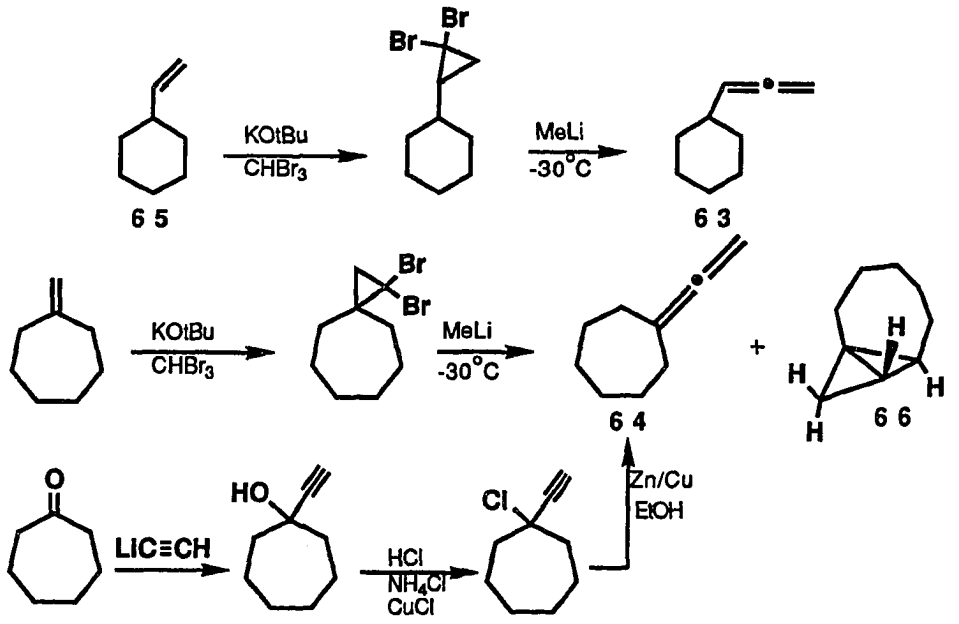
Doering-Moore-Skattebol approach led to some unexpected results. In one case, cyclohexyl-1,2-propadiene[32] (**63**) was conveniently prepared from commercially available vinylcyclohexene (**65**) by dibromocarbene addition and subsequent ring opening with methyllithium at reduced temperatures (Scheme 26). An analogous approach to vinylidenecycloheptane[33] (**64**), however, resulted in the formation of a substance characterized (*vide* infra) as tricyclic **66** (60%), as well as the desired allene **64** (40%). An alternative



Scheme 26

approach, adapted from the reported synthesis of vinylidenecyclohexane,[34] resulted in the efficient preparation of **64**. Samples of both allenes were further purified by preparative GLC (>99%) prior to photochemical studies.

Characterization of tricyclic **66** proved extremely difficult, due in part to the rapidity with which it decomposed. Additionally, separation of tricyclic **66** from allene **64** was impeded by their

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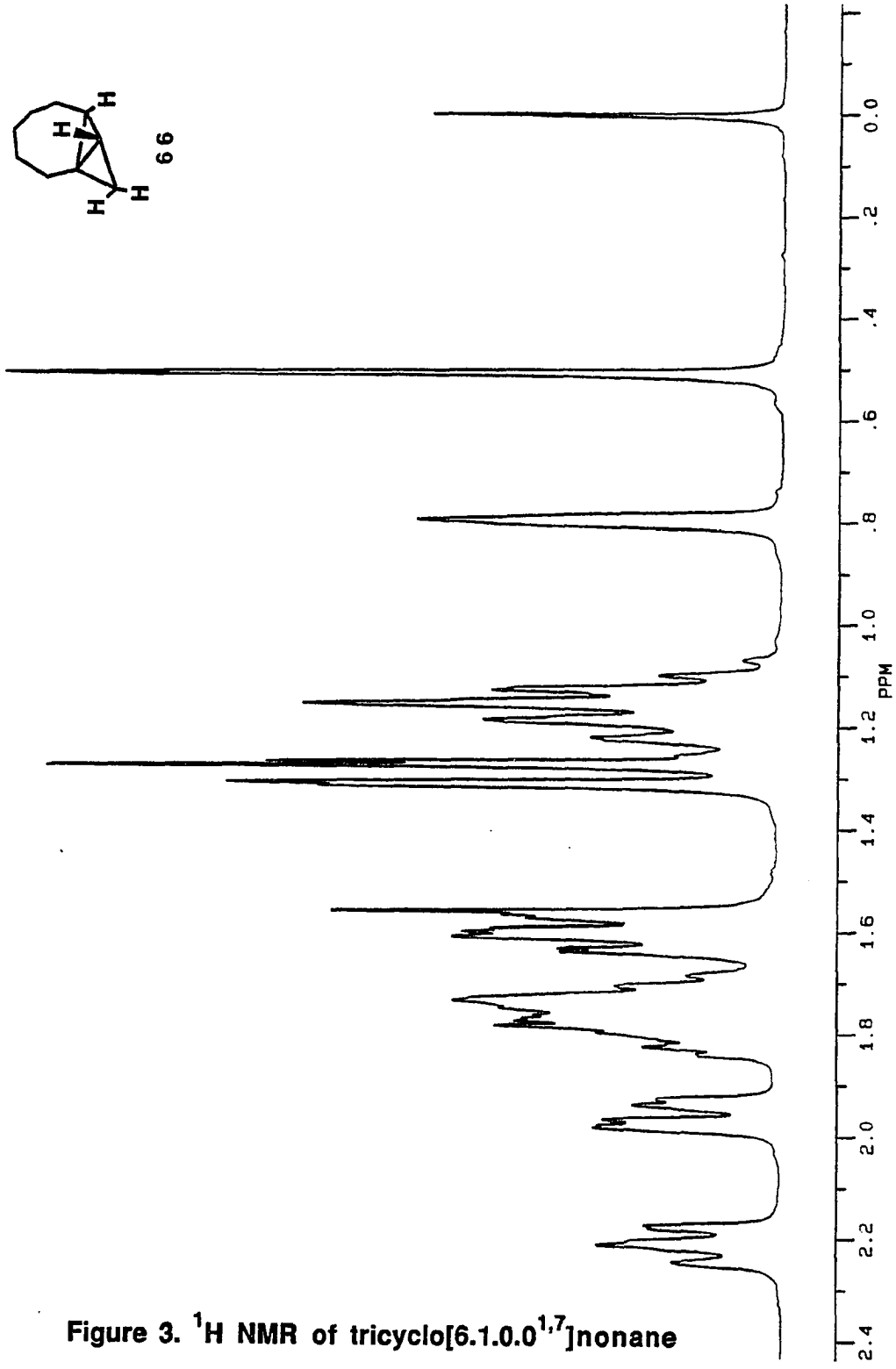

Figure 3. ^{1}H NMR of tricyclo[6.1.0.0^{1,7}]nonane

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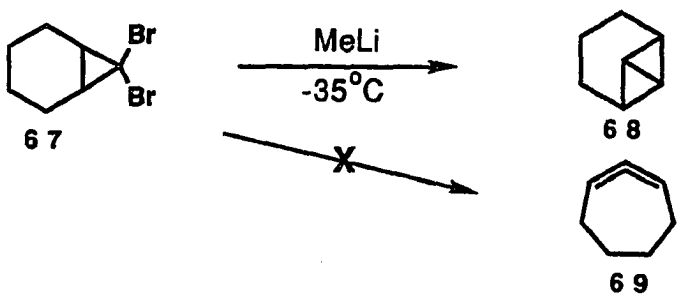
similar retention times. Finally, pure material was obtained from preparative GLC using QF-1 as the mobile phase. Spectral data for **66** include two broad singlets in the ^1H NMR at δ 0.51 and δ 0.79 and two resonances in the ^{13}C NMR at δ 2.61 and δ 14.50, all indicative of the bicyclobutane unit contained in **66**. Homonuclear 2-D NMR provided the connectivity information for further characterization. The spectrum of **66** is shown in Figure 3.

The formation of tricyclic hydrocarbon **66** was unanticipated, but not without precedent. As early as 1961, Moore and co-workers, while attempting the synthesis of 1,2-cycloheptadiene (**69**), isolated tricyclo[4.1.0.$0^{2,7}$]heptane (**68**) from the methyllithium promoted carbenoid cyclization of dibromide **67**. This presumably results from insertion into a proximate C-H bond (Scheme 27).[35]



Scheme 27

Some brief attempt was made to characterize the chemistry of **66**. Reaction of bicyclobutane derivatives with silver catalysts is a well studied process that leads to predictable rearrangement products.[36] Exposure of bicyclobutane **66** to silver triflate in dry benzene led to the formation of vinylcycloheptene (**79**) and bicyclo[5.2.0]non-1-ene (**80**, 50:50) in 64% yield. Both compounds were isolated by preparative GLC and characterized by comparison of spectral data with those reported previously.[37,33] Bicyclic **80** probably results from further rearrangement of initially formed

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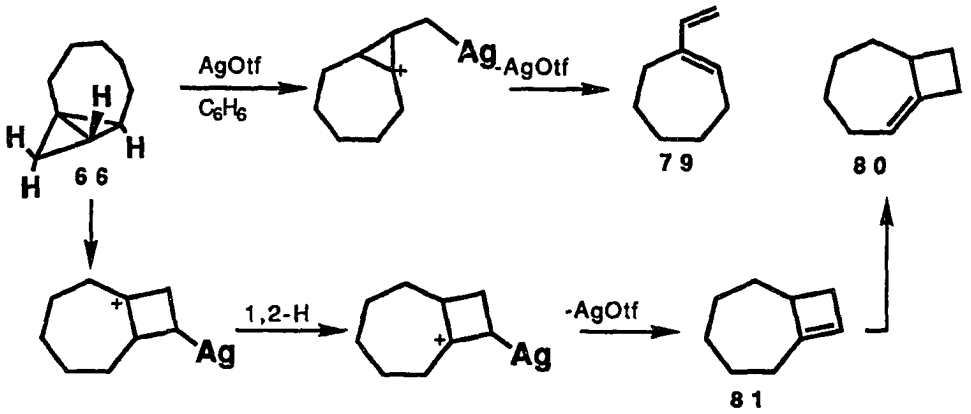
bicyclo[5.2.0]non-1(9)-ene (**81**). This result provides additional proof for the structure of **66** (Scheme 28).



Scheme 28

Benzene sensitized vapor phase irradiation of cyclohexylallene (63)

Irradiation at 254 nm (0.02 mm Hg) of a vapor phase mixture of cyclohexylallene (**63**) and benzene, afforded a complex mixture of eight new products as determined by capillary GLC (Scheme 29). The ratio (Table 1) of these products varied greatly depending on irradiation time; this indicated that secondary photochemistry was occurring. Attempts to separate all of the products by preparative GLC were met with limited success, due to the similarities of retention times. 1,3,8-Nonatriene (**82**), and bicyclics **45** and **83** were isolated and their structures were unambiguously assigned by comparison of spectral data with those previously reported.[37]

Complete characterization of the collection of bicyclo[3.2.0]-heptanes **84**, **85**, and **86** proved extremely difficult because of their similar retention times. The separation of one isomer, however, allowed it to be identified spectroscopically as a member of the above series. Spectral data for the separated isomer (it was impossible to determine from spectroscopic data which of the three isomers **84**, **85**, or **86** was isolated) include a ddd and a multiplet in

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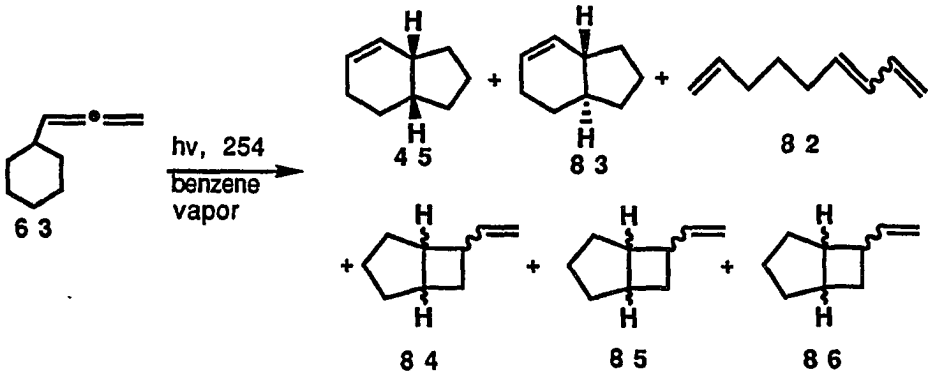
the ^1H NMR at δ 6.02 (1H) and δ 4.91 (2H) respectively; both are char-



Scheme 29

ecteristic of a vinyl group. Furthermore, multiplets at δ 2.63 (1H) and δ 2.32 (1H), assigned to the bridgehead hydrogens, provide support for the bicyclo[3.2.0]heptane backbone. The ^{13}C spectrum of the isomer showed nine resonances. Two resonances at 144 and 111 ppm provide further evidence for the presence of a vinyl group. The two remaining isomers showed similar patterns in the vinyl region. One isomer displayed a ddd at δ 6.00 and a multiplet at δ 5.05, while the other showed a ddd at δ 5.82 and a multiplet at δ 4.98.

The remaining component **87**, while consistently detectable by capillary GLC, was never isolated in a pure enough form to make a reliable assignment.

Benzene sensitized vapor phase irradiation of vinylidene-cycloheptane (64)

Irradiation at 254 nm (0.02 mm Hg) of a vapor phase mixture of benzene and vinylidenecycloheptane (64) for periods up to 20 hours resulted primarily in the formation of polymer. Irradiation for shorter times (e.g. 1 hr.), led to no products which could be observed by capillary GLC or NMR analysis; starting material was recovered unchanged (Scheme 30).

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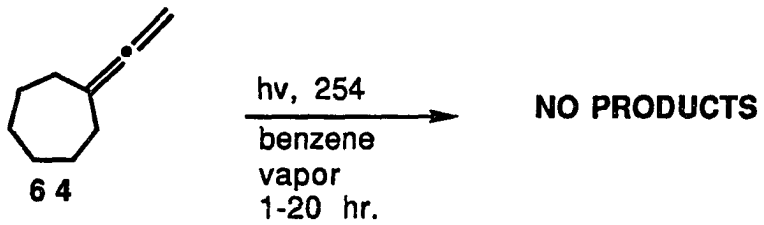
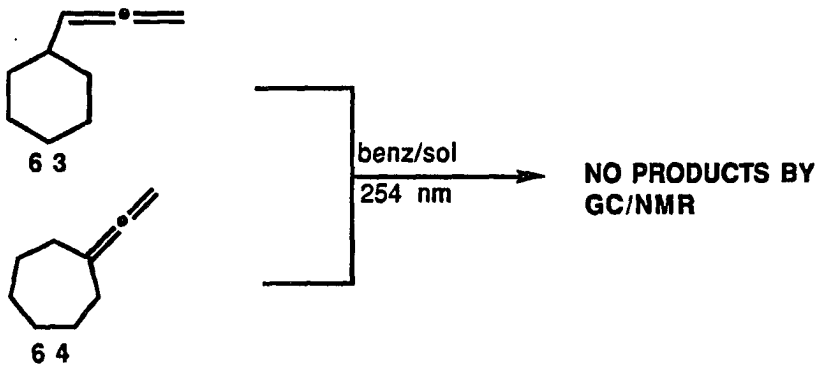


Scheme 30

Benzene Sensitized Solution Phase Irradiation of Cyclohexylallene (**63**) and Vinylidenecycloheptane (**64**)

Irradiation of either cyclohexylallene (**63**) or vinylidene-cycloheptane (**64**) in degassed benzene solutions at 254 nm yielded



Scheme 31

no products observable by capillary GLC or NMR. These solutions could be irradiated for periods up to 48 hours with complete recovery of starting material (Scheme 31).

Discussion of benzene sensitized vapor phase irradiation of cyclo-hexylallene (**63**)

In the benzene vapor phase irradiation of cyclohexylallene (**63**), we considered two intermediates to be directly accessible from the triplet excited state of **63**: triplet cyclopropylidene **88**, and planar

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triplet allene **89**. In theory, pathways to all products may be drawn from either species. Both pathways will be discussed below.

Table 1 shows the relative percentages of products observed at various conversions. At the lowest conversion (4.5%), triene **82**

Irradiation time % conversion	**82**	**84**	**85**	**86**	**83**	**?**	**45**
45 sec 4.5%	46.8	21.9	12.3	10.8	2.30	2.89	3.00
4 min 11%	19.1	40.2	19.2	8.90	4.75	3.03	4.80
30 min 31%	10.1	49.4	18.9	6.20	5.00	5.20	5.20
1 hr 43%	5.50	55.9	18.7	4.08	5.60	4.40	6.46

Table 1. Relative Percentages of Products From Irradiation of Cyclohexylallene

(69%*trans*, 31% *cis*, as determined by ^{1}H NMR) constitutes almost 50% of the photolysate; at the highest conversion (42.5%), it drops to 5.5%. Meanwhile, the relative percentages of compounds **45, 83-86** increase steadily. These data implicate the primary nature of triene **82**, while suggesting that the remaining compounds may all be secondary. In fact, it seems likely that a series of triplet sensitized [4+2] and [2+2] reactions from triene **82** may explain all of the observed secondary chemistry.

The solution phase, triplet photochemical reactions of alkenes and dienes[38] have been extensively studied and are well characterized; however, their vapor phase counterparts remain poorly understood. We believe the most direct approach to the formation of bicyclics **45, 83-86** should involve triplet sensitized [4 + 2] and [2 + 2] reactions of triene **82**. Direct light absorption by triene **82** seems unlikely as it does not efficiently absorb light in

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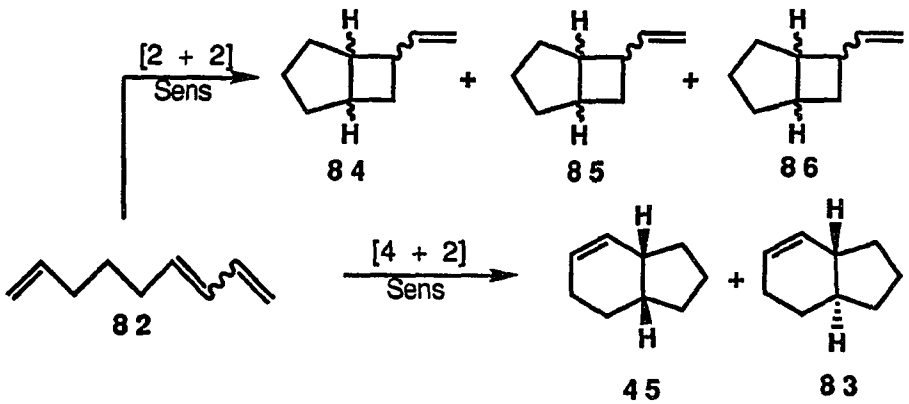
this region (254 nm). Reaction through a triplet excited state of



Scheme 32

triene **82** would presumably be stepwise; this accounts for the large collection of bicyclo[3.2.0]heptanes **84-86** observed in the reaction. Additionally, it is unlikely that bicyclics **45** and **83** (for which unequivocal proof of existence has been demonstrated) could be formed by any other pathway (Scheme 32).

The question still remaining is the precise mechanism by which triene **82** is formed. In theory, either mechanistic pathway shown in Scheme 33 may explain the observed formation of **82**. Along one pathway, sequential energy transfer, π bond rotation, and hydrogen abstraction yield diradical **90**. After intersystem crossing, this diradical can open forming **82**. Alternatively, closure first to cyclopropylidene **88**, followed by hydrogen abstraction, and opening of the resultant cyclopropyl radical **91**, yields the same intermediate **90**. A third possibility is that **88** may open to planar allene **89** (Scheme 33). Ring opening in these last two cases is expected to be exothermic due to relief of cyclopropyl strain; however, both reactions probably have modest barriers.[39]

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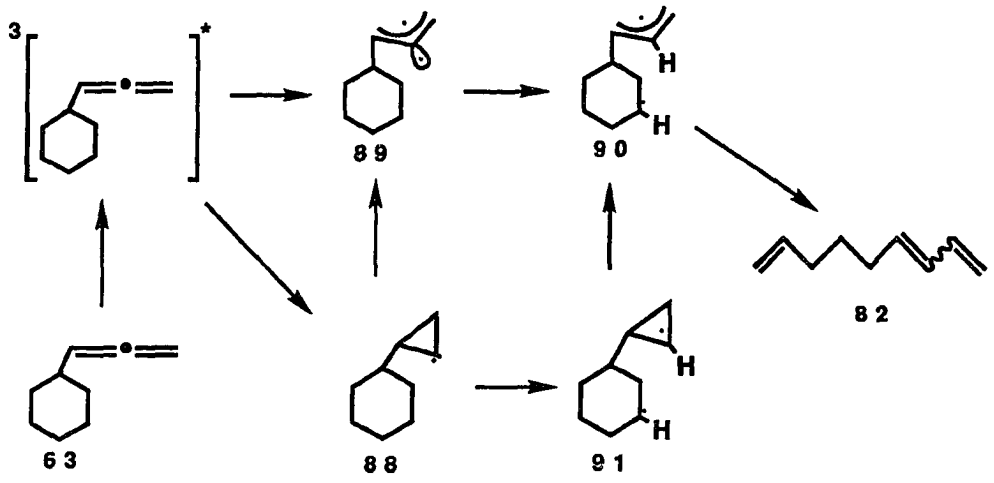

Scheme 33

The strongest evidence against the initial formation of **88** is the absence of any identifiable tricyclic photoproducts. In theory, three possible isomers could be formed. All involve initial hydrogen abstraction yielding a diradical, followed by intersystem crossing, and subsequent closure to the tricyclic. Dreiding models indicate that the diradical precursor to tricyclo[3.3.1.$0^{2,4}$]nonane (**92**) should be easily accessible from a chair conformation of **88** (Scheme 34). Likewise, the precursor to tricyclo[4.3.0.$0^{7,9}$]nonane **93** appears accessible from a chair conformation; however, in this case, models indicate a bonding distance of ≈ 2.3Å. The precursor to tricyclo-[3.2.2.$0^{2,4}$]nonane (**94**) requires hydrogen abstraction from a boat conformation, which is considerably higher in energy, making this pathway less attractive. After partial separation of the crude photolysate by GLC and comparison of spectral data with those from the literature,[40] no evidence for any tricyclic product could be found. Specifically, the high field resonances characteristic of cyclo-propane ring hydrogens were absent in the ^{1}H NMR.

The most logical precursor to biradical **90**, then, appears to be

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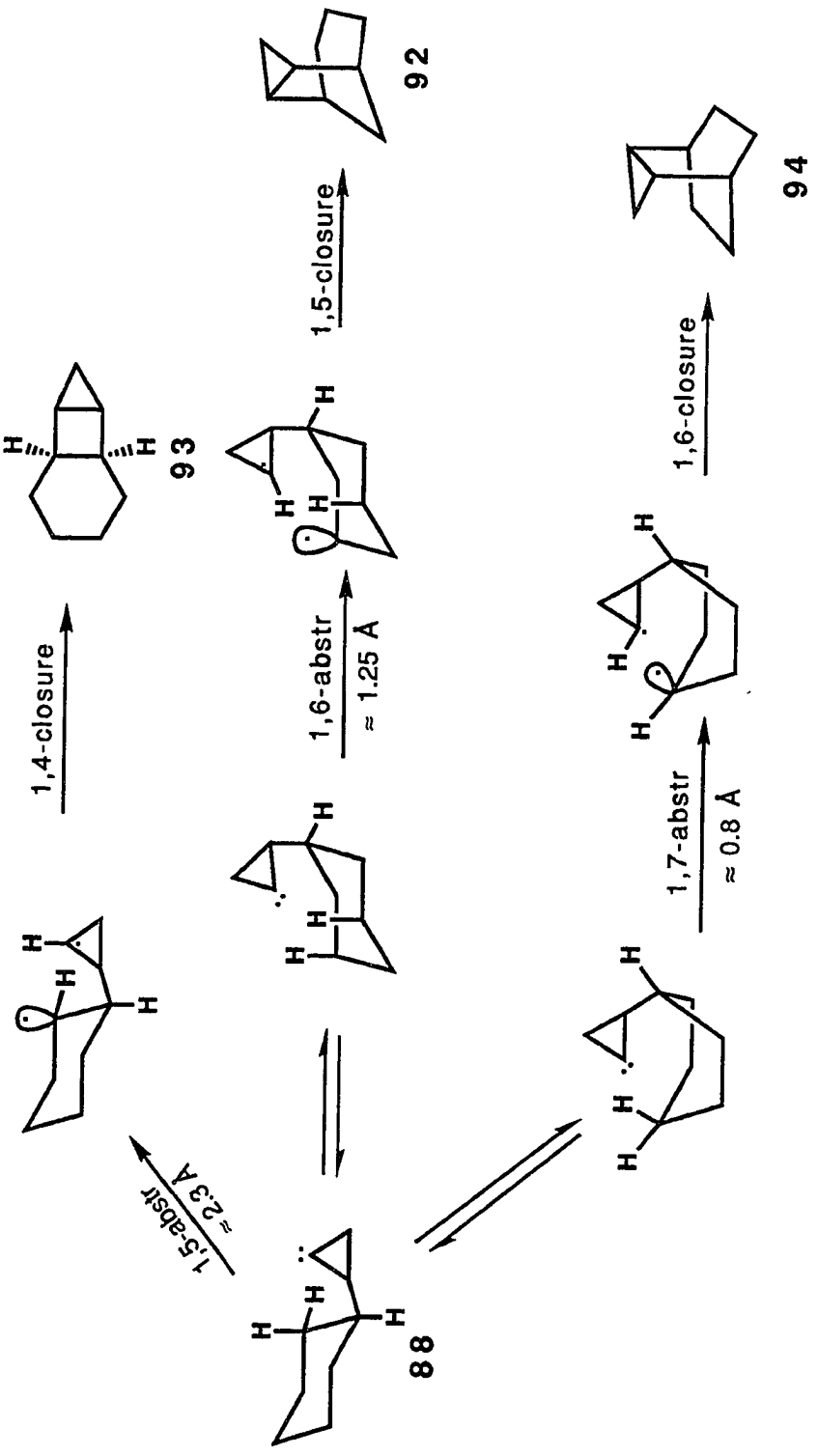

Scheme 34

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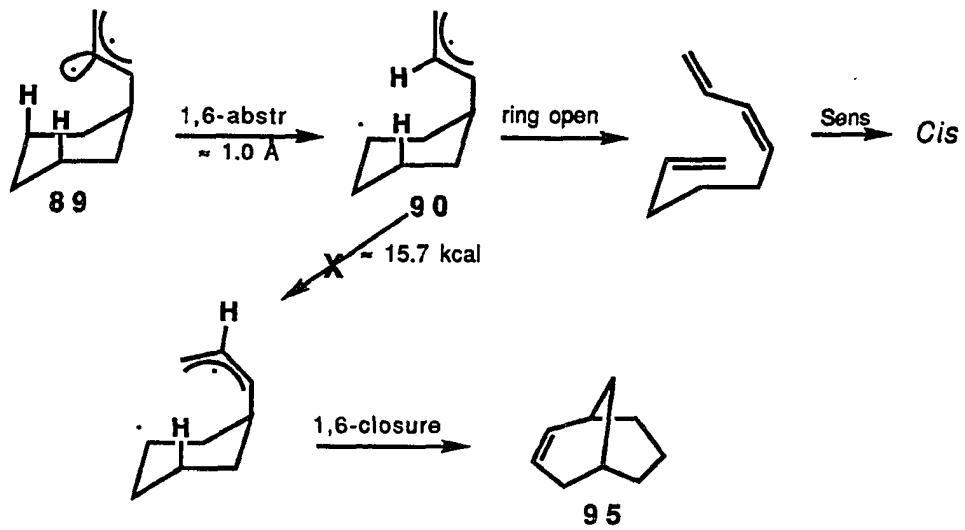
planar triplet species **89**. Dreiding models indicate that bent **89** is positioned well to abstract a hydrogen from the C-3 carbon (≈ 1.0Å), resulting in the formation of biradical **90**. This presumably occurs through a chair conformation in which the substituent occupies the axial position. The absence of any other products derived from biradical **90** is attributed to the ease with which 1,4-biradicals fragment to dienes. Additionally, closure of biradical **90** to bicyclo[3.3.1]non-2-ene (**95**) requires rotation of the allyl radical; Sustmann *et al.* have determined this process to have an activation energy of ≈ 15.7 kcal/mol, which may be sufficient to preclude this process (Scheme 35).[41]



Scheme 35

To further investigate the process of hydrogen abstraction by cyclohexylallene (**63**), we explored its thermal chemistry. In principle, two retro-ene reactions are possible: the first involves fragmentation to cyclohexene (**95b**) and propyne (**24**), the second involves ring opening to triene **82**. Both modes may be described as

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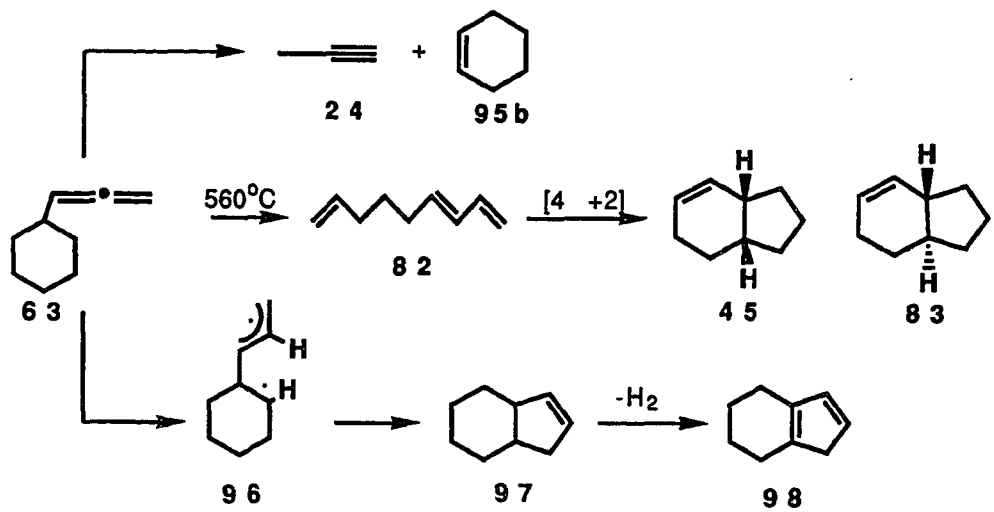
symmetry allowed [σ2 + σ2 + π2] six electron processes. Passage of allene **63** through a quartz tube at 610° C (0.02 mm Hg) resulted in the formation of products shown in Scheme 36. All of these compounds (except propyne **24**) were isolated by preparative GLC and their structures unambiguously assigned by comparison of spectra with those reported previously.[37] At the lowest conversions (7%, 560° C), triene **82** constituted 48% of the observed products, indicating the relative ease with which it is formed. Bicyclics **45** and **83** are secondary products, both arising from well-precedented intramolecular Diels-Alder reactions. The 2:1 ratio for **45** and **83** respectively, agrees well with data for the thermolysis of **82**



Scheme 36

generated by an alternate route.[42] Bicyclic **97** probably results from intramolecular hydrogen abstraction of biradical **96** followed by closure. The subsequent loss of H_2 yields **98**.

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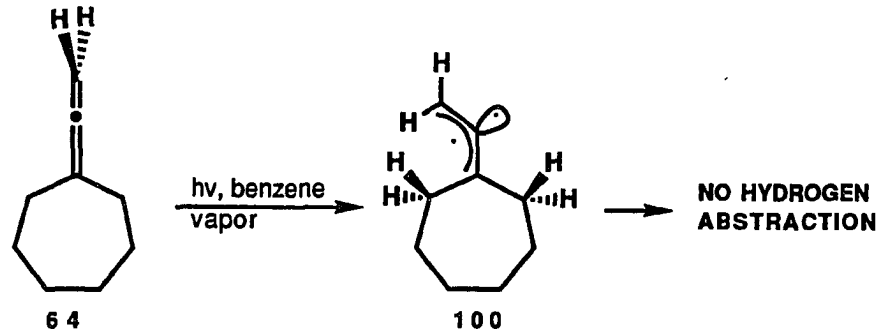
Discussion of benzene sensitized vapor phase irradiation of vinylidenecycloheptane (64)

The total lack of reactivity observed with allene **64** can only be attributed to its inability to abstract a proximate hydrogen from one of the methylene carbons. Dreiding models indicate that neither intermediate, the cyclopropylidene **99** or the planar allene **100**, is particularly well suited for this process to occur. Cyclopropylidene **99** appears capable of hydrogen abstraction from C-4; however, models indicate the distance to hydrogen abstraction is ≈ 1.7Å, as measured from the twist-boat conformation. The lack of observed reactivity with planar intermediate **100** is directly attributable to



Scheme 37

the geometry of the half-filled p-orbital at C-2. Formation of intermediate **100** (through bending and twisting) requires that this orbital be almost orthogonal to any abstractable hydrogens (Scheme 37). Thus, while it appears likely that intermediate **100** is formed, it is very unlikely that hydrogen abstraction and subsequent reactions are possible. The next higher homologue in the series, vinylidenecyclooctane, enjoys much greater conformational mobility; however, this system was not examined. It is interesting to note that the carbenoid, formed in the generation of allene **64** by

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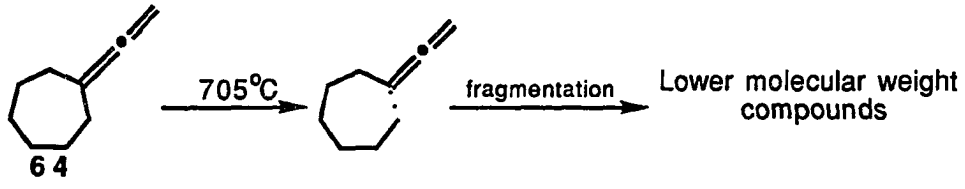
the Doering-Moore-Skattebol approach, allows for efficient insertion into neighboring C-H bond (Scheme 26) resulting in tricyclic **64**. The carbenoid is therefore large enough to allow adequate overlap for insertion to take place.

The observed photochemical inertness of allene **64** was paralleled by its thermal chemistry. Passage of allene **64** through a quartz tube at 680° C (0.02 mm Hg) resulted in quantitative isolation of starting material; no observation of any retro-ene products could be observed in the pyrolysate. At 705° C, lower molecular weight molecules were observed by GC-MS. These compounds presumably arise through alpha cleavage and subsequent fragmentation (Scheme 38). No attempt was made to characterize these fragmentation products. Hopf *et al.* investigated the thermal chemistry of vinylidenecyclohexane (and related compounds), and found that it too required harsh conditions (760° C) before isomerization occurred; the pyrolysate contained only aromatic species.[43]



64

Scheme 38

Discussion of Benzene Sensitized Solution Phase Irradiation of Cyclohexylallene (**63**) and Vinylidenecycloheptane (**64**)

Irradiation of **63** or **64** in benzene solutions at 254 nm yielded no products observable by capillary GLC or NMR. This result is in contrast to those reported by Gilbert *et al.* for irradiation of parent allene **22** and 1,2-cyclononadiene (**20**) under similar conditions.[30]

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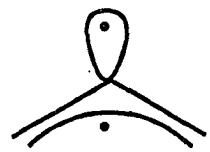
They reported the formation of two benzene cycloadducts, albeit in very low yields, and only after extensive irradiation. The general inertness of triplet allenes in the solution phase is best attributed to the rapid spin inversion of the planar biradical geometry **61** (Figure 4). Ab initio MCSCF calculations on **61** indicate a singlet ground state and a small singlet/triplet gap.[44]



61

Figure 4. Planar triplet allene (61)

Conclusion

The triplet photochemistry of cyclohexylallene (**63**) shows a remarkable phase dependence. Vapor phase reactions of **63** are best described as resulting from the planar triplet species **89**; none of the products is consistent with the intermediacy of cyclopropylidene **88** unless the opening of **88** to **89** is facile. In solution, **63** is presumably formed, however, rapid spin inversion through intersysten crossing results in singlet **63**. One explanation is that low pressure vapor reactions of **63** involve a vibrationally "hot" triplet species which follows a higher energy pathway; in solution, a vibrationally "cold" triplet quickly relaxes to the ground state.[31]

The total lack of reactivity observed by triplet **64** in the vapor phase presumably is a result of its inability to abstract a proximate hydrogen. Because cyclopropylidene **99** appears to be the only species capable of hydrogen abstraction, its formation is clearly in question. The data seem more consistent with the formation of a

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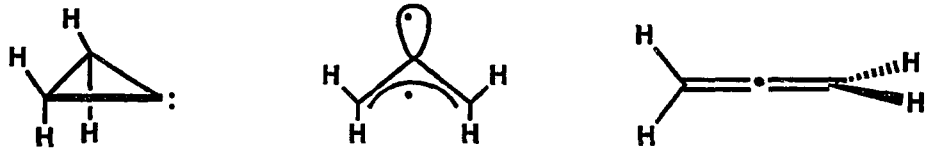
planar triplet species **100** which is simply unable to abstract a hydrogen, and therefore, undergo further reaction. The solution phase triplet chemistry is more easily rationalized in view of the above result. Rotation to a planar triplet allene **100** results in a species which is incapable of hydrogen abstraction; spin inversion then, simply yields the starting allene **64**.

Ab Initio Study of Hydrogen Abstraction by Triplet Cyclopropylidene (52) and Planar Triplet Allene (61)

Introduction

Hydrogen atom abstraction is a common reaction of triplet excited states, and odd electron species, such as carbenes and radicals.[45,46] Triplet excited state photoreactions of simple allene (1,2-propadiene) derivatives are characterized predominantly by intramolecular hydrogen abstraction at proximate C-H bonds.[24,28b,47,48,25,31] These reactions were first investigated during the 1960s by Ward and Karafiath, who proposed two intermediates (Figure 5): triplet cyclopropylidene (**52**) and planar triplet allene



52 **61** **22**

Figure 5. Cyclopropylidene (52), planar triplet allene (61), and allene (22)

(**61**).[28b] These can result from allene (**22**) through either π bond rotation and closure, or rotation and bending, respectively. In the well studied case of 1,2-cyclononadiene (**20**, Scheme 39),

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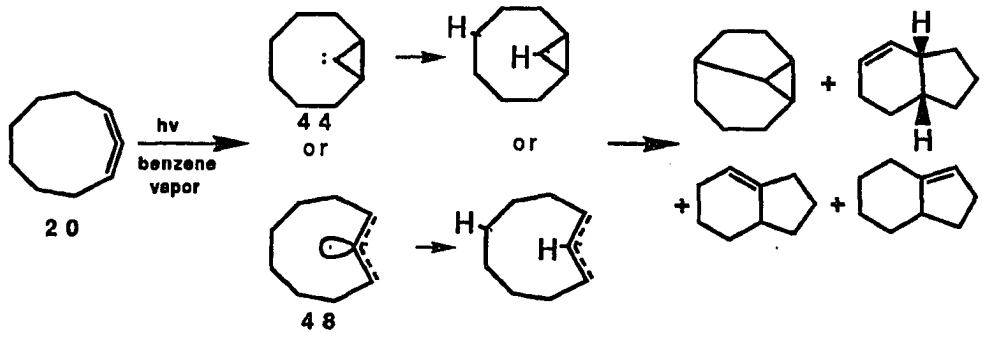
intramolecular hydrogen abstraction by either **44** or **48** can lead to the observed products.[28b,25]



Scheme 39

Allene triplet states usually are generated by benzene sensitization.[24,28b,47,48,25,31] Allene T_1 and T_2 (4.3 and 4.9 eV[49]) lie above the 3.66 eV triplet energy of benzene, which indicates that energy transfer to allene must be "nonvertical".[50] Thus **52** and **61**, which are lower energy (ca 3.4 and 2.2 eV, respectively) minima on the triplet C_3H_4 surface,[25,48] are logical intermediates in these reactions.

Cyclopropylidenes have resisted matrix isolation attempts and remain relatively poorly characterized among carbenes.[51] Singlet **52** is predicted to undergo ring opening to allene, with a barrier of 12-14 kcal/mol.[52] The ground state multiplicity of **52** is not known from experiment, but recent ab initio studies predict a singlet ground state, with a singlet-triplet gap of 12-15 kcal/mol.[25,48,52] For allene, pi bond rotation results in a planar triplet (**61**), which has been predicted to have a bent structure,[53] and to lie ca 1 eV below triplet **52**.[25,48,52b] This diradical is electronically similar to a triplet carbene, except that the pi nonbonding orbital will have a node at C-2. MCSCF calculations on diradical **61** predict a singlet

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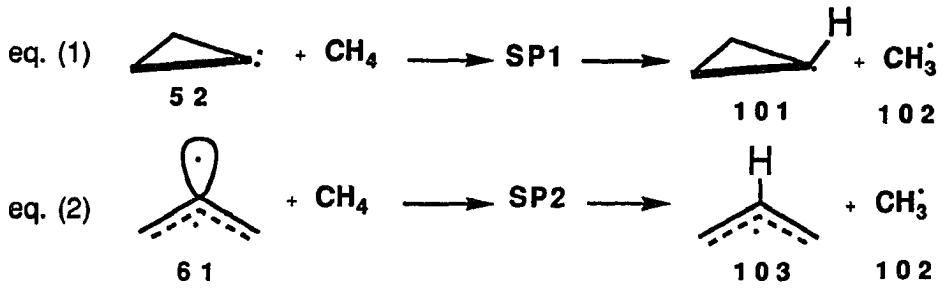
ground state, with a singlet-triplet gap of 4.8 kcal/mol.[54] This small singlet-triplet gap undoubtedly contributes to a short lifetime for **61**. Ab initio calculations predict a 23.7 kcal/mol barrier for opening of triplet **52** to **61**.[52b]

Experimental studies indicate that reaction mechanisms are quite dependent on structure.[24,28b,47,48,25,31] In the case (Scheme 39) of 1,2-cyclononadiene,[28b,25,48] Stierman and Johnson isolated minor reaction products which seem best derived from a common 1,3-biradical; this implies late formation of the three membered ring, and hydrogen abstraction by **48** rather than **44**. Other acyclic examples do not require cyclopropylidene formation.[28b,47] Recent studies by Price and Johnson on a t-butyl-1,2-cyclooctadiene also argue against a cyclopropylidene (*vide* supra).[29] Compelling evidence for a triplet cyclopropylidene is provided by the reactions of 1,2-cyclodecadiene.[25] In this case, the remarkable array of strained tricyclic products seems most consistent with stepwise reaction and initial three membered ring formation. What is puzzling about this reaction is its low selectivity, which implies minimal geometric requirements for hydrogen abstraction.

Described here are the results of ab initio calculations on



the hydrogen abstractions depicted in equations (1) and (2). Our goals were to determine the relative activation energies for these

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fundamental reactions, the saddle point geometries (SP1 and SP2), and their sensitivity to approach angle of the hydrogen.

Computational Methods

Hartree-Fock (UHF and RHF) and Moller-Plesset calculations were performed with a standard VAX version of GAUSSIAN 82.[55] Most calculations reported are at the UMP3/6-31G*//UHF/3-21G level.[56] Geometries were optimized within appropriate symmetry constraints. Multiconfiguration SCF (MCSCF) calculations were performed with GAMESS.[57]

Geometries for triplets, doublets, and saddle points were taken from UHF/3-21G calculations. A final single point calculation was then performed at the MP3/6-31G* level.[56] Geometric data for reactants (**52**, **61** and CH_4) and products (**101-103**) were either taken from, or agreed well with previous calculations.[58] Methyl (**102**) and allyl (**103**) radicals are predicted to have planar, symmetrical structures, while cyclopropyl (**101**) is pyramidalized[58a] (38° out of plane bending at C-1) with a low barrier to planarity.[39b] Triplet species **52** and **61** are predicted to be bent by 63.4° and 137.4°, respectively. Saddle points for hydrogen abstractions were located approximately by initial reaction path calculations and then more rigorously characterized as points having a single imaginary frequency.

Results of Calculations

Total energies for reactants, products, and saddle points are summarized in Table 2. Relative reaction energetics and schematic potential energy curves at the UMP3/6-31G*//3-21G level are depicted in Figure 6. Table 3 provides a summary of calculated activation energies and reaction energies.

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Table 2 Summary of Computational Results

Total Energies (hartrees)[a]

species	HF/3-21G	HF/6-31G*	MP2/6-31G*	MP3/6-31G*
52 ($^3B_2$)	-115.11324	-115.76955	-116.10973	-116.13496
61 ($^3A_2$)	-115.17110	-115.81588	-116.14067	-116.17170
CH_4	-39.97688	-40.19517	-40.33242	-40.34844
CH_3	-39.34261	-39.55899	-39.66864	-39.68448
103	-115.82304	-116.46807	-116.80960	-116.84144
101	-115.75660	-116.41500	-116.77686	-116.80552
SP1[b]	-155.05734	-155.92735	-156.41481	-156.45673
SP2	-155.11162	-155.97056	-156.44504	-156.49017
104 ($^3A'$)	-115.14252	-115.78737	-116.10044	-116.13281

(a) All calculations employed RHF of UHF wavefunctions and geometries optimized with the 3-21G basis set.

(b) SP1 and SP2 are saddle points. See figure 7.

The saddle point structures for these two hydrogen abstractions are shown in Figure 7. Both are predicted to be linear, with the abstracted hydrogen and four carbon atoms essentially coplanar. As indicated by the relative C-H distances, the saddle points lie slightly closer to reactants than products. This is consistent with the modest predicted exothermicities.

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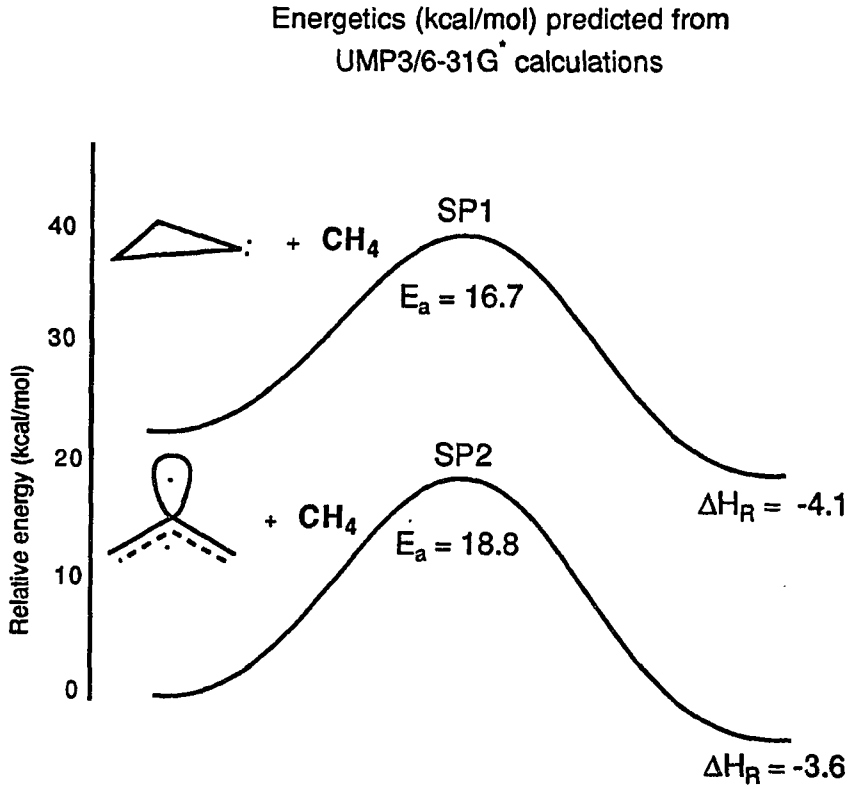

Figure 6

Table 3 Summary of Reaction Energetics (kcal/mol)

Level of Calculation	Predicted Activation Energies SP1	SP2	Reaction Energies eq. (1)	eq. (2)
UHF/3-21G	20.6	22.8	-5.7	-11.1
UHF/6-31G*	23.5	25.4	-5.8	-10.5
MP2/6-31G*	16.0	17.6	-3.2	-3.2
MP3/6-31G*	16.7	18.8	-4.1	-3.6

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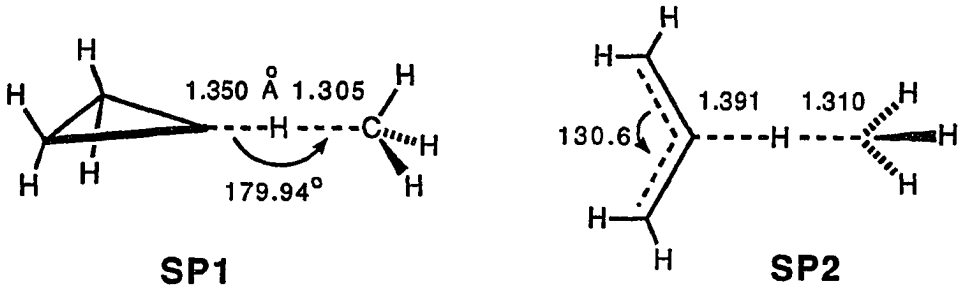

Figure 7. Saddle point geometries for hydrogen abstraction by cyclopropylidene and planar triplet allene

Results and Discussion

At the highest computational level employed, predicted barriers for hydrogen abstraction are 16.7 kcal/mol for triplet cyclopropylidene (equation 1) and 18.8 for planar triplet allene (equation 2). Abstraction of a secondary hydrogen, as in cyclic allene **20**, should diminish this barrier by 2-3 kcal/mol. Gordon has recently reported a very comparable barrier of 17.9 kcal/mol for hydrogen abstraction (equation 3) by triplet methylene.[46d]

eq. (3) $^3CH_2$: + CH_4 ⟶ 2 CH_3·

In one earlier study, Schaefer and co-workers predicted a barrier of 18-23 kcal/mol for this reaction.[46e] BEBO[46f] and MINDO/2[46g] methods afford predicted barriers of 25.6 and 3.8 kcal/mol, respectively. Predicted and experimental values for hydrogen abstraction by simple alkyl radicals (eg. CH_3· + CH_4) are generally 10-20 kcal/mol.[45,46] Our predicted activation energies are probably too high by several kcal/mol.

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Based on our calculations, we conclude that the reactions in equations (1) and (2) should have comparable activation energies and exothermicities, and will follow essentially parallel surfaces. Both are predicted to have a linear transition state.

Saddle point geometries such as these are of fundamental interest, but we believe that more chemical significance should attach to their sensitivity to geometric distortion. Intramolecular hydrogen abstraction in **20** or 1,2-cyclodecadiene[29] must proceed through a substantially nonlinear geometry. Estimates of saddle point "flexibility" are available for **52** and **61**. Initial attempts to locate the saddle point for **52** with a UHF/STO-3G wavefunction gave two geometries, SP3 and SP4, both with α = ca 150°. With the 3-21G basis set, both SP3 and SP4 (Figure 8) collapsed to the linear SP2 geometry, however, both were only 1.3 kcal/mol (UHF/3-21G) higher than SP1. This result indicates that substantial out of plane bending will have a very small effect on the saddle point energy. Indeed, entropic differences might cancel these small differences in enthalpy. As a consequence, intramolecular hydrogen abstraction or

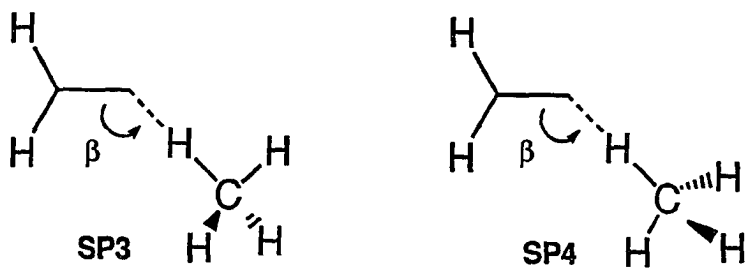

Figure 8. STO-3G Geometries for cyclopropylidene

abstraction in matrices may be insensitive to modest geometric changes. We are exploring the generality of this observation for other triplet carbenes. For planar triplet allene (**61**), we performed similar calculations in which β was systematically varied,while the

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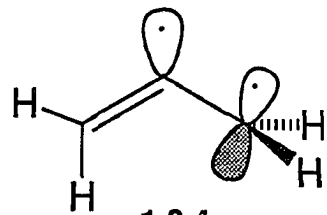
C1-H distance was fixed at the SP2 value. At the UHF/3-21G//STO-3G level, relative energetics were: θ = 180°, 0.0 kcal/mol; 170°, 1.6; 160°, 5.3; 150°, 10.6; 140°, 25.1. These data indicate that hydrogen abstraction by **61** should be much more sensitive to geometry. These differences presumably arise because the half-filled out of plane orbital in **52** is concentrated at C1, while in **61**, there is a node at this site.

Predicted activation and reaction energies (Table 3) are not strongly dependent on the level of calculation. It is remarkable that the HF/3-21G calculation compares well to UMP3/6-31G*, which requires ca. 50 times the computational effort for a single point.

One additional question is the existence of other triplet C_3H_4 species. We conducted a limited search using triplet MCSCF or UHF wavefunctions. Intermediates with D_2h, D_2, or C_2 symmetry all collapsed to **61**. In addition to π bond twisting (D_2d C_2 or D_2d D_2), inplane bending (D_2d Cs) leads to substantial stabilization of the lowest triplet state of allene.[59,44] MCSCF or UHF geometry optimization, with restriction to Cs symmetry, gives a 3A' species, best characterized as **104** (Figure 9). Energetics of this species are



104

Figure 9. Bisected allene (104)

summarized in Table 2. This structure is 18 - 24 kcal/mol above **61**, and UHF/3-21G vibrational analysis gave a single imaginary frequency. We thus conclude that **104** is a saddle point for rotation

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of **61**, rather than an intermediate. Martin, Yates, and Csizmadia recently reported calculations on a 3A" (Cs) allene triplet state; this is predicted to be much higher energy than **104** and hence seems an unlikely intermediate.[60] We find no computational evidence for low energy triplet C_3H_4 intermediates other than **52** and **61**.

Conclusions

Hydrogen abstractions by triplet cyclopropylidene (**52**) and planar triplet allene (**61**) are predicted to have nearly identical activation energies of <19 kcal/mol. Because of limitations in the quantum mechanical model, these numbers are likely to be somewhat high. Both reactions are slightly exothermic. Predicted barriers are similar to those of other free radicals and triplet carbenes. Our results support previous conclusions that intermediates like both **52** and **61** are involved in triplet allene photoreactions. Both saddle points are predicted to have linear C--H--C geometries, however, abstraction by cyclopropylidene is found to be quite insensitive to out of plane bending. This saddle point flexibility may explain the facility and remarkably unselective intramolecular hydrogen abstraction in reactions of cyclic allenes.

Deuterium NMR Studies

During the 1960s, the application of deuterium NMR as a mechanistic probe was first demonstrated. Today, the synthesis and subsequent analysis of suitably labeled material provide a common technique in the study of reaction mechanisms. To a much lesser extent, natural abundance deuterium NMR has been used to achieve similar results. One of the major goals of this project, therefore, was the implementation of this latter technique in studying the

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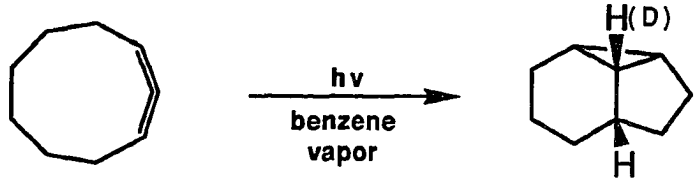
kinetic isotope effect (KIE) for photorearrangement of **20** to **29** (Scheme 40). The project was partly exploratory in nature, designed to ascertain the usefulness of the technique itself, while providing further insight into the triplet sensitized vapor phase photochemistry of allenes.



20 **29**

Scheme 40

The second principal goal of the project was the synthesis of *cis*-6,7-dideuterio-1,2-cyclononadiene (**63**), a potential probe for investigating the mechanism by which **20** photorearranges to **29** in the triplet state. A detailed analysis of tricyclic **29** by deuterium NMR, should theoretically allow for differentiation between the two possible pathways displayed in Scheme 43.

Natural Abundance Deuterium NMR

Natural abundance deuterium (^2H) NMR spectroscopy has received scant attention as a means of measuring KIE's in organic reactions. This relatively new technique should become more routine, however, with the continued improvement of high field instrumentation and availability of new multi-pulse techniques. The experiments require considerably larger sample sizes because of the low natural abundance (ca 0.015%) and sensitivity (0.00965) of ^2H relative to ^1H; however, the technique offers a practical alternative to labeled compounds which often require extensive preparation and,

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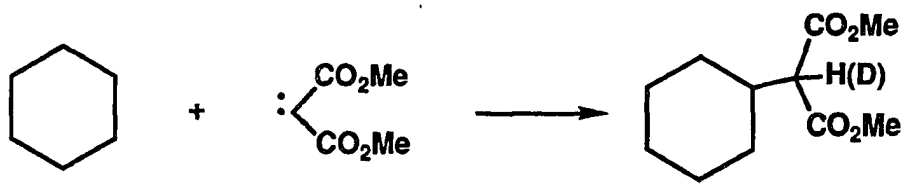
in biological systems, precise knowledge of label location in both the starting materials and products.

Pascal and co-workers first employed this technique to investigate KIE's of several organic and biological systems.[61] By comparing the relative integrations between ^1H and ^2H spectra for a given system, they measured both primary and secondary effects. In one example, which involved the insertion of a singlet carbene into a



Scheme 41

C-H (C-D) bond, they observed k_H/k_D = 2.2 (Scheme 41).[61] In a more dramatic example, the dehydrobromination of (2-bromoethyl)-benzene, they observed k_H/k_D = 7.9. Significantly, both values agreed well with those obtained from labeled compounds. Moreover, they demonstrated the validity of this technique in assessing the "chemical history" of compounds, specifically n-propylbenzene (**105**), formed from 1-phenylpropyne. Integration of the ^2H spectrum of **105** revealed a 3:0.6:0.6 ratio (expected 3:2:2) for the propyl hydrogens; they attributed the observed isotope effect to at least two steps in its chemical history.

Our group recently demonstrated the remarkable effectiveness of this technique.[62] Secondary isotope effects were determined at multiple sites in the di-π- methane rearrangement of benzonorbornadiene (**106**) to tetracyclic **107** (Scheme 42). The experiment should have permitted simultaneous determination of

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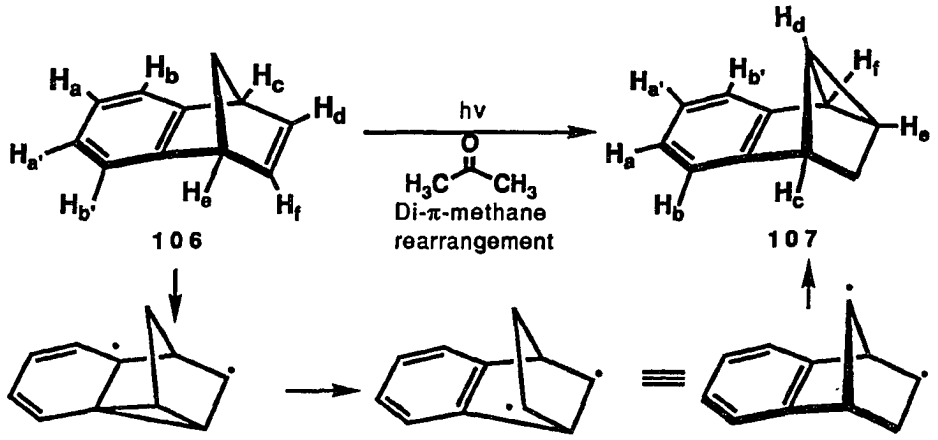
four isotope effects, however, line dispersion of the aromatic region posed some difficulty for accurate integration of protons H_a and H_b. Measurement of H_c and H_d yielded k_H/k_D = 1.31 and 1.40 respectively, in good agreement with values previously reported by Paquette.[63] It is believed that experimentaton at higher fields (500 MHz) will



Scheme 42

allow complete characterization of all four isotope effects, without incorporation of a single, unnatural label.

Investigation of Tricyclic **29** by Natural Abundance Deuterium NMR

Triplet sensitization of 1,2-cyclononadiene (**20**) in the vapor phase results predominantly in the formation of tricyclic **29** (Scheme 43). Two pathways have been proposed for this transformation; presumably, both involve initial hydrogen abstraction from C_6 yielding species **108** and **49**.[25] Closure of diradical **108** or **49** would furnish the observed tricyclic **29**, where H_c is the abstracted hydrogen. Assuming this is the rate determining step, regardless of the pathway traversed, observation of a primary isotope effect is anticipated. To measure this effect, we obtained

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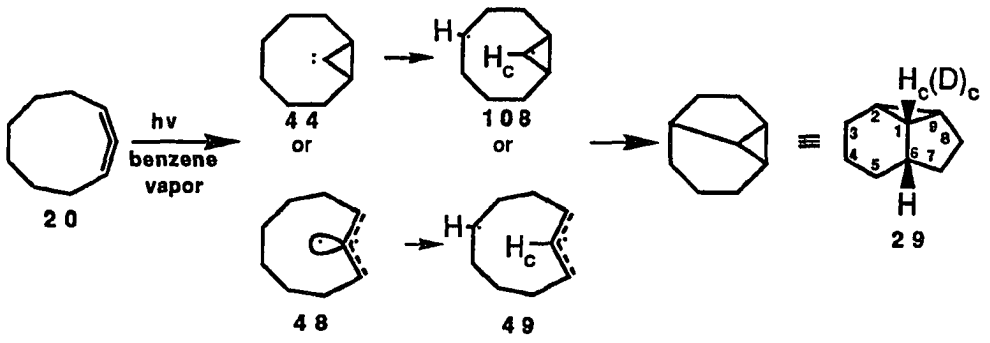

Scheme 43

natural abundance ^2H NMR spectra of tricyclic **29**. Through accurate integration of the abstracted deuterium (D_c) versus other single deuterium resonances in the molecule, we determined efficiently the small, but measurable KIE associated with this process.

Synthesis of tricyclic **29** has been previously described.[28] Material used in NMR experiments was further purified by preparative GLC (>99.5%). A ^1H NMR spectrum of the purified material is shown in Figure 10. The resonances were confidently assigned by a combination of NMR techniques (see Scheme 43 for numbering) on both substituted and unsubstituted **29** as described below. Information was derived from 2D COSY experiments, methyl substitution at C_2 and C_9 (^1H NMR)[48], deuterium substitution at C_2 and C_9 (^2H and ^1H NMR)[37], and deuterium substitution at C_1, C_6, and C_5 (^1H NMR).

The ^2H spectra were recorded at 55.30 MHz on a Bruker AM-360 Fourier transform spectrometer. The sample was prepared as a 1.3 M solution in chloroform in 10 mm (o.d.) tubes. Spectra were obtained using a 90^0 pulse angle and a 4-s pulse delay with CPD decoupling. The spectrometer was run unlocked and spectra were recorded in blocks of 1000 scans. The blocks were individually transformed,

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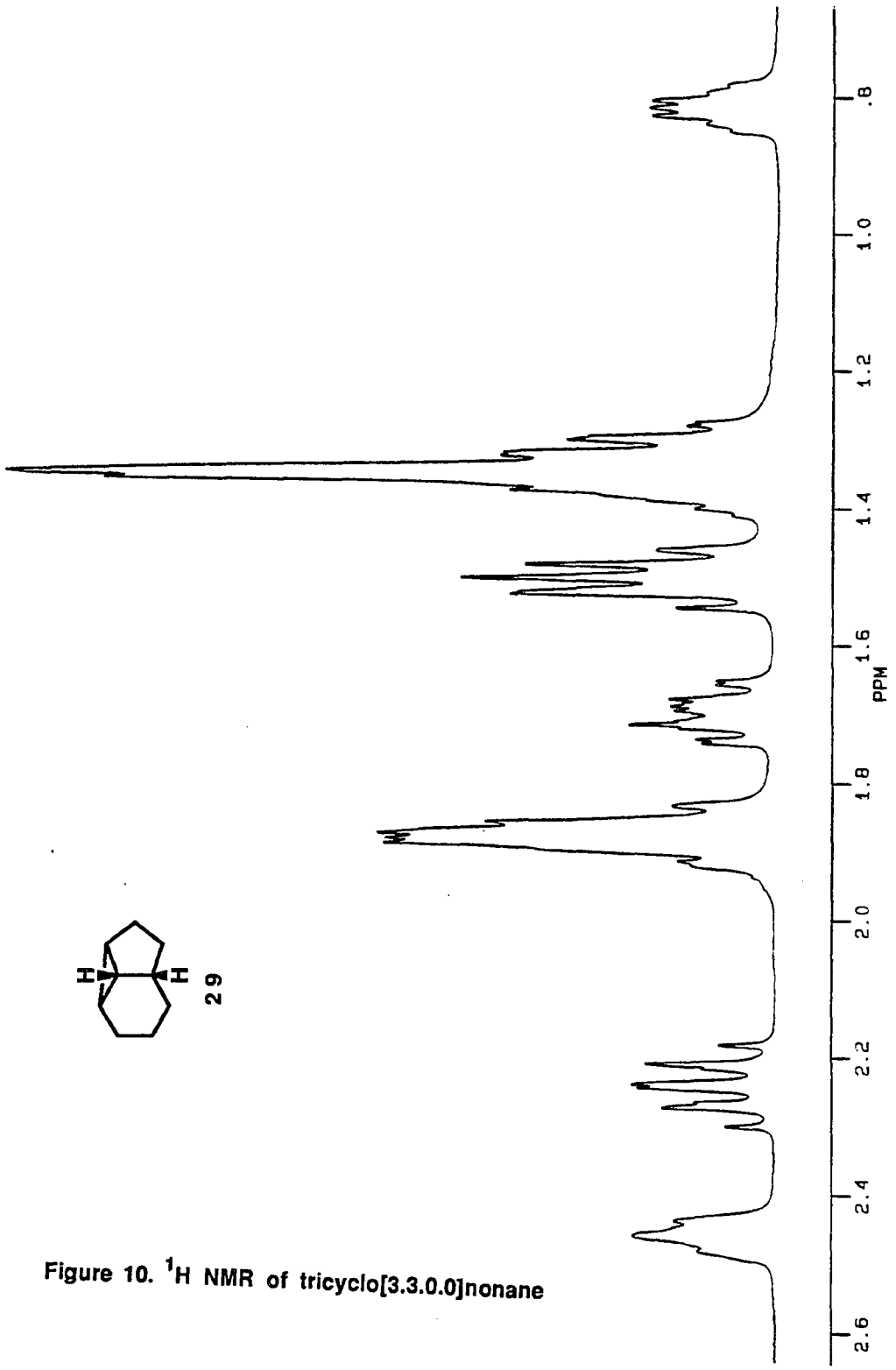

Figure 10. ^{1}H NMR of tricyclo[3.3.0.0]nonane

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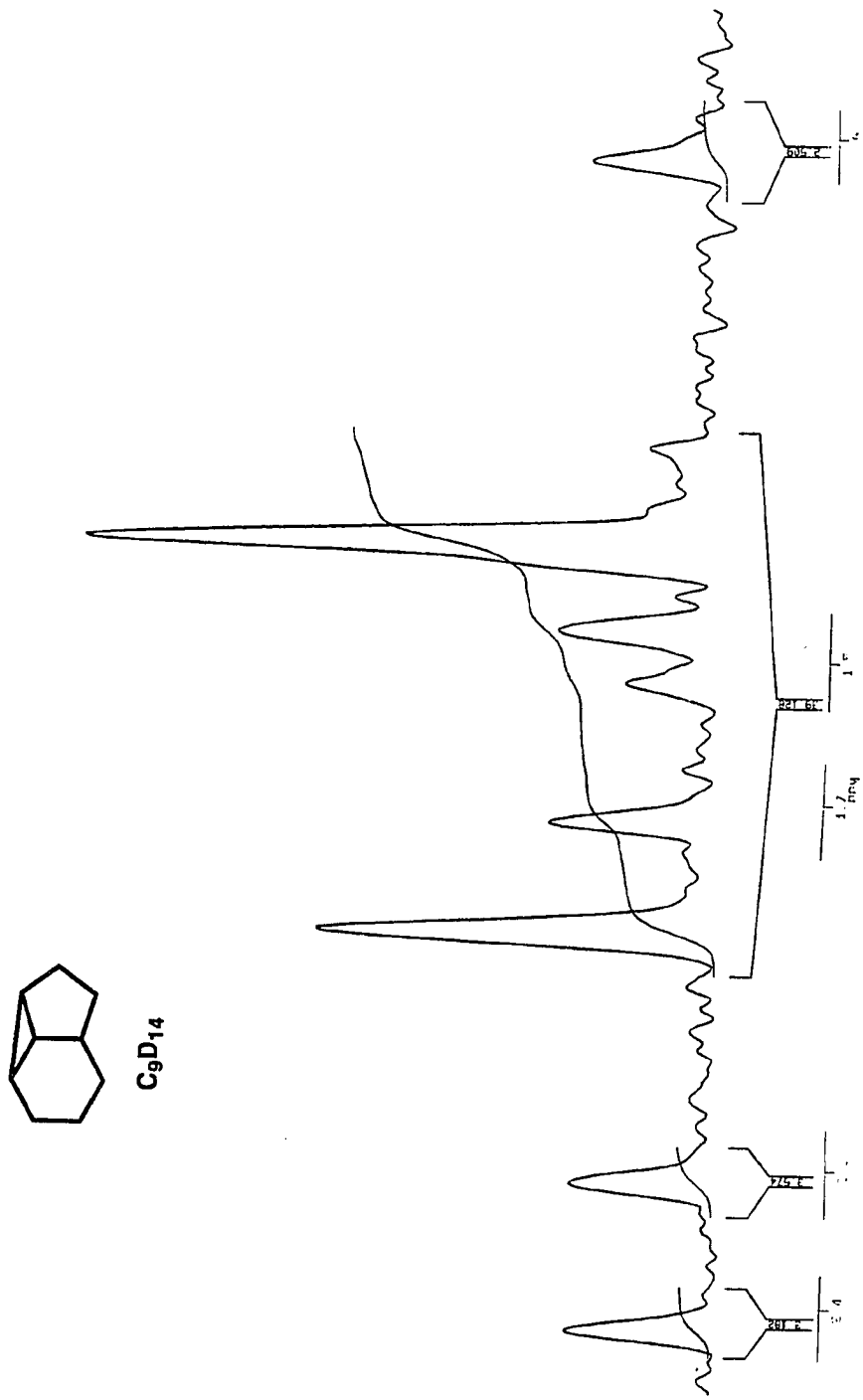

Figure 11. ^2H NMR of tricyclo[3.3.0.0]nonane

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phase and baseline corrected, then added in the frequency domain. Peak areas from the added spectrum were obtained by digital integration and the cut-and-weigh method. There was no significant difference between these two methods.

The deuterium spectrum of tricyclic **29** is shown in Figure 11. The broad resonance at δ 1.51 represents D_c, the abstracted deuterium. Upon visual observation, the area under this resonance clearly is considerably less than that of other single deuterium resonances at δ 2.43, δ 2.23, δ 1.72, and δ 0.81. Quantitative measurements revealed the integral of transferred deuterium D_c was 0.56. Multiple integrations by both methods described above, followed by averaging, yielded $k_H/k_D = 1.79 \pm 0.11$.

For hydrogen atom transfers involving linear transition states, the observation of a large isotope effect indicates the transition state is symmetrical, whereas a small isotope effect indicates it is more reactant or product-like. In our case, the modest exothermicity of hydrogen abstraction (15-20 kcal/mol) precludes interpretation based on the symmetry of the transition state. Conventional wisdom holds that isotope effects may also be interpretated in terms of the linearity of the transition state. This was demonstrated computationally in a classic paper by Moore O' Ferrall,[64] but first put forth by Lewis.[65] In the work by Moore O' Ferrall, an isotope effect of 7.9 was calculated for hydrogen atom abstraction in a linear transition state (180°). When the transition state was bent substantially (60°) this value was reduced to 1.4.

Thus, we believe the observation of a small isotope effect indicates the transition state for the conversion of **20** to **29** is distinctly non-linear. Models indicate that both potential intermediates **49** and **48** must adopt conformations in which the

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transition states for hydrogen abstraction are bent. Therefore, it becomes impossible to distinguish between the two proposed pathways on this data alone.

In summary, the implementation of natural abundance ^2H NMR in determining isotope effects has been demonstrated. The ability to obtain KIE's without unnatural labels is a significant improvement over previous methods, which involve the synthesis of labeled compounds. While we did not use this technique for mechanistic interpretation, it is clear it would offer a nice alternative to labeled compounds in this regard. The only practical limitations of this technique are its low sensitivity, requirement for larger sample sizes, and line dispersion, all of which may be overcome with higher field instrumentation.

Synthesis of *cis*-6,7-Dideuterio-1,2-cyclononadiene (**63**)

In the preceding section, two pathways for the conversion of 1,2-cyclononadiene (**20**) to tricyclic **29** in the vapor phase triplet excited state were presented. To investigate more closely the mechanism by which this transformation occurs, we undertook the synthesis of *cis*-6,7-dideuterio-1,2-cyclononadiene (**63**) as a mechanistic probe. Conversion of labeled **63** to tricyclic **29d**, and analysis of the product by ^2H NMR should, in principle, distinguish between the two possible pathways.

To understand completely the merits of the experiment, a closer look at both transition states is necessary. Hydrogen abstraction by triplet cyclopropylidene **44** is presumed to take place from two equally probable tub-shaped conformations (**44a** and **44b**) in which no choice between H or D exists (Scheme 44). Abstraction, followed by insertion should yield tricyclic **29d** with equal

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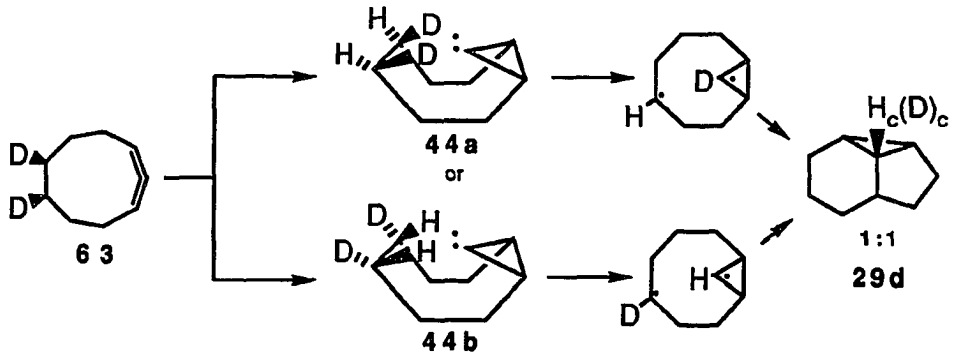
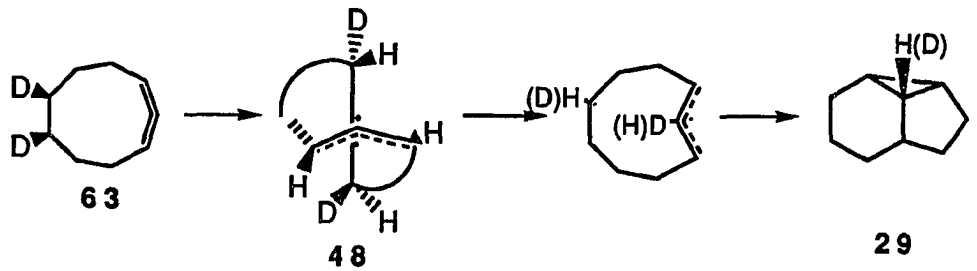


Scheme 44

proportions of H and D at C_1 and C_6. Confirmation of this should be readily achieved by ^2H NMR. By contrast, abstraction by planar triplet allene **48** requires that it adopt C_2 symmetry in which H and D are in identical and competing positions (Scheme 45). In this case, a choice between both nuclei exists, and a primary isotope effect (i.e. less ^2H at C_1 than at C_6) is anticipated.



Scheme 45

The most direct approach to **63** is through MeLi promoted ring opening of an appropriately labeled dibromoocyclopropane precursor, namely, *cis*-9,9-dibromo-6,7-dideuteriobicyclo[6.1.0]nonane (**111**). Synthesis of **111** should be accomplished through addition of

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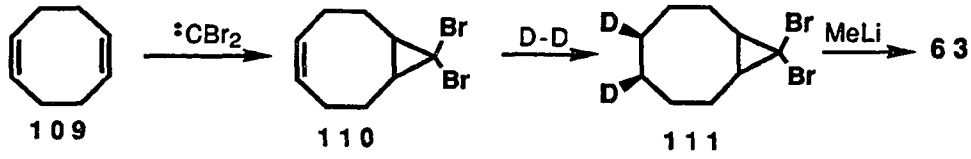

Scheme 46

deuterium by one of several methods to alkene precursor **110**. Dibromide **110** may be prepared by dibromcarbene addition to 1,5-cyclooctadiene (**109**, Scheme 46).

The method chosen for addition of deuterium to **110** was critical, as only *cis* deuteration was desired. Normal methods of catalytic reduction invariably result in small amounts of anti addition, exchange of hydrogens, and double-bond isomerization. To avoid this, we chose diimide, which adds stereospecifically syn, and without isomerization.[66]

Dideuteriodiimide was generated from the addition of deuterio acetic acid to dipotassium azodicarboxylate. Generation of deutero-diimide in the presence of alkene **110** resulted in anywhere from 10%-30% reduction. This yield was improved to 85% by performing several reductions on the same batch. Separation of the reduced **111** from alkene **110** was accomplished by MCBPA oxidation of the crude mixture, followed by passage through neutral alumina (pentane) to remove the epoxide. In this fashion, **111** was obtained in 76% overall yield after distillation (Scheme 47). Analysis of **111** by MS, however, indicated it to be ≈ 66% dideuterated and 34% monodeuterated. Numerous attempts at eradicating the source of hydrogen through the use of deuterated solvents and extensive drying did not significantly alter the isotopic purity.

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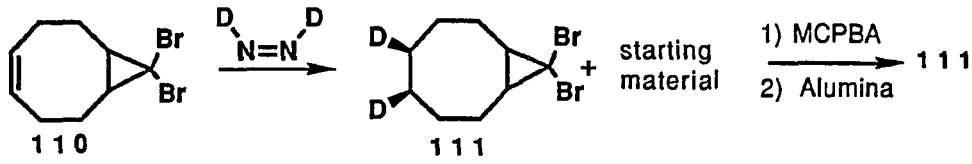

Scheme 47

The above results were indeed very puzzling. Great care was exercised to exclude water from the system, and the dipotassium azodicarboxylate (diimide precursor) salt was dried for 24 hr (0.02 mm Hg) prior to use. All solvents were purchased from Aldrich and supposedly >99% isotopically pure. The purity of these solvents was never questioned, however, it would seem unlikely that they were the source of hydrogen. Statistically, the mere fact that several runs were made on each batch increases the probability of introducing water. The formation of monodeuterated product deterred us from continuing the study, as the reliability of NMR data would surely be in question. Nonetheless, **63** was converted to **29d**, whose ^{1}H NMR aided in assigning the spectrum of the unsubstituted material **29**.

The idea of using labeled allene **63** as a mechanistic probe is, in principle, a very good one. There are at least two other methods for introducing deuterium in a *cis* fashion: Wilkinson's catalyst, and boron reagents. Both of these methods were explored; however, the results were mixed and reaction conditions never fully optimized. Continued investigation employing either methodology may eventually lead to the synthesis of **63**.

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CHAPTER 3

SYNTHESIS AND TRAPPING OF STRAINED CUMULENES

General Introduction to Strained Molecules

One fundamental challenge posed to chemists over the years has been the synthesis and investigation of strained hydrocarbons. The concept of strain was first introduced more than a century ago by Adolf von Baeyer, and work in his laboratory led to syntheses of the first cyclopropane and cyclobutane derivatives.[67] Sixty five years passed, however, before quantitative strain estimates for these compounds would become available.[68] Today, a remarkable collection of strained hydrocarbons is known. In past years, many of these would have been viewed as unlikely candidates for synthesis. This explosion in the field of strained molecule chemistry is due principally to vast improvements in synthetic methodologies. Because of their unusual electronic properties, strained molecules have also provided fertile ground for study by theoreticians. In fact, synergism between these two disciplines has aided the study of this rich and diverse field.

The field of strained organic chemistry has been reviewed extensively in recent literature;[68,69] however, a brief discussion on the origin of strain and several representative examples are included for completeness.

The origin of strain in organic molecules is a departure from the optimal value of at least one of several geometric parameters inherent in all molecules. Molecular strain manifests itself through

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a bewildering compilation of molecules whose structure, energetics, and reactivity may vary considerably. Estimates of strain energy for a molecule may be derived from its heat of formation from the elements (ΔH_f) by comparison with a hypothetical "strainless" model.[68,69] The ΔH_f may derive from experiment or from high level calculations.

Molecular strain is described in terms of four principal components: bond length distortion, bond angle distortion, torsional terms, and steric (nonbonded) interactions. Any deviation from an "optimal" value for a given system by any of the terms contributes to the overall strain in the molecule.

Small rings are a classic example of strained compounds. The two most significant contributors to strain in these molecules are angle and torsional strain. For example, the internal C-C-C bond angle in cyclopropane is ≈ 60°. The "normal" bond angle for a tetrahedral carbon is 109.5°; therefore, cyclopropane experiences considerable angle strain. In fact, the strain energy for this molecule is estimated to be ≈ 27.5 kcal/mol.[68]

Eclipsing methylene groups increase torsional strain, in addition to angle strain. In the next higher homologue of the series, cyclobutane, a perfectly planar arrangement (90° C-C-C angles) of carbons would have all methylenes eclipsed, increasing the torsional component. To minimize this effect, the ring adopts a puckered conformation, thus decreasing the internal C-C-C angle to 88° and allowing the torsional angle to increase to 24°.

Several examples of molecules whose strain is engendered by the presence of small saturated rings are shown in Figure 12. [1.1.1]-Propellane (**112**), first synthesized by Wiberg in 1982, has a strain energy of ≈ 98 kcal/mol.[70] The molecule is forced to adopt an

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inverted tetrahedral geometry at the bridgehead position, and calculations suggest that the central bond has > 90% p character.[70b]

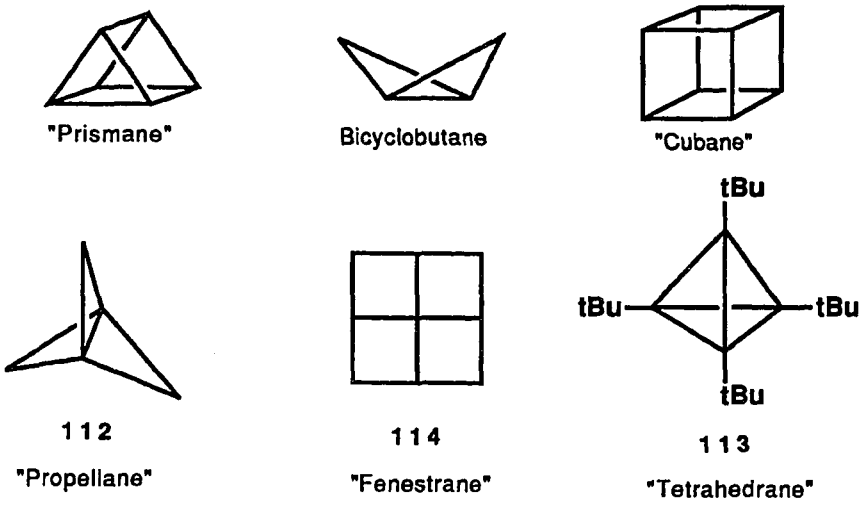

Figure 12. Strained Saturated-Ring Compounds

The molecule is extremely reactive and undergoes rapid addition to its central bond, leading to a host of 1,3-disubstituted bicyclo[1.1.1]-pentanes. Tetrahedranes such as **113** have also been the object of much synthetic endeavor. Tetrahedrane **113** was made in 1981 by Maier *et al.* through photochemical extrusion of CO from the appropriate precursor.[71] While no strain estimates exists for **113**, the calculated value for the parent compound is ≈ 140 kcal/mol![68]

Fenestranes such as **114** (Figure 12), also have been targets of considerable synthetic effort. Strain in these molecules is derived in principle from a shortening of the centralized C-C bonds by as much as 0.05Å, as well as severe angle distortion. Some fenestranes are predicted to have a near planar central carbon atom.[72]

In the preceding discussion, small saturated rings engender considerable strain in a variety of different compounds. Not surprisingly, there exist a large collection of small ring compounds

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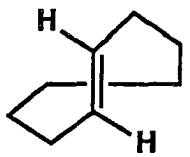
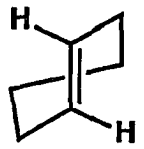
whose strain is due to the presence of multiple bonds. The following is a brief discussion on the origin of strain in alkenes; allenes, alkynes (including enynes), and butatrienes have been omitted here, as they are the major focus in forthcoming sections.

Strain in most alkenes originates through twisting or bending of the π bond. Twisting is introduced through incorporation of a double bond *trans*-fused in rings, the synthesis of anti-Bredt compounds, or severe steric crowding.[68]

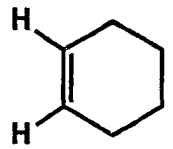
The smallest isolable *trans*-fused system is *trans*-cyclooctene (**115**, Figure 13). Analysis of **115** by electron diffraction revealed its π system was bent away from planarity by 44°,[73] increasing the strain energy by ca. 12 kcal/mol relative to the *cis* isomer. *trans*-Cycloheptene has also been prepared; however, at 1°C it reverts back



115



117



118

Figure 13. *trans*-Cycloalkenes

to the *cis* isomer with a half-life of approximately 10 min.[74] Stabilization of this molecule by coordination to transition metals led to the isolation of a copper(I)-*trans* complex **116**. The NMR spectrum of **116** has been recently reported.[75]

trans-Cyclohexene (**117**) has been proposed as an intermediate; however, unequivocal proof of its existence through either trapping or matrix isolation has not yet been reported. Several groups from the Netherlands conducted theoretical studies on **117** and found it to be an energy minimum.[76] Calculations at the 6-

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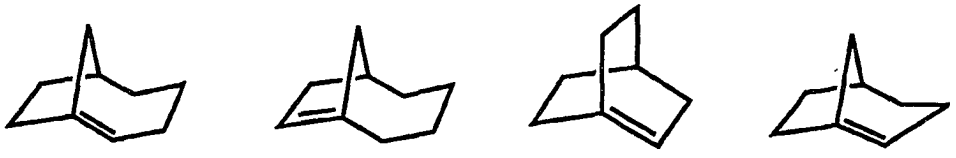
31G level predicted an energy difference of 56 kcal/mol between **117** and its *cis* isomer **118**, while estimating the barrier to *trans-cis* interconversion at 15 kcal/mol. The π bond was distorted from planarity by approximately 81°.

Bridgehead alkenes, also known as Anti-Bredt molecules, represent another class of distorted alkenes whose strain is introduced through twisting of π bonds. Several examples are shown in Figure 14. Of these, **119** and **120** are isolable, while **121** and **122** have been generated and trapped as reactive intermediates.[69] In general, anti-Bredt compounds with double bonds in eight-membered rings or larger are isolable.[69]



119 **120** **121** **122**

Figure 14. Bridgehead Alkenes

Twisting of π bonds may also result from severe steric crowding. The classic example demonstrating this is the series of *tert*-butyl-substituted ethylenes (Figure 15). *cis*-1,2-di-*tert*-Butylethylene is bent from planarity by 5°.[69] The introduction of a third *tert*-butyl group imparts strain in the molecule; to alleviate this strain, the torsion angle is increased to 16°. Tetra-*tert*-butylethylene has not yet been synthesized; however, calculations predict a very high strain energy, and a torsion angle of 75°.[69]

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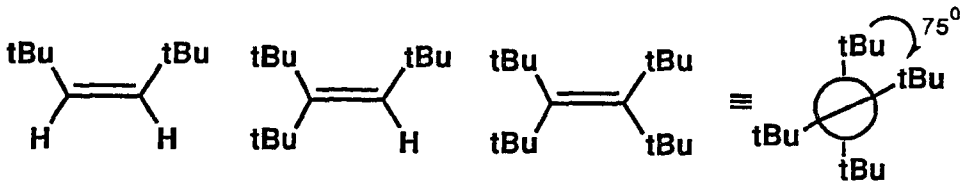

Figure 15. *tert*-Butylethylenes

Strain in cyclic alkenes may be introduced through bending, or pyramidalization of the π bond away from its idealized geometry. A remarkable number of strained compounds exist with very distorted double bonds, four of which are displayed in Figure 16. As mentioned previously, these are some recent examples; for more exhaustive coverage, the reader is referred to several reviews.[77]

Figure 16. Strained bicycloalkenes

Perhaps the most distinguished in the series is bicyclo[1.1.0]-but-1(3)-ene (**124**, Scheme 48). Szeimies *et al.* invoked **124** as an intermediate in the conversion of **123** to **125**; however, labeling experiments implicated **126** rather than **124**.[78] Calculations on **124** predict a puckered geometry, with the C-C-C bridgehead angle = 214°.[68] The strain energy was estimated at 130 kcal/mol, which is substantial for such a small framework, and may prohibit its eventual synthesis.

Several derivatives of **124** have been reported. Szeimies reported several methods for the synthesis and trapping of **127** (Scheme 49).[79] With an additional double bond, **129** was suggested

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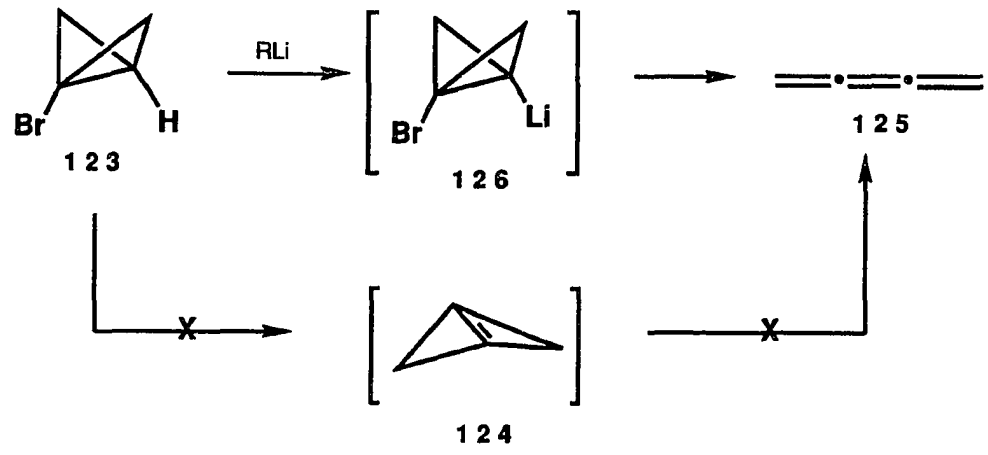
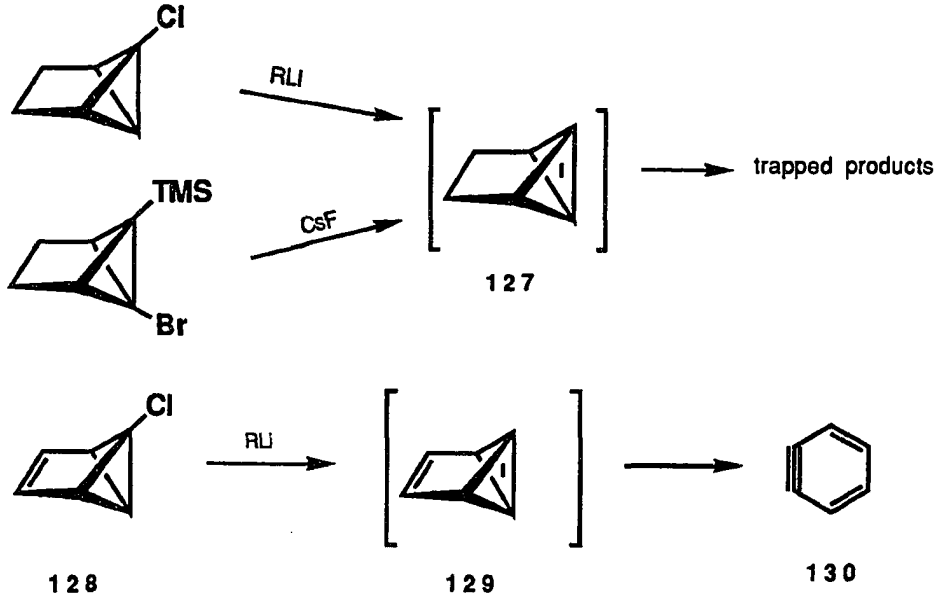


Scheme 48

as an intermediate in the conversion of **128** to **130**. Attempts to trap **129** at lower temperatures (-105° C) resulted in the sole isolation of trapped **130**.[79b] This result clearly indicates that incorporation of the bridgehead double bond in **129** induces more strain than the triple bond in benzyne (**130**).



Scheme 49

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Statement of the Goals

For some time, our group has been interested in strain and the resultant reactivity derived from the incorporation of multiple bonds into smaller and smaller ring systems. This interest stems from a natural desire to further understand the nature and limitations of chemical bonding. Additionally, a comprehensive understanding of structure, isolability, and chemical reactivity should make many strained species available as reaction intermediates, in much the same way that benzyne (**130**) is used today. Indeed, a remarkable observation with such molecules is their smooth transformation from being shelf-stable to reactive intermediates with decreasing ring size. A general goal of this research then, was to define the limitations of bonding in specific multiply-bonded systems, and to develop new and general syntheses that would allow convenient access to these systems.

In the course of research directed toward the synthesis of 1,2-cyclopentadiene (**131**), we developed a new methodology for introducing strained double bonds into cyclic allenes. Eventually, the method was adapted to syntheses of several other strained systems. The purpose of this chapter then, is to present the results of our studies focused on the following three cyclic systems: allenes, butatrienes, and enynes.

Cyclic Allenes: Synthesis and Trapping of 1-Phenyl-1,2-cyclohexadiene (137) and Attempts at the Synthesis of 1,2-Cyclopentadiene (131)

Introduction to Strained Allenes

Allenes (1,2-propadienes) comprise the second group of the homologous series of unsaturated hydrocarbons known as

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cumulenes. The centrally bonded carbon is sp hybridized; therefore, "strain free" allenes prefer linear geometries. Ring constraints engender substantial strain in allene systems; it is well known that the kinetic stability of allenes is decreased with smaller ring sizes. This is manifested through a gradual change from shelf-stable species to reactive intermediates as ring size is decreased.

Strain in allenes is introduced through bending of the system away from its ideal linear geometry. Concomitant with bending, a twisting motion contorts both pairs of orthogonal substituents towards planarity, adding a torsional component. Calculations predict these motions are coupled; as further bending is induced through ring constraints, additional twisting towards planarity is observed.[80] The series of allenes from nine- to five-membered rings is shown in Figure 17. Bending angles and out-of-plane

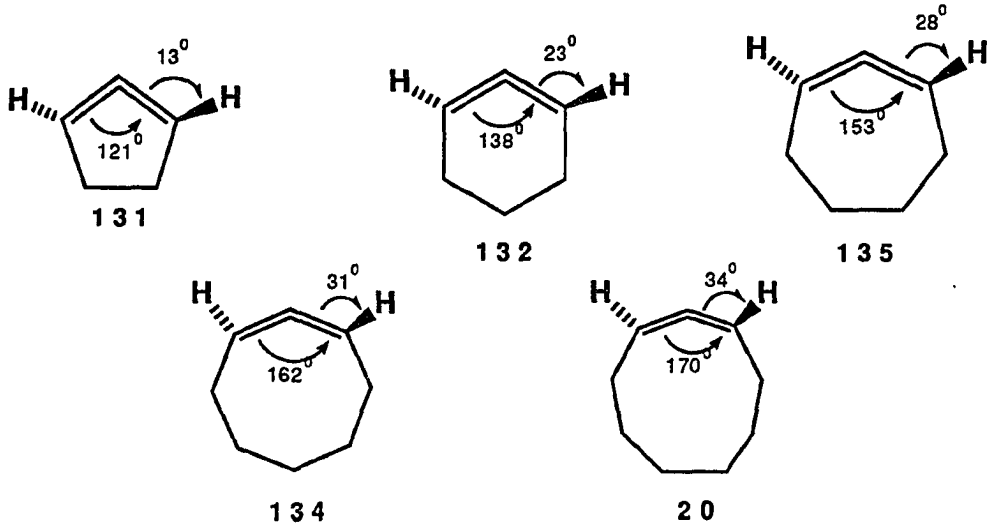

Figure 17. Bending and twisting angles of cyclicallenes

torsional angles were estimated using semiempirical methods.[81] The bending potential for allenes is predicted to be quite soft; during the

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first 20°, the strain increases by only 4 kcal/mol.

Considerable uncertainity originally surrounded the structure of small ring cumulenes. The smallest existing cyclic allene is 1,2-cyclohexadiene (**132**). Several possible electronic representations for ground state **132** are shown in Figure 18. Early experiments by Moore and Moser led them to posit either singlet diradical **132d** or zwitterion **132b** as the ground electronic state for **132**.[82] They concluded, "both formal representations imply high reactivity." The latter species received support from INDO-MO calculations performed by Dillon and Underwood; however, they appear to have calculated the wrong state.[83]

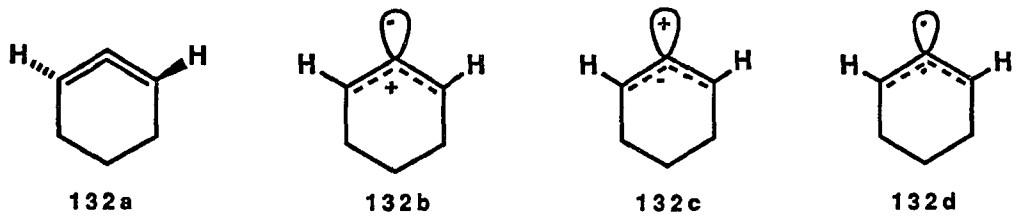

Figure 18. Electronic configurations of 1,2-cyclohexadiene

The strongest support for the proposed intermediacy of chiral species **132a** came from experiments by Balci and Jones (Scheme **50**).[84] The recognition that only **132a** is inherently chiral, led the authors to synthesize and trap optically active **132**. Optical activity in the products was competitive with recemization at 80° C, which implies a low barrier to racemization for **132**. In fact, this low barrier, and the preference for chiral **132a**, was further supported by Johnson *et al.*[81] Ab initio calculations predicted an inversion barrier of 15-24 kcal/mol for **132**.[81,85]

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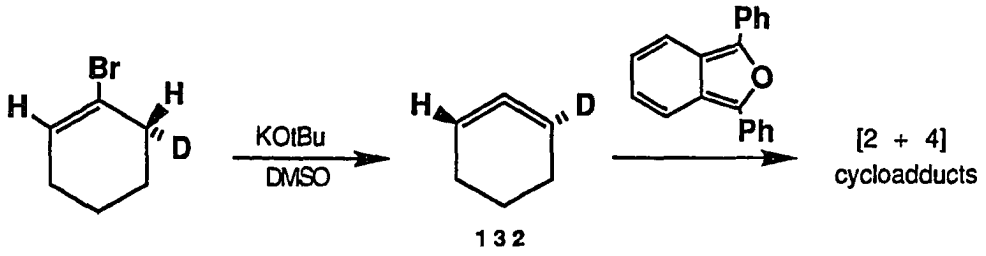
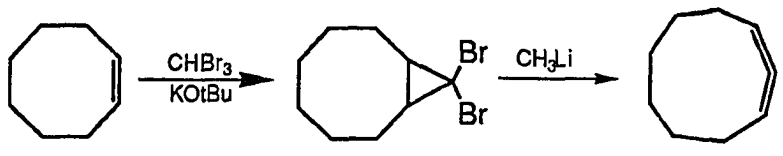


132

Scheme 50

The next lower homologue, 1,2-cyclopentadiene (**131**), is also predicted to have a chiral ground state geometry; however the authors indicate the 4.9 kcal/mol favoring this structure are within reasonable estimates for computational error bounds.[81] Work to define the structure of 1,2-cyclobutadiene is in progress at present.

One fundamental question concerns the limitations of isolability and existence of strained cyclic allenes. Models indicate the smallest ring in which an allene unit may be incorporated without bending is 1,2-cyclodecadiene (**50**). 1,2-Cyclononadiene (**20**) is the smallest unsubstituted cyclic allene which is isolable under ordinary conditions. Calculations and experiments[86] indicate the allenic moiety is bent 10^0 away from linearity. Allene **20** is conveniently prepared in excellent yields by opening dibromocyclopropane precursor **133** with methyllithium at reduced temperature.[87] This two-step procedure (Scheme 51) is a very general route to cyclic allenes.



133 20

Scheme 51

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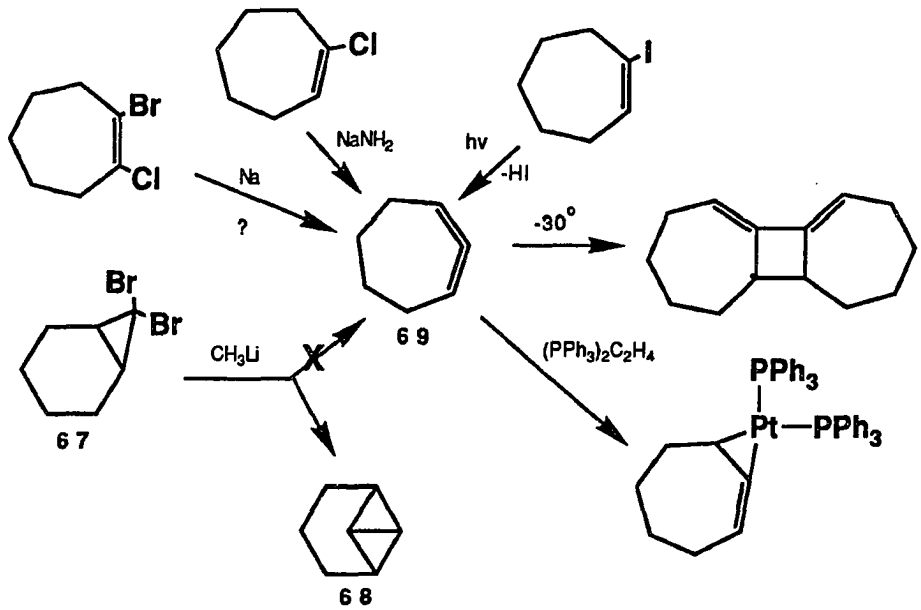
1,2-Cyclooctadiene (**134**) dimerizes rapidly at room temperature, however, spectroscopic data supporting the existence of this molecule proved measurable at -60° C.[88] Appendage of a *tert*-butyl-group by a member in our group induced sufficient kinetic stability to arrest dimerization and allow isolation of what is now the smallest substituted allene.[31] In fact, the molecule was stable to purification by GLC.

1,2-Cycloheptadiene (**69**) has been synthesized through a variety of different routes (Scheme 52);[90] however, **69** was too



Scheme 52

reactive to be observed spectroscopically.[89] Interestingly, the conventional route to this molecule through opening of the suitable dibromocyclopropane precursor **67** fails. Insertion of the carbenoid into a proximate C-H bond results in the isolation of tricyclic **68**.[35]

The next lower homologue in the series, 1,2-cyclohexadiene (**132**) is, to date, the smallest existing allene. Diene **132** is

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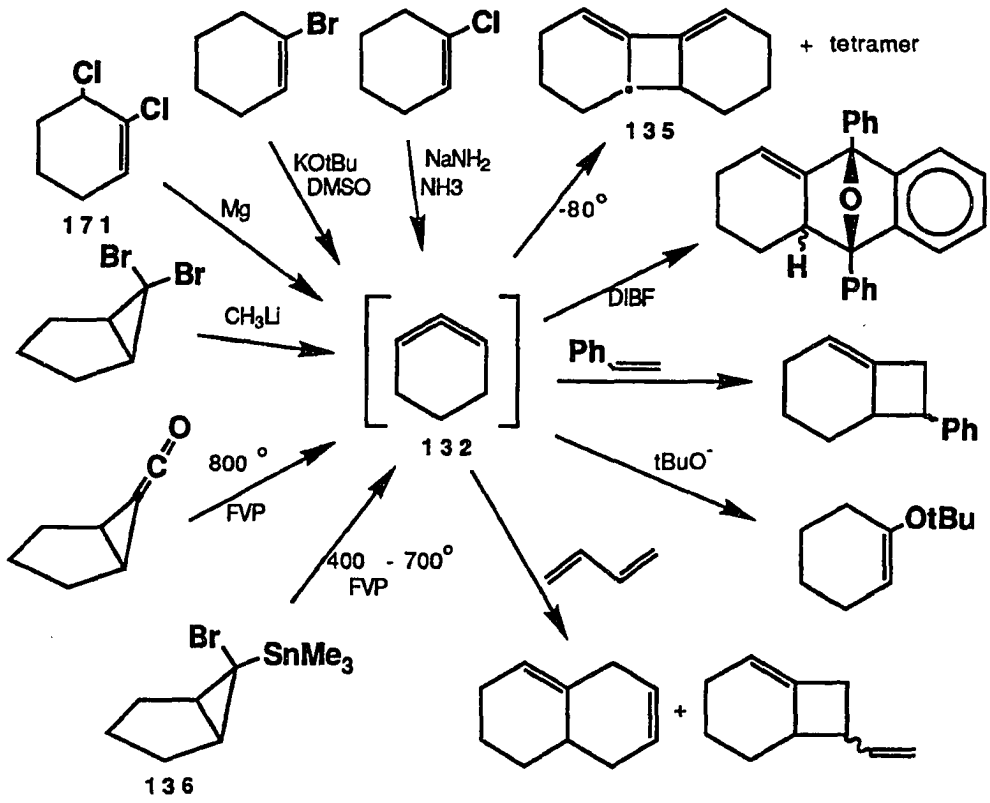
prepared by the conventional route, or through a host of other pathways (Scheme 53).[90] Both calculation and experimentation implicate chiral **132** as the equilibrium structure. Calculations predict the allene unit is bent 50° away from linearity, while the allenic hydrogens are bent in opposite directions, 30° out-of-plane.[81]



Scheme 53

There have been two reports of **132** being trapped in a cryogenic matrix. Wentrup has trapped pyrolytically generated **132** in an argon matrix at 11K and observed an IR stretching frequency at 1886 cm^{-1}, which he attributed to the bent allene unit. Upon

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warming of the matrix he isolated the dimer **135** (Scheme 53).[91] More recently, Runge and Sander pyrolyzed bicyclic **136** and trapped an intermediate with an IR stretching frequency at 1829 cm-1.[92] These discrepancies led us to calculate (*vide* infra) the absorbtion of **132** using semiemperical methods. After calibration versus experimentally determined frequencies, we predicted a vibrational frequency of 1809 cm-1.

Synthesis and Trapping of 1-Phenyl-1,2-cyclohexadiene (137)

Introduction. It has been shown that the kinetic stability of cyclic allenes may be greatly enhanced through substitution.[90] For example, while 1,2-cyclooctadiene dimerizes rapidly at ambient temperature,[90] the 1-methyl derivative of **134** enjoys greater kinetic stability and dimerizes with a half-life of 10-15 minutes at room temperature.[93] Further buttressing by the addition of a *tert*-butyl group imparts even greater kinetic stability, and permits

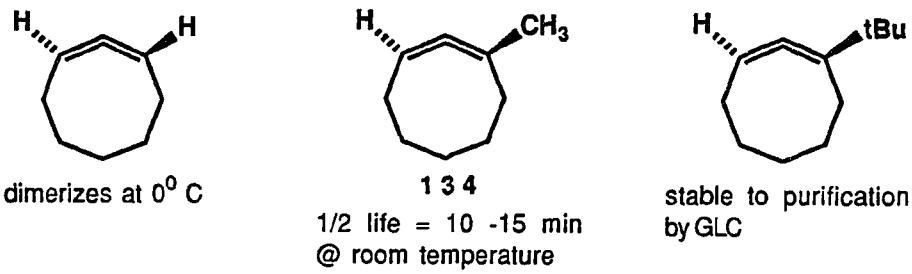

Figure 19. Kinetic stability of some 1,2-cyclooctadienes

isolation by GLC (Figure 19).[31] Our group was interested in investigating the kinetic stability of a series of 1-phenyl-substituted cyclic allenes and the effect imparted by the phenyl group through either electronic or steric interactions. Additionally, it was conjectured that incorporation of a phenyl group would

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facilitate studies on the kinetics of dimerization by acting as an auxochrome for UV analysis.

The syntheses and inherent stabilities of several members in the series of 1-phenyl-substituted allenes has been described previously by Loiselle and Johnson.[94] Figure 20 displays the series from 10- to 6-membered rings and the kinetic stability associated

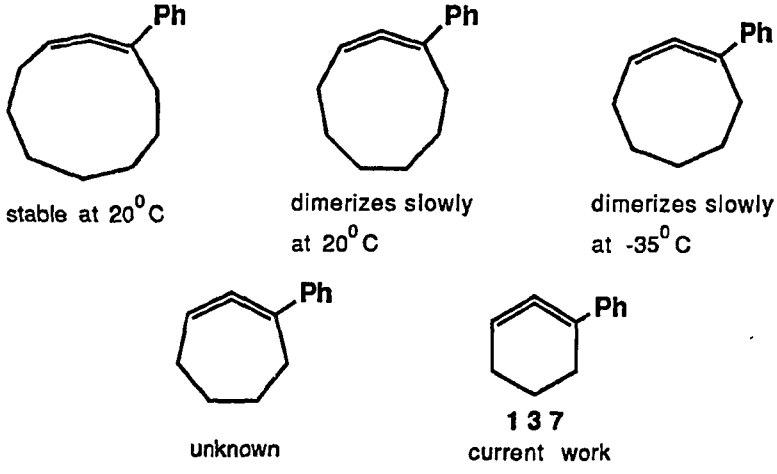

Figure 20. Kinetic stability of some phenyl-substituted cyclic allenes

with them. Described here are recent efforts toward the synthesis of 1-phenyl-1,2-cyclohexadiene (**137**), the smallest existing phenyl-substituted cyclic allene reported to date.[95] This work was initiated independently, then later developed as a collaboration with Professor Laren Tolbert and Md. Nural Islam at the Georgia Institute of Technology. Tolbert and Nural Islam investigated photo-dehalogenation of chlorocarbanion **138**. Their approach to **137** is shown in Scheme 54; however, a detailed discussion of their work will not be given here.

Results and Discussion The synthesis of **137** is outlined in

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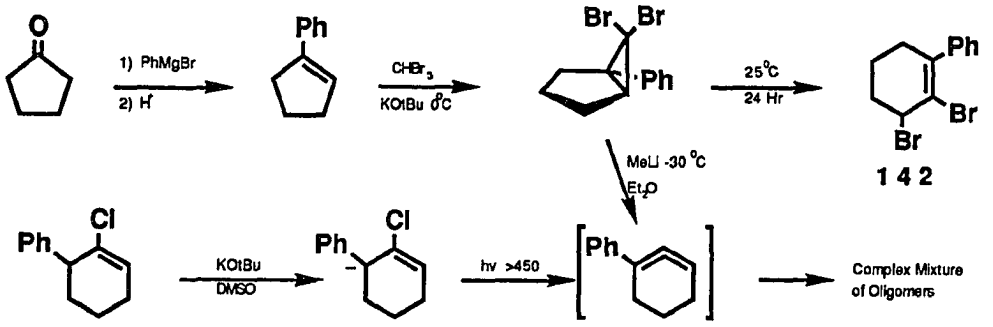
Scheme 54. This follows the general carbenoid route employed in the synthesis of most cyclic allenes.[87] Reaction of cyclopentanone (**139**) with phenylmagnesium bromide yields the corresponding alcohol which is dehydrated with *p*-toluenesulfonic acid to give 1-phenyl-1-cyclopentene (**140**) in 84% yield after distillation. Addition of dibromocarbene to **140** afforded thermally unstable adduct **141** in 20% yield. Dibromide **141** was characterized by ^{1}H and ^{13}C spectra. This strained bicyclic dibromide proved extremely labile, ring opening cleanly to 1,6-dibromo-2-phenyl-1-cyclohexene (**142**) upon standing in chloroform at ambient temperature for 24 hr. Spectra for **142** include a broad singlet in ^{1}H NMR at δ 5.05 and ten resonances in the ^{13}C NMR. Additionally, a strong absorption at 1625 cm^{-1} in the IR spectrum is characteristic of vinylbromides.



Scheme 54

Facile isolation of unrearranged adduct **141** was somewhat surprising, as literature precedent indicated that this might be difficult. The parent compound has been synthesized and is distillable at 60° C under reduced pressure.[82] Substitution has been shown to accelerate rearrangement. In the synthesis of the methyl analogue **141a**, facile rearrangement to isomers **143** and **144** has been reported by Cristl and co-workers (Scheme 55).[96]

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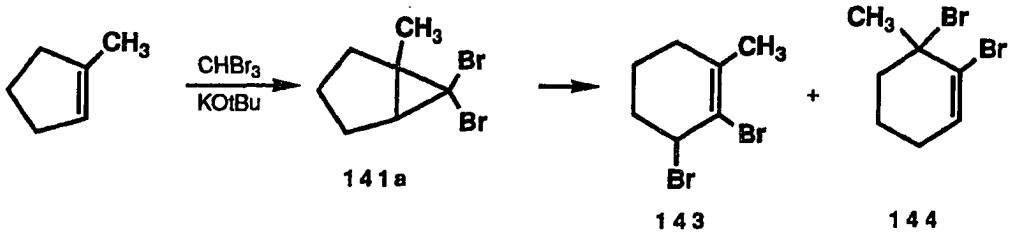
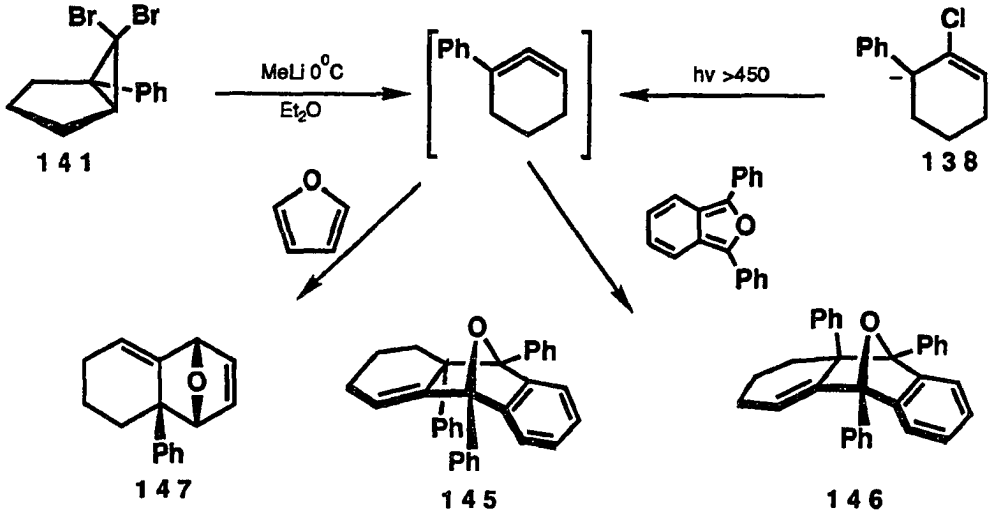


Scheme 55

The addition of methyllithium to **141** at temperatures ranging from -40° C to 0° C resulted in a complex mixture of oligomers. Screening of these mixtures by both HPLC and ^{1}H NMR indicated the presence of up to twelve components. The complexity of the mixtures precluded isolation of individual components. Treatment of **141** with methyllithium in the presence of diphenylisobenzofuran (DPIBF), however, gave adducts **145** and **146** in a ratio of 1:4 (Scheme 56). Importantly, this ratio proved identical with that obtained by photo-dehalogenation of carbanion **138**.



Scheme 56

Assignment of **146** as the *exo* isomer was facilitated by comparison of spectral data with that from adduct **147** (Scheme

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56), for which the exact stereochemistry was determined by X-ray diffractometry.[95] Spectral data for **146** include a doublet of doublets in the ^1H NMR at δ 5.94, a triplet of doublets at δ 2.67, and a doublet of triplets at δ 0.95. The ^{13}C NMR showed 26 resonances. A 2-D COSY spectrum revealed the resonances at δ 2.67 and δ 0.95 were coupled, and that both hydrogens were located on C_8. Models indicate the pseudo-axial hydrogen on C_8 is forced into the anisotropic shielding region of the benzofuran moiety, therefore, shifting it upfield to δ 0.95. The substantial downfield shift of the pseudo-equatorial hydrogen on C_8 results from deshielding by the *exo*-phenyl group on C_8' which is conformationally biased due to non-bonded interactions.

Spectral data for the *endo* isomer **145** seem less influenced by phenyl substituents. The vinyl resonance appears as a doublet of doublets in the ^1H NMR at δ 5.77, and the aliphatic region displays three multiplets at δ 1.25, δ 1.48, and δ 1.94.

The cycloaddition of allene **137** with DPIBF is regiospecific and displays high stereoselectivity, despite the high reactivity and expectation of a highly nonsynchronous mechanism.[97] Initial bonding at the central allene carbon relieves ca. 30 kcal/mol of strain;[81] this is followed by closure at the sites of higher odd electron density. AM1 calculations of **137** predict a chiral allenic structure (Figure 21), with C1-C2-C3 angle of 134°, slightly less than the parent compound. Frontier MO coefficients are greater at the styryl centers, which is also consistent with the observed regiospecificity.

In conclusion, 1-phenyl-1,2-cyclohexadiene (**137**) has been synthesized and trapped using the standard carbenoid approach. It now represents the smallest member of its homologous series. Tolbert and Nural Islam attempted a synthesis of the next member in

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the series, 1-phenyl-1,2-cyclopentadiene, by photodehalogenation of the appropriate precursor, however, this appears to have failed.[95]

Attempts at the Synthesis of 1,2-Cyclopentadiene (131)

Introduction. 1,2-Cyclohexadiene (**132**) is currently the smallest cyclic allene for which unequivocal proof of existence has been demonstrated.[90] The next lower homologue, 1,2-cyclopentadiene (**131**), has remained elusive, even though its synthesis was first attempted in 1935 by Favorski.[98] The primary objective of this research therefore, was the synthesis and trapping of **131**. Eventually this led to the development of a new synthetic methodology, which has allowed access to several classes of highly strained molecules (*vide* infra).

Johnson *et al.* reported theoretical studies on the structure and barrier to inversion of several small-ring cyclic allenes.[81] Their calculations led to the prediction that **131** may exist as a chiral allenic structure, with a low barrier for racemization. They concluded that, "confirmation must await the results of careful experimentation."

There are several reports on efforts directed toward the synthesis of **131** or derivatives thereof. Favorski first attempted the synthesis of **131** in 1935 by reaction of sodium with dibromide **148** (Scheme 57).[98] Although successful for larger rings, this approach appears to have yielded only diene **149**. In 1972, Wittig and Heyne investigated the dehydrohalogenation of 1-bromo-1-cyclopentene (**150**), a technique employed successfully for the synthesis of 1,2-cyclohexadiene. Allene **131** was not produced; instead, cyclopentyne (**151**), the smallest known cyclic alkyne,

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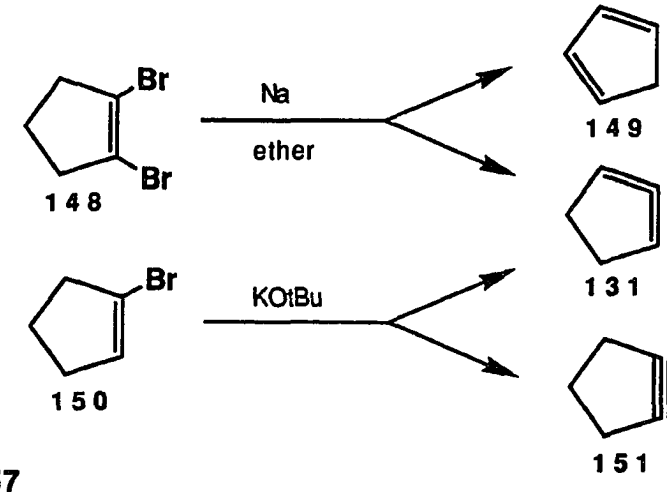
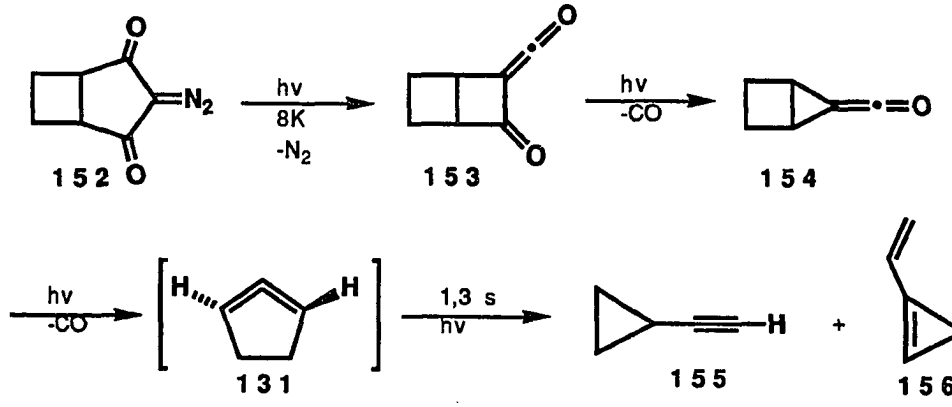


Scheme 57

was trapped.[99] Chapman has postulated the existence of **131** generated in a low temperature argon matrix (Scheme 58).[100] Photochemical Wolff rearrangement of diazodione **152** at 8K gives keto-ketene **153** which undergoes photodecarbonylation to **154**. Irradiation of **154** yields cyclopropylacetylene (**155**) and 1-vinylcyclopropene (**156**), products which the authors suggest are sensibly derived by [1,3s] sigmatropic rearrangement from **131**. The rate of destruction of **131** was too rapid to allow its detection by IR. These experiments have only briefly been described in a rather terse review.[100]



Scheme 58

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Several other structures containing the five-ring allene subunit have been proposed (Figure 22). The possibility that cyclopentatriene **157** may exist as a chiral structure was ruled out on the basis of ESR studies, which favored $^3B_1$ **158** as the ground electronic state.[101] Confirmation of this came from ab initio (HF/3-21G) calculations which predicted **158** to be a minimum.[102] Tolbert and Siddiqui explored the potential intermediacy of the 4,5-benzannelated allene **159**; however, all of the observed chemistry was best described as originating from isoindenylidene **160**.[103]

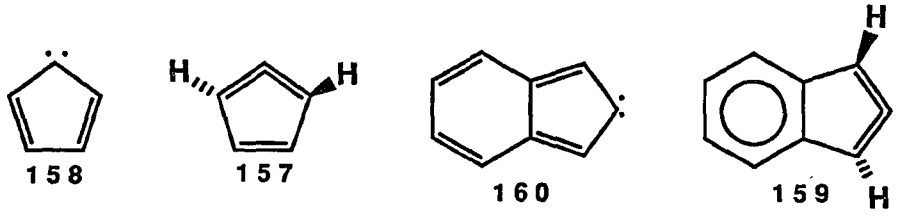
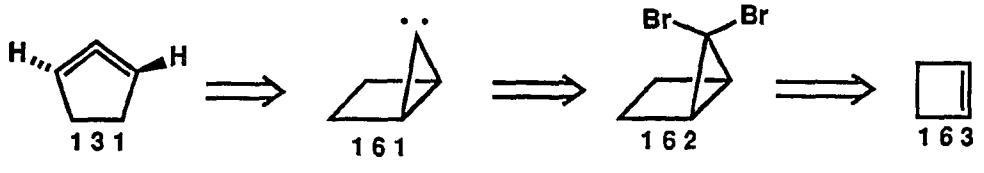


Figure 22. Derivatives of 1,2-cyclopentadiene

The most logical approach to **131** should be through cyclopropylidene **161**, which is accessible from dibromocyclopropane **162** upon reaction with methyllithium. Dibromide **162** should be available directly from addition of dibromocarbene to cyclobutene (**163**, Scheme 59). We anticipated that adduct **162** would be extremely labile, however, its generation and subsequent reaction at low temperature should obviate the need for isolation.



Scheme 59

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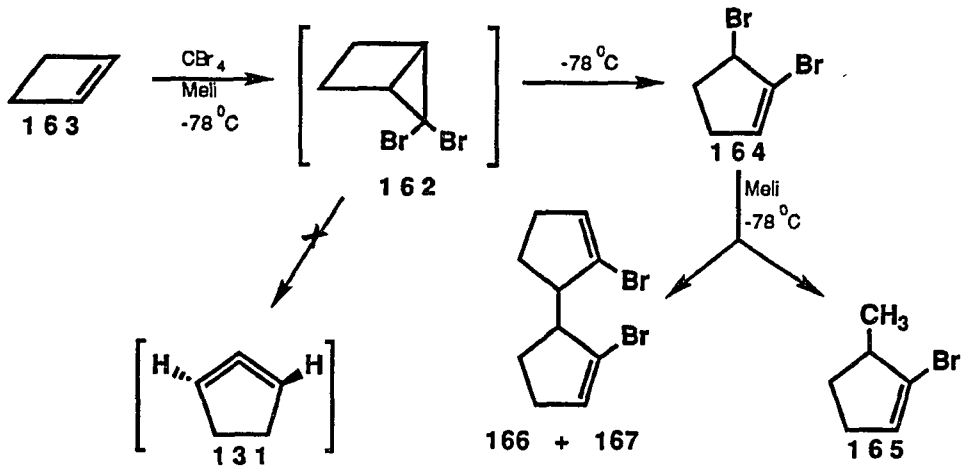
Results and Discussion The synthesis of cyclobutene (**163**) has been reported.[104] This is conveniently prepared from cyclopropylmethanol in three steps. To determine the stability of **162**, it was first generated at low temperature by addition of dibromocarbene (CBr_4/MeLi) to **163**, followed by warming to ambient temperature, and normal work up. Crude ^1H NMR revealed that it had apparently ring-opened to 1,5-dibromo-1-cyclopentene (**164**, Scheme 60). The structure of **164** was unequivocally assigned after isolation by low temperature chromatography (-11° C) and further characterization (^1H, ^{13}C, GC-MS). We have learned that Christiansen has independently prepared **164**.[105]



Scheme 60

In order to synthesize allene **131**, **162** was generated at -78° C, allowed to stir for 15 minutes, and reacted with an additional equivalent of methyllithium. After warming to 0° C, workup under nitrogen yielded three compounds, as determined by capillary GC (1:2:2). The first was identified as 1-bromo-5-methyl-1-

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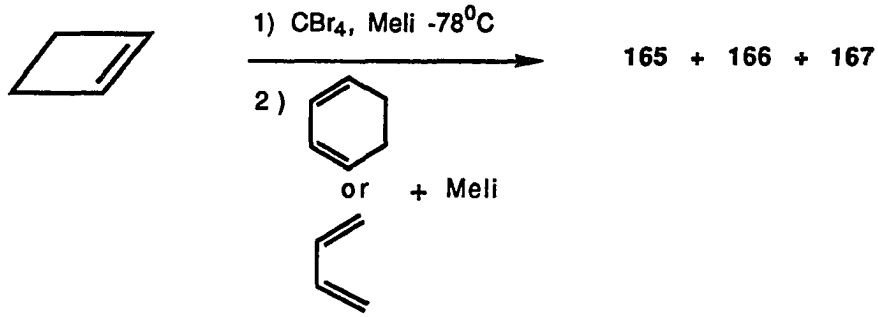
cyclopentene (**165**, ^1H, ^{13}C, GC-MS) after isolation by GLC on QF-1. The remaining two compounds were separated by GLC, and determined to be $C_{10}H_{12}Br_2$ isomers by GC-MS. Both compounds displayed an apparent quartet at δ 5.93, multiplets at δ 3.20 in the ^1H NMR, and five ^{13}C resonances. A DEPT sequence provided the carbon multiplicities and the structures were assigned as stereoisomeric products **166** and **167** (*meso* and *dl*).

The possibility that small amounts of **131** were being produced and not dimerizing in the fashion predicted, led us to perform several trapping experiments. After initial generation of dibromocyclopropane **162** as described above, 1,3-cyclohexadiene was added before the second equivalent of methyllithium was introduced. Workup under nitrogen, however, again yielded only the three adducts **165-167** described above. Reactions with DPIBF as the trap led to similar results (Scheme 61).



Scheme 61

The above data imply that dibromocyclopropane **162** is formed at -78° C and rearranges in its nascent state to the more stable 1,5-dibromide **164**. This then reacts with an additional equivalent of methyllithium, yielding **165**, or promotes coupling to **166**, and **167**. The extreme lability of **162** at -78° C was indeed surprising as the

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next higher homologue in the series, the precursor to 1,2-cyclohexadiene (**132**), is a distillable liquid at 60° C (10 mm Hg),[82] 138° C higher in temperature!

To increase the possibility of observing reactions of **131**, we attempted its generation at lower temperatures. Methyllithium was added to an etheral solution containing cyclobutene (**163**) and carbon tetrabromide at -105° C. The mixture was stirred for several minutes before an additional equivalent of methyllithium was added. After warming to 0° C, and workup, no evidence could be found for the formation of **131** (^{1}H, GC-MS). Reactions in the presence of several traps yielded similar results. Throughout these experiments, GC-MS proved to be an efficient method for screening reaction mixtures.

It is well documented that dichlorocyclopropanes undergo ring opening less easily than their dibromo counterparts.[106] We therefore undertook the synthesis of **168**, the dichloro analogue of **162** with expectations that increased stability would prevent ring opening. Bicyclic **168** was synthesized by the addition of dichlorocarbene (CCl_4/nBuLi) to cyclobutene (**163**) at -78° C (Scheme 62). Upon warming to ambient temperature, however, **168** ring-opened to 1,5-dichloro-1-cyclopentene (**169**)[107] as determined spectroscopically (^{1}H, ^{13}C, GC-MS). Generation of **168** at -78° C, followed by a second equivalent of nBuLi, yielded **170** as the primary product (> 64%) as determined by ^{1}H NMR and GC-MS.[108] No evidence for the formation of **131** could be observed. Attempted generation of **131** in the presence of 1,3-butadiene or 1,3-cyclohexadiene as traps resulted again in formation of **170**.

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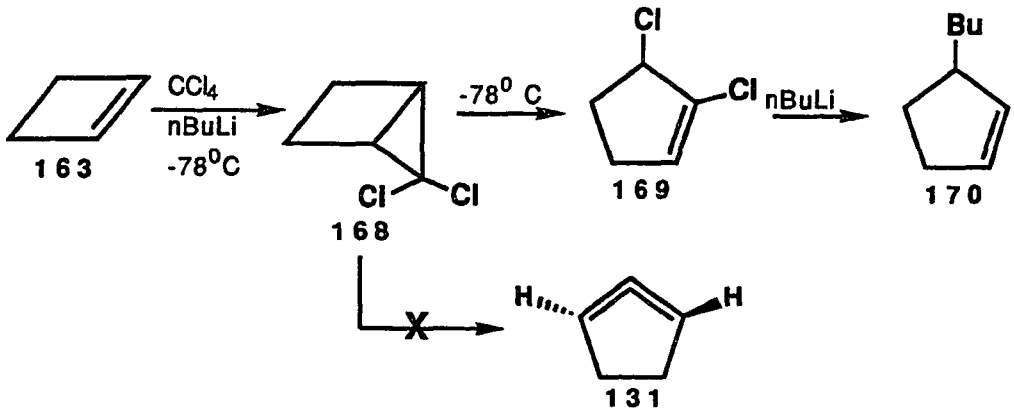
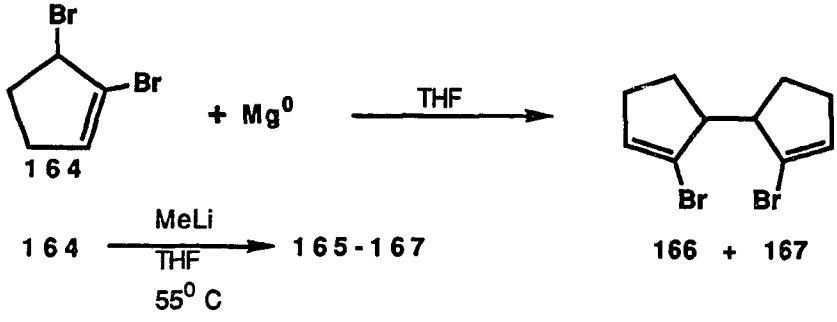


Scheme 62

As with the dibromo adduct **162**, **168** appears to rearrange immediately at temperatures as low as -78° C. In the presence of excess nBuLi, substitution at the allylic position, followed by lithium-halogen exchange at C-1, results predominantly in the formation of **170**.

Our inability to find a suitably stable precursor to **131** led us to investigate the potential of rearranged dibromide **164** as a progenitor to allene **131**. This method has been used successfully in the synthesis of 1,2-cyclohexadiene (**132**), by reaction of dichlorocyclohexane **171** with either sodium or magnesium



Scheme 63

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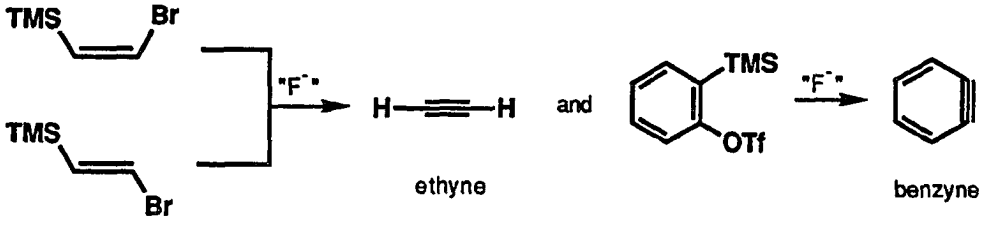
(Scheme 63).[90] Dibromide **164** was reacted with activated magnesium[109] at a variety of temperatures (0° C - (+) 60° C), with and without chemical traps (Scheme 63). Under all circumstances, coupling adducts **166** and **167** were observed as the major products; no evidence for the formation of **131** could be detected. In addition, **164** was reacted with methyllithium at elevated temperatures (60° C), however, only **165-167** could be detected.

We then began to research alternative methods for introducing strained double bonds. It has been known for some time that ß-halosilanes are suitable precursors to alkenes. Exposure to alkoxide or hydroxide ion leads to an "E2-like" mechanism.[110] Cunico and Dexheimer extended the methodology to the synthesis of alkynes through fluoride induced elimination of ß-halovinylsilanes, eventually developing suitable precursors to benzyne (Scheme 64).[111]



Scheme 64

Implementation of the methodology in syntheses of strained alkenes was first demonstrated by Chan and Massuda, who synthesized and trapped **173** from reaction of **172** with cesium fluoride.[112] (Scheme 65) Since that time, a host of additional strained alkenes have been generated by similar methods (Scheme 66).[79,113] Perhaps the most remarkable aspect of this reaction is the extremely mild conditions under which the reaction is carried out,

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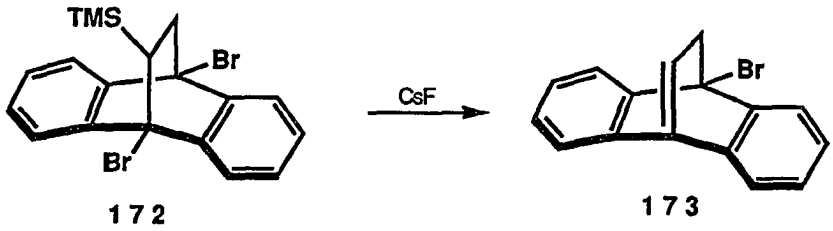
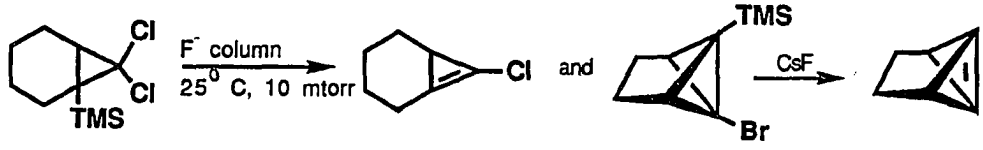


172 173

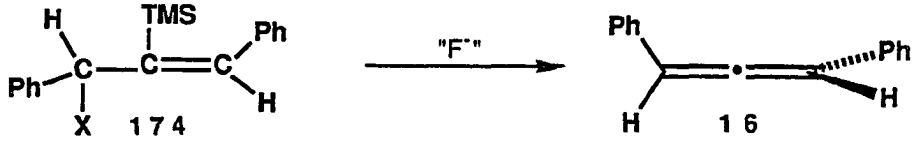
Scheme 65

typically 20° C, CsF/DMSO. This allows for generation of these species in the presence of other functional groups, which is important if they are to find more use as reactive intermediates in the synthesis of complex molecules.



Scheme 66

This methodology should also lend itself to the synthesis of allenes. In 1974, Chan and Mychajloskij synthesized diphenylallene (**16**) from the fluoride induced elimination of trimethylsilane **174**



174 16

Scheme 67

(Scheme 67). They later extended the methodology to a variety of substituted allenes reporting very clean reactions and moderate yields.[114] In principle, a similar approach should yield strained

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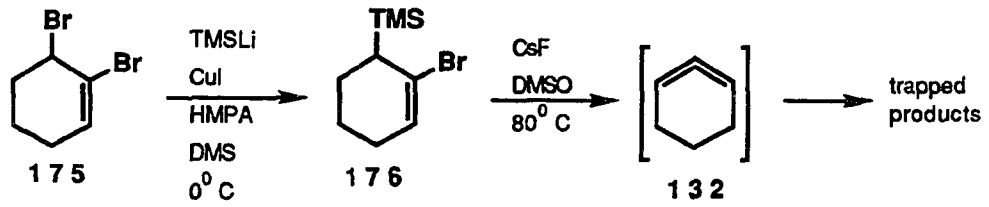
allenes; however, a thorough investigation of the literature produced no examples supporting this notion.

In order to explore the potential of this methodology in the synthesis of strained allenes, we chose 1,2-cyclohexadiene (**132**) as a target molecule. Diene **132** embodies considerable strain (≈ 31 kcal/mol), and the chemistry of **132** is relatively well characterized.[90] A suitable precursor to allene **132** is the substituted silane **176** which was synthesized several years ago by Denmark.[115] Silane **176** is conveniently prepared through a coupling reaction of the corresponding allylic dibromide **175** with TMSCuLi, following a general protocol first reported by Smith (Scheme 68).[116] Treatment of **176** with CsF in DMSO in the presence of DPIBF at 80° C, resulted in a 76% combined yield of two stereoisomeric cycloadducts in a ratio identical with that previously reported.[117,90]



Scheme 68

The remarkable efficiency and apparent generality of the above method in the synthesis of strained allenes should make it an excellent alternative to existing methods, particularly in the presence of other functional groups. With this new methodology in hand, we next returned to the synthesis of 1,2-cyclopentadiene (**131**).

A synthesis of appropriately substituted trimethylsilane precursor **177** had been previously described in the literature.[115] It

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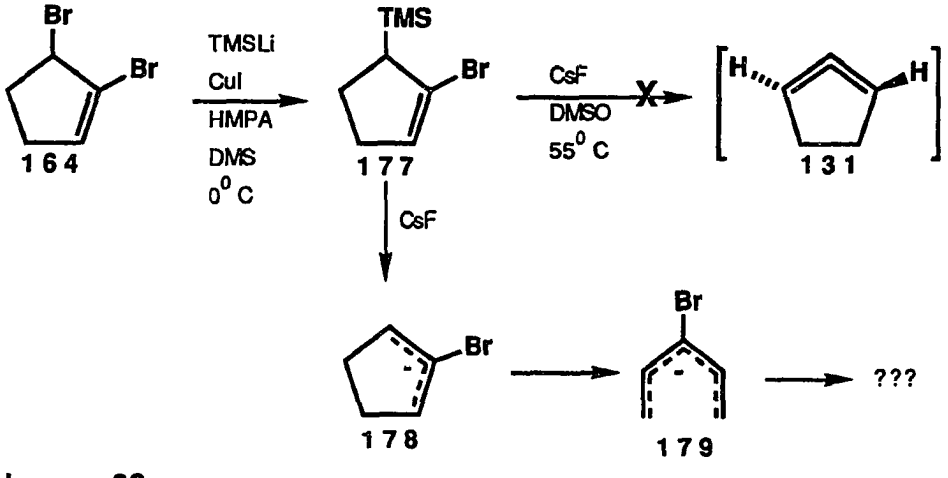
was prepared through a coupling reaction of allylic dibromide **164** with TMSCuLi in 33% yield after chromatography on silica gel (hexane, -11° C). Treatment of **177** with CsF in DMSO in the presence of DPIBF at ambient temperature yielded no adducts which could be attributed to the intermediacy of allene **131**. The reaction was conducted at 30° C, 60° C, and 80° C; however, this did not significantly alter the results. ^{1}H NMR analysis of the crude material indicated that starting silane **177** had been completely consumed, however, there were no aliphatic resonances which would result from adduct formation. Chromatography on silica gel yielded only DPIBF (Rf = 0.49, hexane/chloroform, 3:1) and baseline material. ^{1}H NMR of the baseline material showed only aromatic resonances, no aliphatic resonances were present. Attempts to trap any volatile components formed in the reaction mixture failed.



Scheme 69

Perhaps more disturbing than our apparent inability to generate 1,2-cyclopentadiene (**131**) is the absence of any isolable products suggesting alternative reactions. By ^{1}H NMR the starting silane **177** is completely consumed; however, it is unclear what is

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being generated. Attack by fluoride ion on silicon would be accompanied presumably by loss of bromide ion in accordance with the accepted E2 mechanism. This suggests that allene **131** may be formed initially, but is so short lived, it escapes trapping and undergoes further chemistry. An alternative mechanism is one involving more E1cb character. Initial elimination of the TMS group would yield allyl anion **178**, which can undergo disrotatory electrocyclic ring opening to give pentadienyl anion **179** (Scheme 69).[118] This second mechanism may be more favorable than that involving allene formation, as that would be accompanied by a considerable increase in total strain energy (≈ 41 kcal/mol).

Future Work. There are several other routes which in principle may yield allene **131**. The first employs a regioisomer of previously described silane **177** where the TMS group is now substituted at the vinyl position. The possibility of ring opening as postulated for **177** is then diminished, and the propensity for allene formation may be increased.

Scheme 70 outlines a logical route to a substituted vinylsilane **183** where X represents a good leaving group. A synthesis of allylic alcohol **182** was eventually achieved, however, conversion of the alcohol functionality to a suitable leaving group was only briefly investigated. 2-Trimethylsilyl-2-cyclohexen-1-one (**181**) was prepared in six steps from the parent cyclopentenone **180** as described in the literature.[119] Reduction of **181** with Luche's reagent ($NaBH_4/CeCl_3$) resulted in the formation of alcohol **182**; however, considerable amounts of the fully saturated alcohol were also present (4:1). This problem was overcome by reduction with 9-BBN which resulted in the sole formation of allylic alcohol **182** in 56% overall yield after chromatography.

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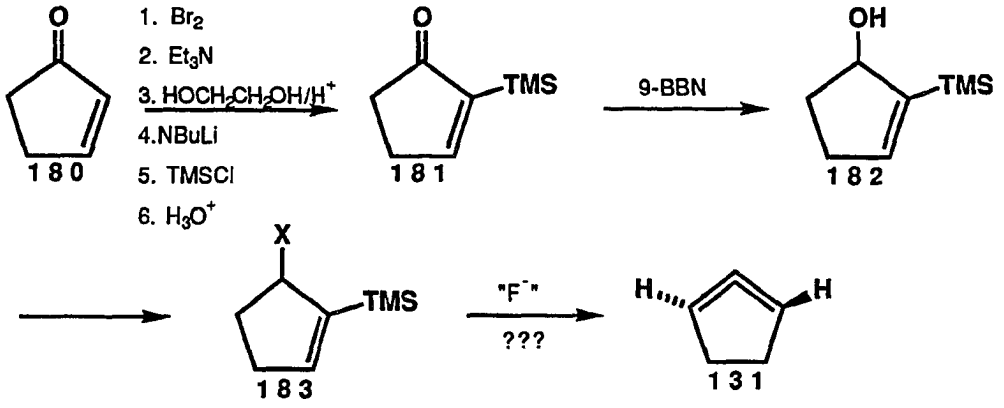

Scheme 70

Conversion of the alcohol functionality to a suitable leaving group X was briefly explored, and preliminary results suggest that these compounds may be extremely unstable. Attempted formation of the triflate using trifluoromethanesulfonic anhydride/triethylamine (0° C) resulted in formation of a black intractable mixture. The chloride (X = H) was eventually synthesized and isolated by reaction of alcohol **182** with tosyl chloride/pyridine (catalytic DMAP) in methylene chloride; however, limited quantities prohibited rigorous characterization. Alternatively, generation of an appropriate leaving group in situ, and further reaction with cesium fluoride, may be necessary.

The second potential pathway to **131** is through bromofluoro-cyclopropane **184**, which should be attainable from the addition of bromofluorocarbene to cyclobutene (**163**, Scheme 71). The strength of the C-F bond makes fluorine less susceptible to migration than either bromine or chlorine and would in principle stabilize cyclopropane adduct **184**. This should then open to allene **131** upon addition of MeLi at reduced temperatures. Several years ago, Christl and Braun reported the isolation of **185**, whereas the

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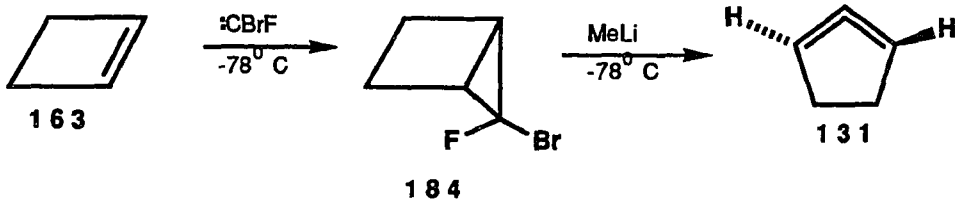
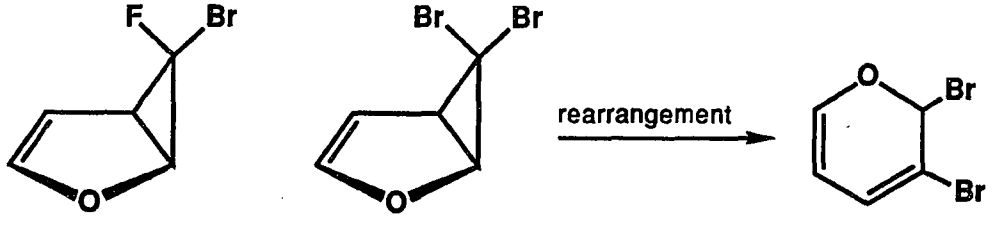
dibromo analogue **186** underwent rapid rearrangement (Scheme 72).[96] This differential stability is a consequence of well known stereoelectronic requirements for disrotatory ring opening.



163 **184** **131**

Scheme 71



185 **186**

Scheme 72

In summary, the results concerning the synthesis of 1,2-cyclopentadiene are inconclusive. The standard carbenoid route using dibromocarbene or diclorocarbene fails due to the inherent instability of both cyclopropane precursors. The instability of both precursors was indeed surprising as the dibromocarbene precursor to the next higher homologue in the series, 1,2-cyclohexadiene, is a distillable liquid at 60° C (12 mm), 138° C higher in temperature. A synthesis of the bromofluoro analogue may eventually permit the synthesis of **131**.

The inability of substituted silane **177** to undergo fluoride induced elimination to **131** was suprising in light of the ease with

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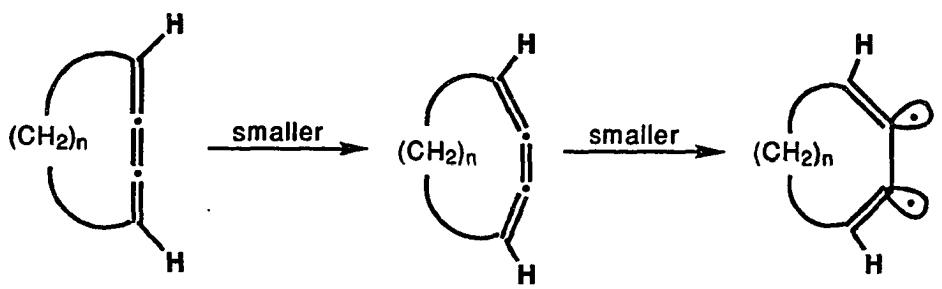
which 1,2-cyclohexadiene (**132**) was made by the same route. It would appear to be a direct reflection of the increase in strain in going from **132** to **131**. Nonetheless, the route should allow convenient access to larger ring allenes under relatively mild conditions. This is currently being investigated in our laboratory.

Cyclic Butatrienes: The Synthesis of 1,2,3-Cyclohexatriene (199)

Introduction

Butatrienes comprise the third member of the homologous series of unsaturated hydrocarbons known as cumulenes. The two central carbon atoms are sp hybridized; therefore, the preferred geometry for acyclic systems is linear. Bending of the triene functionality through incorporation into successively smaller rings engenders considerable strain, and like allenes, a smooth transformation from shelf stable species to reactive intermediates is observed. The increased strain in cyclic butatrienes is due principally to in-plane bending of the central C_2-C_3 π bond away from linearity. Bending will be accompanied by rehybridization (Scheme 73) at C_2 and C_3 from sp to sp^2.



Scheme 73

Strain estimates for the series of cyclic butatrienes from C_9 to C_5 have been reported by Johnson and Angus, who employed MNDO calculations.[120] The corresponding values of 8.0, 14.0, 31.5, 60.5,

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and 130 kcal/mol, were estimated by bending 1,2,3-butatriene, and comparison with predicted cyclic structures. These results indicate

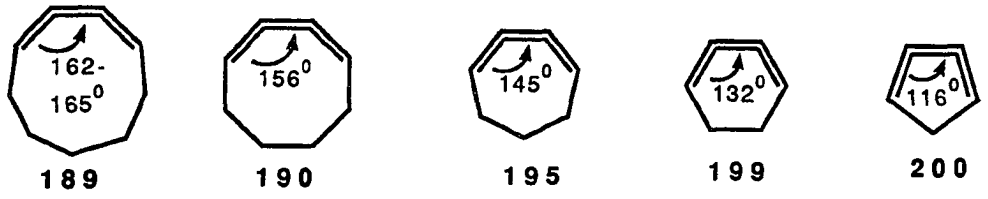
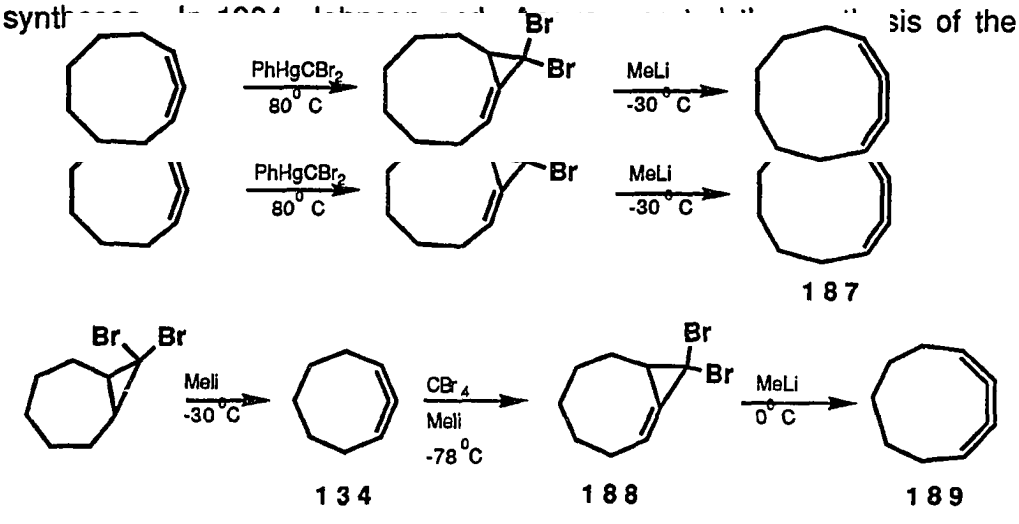


Figure 23. Bending angles of cyclic butatrienes

an approximate doubling of the strain energy for each subsequent removal of a methylene group. The internal C_1-C_2-C_3 bond angles decrease from 163° to 116° in going down the series (Figure 23).

1,2,3-Cyclodecatriene (**187**) is the smallest unsubstituted cyclic butatriene for which there should be little distortion of the triene moiety. Triene **187** was first reported by Moore and Ozretich in 1967.[121] The authors employed standard carbenoid chemistry (Scheme 74) in the synthesis of **187**, a protocol used in allene synth[illegible]sis of the



Scheme 74

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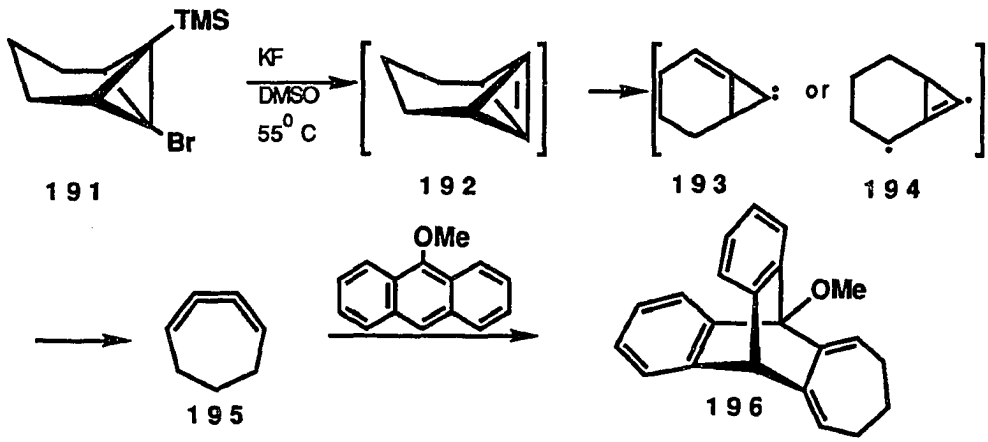
next lower homologue in the series, 1,2,3-cyclononatriene (**189**), through the use of similar chemistry. Generation of allene **134** at -30° C, followed by the addition of dibromocarbene yielded **186**, which ring opened to **189** upon exposure to methyllithium at reduced temperature (Scheme 74).[120] Butatriene **189** proved stable at ambient temperature in dilute solutions, but rapidly polymerized upon concentration or exposure to air. A synthesis of 1,2,3-cyclooctatriene (**190**) has not been reported, although strain estimates indicate it should be easily made. Its kinetic stability is unpredictable.

Szeimies *et al.* reported a truly remarkable synthesis of the next member of the series 1,2,3-cycloheptatriene (**195**).[79a] Treatment of **191** with KF in DMSO at 55° C yielded alkene **192** which was trapped with a variety of dienes. Unexpectedly, triene **195** was formed and trapped with 9-methoxyanthracene to give adduct **196.** The authors proposed rearrangement of initially formed alkene **192** to triene **195** by either intermediate **193** or **194**, followed by subsequent trapping.



Scheme 75

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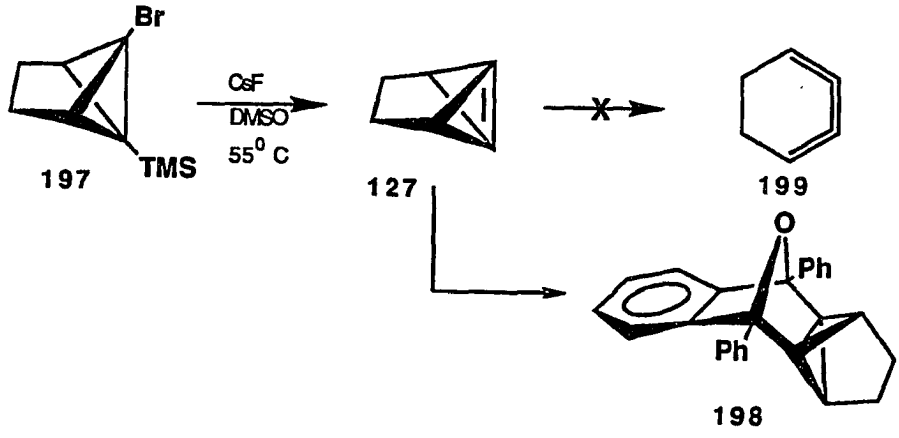
In view of the preceding result, the authors attempted a similar approach to 1,2,3-cyclohexatriene (**199**).[79b] Starting with the appropriately substituted bicyclic silane **197**, treatment with CsF in DMSO at 80° C in the presence of DPIBF yielded only adduct **198** (Scheme 76). The authors noted that transformation of **127** to **199** is considerably more exothermic than isomerization of **192** to **195** and, therefore proceeds at lower temperatures. This is corroborated by strain estimates which predict that **199** is roughly twice as strained as **195**.[120] There have been no reports on the synthesis of the next member in the series, 1,2,3-cyclopentatriene (**200**).



Scheme 76

From the preceding discussion it is clear that routes to cyclic butatrienes are sparse. The addition of dibromocarbene to cyclic allenes followed by ring opening, is suitable for larger systems, however, its adaptation in construction of smaller homologues is foiled by the instability of small ring allenes.[90] One fundamental goal of this project was the development of a synthetic methodology that would allow access to cyclic butatrienes, independent of ring

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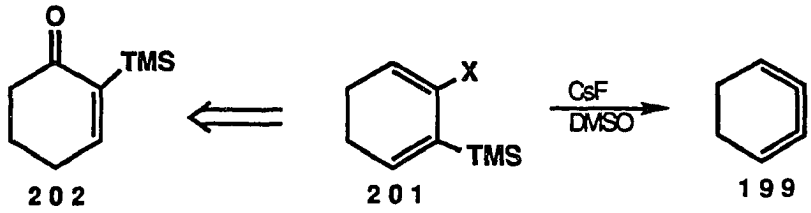
size. Such a methodology would render such compounds readily available and increase their use as reactive intermediates in synthesis.

Another goal of the project was to redefine the current known limitations of cyclic butatrienes. To date, the smallest existing cyclic compound containing three contiguous double bonds is 1,2,3-cycloheptatriene (**195**). The synthesis of 1,2,3-cyclohexatriene (**199**) would not only redefine this limitation, but it would also be of interest as a new isomer of benzene isomer.

Synthesis and Trapping of 1,2,3-Cyclohexatriene (199)

The most logical precursor to triene **199** was thought to be vinylsilane **201**, where X is a good leaving group (Scheme 77). As described previously for 1,2-cyclohexadiene (**132**) and several strained alkenes, **199** should be accessible by introduction of the strained π bond through fluoride induced elimination of vicinal trimethylsilyl and X groups. We chose this route because of the extremely mild conditions under which **199** may be generated. Retrosynthetically, **201** was best envisioned as originating from TMS-enone **202** whose synthesis has been described in the literature.[119]



202 **201** **199**

Scheme 77

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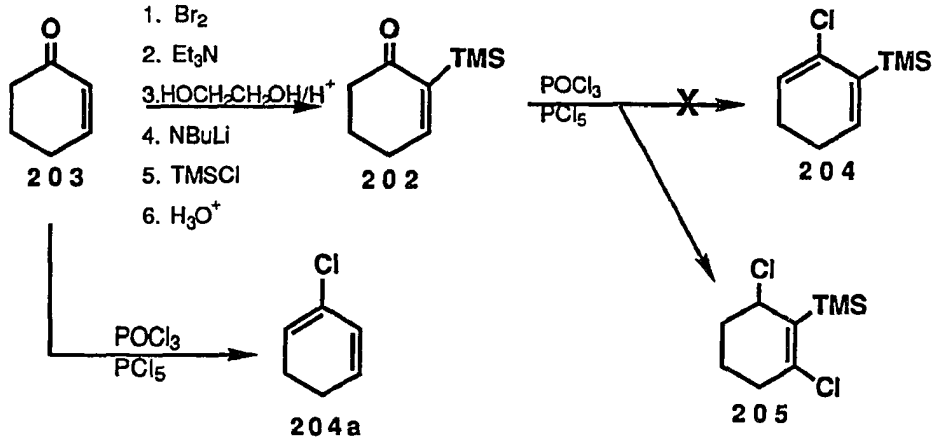
The synthesis of starting TMS-enone **202** was accomplished in six steps from 2-cyclohexen-1-one (**203**) as described in the literature (Scheme 78).[119] Reaction of **202** with an equimolar mixture



Scheme 78

of PCl_5 and $POCl_3$[122] resulted in the formation of dichloride **205**, however, instead of the desired diene **204**. Dichloride **205** was characterized by normal spectroscopic methods (^1H, ^{13}C NMR, GC-MS) after isolation by chromatography (silica gel/hexane, 38% yield). The formation of alkene **205** was surprising; Axelrad had reported the conversion of enone **203** to 2-chloro-1,3-cyclohexadiene **204a** in 98% yield by the same methodology.[122]

Upon further scrutiny, it became apparent that dichloride **205** was a suitable precursor to diene **204** provided 1,4-elimination could be achieved in preference to 1,2-elimination. Reaction of **205** with DBU/DMSO at room temperature resulted in both dienes **204** and **206** (3:2, GLC) in 38% overall yield (Scheme 79). These isomers were inseparable, however, by normal chromatographic methods. Separation was achieved by capillary GC, but, all attempts using preparative columns resulted in complete aromatization.

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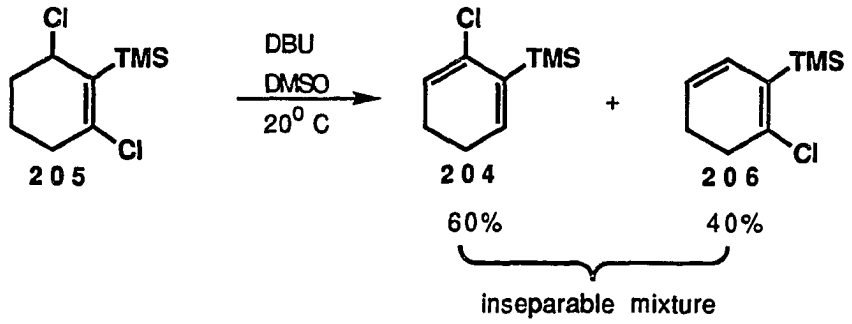

Scheme 79

An alternative route to diene **201** involves quenching of enolate **207** with a reagent capable of generating a good leaving group at that position. McMurry and Scott had previously published a report on the conversion of several enones to enolates, and their subsequent conversion to triflates upon reaction with N-phenyltriflimide.[123] In principle then, a similar reaction with TMS-enone **202** would yield the corresponding diene **208** with the triflate in the proper ß-position. Significantly, this methodology would appear to be ring size independent, and should permit the synthesis of many butatrienes.

Deprotonation of TMS-enone **202** under kinetic conditions with lithium diisopropylamide (LDA), followed by addition of N-phenyltriflimide (Scheme 80), gave the 1,3-diene **208** in 58% yield after chromatography (silica gel/hexane). Spectral data for **208** include two triplets at δ 6.28 and δ 5.75 in the ^1H NMR, seven resonances in the ^{13}C NMR, and $M^+ = 300$ in the mass spectrum.

The conversion of diene **208** to 1,2,3-cyclohexatriene (**199**) followed the normal desilyation protocol for introduction of strained double bonds. Reaction of **208** with CsF in DMSO at 25° C in the presence of DPIBF afforded crystalline adduct **209** in 24% yield after chromatography (silica gel, 3:2 hexane/CH_2Cl_2). Spectral data

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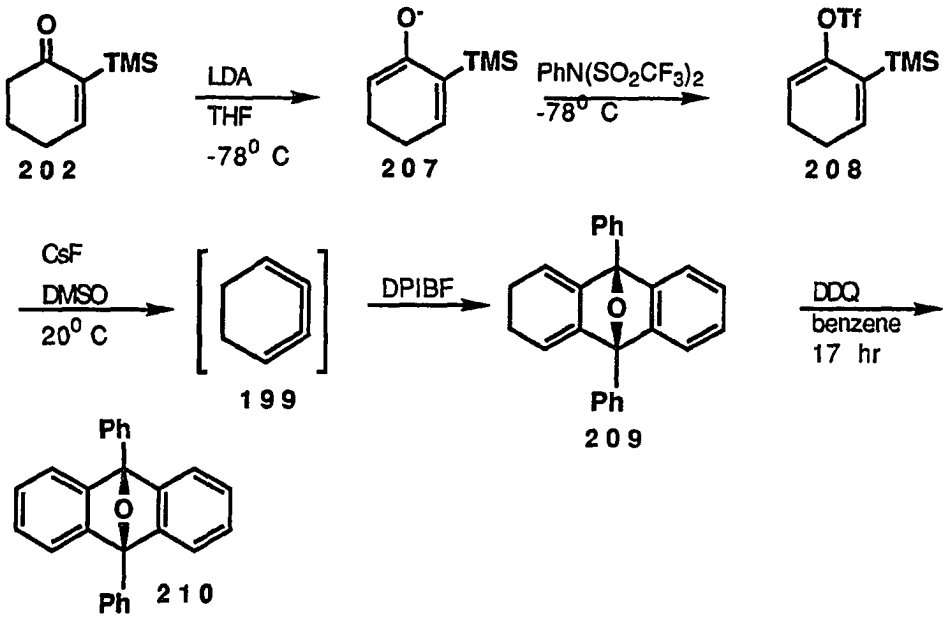

Scheme 80

for **209** include a broad singlet at δ 5.69 and a multiplet at δ 2.20 in the ^{1}H NMR, 11 resonances (C_s symmetry) in ^{13}C NMR, and M+ = 348 in the mass spectrum. Additional support for diene **209** came from its DDQ oxidation to the fully aromatic structure **210**, which was reported previously in the literature.[124]

Ample literature precedent supports the conclusion that **209** is formed from [2 + 4] cycloaddition of cumulene **199** at its most strained π bond.[77,79b,90] The exclusive reaction at the C_2-C_3 bond is in good agreement with the relief of ca. 50 kcal/mol of total strain energy. Conversely, addition across the C_1-C_2 double bond would result in a substituted allene with ca. 31 kcal/mol of strain energy; it is therefore not observed.

Cumulene **199** is highly strained; it was conjectured that it might undergo thermally allowed disrotatory ring opening to 1,5-hexadien-3-yne (**211**) before reacting with DPIBF (Scheme 81).

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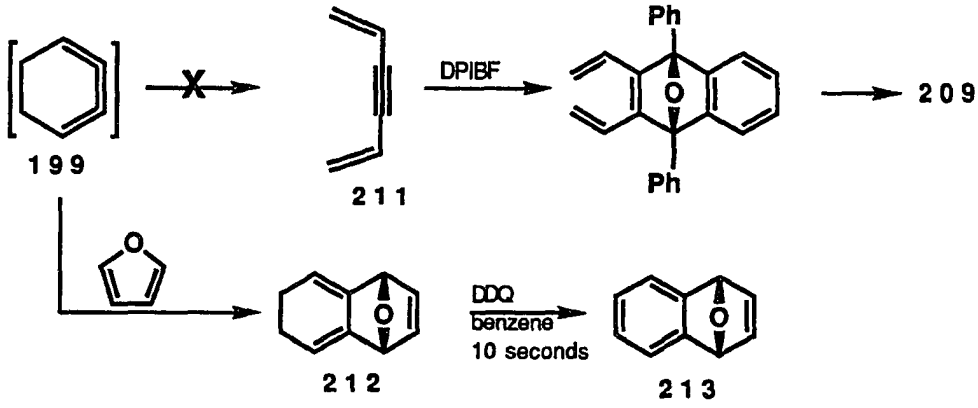

Scheme 81

Reaction of dienyne **211** with DPIBF, followed by thermal ring closure, would also yield the observed adduct **209**. To investigate this possibility, we generated triene **199** in the presence of a less reactive diene trap, which should not undergo Diels-Alder chemistry with dienyne **211**. Generation of **199** in the presence of furan resulted in the sole isolation of adduct **212** in 66% yield after chromatography (silica gel, 9:1 hexane/Et_2O). Spectral data for **212** include three broad singlets at δ 6.40, δ 5.65, and δ 5.19 in the ^1H NMR, five resonances (C_s symmetry) in the ^{13}C NMR, and M+ = 146 in the mass spectrum. Adduct **212** was rapidly oxidized with DDQ to the aromatic structure **213**, whose spectral charateristics have been described elsewhere.[125] We thus conclude that adducts **209** and **212** are formed from [2 + 4] cycloaddition of cumulene **199** at its most strained π bond.

The chemistry of triene **199**, in the absence of traps, was also investigated. Very little is known about the dimerization of strained cyclic butatrienes; however, one might predict formation of dimers, trimers, or tetramers in a manner observed for several cyclic allenes. Generation of **199** in the absence of any traps yielded a

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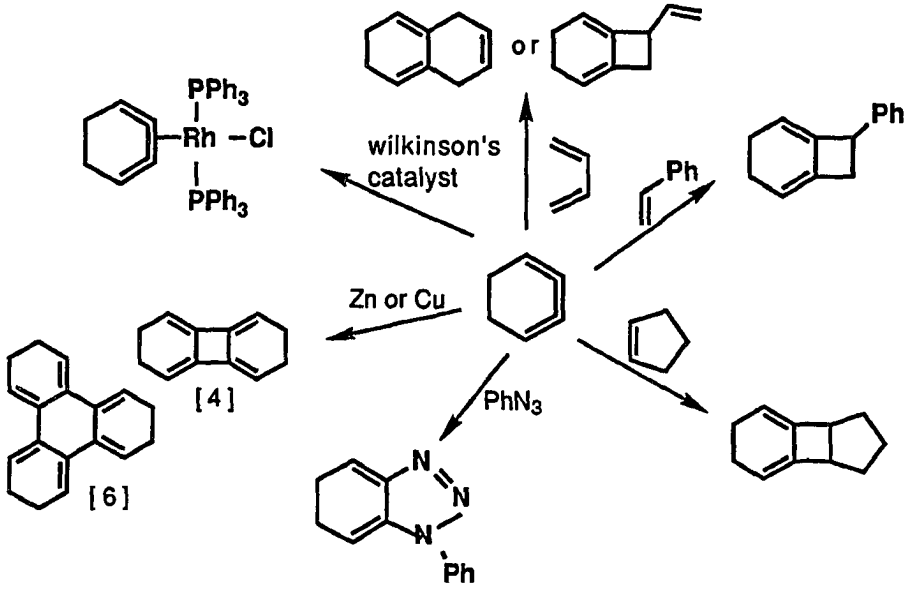
complex mixture of products as determined by ^{1}H and ^{13}C NMR. Attempts at column chromatography failed, leaving only baseline material whose ^{1}H and ^{13}C NMR spectra were extremely complex. The mixture was not intractable, suggesting polymerization did not occur; however, the enormous array of products implies very low selectivity, or highly labile products.

To date, **199** has been trapped only with dienes in Diels-Alder reactions. In the absence of traps, the extreme reactivity of **199** is manifested through its low reaction selectivity and abundance of unrelated products. To completely characterize the chemistry of **199**, its generation in the presence acyclic dienes, alkenes, and dipolar species must be accomplished (Scheme 82). It would also be of interest to trap **199** with transition metals as this might yield a photolytic precursor to butatriene **199**. Additionally, it has been demonstrated that dimerization of acyclic butatrienes is facilitated



Scheme 82

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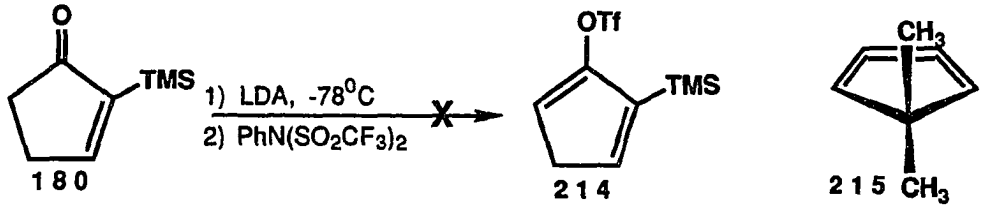
by the presence of metal catalysts such as zinc, nickel, and copper.[126] Generation of **199** in the presence of these might furnish [4]radialene or [6]radialene in the absence of side products (Scheme 82).

Cyclic butatrienes comprise a rich and diverse class of compounds whose chemistry has only recently been investigated. The synthesis of 1,2,3-cyclohexatriene (**199**) redifines the current known limitations for existence of cyclic butatrienes, and



Scheme 83

represents a new benzene isomer. A synthesis of 1,2,3-cyclopentatriene (**200**) would now seem likely but preliminary work on the synthesis of a suitable precursor is, to date, inconclusive. All attempts to convert enone **180** to diene precursor **214**, failed, resulting in very complex mixtures as determined spectroscopically (Scheme 83). Work on a substituted analogue **215**, however, is currently under investigation by another member of the group.

Of perhaps equal importance is the development of what appears to be a very general route to cyclic butatrienes from the corresponding enone. Our group is currently investigating this possibility in the synthesis of both smaller and larger ring homologues. Additionally, preliminary data suggest that 2-TMS-2-

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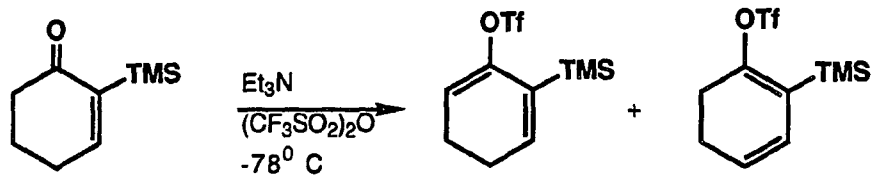
enones may be suitable precursors to cyclic enynes (Scheme 84) depending on reaction conditions. Indeed, routes to these molecules are equally sparse (*vide* infra).



Scheme 84

In summary, 1,2,3-cyclohexatriene may be generated and trapped by well precedented cycloaddition reactions. Both the generality of our synthetic route and the chemistry of this remarkable C_6H_6 isomer are currently subjects of active investigation.

Cycloalkynes and Cycloenynes: Synthesis and Trapping of 1-Cyclohexen-3-yne (240)

Introduction to Cycloalkynes

Cycloalkynes and cycloenynes comprise interesting and fundamental classes of organic molecules for which limitations of structure and isolability have not yet fully been determined. Strain in both classes is introduced by distortion of the linear alkyne moiety through incorporation into consecutively smaller ring sizes. In the case of enynes, the double bond probably contributes very little to total strain. This implies that the smallest ring in which an alkyne functionality may exist, should in principle, accommodate the corresponding enyne. Cyclopentyne (**151**) is the smallest cycloalkyne for which unequivocal proof of existence has been demonstrated; to

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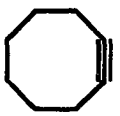
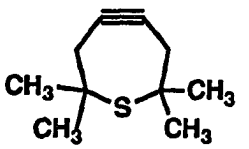
date, no reports on the synthesis 1-cyclopenten-3-yne (**216**) have appeared in the literature.

A large collection of data pertaining to cycloalkynes has been reported in the literature since 1953 when Bloomquist and Liu[127]



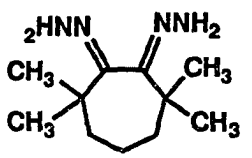
217
stable

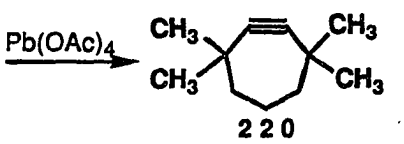
218
1/2 life =
1 min, -25^{0}C



221
stable to 140^0 C

222





220
1/2 life =
1 hr, ambient

Scheme 85

first assuredly synthesized cyclooctyne (**217**).[128] This shelf stable molecule is predicted to have only 10 kcal/mol of strain.[69] A normal C≡C infrared stretch of 2210 cm^{-1} (unstrained typically 2100 cm^{-1}), belies the 22^0 deformation from linearity, reported from electron diffraction studies.[129]

The next member in the series, cycloheptyne (**218**) could not be isolated; it has a half-life of less than a minute in solution at -25^0 C and about one hour at -76^0 C.[130] Krebs and Kimling reported the synthesis of isolable tetramethylcycloheptyne (**220**) from reaction of **219** with lead tetraacetate (Scheme 85).[131a] This substance had a half-life towards dimerization of about one hour at ambient temperature. Remarkably, the sulfur analogue **221** is thermally stable, showing no tendency to dimerize or oligomerize up to 140^0 C![131b] The greater stability of **221** relative to **220** is attributable to

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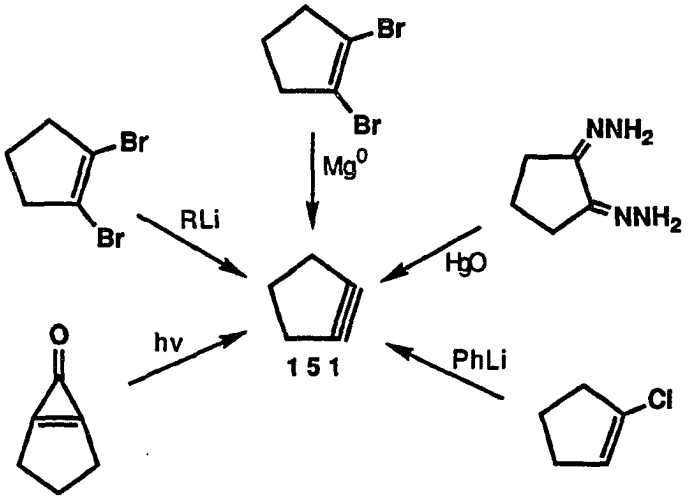
longer carbon-sulfur bonds which ultimately decrease distortion of the triple bond. Cyclohexyne (**222**), the next member in the series, has been observed in an argon matrix and its IR spectrum has been recorded; however, it remains too reactive for study in solution. It has been trapped with platinum and zirconium, and its formation has been inferred from cycloaddition products.[132]

Cyclopentyne (**151**) is the smallest unsubstituted cycloalkyne for which compelling evidence of existence has been demonstrated. MNDO calculations (with CI) predict **151** to be an energy minimum with the C-C≡C-C group distorted some 63° from linearity, and a C≡C bond distance intermediate between double and triple-bond lengths (1.263Å).[133] Interestingly, at the ROHF/3-21G level of theory, the bond angle remains the same; however, the bond length is reduced to 1.238Å.[133] After empirical correction, the ab initio study yielded a C≡C stretching frequency of 1828 cm^{-1}. A number of syntheses of **151** have been reported; several are shown in Scheme 86.[128b]



Scheme 86

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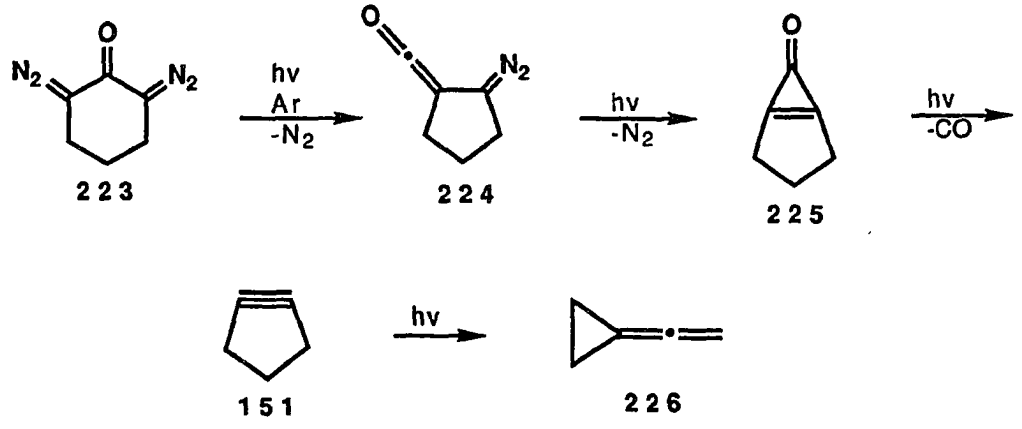
In 1979, Chapman reported on the potential intermediacy of **151** generated in an argon matrix (Scheme 87). Formation of **224** through a photochemical Wolff rearrangement of diazocyclohexanone (**223**), followed by carbene generation and insertion, yielded **225**. Decarbonylation of **225** gave what the authors believed was highly photolabile species **151**, which rearranged immediately to allene **226**.[100] Several other homologues of five ring alkynes are shown in Figure 24.[152]



Scheme 87

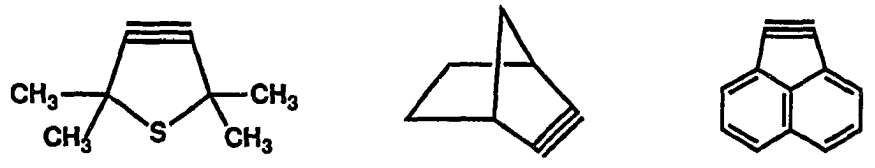


Figure 24. Derivatives of cyclopentyne

The potential existence of the next member in the series, cyclobutyne (**227**), has attracted theoreticians and experimentalists alike as **227** must clearly represent the smallest ring in which this functionality may exist. A report in 1983[134] that **227** represents a

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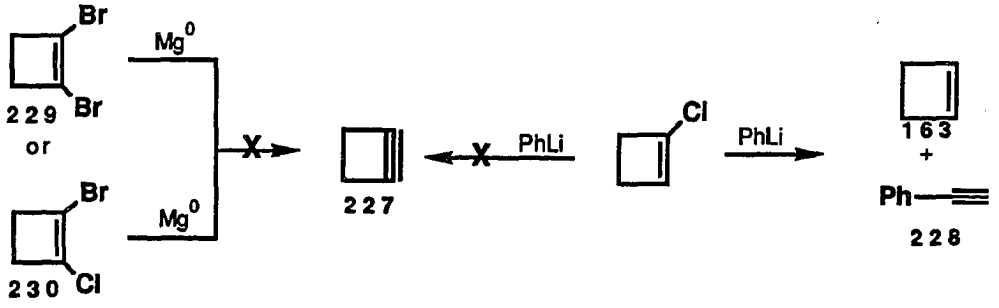
relative minimum on the C_4H_4 potential-energy hypersurface promoted renewed interest; derivatives of **227** now are among planned investigations in our laboratory. Cyclobutyne (**227**) was predicted to have a weak triple bond, however, as indicated by either bond distance (1.26Å) or stretching vibrational frequency (≈ 1700 cm^{-1}). In support of this notion, the electronic wave function for singlet **227** shows signs of biradical character. Thus, while **227** appears to be an energy minimum, the well is undoubtedly very shallow.

There have been several efforts directed toward the synthesis of **227**, or derivatives thereof. Montgomery and Roberts employed methodology used in the synthesis of **151**, but in this case



Scheme 88

isolated only acyclic alkyne **228** and cyclobutene (**163**).[135] Wittig and Wilson attempted dehalogenation of **229** and **230** but could glean no evidence for the putative intermediacy of **227** (Scheme 88).[136] Chapman argued that the possible existence of **227** was mired by facile rearrangement to butatriene; however, he attempted the synthesis of substituted cyclobutyne **233** through low temperature matrix chemistry.[100] Irradiation of **231** at 8 K in an argon matrix yielded cyclopropenone **232**; however,

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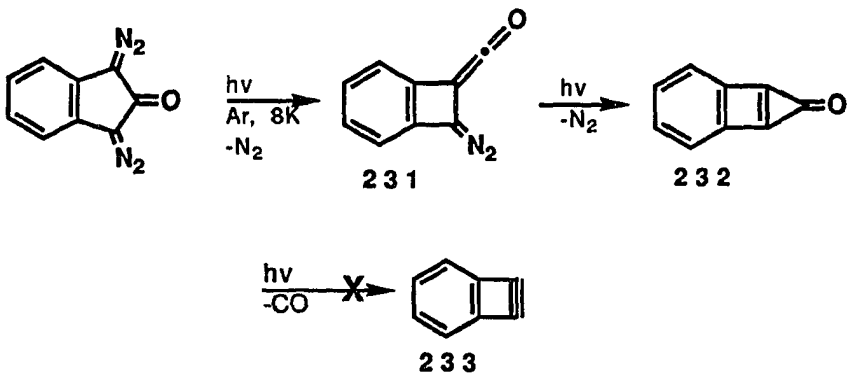
photodecarbonylation to cyclobutyne **233** was not observed. Calculations on the next member in the series, cyclopropyne, predict it to be an intermediate in the degenerate rearrangement of propadienylidene, rather than an energy minimum.[137]



Scheme 89

Introduction to Cycloenynes

Far less is known about the corresponding series of cycloenynes, although limitations of structure and isolability should roughly mimic those of the parent cycloalkynes. An explosion in the field of endiynes, however, was precipitated by the recent discovery of two remarkable series of naturally occurring compounds, the calichemicins **234** and the esperamicins **235**, as potent antibacterial and antitumor agents (Scheme 90).[138] Their ability to perform as antitumor agents centers around closure of the endiyne to 1,4-diradicals **236** and **237**, which subsequently cleave DNA. Apparently crucial for closure of **234** to **236** is the rehybridization that occurs at C_1 (sp^2 to sp^3) as a result of conjugate addition by thiolate ion. This shortens the distance between the two acetylenic groups, increasing the strain, which triggers the Bergman cyclization.

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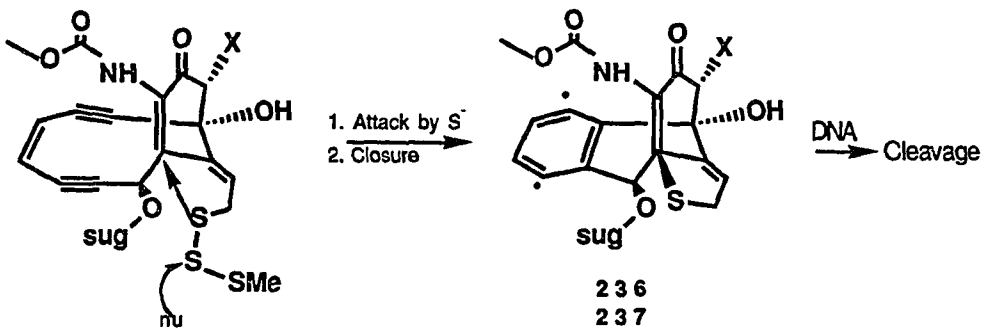
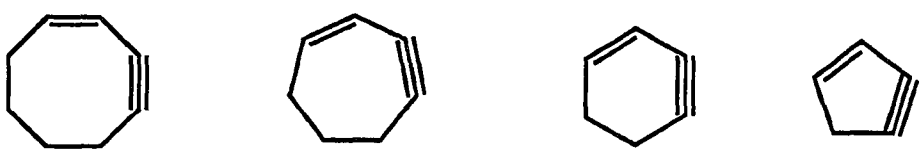


234 Calicheamicin, X = H
235 Esperimicin, X = OR

236
237

Scheme 90

In the series of cycloenynes, the smallest member whose existence has been inferred from trapping is 1-cyclohepten-3-yne (**239**).[139] The eight ring homologue **238**, as might be predicted, is stable at ambient temperature (Figure 25). In general, three methods have been employed in syntheses of these compounds; all introduce the triple-bond last through either dehydrohalogenation, oxidation of 1,2-dihydrazones and 1-amino-1,2,3-triazoles, or by fragmentation of 1,2,3-selenadiazoles.[139] In the course of work on the synthesis of 1,2,3-cyclohexatriene (**199**) we came upon what appeared to be a logical precursor to cyclohexen-3-yne (**240**) by an alternative route.



238 **239** **240** **241**

Figure 25. Series of cyclicenynes

Specifically, one involving fluoride induced elimination of an appropriately substituted vinylsilane. Remarkably, no references to this novel compound exist. 1-Cyclohexen-3-yne (**240**) represents the

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smallest member of its series as well as being a new isomer of benzene.

Synthesis and Trapping of 1-Cyclohexen-3-yne (240)

In accordance with methodology previously described for the synthesis of 1,2,3-cyclohexatriene (**199**), substituted silane **245** was viewed as the logical progenitor to enyne **240**. Treatment of **245** then with CsF in DMSO at ambient temperature should furnish **240**. The synthesis of diene **245** is outlined in Scheme 91. The starting 1-TMS-1-cyclopentene (**242**) was made in two steps from cyclopentanone as described elsewhere.[140] Addition of dibromocarbene ($CHBr_3$/KOtBu) to **242** resulted in thermally unstable adduct **243** which was characterized by ^1H and ^{13}C NMR. Cyclopropane **243** was was never isolated pure, but rather gently heated in chloroform at 50° C to afford ring opened dibromide **244** in 51% yield after chromatography (silica gel/hexane, -11° C). Spectra for **244** include a broad singlet at δ 4.83 in the ^1H NMR, seven resonances in the ^{13}C NMR, and a strong absorption at 1600 cm^{-1} in the IR, characteristic of vinyl bromides.

From here, reaction with base may proceed by either 1,2 or 1,4-elimination, yielding dienes **245** and **246** respectively. Treatment of **244** with DBU in DMSO (20° C) for eight hours furnished dienes **245** and **246** in roughly a 1:9 ratio as determined spectroscopically. Diene **245** exhibited two triplets at δ 6.11 and δ 6.21 in the ^1H NMR while **246** displayed a doublet of triplets at δ 5.98 and a triplet of doublets at δ 5.86. Separation of the two isomers was achieved with chromatography on silica gel (hexane, -11°C). Further characterization of **246** came from two IR bands at 1611 cm^{-1} and 1560 cm^{-1}, and a strong absorption at 275 nm in the UV, both characteristic of dienes.

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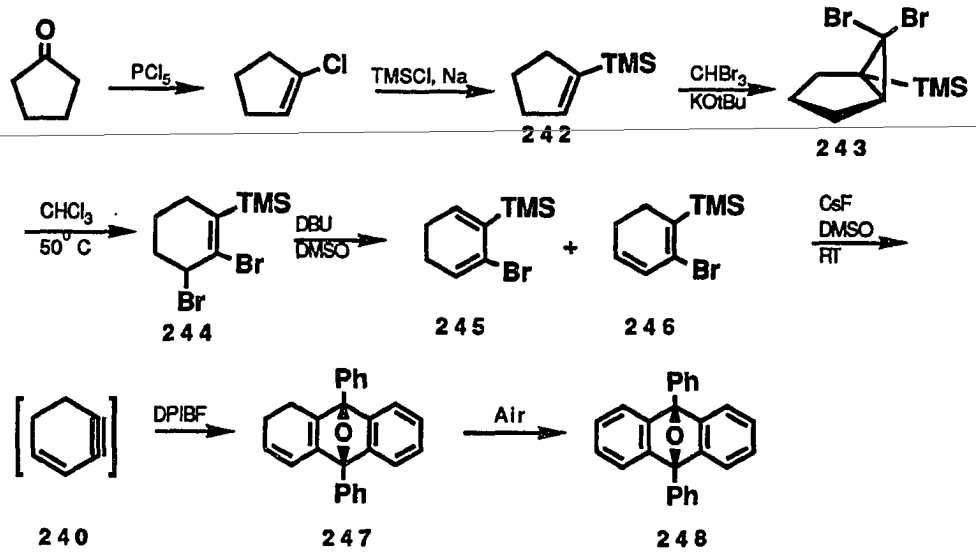

Scheme 91

Diene **246** was cleanly transformed to enyne **240** using the desilyation protocol described earlier. Reaction of **246** with CsF in DMSO at room temperature in the presence of DPIBF resulted in isolation of adduct **247** in 30% yield after chromatography. Spectral data for **247** include a broad doublet at δ 6.18 and triplet of doublets at δ 5.68 in the ^{1}H NMR, and 21 resonances in the ^{13}C NMR. Adduct **247** proved extremely susceptible to oxidation, and quickly aromatized to **248** upon attempts at recrystallization. The possibility of diene **246** reacting with DPIBF before desilyation was ruled out by appropriate control experiments. Thus, we attribute the formation of **247** to cycloaddition of DPIBF with enyne **240** at its most strained triple-bond.

The synthesis of **240** redefines current known limitations for strained cycloenynes, in addition to being a new isomer of benzene. The existence of **240** is not particularly surprising as benzyne (**130**) and cyclohexyne (**222**) have both been reported. Enyne **240**

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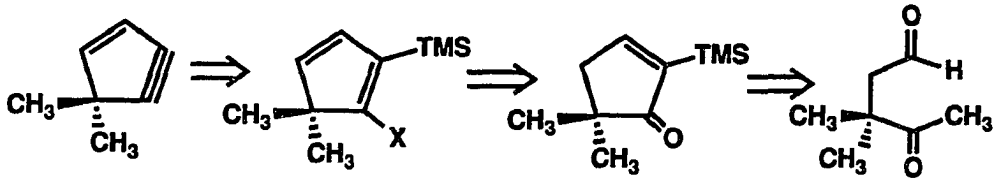
should be only slightly more strained than both **130** and **222**, owing to an increase in the torsional component brought about by eclipsing methylenes at C_3 and C_4. Perhaps of greater significance is the potential generality the method offers in the syntheses of both smaller and larger ring homologues. Additionally, the remarkably mild conditions under which these compounds may be generated makes them extremely attractive as reactive intermediates in synthesis.

The next lower homologue in the series, **241**, should resist synthesis only because the acidic (P_{ka} ≈ 15-18) hydrogens on a suitable diene precursor would prevent its isolation. The 5,5-dimethyl derivative **249** should be amenable to synthesis, however; and a retrosynthetic pathway is outlined in Scheme 92.



249

Scheme 92

In conclusion, cyclohexen-3-yne (**240**) may be generated and trapped by well precedented cycloaddition reactions. The molecule is of fundamental interest as a new isomer of benzene and currently represents the smallest reported member in its series.

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Semiempirical Calculations of Allene Vibrational Frequencies: The MNDO Method

Introduction

During recent years the calculation of vibrational frequencies by semiempirical molecular orbital methods has become an increasingly popular technique for predicting IR and Raman spectra. Specific applications of MINDO/3,[141] MNDO,[142] CNDO/2,[143] and INDO[144] have been reported; however, the technique generally appears to have been limited to smaller molecules. On average, the calculated values are within ±10% of experimentally determined numbers. This same overestimation of frequencies occurs with ab initio methods.[142] We report here the vibrational stretching frequencies for 20 allenes, calculated using the MNDO method. Comparison of the calculated frequencies for 14 allenes with numbers determined experimentally permits us to calculate a coefficient which can be used to predict frequencies with an accuracy of 98.8%.

For the identification of allenes, two infrared absorption bands are of particular interest. The first absorption (ν_1) occurs between 2100-1900 cm^{-1} and is due to the antisymmetrical C=C=C stretching vibration. In the case of terminal allenes which contain an electron withdrawing group (-CO_2H, -CO_2R, -$CONH_2$, -COCl, -COR, CF_3, -CN), this vibration may appear as a doublet.[145] The origin of this splitting is presently unclear. The second absorption (ν_2) occurs near 850 cm^{-1} and is due to the torsional motion of the terminal methylene group. In cyclic allenes, this band is absent. Because of our interest in cyclic systems, we focused exclusively on ν_1 in calculating the coefficient, as this would be applicable to both cyclic and acyclic systems.

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Computational Procedure

Our calculations followed a standard procedure. For all calculations, the AMPAC semiempirical molecular orbital package was used with MNDO Hamiltonians. Calculations were performed by initial analytical determination of first derivatives of the energy with respect to Cartesian coordinates. The Hesian, that is the matrix of second derivatives of the energy with respect to displacement of all pairs of atoms in X, Y, and Z is then calculated. Upon diagonalization, this gives the force constants for the molecule. The force matrix, weighted for isotopic masses, is then used for calculating the vibrational frequencies.[146] In order to ensure sufficient accuracy in the calculation of derivatives, a more stringent criterion of SCF convergence was used in each case.

Results and Discussion

The calculated and observed frequencies[145b,147] are presented in Table 4 and are graphically displayed in Figure 26. On average, the calculated values overestimate the stretching frequencies by approximately 11%. The results are evaluated by correlation coefficients (Q) formed by the quotient between experimental and calculated values. Our collection of allenes included the cyclic series from 6-9 membered rings, as well as a variety of acyclic derivatives. In some cases, experimental values have been reported, or were measured here by FT-IR. The mean value of Q obtained from the 14 entries for which experimental frequencies were available was 0.8912 ± 0.04. When this value was used to predict experimental frequencies from calculated ones, the accuracy was a very acceptable 98.85 ± 2.26%. In the three cases where doublets have been observed experimentally (entries **7**, **13** and **14**), the calculations yielded a single vibrational frequency.

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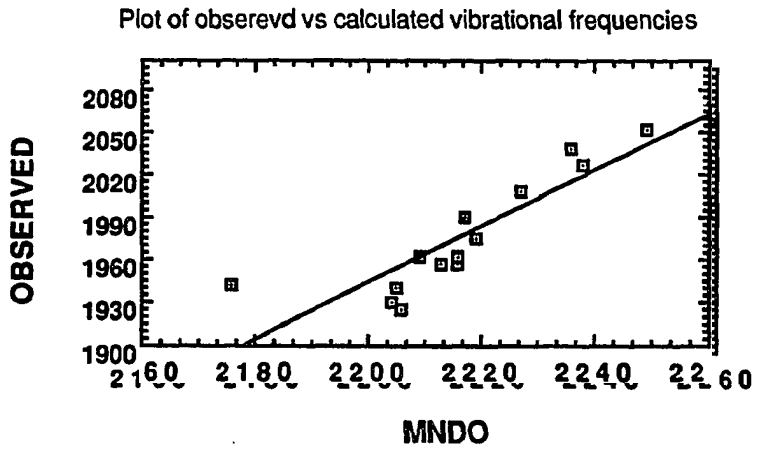

Figure 26

Table 4 displays the calculated and experimentally (where available) determined C=C=C stretching frequencies for the 20 allenes investigated. Within the series of cyclic allenes, the calculated stretching frequency steadily decreases upon incorporation of the allene chromophore into smaller and smaller rings. This is a direct manifestation of the increase in C=C bond length that accompanies this process. As more strain is imparted to the system, the bond length increases (force constant decreases) to reduce the strain.

Alkyl substitution on the allene functional group should reduce the stretching frequency by acting as an electron donor. Comparison of the calculated values for 1,2-cyclooctadiene (entry 3) and 1-*tert*-butyl-1,2-cyclooctadiene (entry 6) shows a marked decrease from 2185 to 2176 cm^{-1}, respectively. Interestingly, the calculated value for 1-methyl-1,2-cyclononadiene (entry 5) is less than that of the parent (entry 4); however, experimentally this observation is reversed. Appendage of a fluorine onto the allene chromophore (entries 13, 15, 16, 17) has the opposite effect to that observed for

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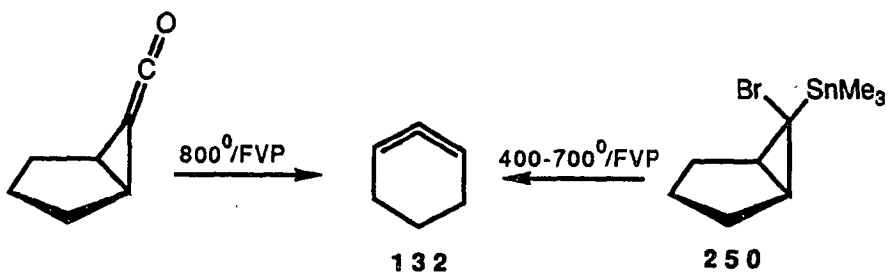
Table 4 Calculated and observed vibrational frequencies (cm^{-1})

	calculated	observed	coeff. (Q)
1) 1,2-Cyclohexadiene	2030	1829(1886)	NA
2) 1,2-Cycloheptadiene	2140	NA	NA
3) 1,2-Cyclooctadiene	2185	NA	NA
4) 1,2-Cyclononadiene	2213	1956	0.8839
5) 1-methyl-1,2-Cyclononadiene	2209	1961	0.8877
6) 1-tbutyl-1,2-Cyclooctadiene	2176	1942	0.8925
7) 1,2,4,6-Cycloheptatetraene	2073	1824(1816)	NA
8) Allene	2216	1961	0.8830
9) 1-Methylallene	2216	1961	0.8850
10) 1,1-Dimethylallene	2204	1930	0.8750
11) 1,1,3-Trimethylallene	2205	1940	0.8798
12) 1-Phenylallene	2206	1925	0.8720
13) 1,1,3-Trifluoro-3-methylallene	2208	2000(1970)	NA
14) 1-Carboxylallene	2207	1930(1900)	NA
15) 1-Fluoroallene	2219	1975	0.8900
16) 1,1-Difluoroallene	2238	2026	0.9053
17) 1,1,3-Trifluoroallene	2236	2038	0.9144
18) 1,1,3,3-Tetrafluoroallene	2244	2052	0.9124
19) 1-Deuterio-3,3-trifluoroallene	2227	2008	0.9107
20) 1,1-Dideuterio-3,3-difluoroallene	2217	1990	0.8976

alkyl substitution. By removing electron density, the force constant, and therefore the observed frequency, is increased.

While these calculations are of fundamental interest, the results may be of practical value in assigning observed vibrational frequencies for transient species whose identities are uncertain. For example, there have been two reports that 1,2-cyclohexadiene (**132**) may be observed in a cryogenic matrix. Wentrup[91] has trapped pyrolytically generated **132** in an argon matrix at 11K and observed a stretching frequency at 1886 cm^{-1}, which he attributed to the antisymmetrical C=C=C stretch. More recently, Runge and Sander[92] pyrolyzed bicyclic **250** (Scheme 93) and trapped an intermediate



Scheme 93

with a stretching frequency of 1829 cm^{-1}. The calculated absorption using the above method (entry 1) was 2030 cm^{-1}; however, when the correction was applied, the value was reduced to 1809 cm^{-1}. The predicted value then is approximately 4% and 1% smaller than those reported experimentally. Given the slight error associated with the correction it would be difficult to rule out either value, although, the frequency reported by the latter authors is obviously in better agreement.

In another example, Chapman *et al.* reported that irradiation of phenylmethylene (**251**, Scheme 94) in an argon matrix at 15K

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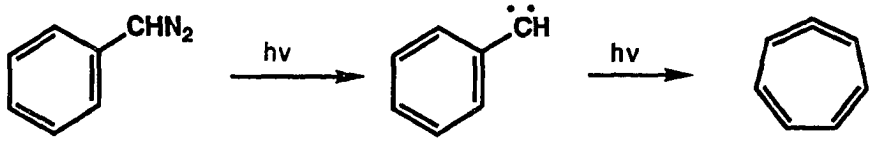
resulted in the formation of 1,2,4,6-cycloheptatetraene (**252**).[148] Evidence supporting this centered around the observation of two stretching frequencies at 1824 cm^{-1} and 1816 cm^{-1} in the IR spectrum. The calculated absorption using the above method (entry 7) was 2073 cm^{-1}; however, after correction, this value was reduced to 1847 cm^{-1}. This represents a small overestimation of 1.3% and 1.7% respectively. Thus while the calculated value appears to be in good agreement, it does not account for the experimentally observed doublet reported by the authors.



251 **252**

Scheme 94

The use of semiempirical molecular orbital calculations to predict the stretching frequency of 20 allenes has been presented. The MNDO Hamiltonian overestimates this stretch by approximately 11%, however, after the correction has been applied, the vibrational frequency may be predicted with 98.5 ± 2.26% accuracy. The use of these calculations to predict stretching frequencies where the assignment was uncertain, has also been demonstrated. When the calculated coefficient was used to predict the stretching frequency of 1,2-cyclohexadiene and 1,2,4,6-cycloheptatetraene, the corrected values agreed well with those observed experimentally.

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EXPERIMENTAL SECTION

General Experimental

Instrumentation:

^{1}H NMR Spectra were recorded on a Bruker AM-360 Fourier transform spectrometer and a Varian EM-360A spectrometer. All spectra were measured with $CDCl_3$ as solvent and TMS as reference unless otherwise noted.

^{2}H NMR Spectra were recorded at 55.30 MHz on a Bruker AM-360 fourier transform spectrometer. Spectra were measured with $CHCl_3$ as solvent and reference.

^{13}C NMR Spectra were recorded at 90.52 MHz on a Bruker AM-360 fourier transform spectrometer. All Spectra were measured with $CDCl_3$ as solvent and TMS as reference unless otherwise noted.

Infrared Spectra were recorded on a Perkin-Elmer 283B grating spectrometer. Absorptions were reported in wavenumbers (cm^{-1}), with polystyrene (1601 cm^{-1}) as the calibration peak.

Ultraviolet Spectra were recorded on a Schimadzu Bausch & Lomb Spectronic 200 UV spectrometer.

Low Resolution Mass Spectra were obtained through the University Instrumentation Center on a Perkin-Elmer Hitachi RMU-60 mass spectrometer and a Hewlett-Packard 5988A spectrometer.

Gas Chromatography Mass Spectra were obtained through the University Instrumentation Center on a Hewlett-Packard 5988A spectrometer equipped with a 12 meter crosslinked methyl silicone capillary column.

Optical Rotations were measured on a Zeiss LEPA2 polarimeter.

Melting Points were recorded on a MEL-TEMP capillary melting point apparatus and are uncorrected.

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CHN Analyses were obtained through the University Instrumentation Center on a Perkin-Elmer 240B elemental analyzer.

Analytical Gas Chromatography was performed with a Hewlett-Packard 5793A instrument equipped with a flame ionization detector and an attached model 3390A integrator. The following columns were used: (A) 10% Carbowax 20M (10' × 1/8' glass column at specified temperatures), (B) Alltech RSL-150 capillary (25 meter polydimethylsiloxane column at specified temperatures).

Preparative Gas Chromatography was performed on a Varian 920 gas chromatograph with a glass-lined injector. The following columns were used: (C) 15% Carbowax 20M (10' × 1/4" stainless steel column at specified temperatures), (D) 15% QF-1 (10' × 1/4" stainless steel column at specified temperatures), (E) 10% FFAP (10' × 1/4" stainless steel column at specified temperatures).

Photochemical Experiments:

In all solution phase photochemical experiments, spectroquality solvents were used. Argon was bubbled through the solution prior to and during irradiations. The light source was either a Rayonet RPR-100 reactor, fitted with 254 nm, or 350 nm lamps, or a 450 W Conrad-Hanovia lamp with sleeve filters. Low temperature experiments (Rayonet only) were performed by flowing nitrogen (pre-cooled in liquid nitrogen) through coils immersed in the reaction vessel. A quartz Dewar vessel was employed. The desired temperature was achieved through flow regulation.

Solvents:

Pentane, hexane, and benzene solvents used in photochemical experiments were spectroquality grade, purchased from Fischer Scientific. The following chromatographic solvents were distilled prior to use; n-pentane, n-hexane, methylene chloride (CH_2Cl_2),

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chloroform ($CHCl_3$), and benzene. The following solvents used for experimentation were distilled from calcium hydride and stored under nitrogen: hexamethylphosphoric triamide (HMPA) and dimethyl sulfoxide (DMSO). Tetrahydrofuran (THF) and diethylether (Et_2O) were freshly distilled from purple sodium benzophenone ketyl under a nitrogen atmosphere and used immediately. Diisopropylamine was distilled from potassium hydroxide and stored over 4Å molecular sieves under nitrogen. Ethylene glycol was distilled from magnesium sulfate. N,N-Dimethylformamide (DMF) was pre-dried over potassium hydroxide and then distilled from barium oxide.

Column Chromatography & Adsorbents:

Low temperature (0^0 C-(-)20^0 C) column chromatography was performed using jacketed columns. Temperature was controlled with a Lauda RC3 refrigerated recirculating bath.

Silica Gel: 60-200 mesh Davison Chemical silica gel was used as obtained from the company. Where necessary, the silica gel was doped with Sylvania 2282 green phosphor to allow observation with ultraviolet light in quartz chromatography columns.

Preparative TLC: Silica gel (1 mm) preparative TLC plates were purchased from Analtech. These plates were oven dried for 24 hr prior to use.

Alumina: 50-200 mesh Baker analyzed neutral grade alumina was used as obtained from the company.

Experimental

(R)-(+)-4,5,6,7-Tetrahydrodinaphtho[2,1-*g*:1',2'-*i*][1,6]dioxecine (10)

Ether **10** was prepared in 89% yield from (R)-(+)-1,1'-bi-2-naphthol (Aldrich Chemical Co.) by the method of Simpson, Daub, and Hayes[15]. No physical data were reported previously. mp 251-252^0 C;

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^{1}H NMR ($CDCl_3$) δ 7.93 (bd, 2H, J = 9.0 Hz), 7.85 (bd, 2H, J = 8.1 Hz), 7.47 (d, 2H, J = 9.0 Hz), 7.32 (td, 2H, J = 6.7, 1.2 Hz), 7.18 (td, 2H, J = 6.8, 1.3 Hz), 7.09 (bd, 2H, J = 8.4 Hz), 4.50 (m, 2H), 1.76 (m, 4H), 4.09 (t, 2H, J = 9.5 Hz); ^{13}C NMR δ 153.3, 134.1, 129.7, 129.3, 127.9, 126.3, 125.7, 123.9, 122.4, 117.4, 70.3, 25.2; UV (hexane) λ_{max} 331 (ε6789); $[\alpha]^{20}_D$ ($CHCl_3$) = -215.9°.

Asymmetric sensitized irradiation of 1,3-diphenylallene (16)

A solution of allene **16** (272 mg) and sensitizer **10** (32.6 mg), in 5 ml of $CHCl_3$, was added to 150 ml of hexane. The mixture was irradiated at 350 nm for 42.5 hr, and concentrated under reduced pressure. Chromatography on silica gel (1 × 10 cm, hexane), yielded 192 mg (72% recovery) of **16** as a white solid, α = 0.18°, $[\alpha]^{20}_D$ ($CHCl_3$) = + 7.53° (e.e = 0.66%[17]).

In another experiment, a solution of allene **16** (275 mg) and sensitizer **10** (32.6 mg), in 5 ml of $CHCl_3$, was added to 150 ml of hexane. The mixture was irradiated at 350 nm at -40° C for 16 hr, and the allene was isolated as described above, α = 0.043°, $[\alpha]^{20}_D$ ($CHCl_3$) = + 0.726 (e.e. = 0.064%).

Asymmetric sensitized irradiation of *cis,cis*-1,3-cyclooctadiene (17)

A solution of diene **17** (300 mg) and sensitizer **10** (30 mg), in 5 ml of $CHCl_3$, was added to 150 ml of pentane. The mixture was irradiated at 350 nm for 2 hr, and the pale yellow solution was concentrated under reduced pressure at -11° C. Chromatography on silica gel (1 × 10 cm, pentane) yielded 252 mg (84% recovery) of a clear oil. GLC (column A, 90° C) showed three components, *cis*-bicyclo[4.2.0]oct-7-ene (**17a**, 11.7%, rt 2.61 min), *cis,cis*-1,3-cyclooctadiene (**17**, 68.4%, rt 3.81 min), *cis,trans*-1,3-

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cyclooctadiene (**18**, 19.9%, rt 4.37 min). Calibration versus the internal standard (decane, 29.7 mg, rt 2.51 min) gave 26.9 mg of **18** which had α = + 0.044°, $[\alpha]^{20}_D$ (EtOH) = + 6.18° (e.e. = 0.95%[19]).

In another experiment, a solution of diene **17** (300 mg) and sensitizer **10** (28 mg), in 5 ml of $CHCl_3$ was added to 150 ml of pentane. The mixture was irradiated at 350 nm at -45° C for 2 hr and purified as described above to yield 223 mg (74% recovery) of a clear oil. GLC (column A, 90° C) showed **17**, **18**, and **17a** (ratio 85.4:10.2: 4.4). Calibration versus the internal standard yielded 12.5 mg of **18** which had α = + 0.056°, $[\alpha]^{20}_D$ (EtOH) = + 22.32° (e.e. = 3.44%)

The experiment was repeated at -80° C. GLC (column A, 90° C) showed **17**, **18**, and **17a** (ratio 86.2:9.1:4.7). Calibration versus the internal standard yielded 10.9 mg of **18** which had α = 0.20°, $[\alpha]^{20}_D$ (EtOH) = + 73.20° (e.e. = 11.30%).

Sensitized irradiation of *cis,cis*-1,3-cyclooctadiene (**17**); Quenching of the singlet state

A solution of diene **17** (3.0 g) and the sensitizer **10** (33 mg) in 5 ml of $CHCl_3$ was added to 150 ml of pentane. Stern-Volmer analysis indicated this concentration of diene **17** would quench ≈ 80% of the singlet state of **10**. Irradiation at 350 nm at -60° C for 7 hr, followed by workup yielded **17**, **18**, and **17a** (ratio 95.6:2.8:1.6), α = 0.16°, $[\alpha]^{20}_D$ (neat) = + 6.86° (e.e. = 1.06%).

Asymmetric sensitized irradiation of *trans*-1,2-diphenylcyclopropane (**1**)

A solution of cyclopropane **1** (200 mg) and sensitizer **10** (28 mg), in 180 ml of benzene was irradiated for 40 hr through a pyrex

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filter. The solution was concentrated under reduced pressure, chromatographed on silica gel (1 × 15 cm, hexane) to yield 168 mg (84% recovery) of a clear oil. GLC analysis (column A, 175° C) indicated two components, (3, 3.0%, rt 6.73 min), and (1, 97%, rt 10.01 min) Calibration versus the standard gave 161 mg of *trans* 1 which had $\alpha = 0.02^{0}$, $[\alpha]^{25}_{D}$ ($CHCl_3$) = + 0.25° (e.e = 0.06%).

Cyclohexyl-1,2-propadiene (63)

Cyclohexyl-1,2-propadiene (**63**) was prepared by the Doering-Moore-Skattebol approach.[87] To a stirred slurry of vinylcyclohexane (5.0 g, 0.045 mol) and potassium t-butoxide (30.6 g, 0.27 mol) in 170 ml of pentane at 0° C, was added dropwise a solution of bromoform (19.9 ml, 6.9 g, 0.23 mol) in 25 ml of pentane. The mixture was allowed to warm to room temperature and was stirred overnight. Water (100 ml) was added and the mixture was neutralized with 10% aqueous HCl. The aqueous and organic layers were separated and the aqueous layer was extracted with pentane (2 × 100 ml). The pentane extracts were combined, washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Distillation yielded 1,1-dibromocyclohexylcyclopropane (4.5 g, 35%, 0.016 mol) as a clear oil, bp 60-63° C at 0.02 mm (lit.[150] 160° C at 14 mm).

Methyllithium (15.4 ml of a 1.5 M solution, 0.0184 mol) was added dropwise to a solution of 1,1-dibromocyclohexylcyclopropane (4.5 g, 0.016 mol) in 30 ml of dry ether maintained at -30°/-40° C. The solution was stirred for 45 min. and then warmed to 0° C and quenched slowly with water (40 ml). The aqueous and organic layers were separated and the aqueous layer extracted with ether (2 × 25 ml). The ether extracts were combined, washed with water, dried

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over magnesium sulfate, filtered, and concentrated under reduced pressure. Distillation gave cyclohexyl-1,2-propadiene (**63**, 1.7 g, 87% 0.014 mol) as a clear oil, bp 40-45° C at 12 mm (lit.[32] 56-57° C at 15 mm). ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.08 (q, 1H, J = 6.6 Hz), 4.69 (d, 1H, J = 3.2 Hz), 4.66 (d, 1H, J = 3.2 Hz), 1.92-2.17 (m, 1H), 1.55-1.80 (m, 4H), 1.08-1.35 (m, 6H).

This material was found to be ca. 94% pure by capillary GLC analysis (column B, 82° C, rt 7.06 min). Further purification to 99% was achieved by preparative scale GLC (column C, 80° C).

Benzene sensitized vapor phase irradiation of cyclohexyl-1,2-propadiene (63)

Cyclohexyl-1,2-propadiene (50 mg) and benzene (80 mg) were placed in a 1.5 L quartz tube; the bottom portion of the tube was cooled to -78° C, and the system was degassed by evacuating to ca. 0.03 mm and backflushing with nitrogen several times. After evacuating to 0.03 mm, the tube was allowed to warm to room temperature and was irradiated for 4.5 min in a Rayonet photoreactor fitted with 254 nm lamps. The reaction vessel was then cooled to -78° C, vented to nitrogen, and the product was collected with pentane. The pentane solution was filtered through silica gel and concentrated under reduced pressure at 0° C to give 27.6 mg of a clear oil. This process was repeated five times. Capillary GLC (column B, 82° C) analysis indicated 4.5% conversion to 8 products. These were partially separated on a preparative scale (column C, 80° C) and identified as follows; *cis* and *trans*-1,3,8-Nonatriene (**82**, 46.8%, rt 4.94 min), Compound A (**84**, 21.9%, rt 5.09 min): ^{1}H NMR (360 MHz, $CDCl_3$) δ 6.00 (ddd, 1H, J = 17.2, 10.2, 7.1 Hz), 4.86-4.94 (m, 2H), 2.58-2.68 (m, 1H), 2.51 (q, 1H, J = 6.5 Hz), 2.28-

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2.38 (m, 1H), 1.98 (ddd, 1H, J = 15.9, 12.2, 9.3 Hz), 1.75-1.92 (m, 2H), 1.38-1.67 (m, 5H); ^{13}C NMR δ 143.9, 111.1, 44.4, 40.9, 34.1, 33.1, 32.8, 30.0, 25.0. Compound B (**85**, 12.3%, rt 5.88 min) ^{1}H NMR (partial, $CDCl_3$) δ 6.00 (ddd, 1H, J = 17.3, 9.8, 8.2 Hz), 4.96-5.11 (m, 2H); Compound C (**86**, 10.8%, rt 6.23 min): ^{1}H NMR (partial, $CDCl_3$) δ 5.82 (ddd, 1H, J = 16.9, 10.1, 7.8 Hz), 4.86-5.02 (m, 2H); *trans*-Bicyclo[4.3.1]non-2-ene (**83**, 2.3%, rt 6.68 min); Unknown (2.89%, rt 6.82); *cis*-Bicyclo[4.3.1]non-2-ene (**45**, 3.0%, rt 7.49 min).

Thermolysis of cyclohexyl-1,2-propadiene (**63**)

Cyclohexyl-1,2-propadiene (300 mg) was passed through a horizontal quartz tube packed with quartz chips, maintained at 610° C and at a pressure of 0.03 mm. The product was collected in a cold trap (-78° C), rinsed out with pentane, and concentrated under reduced pressure at 0° C to give 140 mg of a pale yellow oil. Capillary GLC (column B, 82° C) indicated 20% conversion to nine major products. Six of these were isolated on a preparative scale (column C, 80° C) and identified by comparison of ^{1}H spectra with those of authentic compounds. Cyclohexene (**95b**, 5.1%, rt 2.26 min); Unknown (5.5%, rt 2.74 min); *cis* and *trans*-1,3,8-Nonatriene (**82**, 3.6%, rt 4.94 min); Bicyclo-[4.3.0]-nona-1(6),7-diene (**98**, 3.2%, rt 5.94 min); *cis*-Bicyclo[4.3.0]non-7-ene (**97**, 10.7%, rt 6.04 min); Unknown (4.4%, rt 6.16 min); *trans*-Bicyclo[4.3.0]-non-2-ene (**83**, 15.8%, rt 6.67 min); *cis*-Bicyclo[4.3.0]non-2-ene (**45**, 31.2%, rt 7.38 min).

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Benzene sensitized solution phase irradiation of cyclohexyl-1,2-propadiene (63)

A solution of cyclohexyl-1,2-propadiene (50 mg), in 50 ml of benzene was placed in a pyrex tube and thoroughly degassed with argon. The mixture was irradiated in a Rayonet apparatus equipped with 254 nm lamps for 48 hr, then concentrated under reduced pressure to yield 52 mg of clear oil. Capillary GLC (column B, 82° C) analysis indicated only the presence of starting material (**63**, rt 7.08 min).

Route A: Vinylidenecycloheptane (64)

To a stirred slurry of methylenecycloheptane (3.2 g, 0.029 mol) and potassium t-butoxide (9.8 g, 0.087 mol) in 75 ml of pentane at 0° C was added dropwise a solution of bromoform (20.5 ml, 7.1 g, 0.081 mol) in 10 ml of pentane. The mixture was then allowed to warm to room temperature and was stirred overnight. Water (50 ml) was added and the mixture was neutralized with 10% aqueous HCl. The aqueous and organic layers were separated, and the aqueous layer was extracted with pentane (2 × 50 ml). The pentane extracts were combined, washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Distillation yielded 1,1-dibromospiro[2.5]nonane (2.8 g, 33.6%,0.010 mol) as a clear oil, bp 45-49° C at 0.02 mm (lit.[150] 140-142° C at 12 mm).

Methyllithium (1.4 ml of a 1.5 M solution, 0.0069 mol) was added dropwise to a solution of 1,1-dibromospiro[2.5]nonane (1.5g, 0.0053 mol) in 30 ml of dry ether maintained at -30°/-40° C. The mixture was stirred fo 45 min, warmed to 0° C, and quenched slowly with water (40 ml). The aqueous and organic layers were separated and the aqueous layer was extracted with ether (2 × 30 ml). The

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ether extracts were combined, washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Distillation gave 0.35 g (0.0029 mol, 54%) of a clear oil, bp 45-50° C at 12 mm. Capillary GLC analysis (column B, 82° C) showed two products. These were isolated on a preparative scale (column D, 75° C), and in the case of allene **64**, characterized by comparison of spectra with those reported.[33] Vinylidenecycloheptane (**64**, 40%, rt 8.1 min): ^{1}H NMR (360 MHz, $CDCl_3$) δ 4.50 (quint, 2H, J = 2.7 Hz), 2.22-2.29 (m, 4H), 1.43-1.64 (m, 8H); ^{13}C NMR δ 206.6, 103.1, 72.1, 32.1, 29.4, 28.3; IR (neat) 1955 cm^{-1}; Tricyclo[6.1.0.0^{1,7}]nonane (**66**, 60%, rt 7.85 min): ^{1}H NMR (360 MHz, $CDCl_3$) δ 2.16-2.26 (m, 1H), 1.92-1.98 (m, 1H), 1.67-1.85 (m, 3H), 1.55-1.66 (m, 2H), 1.31 (d, 1H, J = 2.7 Hz), 1.27 (d, 1H, J = 2.7 Hz), 1.05-1.27 (m, 3H), 0.80 (bs, 1H), 0.51 (s, 1H); ^{13}C NMR δ 43.8 (d), 32.3 (t), 31.2 (t), 29.6 (t), 28.4 (t), 26.6 (t), 26.4 (t), 14.5 (s), 2.6 (d); IR (neat) 2986, 2910, 2833, 1465, 975 cm^{-1}.

Silver catalyzed isomerization of tricyclo[6.1.0.0^{1,7}]nonane (66)

Tricyclo[6.1.0.0^{1,7}]nonane (20 *ul*) was added to benzene (2 ml) containing several crystals of silver triflate. The mixture was agitated briefly, allowed to stand for 24 hr under nitrogen, and then quenched with 2 ml of 10% sodium hydroxide. The aqueous and organic layers were separated, and the organic layer was dried over magnesium sulfate, filtered, and concentrated at 0° C under reduced pressure. GLC (column B, 82° C) indicated the presence of two isomers which were separated by preparative GLC (column E, 100° C), and shown to be the following compounds by comparison of ^{1}H NMR spectra with those of authentic compounds: Vinylcycloheptene

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(**79**, 49%, rt 8.04 min); Bicyclo[5.1.0]non-1-ene (**80**, 51%, rt 8.43 min).

Route B: Vinylidenecycloheptane (64)

Vinylidenecycloheptane (**64**) was prepared in a manner similar to that described for vinylidenecyclohexane.[34] Lithium acetylide (0.13 mol) was prepared by bubbling acetylene through a solution of dry THF (150 ml) and n-butyllithium (53.6 ml of a 2.5 M solution, 0.13 mol) at -78° C for 0.5 hr. Cycloheptanone (10 g, 0.089 mol), in 20 ml of THF, was added dropwise over 20 min. Stirring was continued for 30 min. The solution was warmed to room temperature and quenched with the dropwise addition of water (250 ml). The mixture was extracted with ether (3 × 150 ml), and the layers were separated. The organic layer was washed with water (3 × 75 ml), dried over magnesium sulfate, filtered, and evaporated under reduced pressure to yield yellow oil. Distillation yielded 1-ethynyl-1-cycloheptanol (7.6 g, 61.6%, 0.055 mol) as a clear oil, bp 72-76° C at 12 mm (lit.[151] 90-92° C at 12 mm).

A flask was charged with powdered ammonium chloride (5.5 g, 0.10 mol), copper (I) chloride (0.8 g, 0.0081 mol), 0.1 g of copper bronze, and 75 ml of 36% HCl. Gaseous HCl (NaCl + H_2SO_4) was introduced with vigorous stirring and cooling at -10°/-15° C. 1-Ethynyl-1-cycloheptanol (7.18 g, 0.052 mol) was then added in two min and stirring was continued for 90 min, while maintaining the temperature of the mixture at -5°/0° C. Ice-water (just enough to effect dissolution of the salts) and pentane (50 ml) were added at 0° C. The aqueous and organic layers were separated, and the aqueous layer was washed with pentane (3 × 50 ml). The combined pentane extracts were washed with water, dried over magnesium sulfate,

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filtered, and concentrated under reduced pressure to yield a pale yellow oil. Distillation yielded 1-chloro-1-cycloheptyl-acetylene (6.2 g, 76%, 0.040 mol) as a clear oil, bp 70-80° C at 15 mm. ^{1}H NMR indicated the material to be ca. 95% pure, and it was used without further purification. ^{1}H NMR (360 Mhz, $CDCl_3$) δ 2.67 (s, 1H), 2.34 (ddd, 2H, J = 14.4, 7.7, 2.2 Hz), 2.15-2.26 (m, 2H), 1.47-1.80 (m, 8H); ^{13}C NMR δ 86.2, 73.2, 65.7, 45.6, 27.5, 23.0.

Dry DMF (75 ml) was added quickly to a finely stirred mixture of zinc dust (30.3 g, 0.046 mol) and $CuSO_4 \cdot H_20$ (11.6 g, 0.046 mol). The reaction was immediately exothermic and external cooling was necessary. After 30 min, 50 ml of 100% ethanol was added and the temperature maintained at 20° C. 1-Chloro-1-cycloheptylacetylene (6.05 g, 0.039 mol), in 5 ml of ethanol, was added slowly over 30 min, and the mixture maintained between 45-50° C for an additional 30 min. The mixture was cooled to room temperature, and the top layer decanted. The remaining black slurry of zinc was rinsed with five portions (50 ml each) of ether. The alcoholic solution and the ether extracts were combined and washed three times with 50 ml portions of 2 N HCL, saturated with ammonium chloride. The organic layer was dried over magnesium sulfate, filtered, and concentrated under reduced pressure to yield 3.6 g of a yellow oil. Capillary GLC (column B, 68° C) indicated **64** was 82% pure. Allene **64** was further purified to 98.6% by preparative GLC (column C, 100° C).

Benzene sensitized vapor phase irradiation of vinylidene-cycloheptane (64)

Vinylidenecycloheptane (50 mg) and benzene (80 mg) were placed in a 1.5 L quartz tube, the bottom portion of the tube was cooled to -78° C, and the system was degassed by evacuating to ca.

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0.02 mm and backflushing with nitrogen several times. After evacuating to 0.02 mm, the tube was allowed to warm to room temperature and was irradiated for 1 hr in a Rayonet fitted with 254 nm lamps. The reaction vessel was then cooled to -78° C, vented to nitrogen, and the product was collected with pentane. The pentane solution was filtered through silica gel and was concentrated under reduced pressure at 0° C to give 46 mg of a clear oil. Capillary GLC (column B, 68° C) analysis indicated only starting material (**64**, rt 8.22 min).

Thermolysis of vinylidenecycloheptane (**64**)

Vinylidenecycloheptane (35 mg) was passed through a horizontal quartz tube, packed with quartz chips, maintained at 705° C at pressure of 0.03 mm. The product was collected in a cold (-78° C) trap, rinsed out with pentane, and concentrated under reduced pressure at 0° C to give 28 mg of a pale yellow oil. Capillary GLC (column B, 68° C) indicated 3.5% conversion to four products which were not isolated.

Benzene sensitized solution phase irradiation of vinylidene-cycloheptane (**64**)

A solution of vinylidenecycloheptane (50 mg), in 50 ml of benzene was placed in a pyrex tube and thoroughly degassed with argon. The mixture was irradiated in a Rayonet apparatus equipped with 254 nm lamps for 48 hr, then concentrated under reduced pressure to yield 50 mg of clear oil. Capillary GLC (column B, 68° C) analysis indicated only the presence of starting material (**64**, rt 8.22 min).

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Sythesis of *cis*-9,9-dibromo-4,5-dideuteriobicyclo[6.1.0]nonane (111)

Acetic acid-*d* (Aldrich, 99% isotopically pure, 28 ml, 0.46 mol) was added to a flask charged with potassium azodicarboxylate (29 g, 0.15 mol) and 9,9-dibromobicyclo[6.1.0]non-4-ene (4.0 g, 0.015 mol) in 50 ml of methyl alcohol-*d* (Aldrich, 99.5% isotopically pure) maintained at 0° C. The mixture was allowed to warm to room temperature and stirring was continued for 24 hr. The mixture was quenched with D_2O and extracted with pentane (2 × 100 ml). The combined pentane extracts were washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure to yield 3.6 g of a crude yellow oil. ^1H NMR (60 MHz, $CDCL_3$) indicated the reaction had gone to approximately 33% completion. It was carried out two more times on the same batch, increasing the overall yield of reduced material to 76% (3.4 g total) as determined spectroscopically.

MCPBA (0.93 g, 0.0054 mol) in 25 ml of choroform was added dropwise to the above mixture (≈ 0.84 g of unsaturated **110**, 0.0030 mol) in 25 ml of chloroform maintained at 0° C. The mixture was allowed to warm to room temperature and stirred for an additional 24 hr before being quenched with water (40 ml). The aqueous and organic layers were separated, and the organic layer was washed with 10% sodium hydroxide (10 ml), saturated sodium bicarbonate (10 ml), and water. The organic layer was dried over magnesium sulfate, filtered and concentrated under reduced presure to yield 3.5 g of a yellow oil. Column chromatography on alumina (2 × 25 cm, hexane) yielded 2.4 g of a clear oil. The chromatographed material was distilled to give *cis*-9,9-dibromo-4,5-dideuteriobicyclo[6.1.0]-nonane (**111**, 2.3 g, 58%, 0.0081 mol), bp 70-75° C at 0.02 mm. Mass

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spectrum, m/z (relative intensity) 281 (74), 282 (143), 283 (120), 284 (244), 285 (99), 286 (120) (for comparison, the mass spectrum of non-deuteriated **111** was recorded, m/z (relative intensity) 280 (45), 282 (87), 284 (42)). By comparing the relative intensities for peaks at 281 and 282 it was possible to determine the percentages of mono- and dideuteriated **111** to be 34% and 66% respectively.

1-Phenyl-1,2-cyclohexadiene (137)

To a stirred solution of 1-phenyl-1-cyclopentene (1.0 g, 0.0069 mol) and potassium t-butoxide (2.3 g, 0.021 mol) in 40 ml of pentane at -15° C was added dropwise a solution of bromoform (1.2 ml, 0.42 g, 0.013 mol) in 3 ml of pentane. The mixture was allowed to warm slowly to room temperature and stirred for 8 hr. The reaction was quenched with water (50 ml), the aqueous and organic layers separated, and the aqueous portion extracted with pentane (2 × 40 ml). The pentane extracts were combined, washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure to give predominantly 6,6-dibromo-1-phenylbicyclo[3.1.0]hexane (**141**, 0.41 g, 20%, 0.0013 mol) as clear yellow oil. This material was used without further purification. ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.22-7.35 (m, 5H), 2.43-2.52 (m, 2H), 2.26-2.38 (m, 2H), 2.06-2.16 (m, 1H), 1.80-1.91 (m, 2H); ^{13}C NMR δ 140.7, 128.2, 128.1, 127.3, 49.7, 46.3, 42.8, 37.8, 30.3, 26.0; IR (neat) 2915, 2810, 1595, 1486, 748 cm^{-1}.

6,6-Dibromo-1-phenylbicyclo[3.1.0]hexane (30 mg, 0.095 mmol) was placed in 1 ml of chloroform and stirred for 24 hr under nitrogen. The mixture was concentrated under reduced pressure, and the residue taken up in 1 ml of pentane. The solution was cooled to -30° C, at which point crystallization occurred. The crystals were

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collected and dried to give 1,6-dibromo-2-phenyl-1-cyclohexene (**142**, 18 mg, 60%, 0.057 mmol) as a white solid, mp 46.5-47° C. ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.20-7.38 (m, 5H), 5.05 (bs, 1H), 2.50-2.62 (m, 2H), 2.18-2.45 (m, 3H), 1.84-1.98 (m, 1H); ^{13}C NMR δ 142.3, 142.0, 128.2, 127.7, 127.4, 120.3, 56.6, 34.0, 33.8, 18.1; IR (KBr) 3018, 2950, 2869, 1625, 1484, 845 cm^{-1}.

Methyllithium (0.81 ml, of a 1.5 M solution, 0.0012 mol) was added dropwise to a solution of 6,6-dibromo-1-phenylbicyclo[3.1.0]-hexane (0.30 g, 0.95 mmol) and 1,3-diphenylisobenzofuran (DPIBF, 0.26 g, 0.95 mmol) in 15 ml of dry ether maintained at 0° C. Stirring was continued for 30 min and then water (20 ml) was added carefully. The aqueous and organic layers were separated and the aqueous layer extracted with ether (2 × 10 ml). The ether extracts were combined, washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure to yield 0.31 g of a yellow solid. TLC analysis (silica gel, 3:1 hexane/CH_2Cl_2) showed three components, one of which was DPIBF (R_f = 0.66). Preparative TLC (silica gel, 3:1 hexane/CH_2Cl_2) of 85 mg gave two components (R_f = 0.41, = 0.31) **146** and **145**, which were both recrystallized from hexane/benzene (9:2). Exo-**146** (11 mg, 8.5%, 0.026 mmol) was isolated as a white solid, mp 193-194° C. ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.99-8.02 (m, 2H), 7.48-7.59 (m, 4H), 7.42-7.44 (m, 2H), 7.12-7.31 (m, 6H), 6.92-6.98 (m, 5H), 5.94 (dd, 1H, J = 4.7, 2.9 Hz), 2.66 (td, 1H, J = 11.6, 3.4 Hz), 1.81-1.99 (m, 2H), 1.46-1.55 (m, 1H), 1.21-1.32 (m, 1H), 0.95 (dt, 1H, J = 12.0, 4.2 Hz); ^{13}C NMR δ 150.0, 147.6, 145.1, 142.1, 137.9, 135.1, 129.6, 128.7, 128.6, 128.4, 127.8, 127.3, 126.9, 126.7, 125.6, 125.5, 125.3, 123.3, 121.9, 117.4, 93.6, 89.2, 56.9, 32.1, 24.1, 18.7; IR (KBr) 3020, 2942, 1601, 1445, 1301, 1150, 1000 cm^{-1}; Anal. C, H.; Endo-**145** (3 mg, 2%, 0.0071 mmol) was isolated as

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a white solid, mp 181-181.5° C. ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.84-7.86 (bd, 2H, J = 7.1 Hz), 7.74-7.75 (bd, 2H, J = 7.2 Hz), 7.56-7.60 (bt, 2H, J = 7.5 Hz), 7.47-7.51 (bt, 2H, J = 7.9 Hz), 7.35-7.45 (m, 5H), 6.83-6.90 (m, 3H), 5.77 (dd, 1H, J = 6.8, 2.4 Hz), 1.84-1.98 (m, 2H), 1.36-1.61 (m, 3H), 1.17-1.31 (m, 1H); ^{13}C NMR δ 148.8, 146.4, 144.7, 141.2, 137.5, 136.4, 129.2, 128.5, 128.0, 127.5, 127.3, 126.9, 126.6, 126.4, 126.3, 125.9, 125.8, 120.7, 119.6, 119.1, 91.9, 89.8, 56.2, 30.4, 21.2, 17.5; IR (KBr) 3020, 2940, 1601, 1446, 1302, 1000, 731 cm^{-1}; Anal. C, H.

Attempted syntheses of 1,2-cyclopentadiene (131)

Route 1: Dibromocarbene addition to cyclobutene (163)

Cyclobutene was prepared according to the procedure of Salaün and Fadel.[104] Methyllithium (7.3 ml of 1.5 M solution, 0.011 mol) was added to a solution of cyclobutene (≈ 0.61 g, 0.011 mol), and carbon tetrabromide (3.8 g, 0.011 mol) in 30 ml of dry ether maintained at -78° C. Stirring was continued for 30 min before it was warmed to 0° C and quenched by the dropwise addition of water (30 ml). The aqueous and organic layers were separated and the aqueous layer extracted with ether (2 × 25 ml). The ether extracts were combined, washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure to yield 1.4 grams of a crude brown oil. TLC analysis (silica gel, pentane) indicated the presence of two components, one of which was carbon tetrabromide (R_f = 0.61). Column chromatography on silica gel (2.5 × 27 cm, pentane, -11° C) of 0.33 g yielded two fractions. The first was carbon tetrabromide and the second (R_f = 0.31) was 1,5-dibromo-1-cyclopentene (**164**, 0.17 g, 28% calculated from crude weight, 0.78 mmol) as a clear oil. ^{1}H NMR (360 MHz, $CDCL_3$) δ 6.16 (t, 1H, J = 2.3

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Hz), 4.94-4.97 (m, 1H), 2.42-2.64 (m, 3H), 2.26-2.38 (m, 1H); ^{13}C NMR δ 137.2, 123.4, 60.8, 35.4, 31.2; IR (neat) 3004, 2951, 1606, 1425, 1010, 820 cm^{-1}; GC-MS, m/z 224, 226 (m + 2), 228 (m + 4).

Methyllithium (7.3 ml of 1.5 M solution, 0.011 mol) was added to a solution of cyclobutene (≈ 0.61 g, 0.011 mol), and carbon tetrabromide (3.8 g, 0.011 mol) in 30 ml of dry ether maintained at -78° C. Stirring was continued for 30 min then methyllithium (1 equivalent) was added dropwise over 25 min, and the mixture held at -78° C for an additional 30 min. The mixture was allowed to warm to 0° C and quenched with the dropwise addition of water (20 ml). The aqueous and organic layers were separated and the aqueous layer extracted with ether (2 × 25 ml). The ether extracts were combined, washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure to yield 1.6 g of a crude brown oil. The mixture was distilled at 0.02 mm, and two fractions collected, one at 20° C (0.15 g), and one at 70° C (0.43 g). The first fraction was further purified by preparative GLC (column D, 100° C) and shown to be 1-bromo-5-methyl-1-cyclopentene (**165**). ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.82 (dd, 1H, J = 4.3, 2.1 Hz), 2.73-2.85 (m, 1H), 2.16-2.34 (m, 3H), 1.52-1.62 (m, 1H), 1.11 (d, 3H, J = 6.9 Hz); ^{13}C NMR δ 130.2, 127.9, 44.4, 31.2, 30.8, 19.8; GC-MS, m/z 160, 162 (m + 2). Capillary GLC of fraction two (column B, 98° C) indicated the presence of two components (1:1) which were isolated by preparative GLC (column D, 150° C) and determined to be the following. Meso or dl Dibromide (**166**, rt 5.75 min), ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.93 (d, 2H, J = 2.1 Hz), 3.24-3.35 (m, 2H), 2.20-2.36 (m, 4H), 1.92-2.03 (m, 2H), 1.51-1.61 (m, 2H); ^{13}C NMR δ 132.1 (d), 124.2 (s), 50.7 (d), 31.4 (t), 22.4 (t); IR ($CHCl_3$) 3005, 2935, 2840, 1664, 1432, 1194 cm^{-1}; GC-MS, m/z 290, 292 (m + 2), 294 (m + 4).

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Meso or dl Dibromide (**167**, rt 6.15 min), ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.91 (dd, 2H, J = 4.4, 2.3 Hz), 3.12-3.19 (m, 2H), 2.22-2.38 (m, 4H), 2.10-2.21 (m, 2H), 1.71 (dddd, 2H, J = 12.7, 9.3, 9.0, 5.5 Hz); ^{13}C NMR δ 133.0 (d), 123.8 (s), 50.7 (d), 31.1 (t), 26.3 (t); IR ($CHCl_3$) 3010, 2935, 2840, 1665, 1437, 1195 cm^{-1}; GC-MS, m/z 290, 292 (m +2), 294 (m + 4).

In another experiment, the above reaction (identical conditions) was run, however, before introducing the second equivalent of methyllithum, 1,3-cyclohexadiene (2.2 g, 0.028 mol) was added as a trap. After workup, ^{1}H NMR, and capillary GLC (column B, 98^0 C) analysis indicated only the presence of **165**, **166**, and **167** (ratio 1:2:2).

Attempted generation of 1,2-cyclopentadiene (**131**) at -105^0 C. Methyllithium (3.6 ml of 1.5 M solution, 0.0055 mol) was added to a solution of cyclobutene (≈ 0.30 g, 0.0055 mol), and carbon tetrabromide (3.2 g, 0.0055 mol) in 20 ml of dry ether maintained at -105^0 C. This temperature was achieved by flowing nitrogen (pre-cooled in liquid nitrogen) through copper coils immersed in pentane/ethanol (1:1). The yellow solution was stirred for 20 min before a second equivalent of methyllithium (3.6 ml of 1.5 M solution, 0.0055 mol) was introduced slowly. The solution was allowed to warm to 0^0 C, and quenched with the dropwise addition of water (20 ml). The aqueous and organic layers were separated and the aqueous layer extracted with ether (2 × 25 ml). The ether extracts were combined, washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure to yield 0.26 g of a pale yellow oil. ^{1}H NMR (360 MHz, $CDCl_3$) showed no vinyl resonances, and a large, undefined lump between δ 1- 2.5.

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In another experiment, the above reaction (identical conditions) was run, however, before introducing the second equivalent of methyllithium, 1,3-cyclohexadiene (1.1 g, 0.014 mol) was added as a trap. After workup and passage through a small plug of silica gel (pentane), 0.29 g of a pale yellow oil remained. Capillary GLC (column B, 68° C) analysis indicated the presence of 5 major components (>92%) which were analyzed by GC-MS and determined to have the following molecular formulas. A (2.2%, rt 3.2 min) C_9H_{14}; B (56.9%, rt 12.6 min) $C_8H_{11}Br$; C (16.4%, rt 14.0 min) C_8H_9Br; D (11.5%, rt 15.8 min) C_8H_{12} ; E (12.5%, rt 17.0 min) $C_9H_{11}Br$.

Route 2: Addition of dichlorocarbene to cyclobutene (163)

n-Butyllithium (3.0 ml of a 2.5 M solution, 0.0076 mol) was added dropwise to a solution of cyclobutene (0.41 g, 0.0076 mol) and carbon tetrachloride (0.73 ml, 1.2, g, 0.0076 mol) in 25 ml of dry ether maintained at -78° C. The mixture was stirred for 30 min, warmed to 0° C, and quenched with the dropwise addition of water (30 ml). The aqueous and organic layers were separated and the aqueous layer extracted with ether (2 × 20 ml). The ether extracts were combined, washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure to yield 0.25 g of pale yellow oil. TLC (silica gel, pentane) analysis showed three components, one of which was major (Rf = 0.66). Column chromatography on silica gel (1 × 25 cm, pentane, -11° C) yielded 0.18 g (17%) of 1,5-dichloro-1-cyclopentene (**169**, >86% pure, column B, 86° C). ^1H NMR (partial, 360 MHz, $CDCl_3$) δ 5.9 (t, 1H, J = 7.8 Hz), 4.65-4.85 (m, 1H); GC-MS, m/z 136, 138 (m + 2).

n-Butyllithium (3.0 ml of a 2.5 M solution, 0.0076 mol) was added dropwise to a solution of cyclobutene (0.41 g, 0.0076 mol) and

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carbon tetrachloride (0.73 ml, 1.2 g, 0.0076 mol) in 25 ml of dry ether maintained at -78° C. The mixture was stirred for 30 min and a second equivalent of n-butyllithium was added. After gradual warming to 0° C, the mixture was quenched by the dropwise addition of water (30 ml). The aqueous and organic layers were separated and the aqueous layer extracted with ether (2 × 30 ml). The ether extratcs were combined, washed with water, dried over magnesium sulfate, filtered, and concentrated to yield 0.38 g of pale yellow oil. Capillary GLC (column B, 86° C) indicated the presence of one major and two minor components (ratio 12:1:1, >76% combined). The major component was partially resolved by preparative GLC (column C, 94° C) and shown to be 3-butyl-1-cyclopentene (**170**) by comparison of ^{1}H NMR and mass spectra with those reported in the literature.[108] ^{1}H NMR (partial, 360 MHz, $CDCl_3$) δ 5.66 (bs, 1H), 2.55-2.69 (m, 1H), 2.22-2.41 (m, 1H), 1.96-2.09 (m, 1H); GC-MS, m/z (relative intensity) 124 (10), 95 (6), 82 (15), 67 (100), 41 (6).

In another experiment, the above reaction (identical conditions) was run, however, before introducing the second equivalent of n-butyllithium, 1,3-cyclohexadiene (0.61 g, 0.0076 mol) was added as a trap. After workup and passage through a small plug of silica gel (pentane), 0.48 g of a clear oil remained. GC-MS indicated **170** (>62%) was again the major component.

Route 3: Reactions of 1,5-dibromo-1-cyclopentene (**164**)

Reaction of 1,5-dibromo-1-cyclopentene (**164**) with activated magnesium. 1,5-Dibromo-1-cyclopentene (0.10 g, 0.44 mmol, in 10 ml of THF) was added dropwise to a mixture of activated magnesium[109] (21 mg, 0.89 mmol) and 1,3-cyclohexadiene (0.14 g, 0.0036 mol) in 20 ml of dry THF maintained at 0° C. The mixture was

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stirred for 3 hr, warmed to room temperature and quenched with the dropwise addition of water (30 ml). The mixture was filtered, and the filtrate extracted with ether (3 × 30 ml). The ether extracts were combined, washed with water (2 × 30 ml), dried over magnesium sulfate, filtered, and concentrated under reduced pressure to give 85 mg of a yellow oil. Capillary GLC (column B, 98° C) analysis indicated 78% conversion to two products (1:1), **166** (rt 5.75 min) and **167** (rt 6.15 min).

Reaction of 1,5-dibromo-1-cyclopentene (**164**) with MeLi at elevated temperatures. Methyllithium (0.63 ml of a 1.5 M solution, 0.44 mmol, in 20 ml of THF) was added dropwise to a solution of1,5-dibromo-1-cyclopentene (0.10 g, 0.44 mmol) in 30 ml of dry THF maintained at 55° C. After addition was complete, the mixture was cooled to room temperature and quenched by the dropwise addition of water (40 ml). The aqueous solution was extracted with ether (3 × 40 ml) and the combined extracts washed with water (2 × 30 ml). The organic layer was dried over magnesium sulfate, filtered, and concentrated under reduced pressure to yield 86 mg of a yellow oil. Capillary GLC (column B, 98° C) indicated 94% conversion to the following three products (1:2:2), **165** (rt 2.76 min), **166** (rt 5.75 min), **167** (rt 6.15 min).

Route 4: Fluoride induced elimination of 1-bromo-5-trimethyl-1-cyclopentene (**177**)

1-Bromo-5-trimethylsilyl-1-cyclopentene (**177**) was prepared in a similar manner to that described by Denmark and Klix.[115] To a solution of hexamethyldisilane (0.38 ml, 0.0019 mol) in 3 ml of HMPA at 0-5° C under nitrogen was added methyllithium (1.2 ml of

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1.5 M solution of Aldrich methyllithium lithium bromide complex in ether, 0.0019 mol) dropwise. After being stirred for 3 min, the resulting red solution was treated with copper (I) iodide (0.35 g, 0.0019 mol) in dimethyl sulfide (1 ml). The resulting black solution was stirred for 3 min and allylic halide **164** (0.17 g, 0.73 mmol) was added rapidly via syringe. The reaction mixxxture was warmed to room temperature and stirred for 1.5 hr. It was then poured into 25 ml of pentane and 25 ml of saturated ammonium chloride (buffered to pH 8 by the addition of ammonium hydroxide), and the mixture was vigorously stirred for 1 hr. The aqueous and organic layers were separated and the aqueous layer extracted with pentane (2 × 50 ml). The combined pentane extracts were washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure to yield 0.18 g of a yellow oil. TLC (silica gel, pentane) analysis indicated the presence of two components, one of which was major (R_f = 0.62). Column chromatography on silica gel (1.5 × 20 cm, pentane, -11° C) yielded 1-bromo-5-trimethylsilyl-1-cyclopentene (**177**, 54 mg, 31%, 0.23 mmol) as a clear oil. Capillary GLC (column B, 80° C) indicated the material to be 98% pure. ^{1}H NMR agreed well with data reported in the literature.[115]

1-Bromo-5-trimethylsilyl-1-cyclopentene (52 mg, 0.23 mmol) was added to 3 ml of dry DMSO containing cesium fluoride (0.14 g, 0.92 mmol) and DPIBF (62 mg, 0.23 mmol) maintained at 80° C. The mixture was stirred overnight, cooled to room temperature, and quenched by the dropwise addition of water (10 ml). The resulting solution was extracted with ether (2 × 50 ml) and the combined ether extracts were washed with water, dried over magnesium sulfate, filtered, and concentrated to yield 72 mg of a yellow solid. TLC analysis (silica gel, 3:1 hexane/chloroform) showed only DPIBF

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(R_f = 0.49). ^1H NMR of the crude material showed only aromatic resonances, no vinyl peaks being observed. Preparative TLC (silica gel, 3:1 hexane/chloroform) analysis of the baseline material by ^1H NMR showed only aromatic resonances.

In other experiments, the reaction temperature was varied between 20° C and 80° C with and without traps; however, this did not significantly alter the above results. Attempts to trap (-78° C) any volatile components failed.

1,2-Cyclohexadiene (132)

1-Bromo-6-trimethylsilyl-1-cyclohexene (**176**) was prepared according to the procedure of Denmark and Klix.[115] Alkene **176** (0.19 g, 0.82 mmol) was added to 20 ml of dry DMSO containing cesium fluoride (0.50 g, 0.0033 mol) and DPIBF (0.22 g, 0.82 mmol) maintained at 80° C. The mixture was stirred overnight, cooled to room temperature and quenched by the dropwise addition of water (30 ml). The resulting solution was extracted with ether (3 × 30 ml) and the combined ether extracts were washed with water (2 × 50 ml), dried over magnesium sulfate, filtered, and concentrated under reduced pressure to yield 0.43 g of a yellow solid. TLC (silica gel, 3:1 hexane/CH_2Cl_2) analysis indicated the presence of three products, one of which was DPIBF (R_f = 0.49). Preparative TLC (silica gel, 3:1 hexane/CH_2Cl_2) gave two components, **A** and **B**, in 73% overall yield. ^1H NMR of both components agreed well with data reported in the literature.[117,90]

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Cyclohexen-3-yne (240)

To a stirred solution of 1-trimethylsilyl-1-cyclopentene (0.10 g, 0.71 mmol) and potassium t-butoxide (0.16 g, 0.0014 mol) in 25 ml of pentane at -11° C was added dropwise a solution of bromoform (0.096 ml, 0.28 g, 0.0011 mol) in 2 ml of pentane. The mixture was maintained at -11° C for 3.5 hr, then quenched by the addition of water (10 ml). The aqueous and organic layers were separated and the aqueous layer extracted with pentane (2 × 30 ml). The combined pentane extracts were washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. 6,6-Dibromo-1-trimethylsilylbicyclo[3.1.0]pentane (**243**, 0.12 g, 54%, 0.39 mmol) was isolated as a yellow oil and used without further purification. ^{1}H NMR (360 MHz, $CDCL_3$) δ 1.89-2.18 (m, 5H), 1.64-1.79 (m, 2H), 0.19 (s, 9H); ^{13}C NMR δ 39.7, 35.0, 34.5, 30.6, 28.7, 26.4, -0.20.

6,6-Dibromo-1-trimethylsilylbicyclo[3.1.0]pentane (0.12 g, 0.39 mmol) was heated in chloroform (5 ml) at 50° C for 3 hr. The resulting mixture was concentrated under reduced pressure and chromatographed on silica gel (1.5 × 20 cm, pentane, -11° C) to yield 1,6-dibromo-2-trimethylsilyl-1-cyclohexene (**244**, 0.11 g, 92%, 0.36 mmol) as a clear oil. ^{1}H NMR (360 MHz, $CDCl_3$) δ 4.83 (bs, 1H), 2.40 (dd, 1H, J = 18.4, 5.3 Hz), 2.18-2.29 (m, 2H), 2.10 (dt, 1H, J = 14.0, 3.1 Hz), 1.92-2.05 (m, 1H), 1.73-1.77 (m, 1H), 0.23 (s, 9H); ^{13}C NMR δ 143.3, 130.9, 57.1, 33.8, 32.2, 17.3, -0.94; IR (neat) 2960, 2900, 1600, 1440, 1253, 1015, 839 cm^{-1}; Anal. C, H.

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 0.28 ml, 0.0018 mol) was added dropwise to 1,6-dibromo-1-trimethylsilyl-1-cyclohexene (0.55 g, 0.0018 mol) in 10 ml of dry DMSO at room temperature. The mixture was stirred for 16 hr, quenched with water, and extracted

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with pentane (2 × 30 ml). The aqueous and organic layers were separated and the organic layer washed with water. The pentane layer was dried over magnesium sulfate, filtered, and concentrated to yield 0.16 g of a yellow oil. Column chromatography on silica gel (1.5 × 25 cm, pentane, -11° C) yielded 1-bromo-2-trimethylsilyl-1,5-cyclohexadiene (**246**, 0.11 g, 26%, 0.47 mmol) as a clear oil (>92% pure). ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.88 (dt, 1H, J = 9.7, 1.8 Hz), 5.85 (dt, 1H, J = 9.7, 4.4 Hz), 2.22-2.27 (m, 2H), 2.05-2.13 (m, 2H), 0.25 (s, 9H); ^{13}C NMR δ 135.3, 130.9, 126.6, 28.5, 21.5; IR (neat) 3042, 2961, 2826, 1611, 1560, 1251, 835 cm^{-1}; UV (hexane) λ_{max} 275 nm (ε4400), 205 (ε3960).

Diene **246** (0.10 g, 0.43 mmol) was added to 7 ml of DMSO containing cesium fluoride (0.15 g, 0.0014 mol) and DPIBF (0.18 g, 0.43 mmol) maintained at 30°/40° C. The mixture was stirred for 16 hr, quenched with water (10 ml), and extracted with ether (3 × 20 ml). The ether extracts were washed with water, dried over magnesium sulfate, filtered, and concentrated to yield 0.16 g of a yellow solid. TLC (silica gel, 3:2 hexane/CH_2Cl_2) analysis indicated the presence of two components, one of which was DPIBF (R_f = 0.62). Preparative TLC (silica gel, 3:2 hexane/CH_2Cl_2) yielded diene **245** (R_f = 0.32, 11 mg, 0.31 mmol) as a white solid, mp 156-157° C. ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.78 (d, 2H, J = 7.1 Hz), 7.69 (d, 2H, J = 7.1 Hz), 7.38-7.53 (m, 6H), 7.23 (t, 2H, J = 7.0 Hz), 2.97 (quin., 2H, J = 7.5 Hz), 6.19 (bd, 1H, J = 9.7 Hz), 5.68 (dt, 1H, J = 9.6, 4.2 Hz), 2.66 (ddd, 1H, J = 17.0, 7.5, 4.8 Hz), 2.28-2.35 (m, 2H), 2.04-2.16 (m, 1H); ^{13}C NMR δ 151.7, 151.5, 150.6, 147.7, 135.2, 134.7, 128.7, 128.2, 127.9, 126.6, 126.1, 125.2, 124.7, 120.1, 120.0, 119.6, 92.5, 92.2, 23.2, 22.7. All attempts to recrystallize **247**, resulted in immediate oxidation to **248** as determined spectroscopically.[124]

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Synthesis of 1,2,3-cyclohexatriene (199)

Route 1: Attempted synthesis of 1-chloro-6-trimethylsilyl-1,5-cyclohexadiene (204).

2-Trimethylsilyl-2-cyclohexen-1-one was prepared according to the procedure of Shih, Fritzen, and Swenton.[119] A 10 ml flask was charged with 2-trimethylsilyl-2-cyclohexen-1-one (0.75 g, 0.0045 mol) and phosphorus pentachloride (0.93 g, 0.0045 mol) under nitrogen. Phosphorus oxychloride (0.41 ml, 0.683 g, 0.0045 mol) was introduced quickly, and the resulting brown mixture was stirred for 22 hr at room temperature. The mixture was poured into water (25 ml) and extracted with ether (3 × 20 ml). The combined ether extracts were washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure to yield 0.86 g of a pale yellow oil. TLC (silica gel, pentane) analysis indicated the presence of three components, one of which was major (Rf = 0.67). Column chromatography on silica gel (1.5 × 30 cm, pentane, -11°C) yielded 1,3-dichloro-2-trimethylsilyl-1-cyclohexene (**205**, 0.38 g, 38%, 0.0017 mol) as a clear oil. ^{1}H NMR (360 MHz, $CDCl_3$) δ 4.78 (bs, 1H), 2.42-2.52 (m, 2H), 2.06-2.11 (m. 2H), 1.86 (td, 1H, J = 10.5, 3.3 Hz), 1.76-1.81 (m, 1H), 0.29 (s, 9H); ^{13}C NMR δ 147.6, 133.8, 59.9, 35.4, 31.0, 18.2, -0.87; IR (neat) 2975, 1602, 1429, 1255, 843 cm^{-1}.

DBU (0.18 ml, 0.0012 mol) was added dropwise to dichloride **205** (0.24 g, 0.0011 mol) in 10 ml of DMSO at room temperature. The mixture was stirred for 20 hr, quenched with water (30 ml), and extracted with pentane (2 × 30 ml). The aqueous and organic layers were separated and the organic layer washed with water. The pentane solution was dried over magnesium sulfate, filtered, and concentrated under reduced pressure to yield 79 mg (38% crude yield) of pale yellow oil. ^{1}H NMR of the crude mixture indicated the

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presence of two components. 1-Chloro-6-trimethylsilyl-1,5-cyclohexadiene (**204**, 60%), ^{1}H NMR (partial, 360 MHz, $CDCl_3$) δ 6.23 (t, 1H, J = 4.1 Hz), 5.8 (t, 1H, J = 4.5 Hz); 1-Chloro-2-trimethylsilyl-1,3-cyclohexadiene (**206**, 40%), ^{1}H NMR (partial, 360 MHz, $CDCl_3$) δ 5.93 (dt, 1H, J = 7.6, 1.7 Hz), 5.7 (quin., 1H, J = 4.4 Hz). The mixture proved inseparable by column chromatography and rapidly aromatized during all attempts at preparative GLC.

Route 2: Fluoride induced elimination of 1-trifluoromethanesulfonic-6-trimethylsilyl-1,5-cyclohexadiene (**208**).

Lithium diisopropylamide (LDA) was prepared by the addition of n-butyllithium (1.20 ml of a 2.5 M solution, 0.0030 mol) to diisopropylamine (0.42 ml, 0.0029 mol) in 8 ml of dry THF at -78^{0}C. 2-Trimethylsilyl-2-cyclohexen-1-one (0.50 g, 0.0029 mol) in 3 ml of THF was then added slowly, and the resulting orange solution stirred for 2 hr at -78^0 C. Trifluoromethanesulfonimide (1.2 g, 0.0033 mol) was added as a solid and the mixture warmed to 0^0 C and maintained for an additional 3 hr. After further warming to room temperature, the resulting red solution was stirred overnight. The mixture was poured into water (50 ml) and extracted with ether (2 × 75 ml). The aqueous and organic layers were separated, and the organic layer was washed with water. The ether layer was dried over magnesium sulfate, filtered, and concentrated to yield 1.1 g of an orange oil. TLC (silica gel, hexane) analysis indicated the presence of two components, one of which was the triflimide (R_f = 0.32). Column chromatography on silica gel (1.5 × 40 cm, hexane) yielded 1-trifluoromethanesulfonic-6-trimethylsilyl-1,5-cyclohexadiene **208**, 0.52 g, 58%, 0.0017 mol) as a clear oil. ^{1}H NMR (360

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MHz, $CDCl_3$) δ 6.29 (t, 1H, J = 4.3 Hz), 5.74 (t, 1H, J = 4.5 Hz), 2.14-2.31 (symmetrical mult., 4H); ^{13}C NMR δ 150.5, 141.2, 133.6, 111.8, 22.6, 21.7; IR (neat) 3010, 2936, 1639, 1420, 1210, 1140, 940, 835 cm^{-1}; UV (hexane) λ_{max} 260 nm (ε2050), 203 (ε2200); GC-MS, m/z 300.

Diene **208** (47 mg, 0.16 mmol) was added to 2 ml of dry DMSO containing cesium fluoride (71 mg, 0.47 mmol) and DPIBF (47 mg, 0.16 mmol) at room temperature. The mixture was stirred for 20 hr, poured into water (10 ml), and extracted with ether (2 × 30 ml). The combined ether extracts were washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. TLC (silica gel, 3:2 hexane/CH_2Cl_2) analysis indicated the presence of two components, one of which was DPIBF (R_f = 0.62). Preparative TLC (silica gel, 3:2 hexane/CH_2Cl_2) yielded 9,10-epoxy-6,7,9,10-tetrahydro-9,10-diphenylanthracene (**209**, 13 mg, 24%, 0.38 mmol) as a white solid, mp 161-162.5° C. ^1H NMR (360 MHz, $CDCl_3$) δ 7.82 (d, 4H, J = 7.2 Hz), 7.54 (t, 4H, J = 7.3 Hz), 7.32 (dd, 2H, J = 5.3, 3.1 Hz), 7.17 (dd, 2H, J = 5.3, 3.1 Hz), 5.69 (bs, 2H), 2.22-2.24 (m, 4H); ^{13}C NMR δ 146.5, 138.7, 135.3, 128.5, 127.9, 126.8, 119.4, 114.3, 88.3, 22.3; IR (KBr) 3025, 3020, 2930, 2830, 1440, 1445, 980, 695 cm^{-1}; Anal. C, H.

Diene **209** (4.4 mg, 0.013 mmol) was dissolved in 0.75 ml of benzene containing 2,3-dichloro-4,5-dicyano-1,4-benzoquinone (DDQ, 2.7 mg, 0.011 mmol). The reaction, monitored by TLC, was determined to be complete after 17 hr. The mixture was filtered and the filtrate concentrated to give a faintly yellow oil. Preparative TLC (silica gel, 3:2 hexane/CH_2Cl_2) yielded 9,10-epoxy-9,10-dihydro-9,10-diphenyl-anthracene (4.1 mg, 91%, 0.012 mmol) as a white solid, mp 191-192° C (lit.[124] mp 193.5-194° C). Spectral data agreed

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well with that reported in the literature.[124]

Diene **208** (70 mg, 0.29 mmol) was added to 1 ml of dry DMSO containing cesium fluoride (0.11 g, 0.72 mmol) and furan (0.21 ml, 0.0029 mol) at room temperature. The resulting purple solution was stirred for 20 hr, quenched with water (10 ml), and extracted with ether (2 × 25 ml). The aqueous and organic layers were separated and the organic layer washed with water (15 ml). The ether portion was dried over magnesium sulfate, filtered, and concentrated to yield 0.12 g of a yellow oil. TLC (silica gel, 9:1 hexane/ether) analysis indicated the presence of a single component (R_f = 0.52). Preparative TLC (silica gel, 9:1 hexane/ether) yielded 1,4-epoxy-1,4,6,7-tetrahydronapthalene (**212**, 24 mg, 66%, 0.19 mmol) as a clear oil. ^{1}H NMR (360 MHz, $CDCl_3$) δ 6.40 (bs, 2H), 5.65 (bs, 2H), 5.19 (bs, 2H), 2.14-2.36 (symmetrical m, 4H); ^{13}C NMR δ 134.7, 134.1, 113.6, 80.2, 22.6; IR (neat) 3005, 2962, 2914, 1442, 1340, 1289, 820 cm^{-1}; UV (hexane) λ_{max} 213 nm (ε3720), 250 (ε2140); GC-MS m/z 146.

Diene **212** (18 mg, 0.12 mmol) was added to 1 ml of benzene containing DDQ (25 mg, 0.11 mmol). The mixture turned orange immediately, and a precipitate formed. The mixture was filtered, and the filtrate concentrated to give a yellow oil. Preparative TLC (silica gel, 9:1 hexane/ether) yielded 1,4-epoxy-1,4-dihydro-napthalene (18 mg, 100%, 0.12 mmol) as a clear oil. Spectral data agreed well with that reported by Aldrich.[149]

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APPENDIX A
SPECTRA FOR COMPOUNDS

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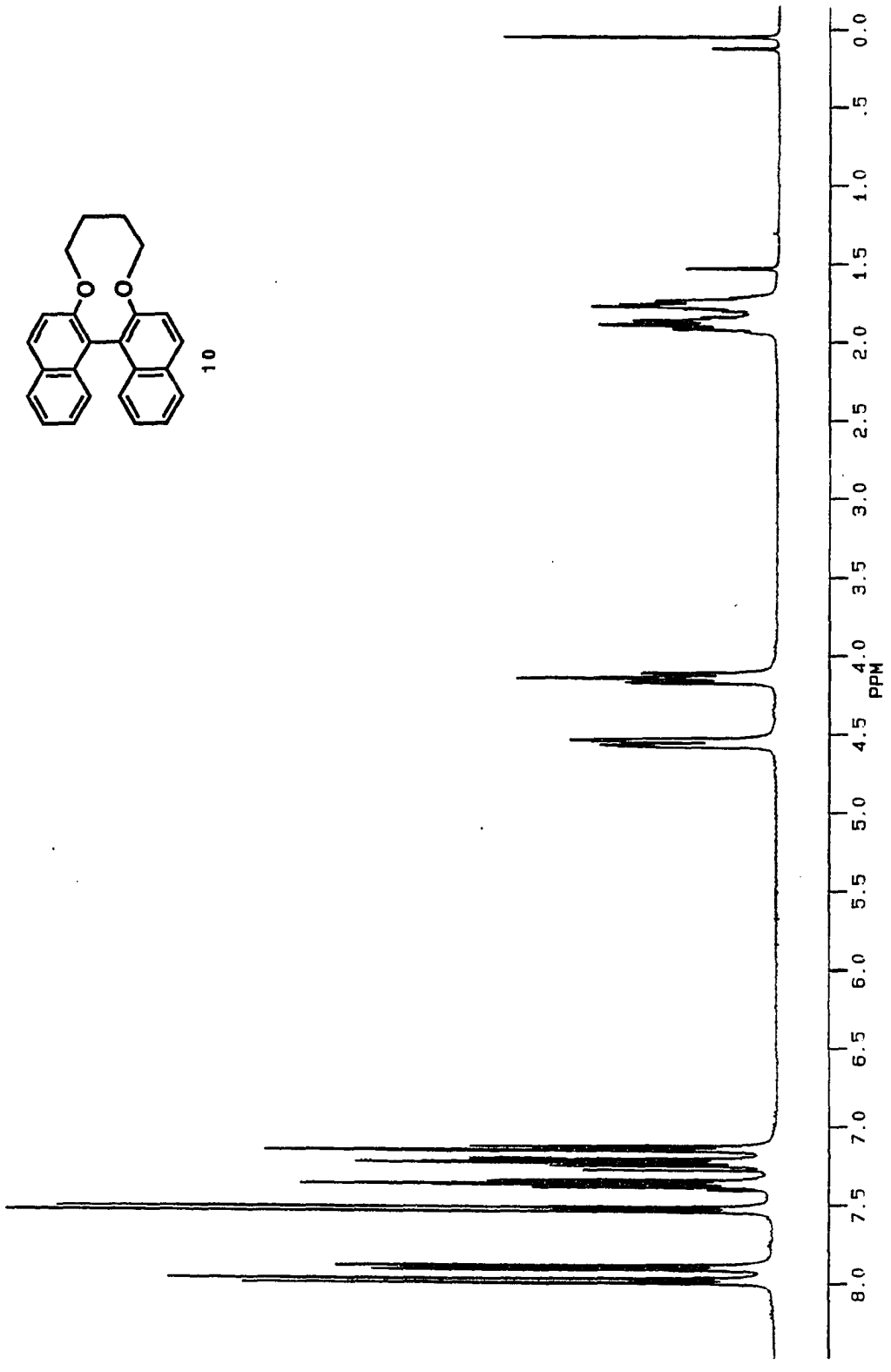

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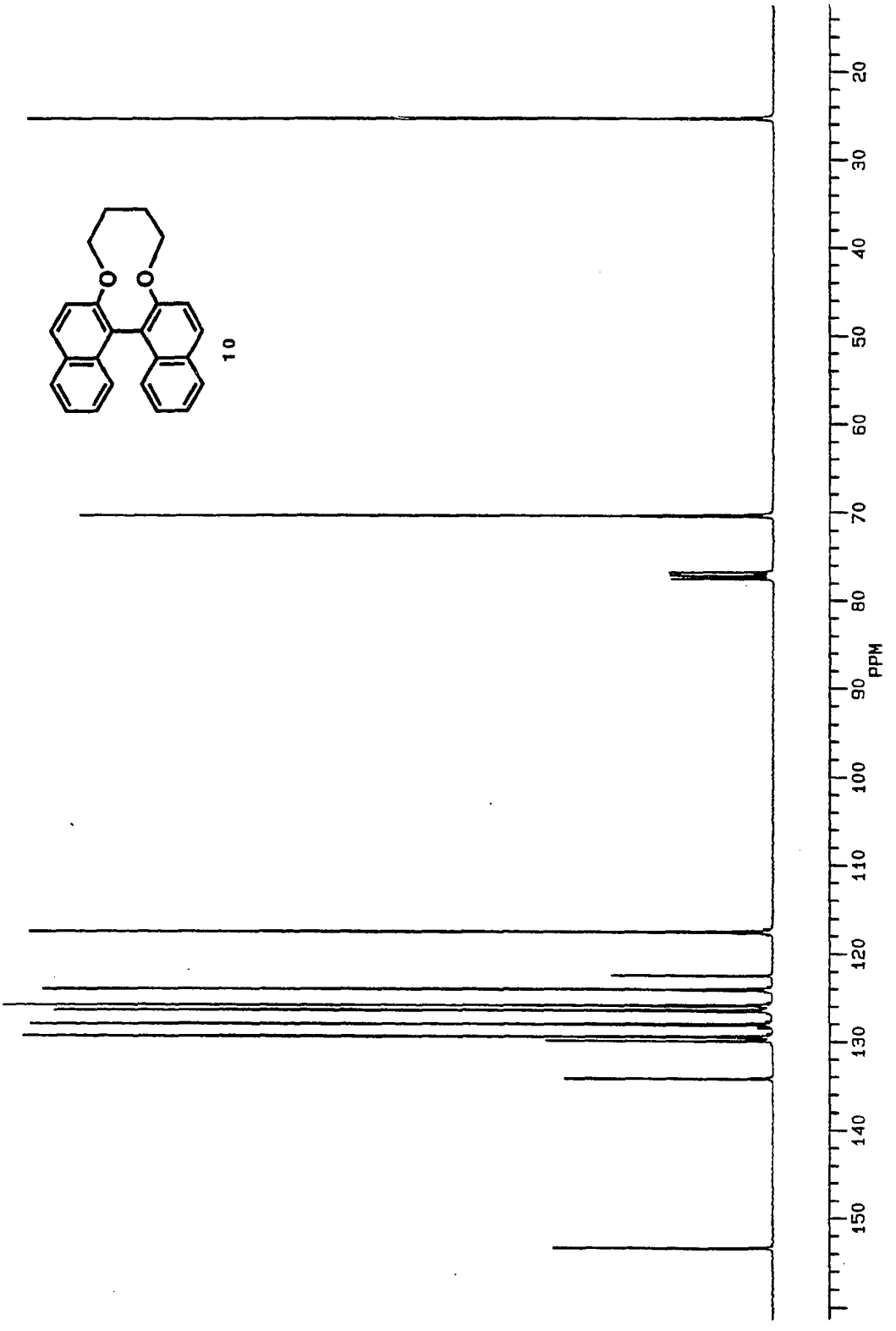

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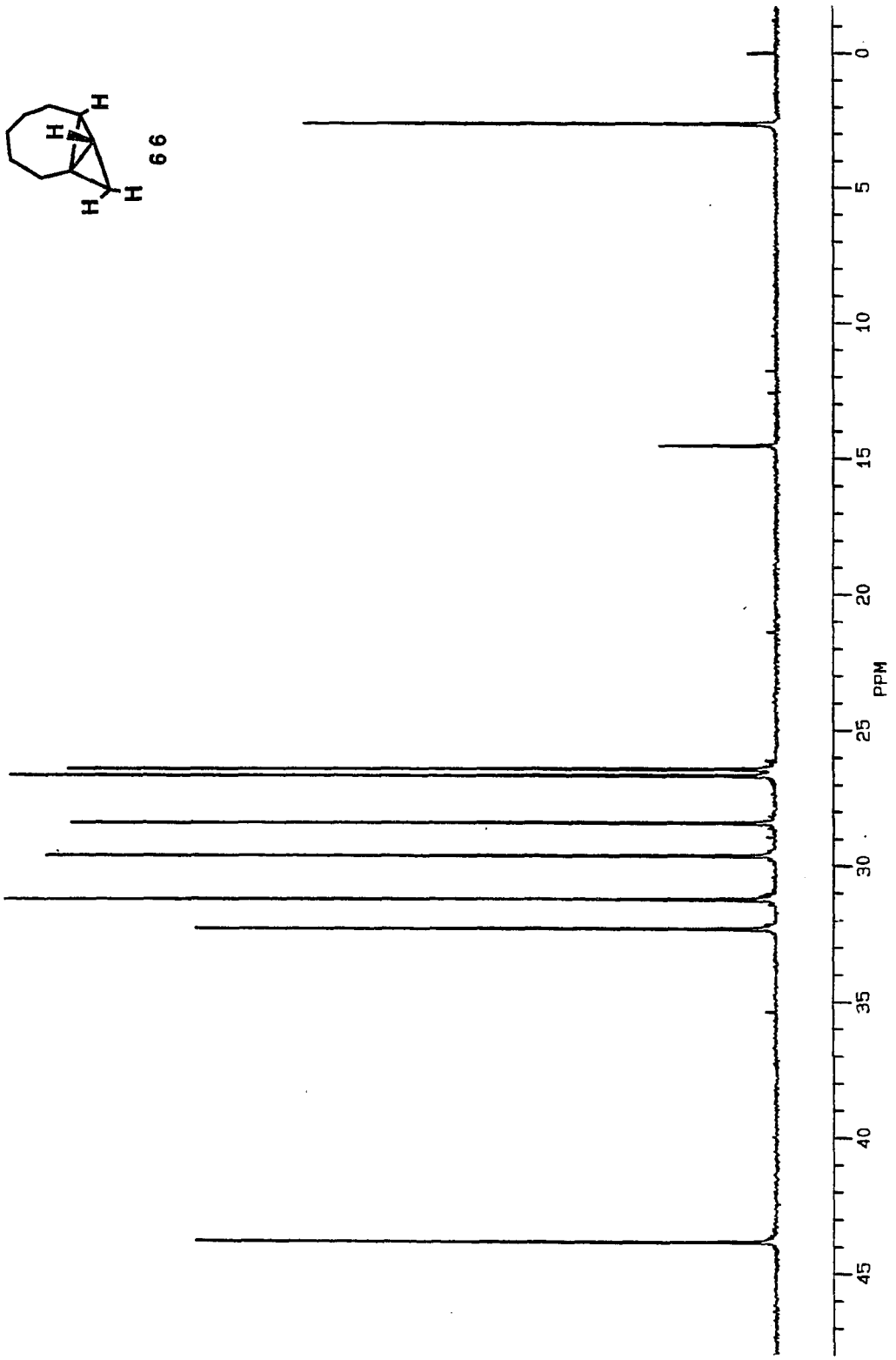

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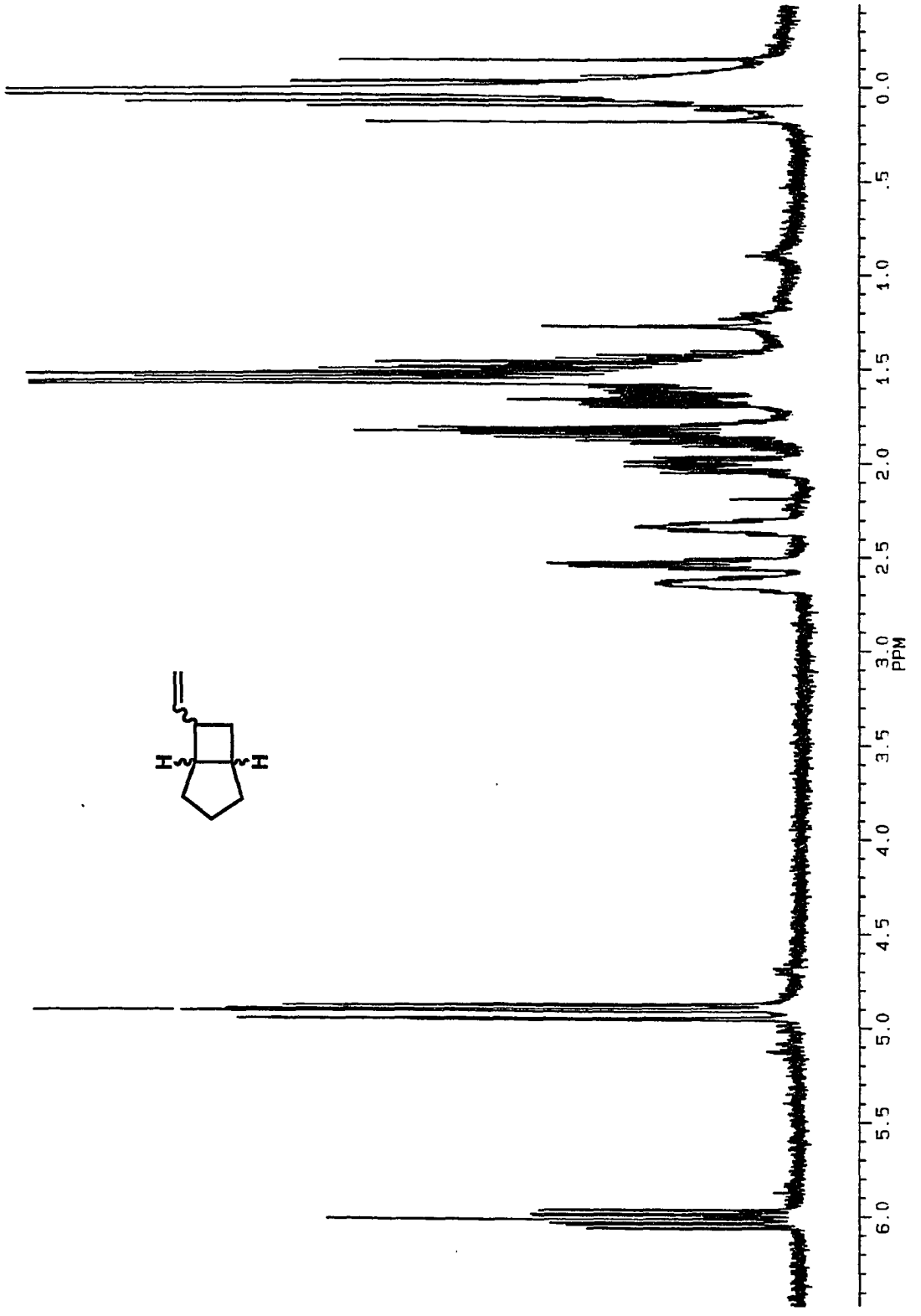

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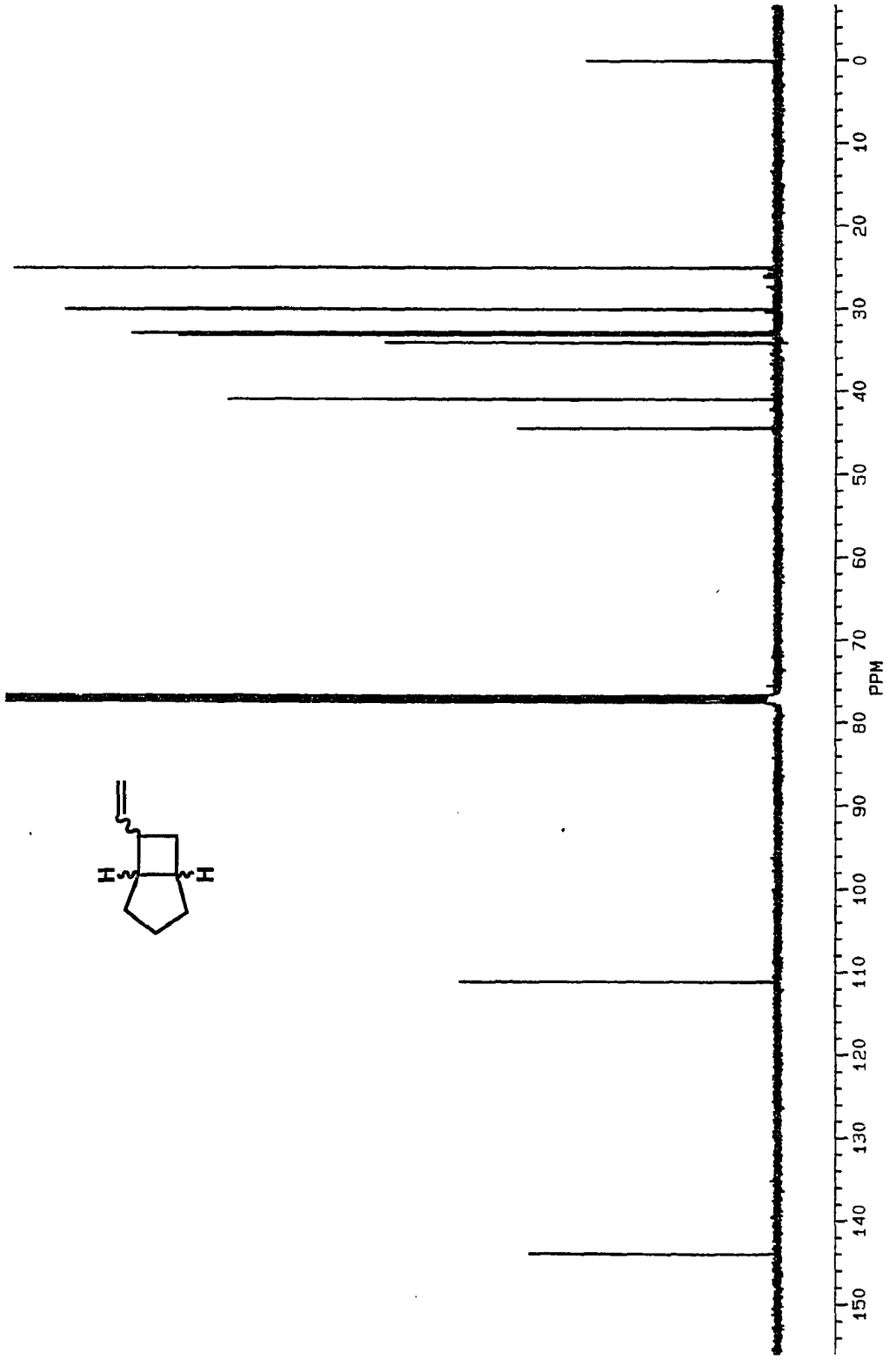

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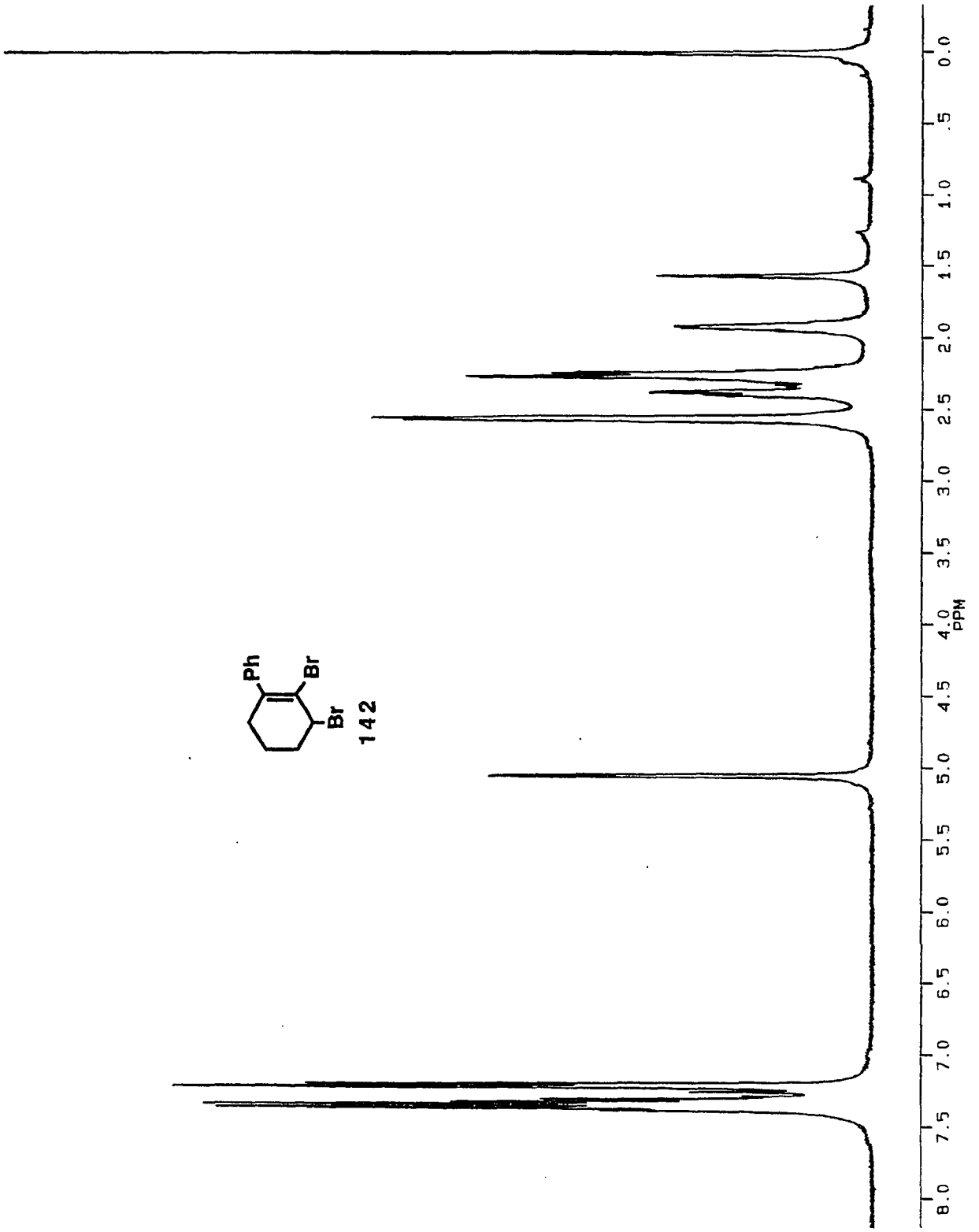

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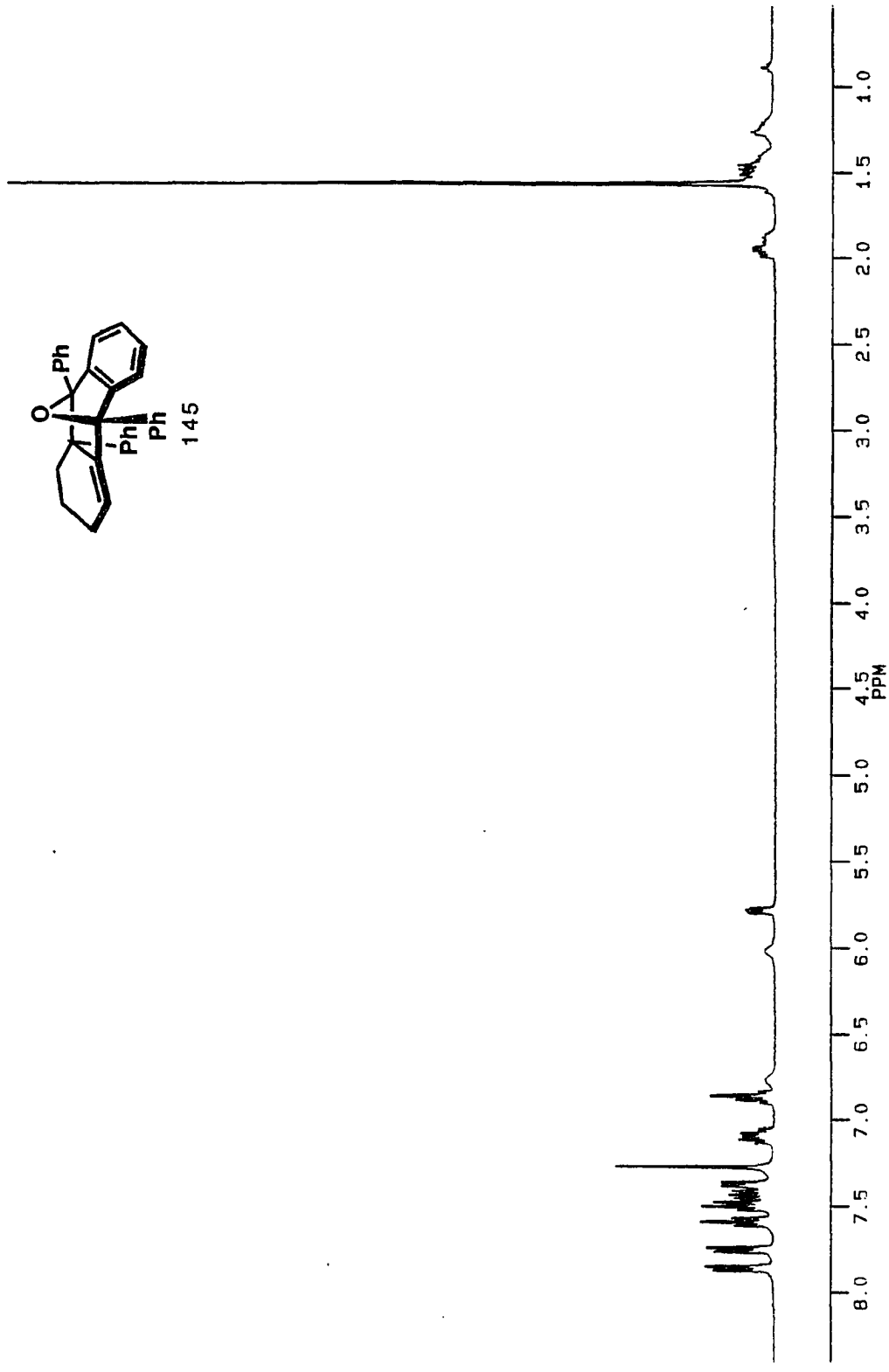

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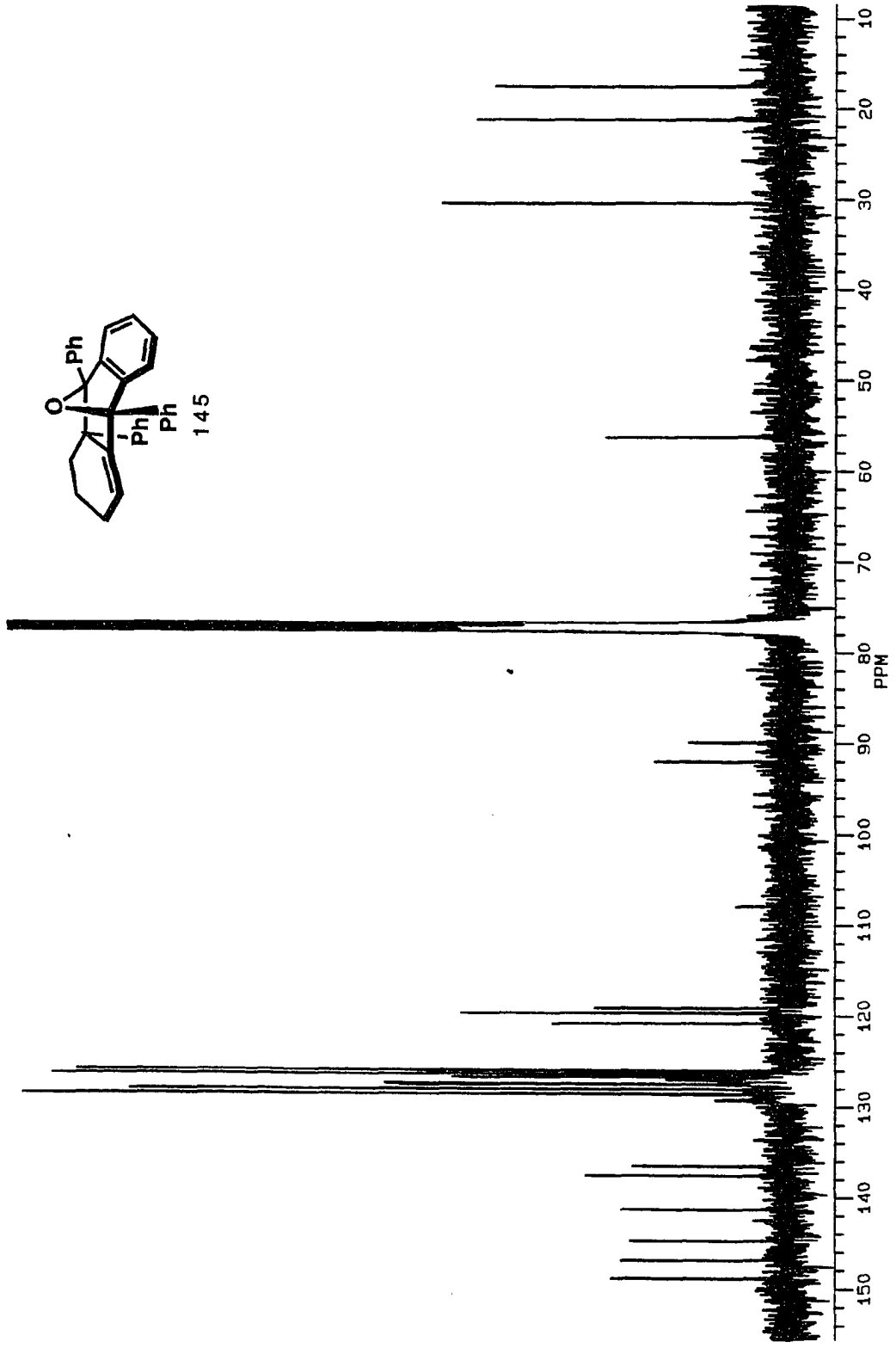

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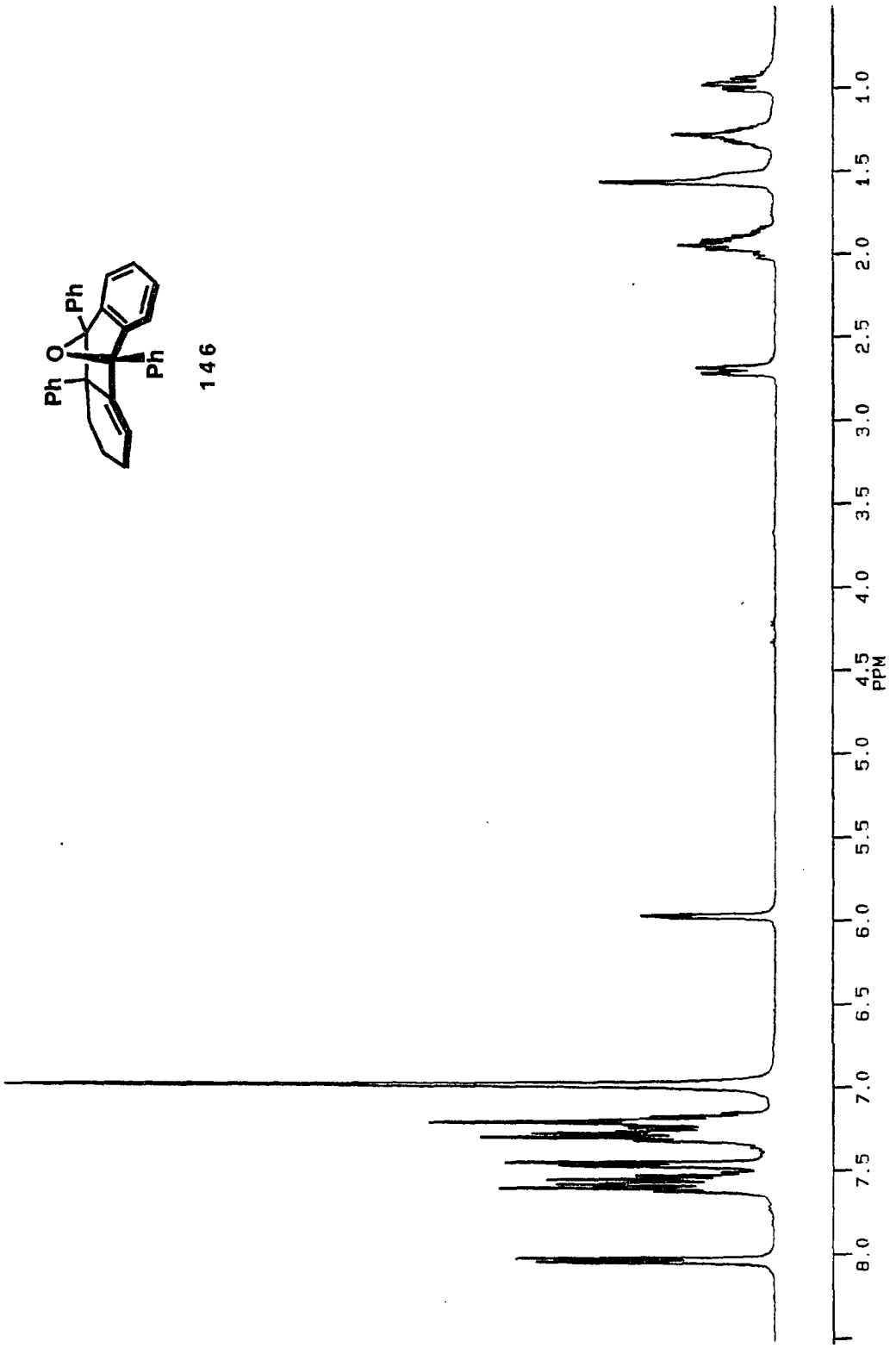

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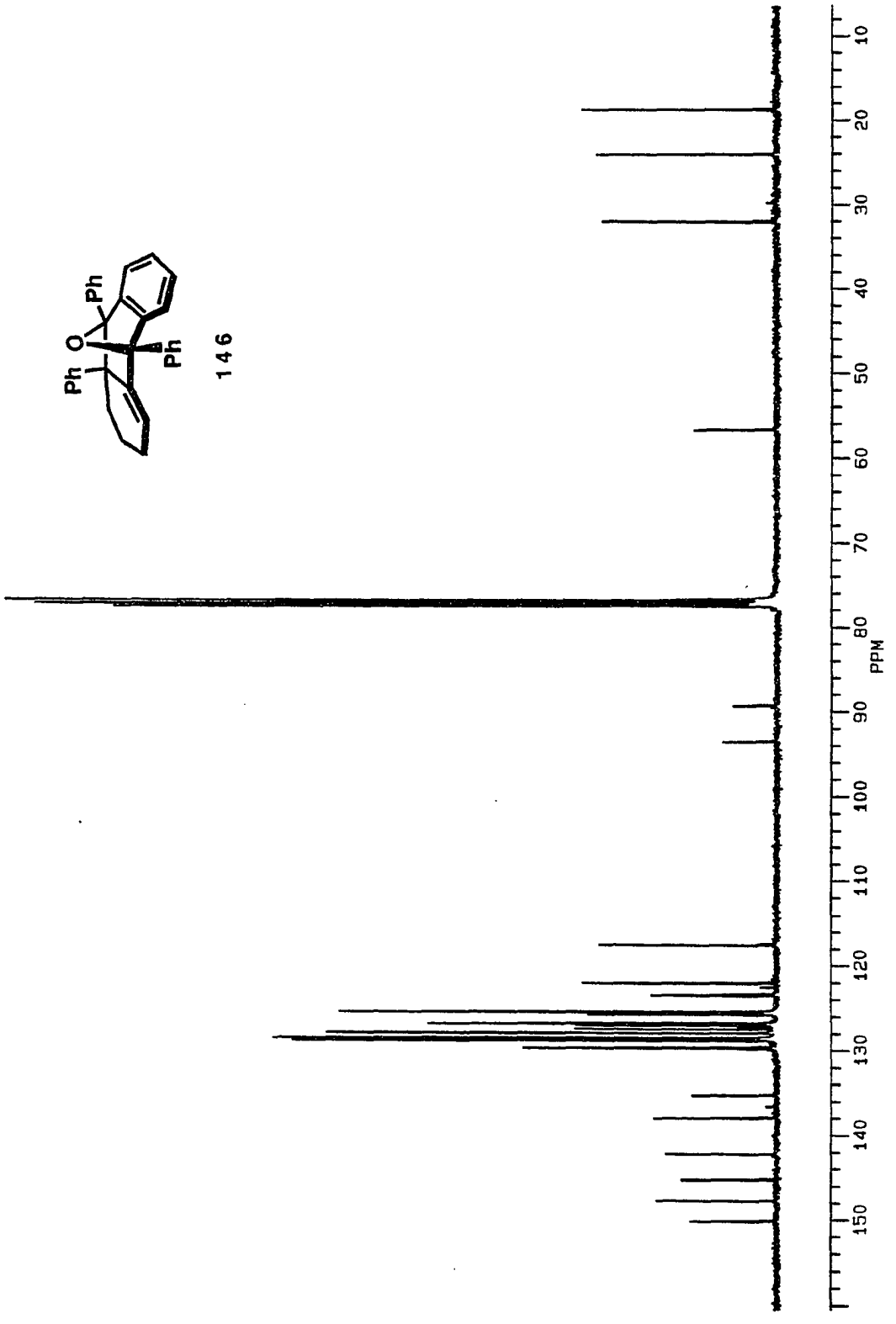

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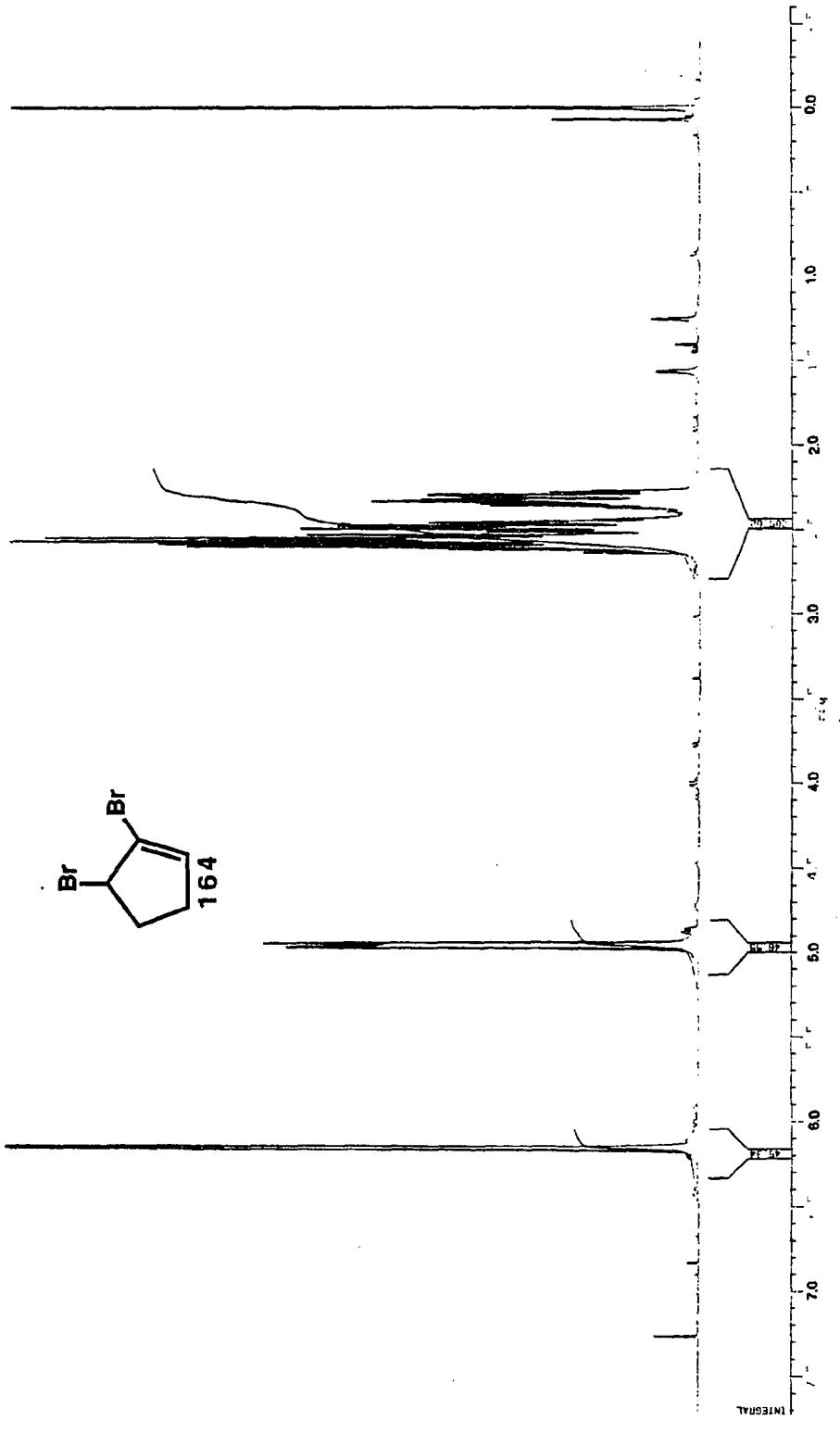

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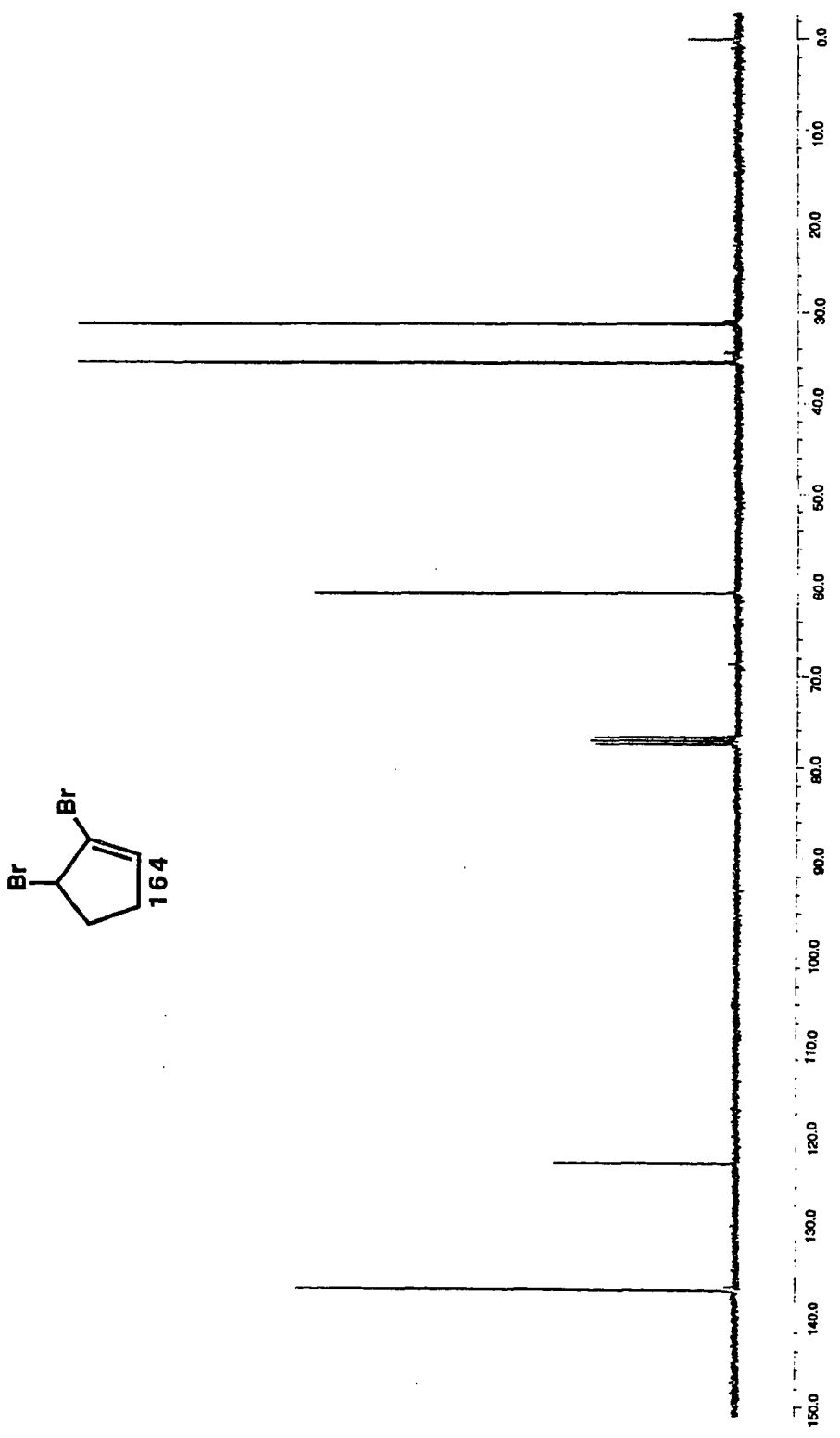

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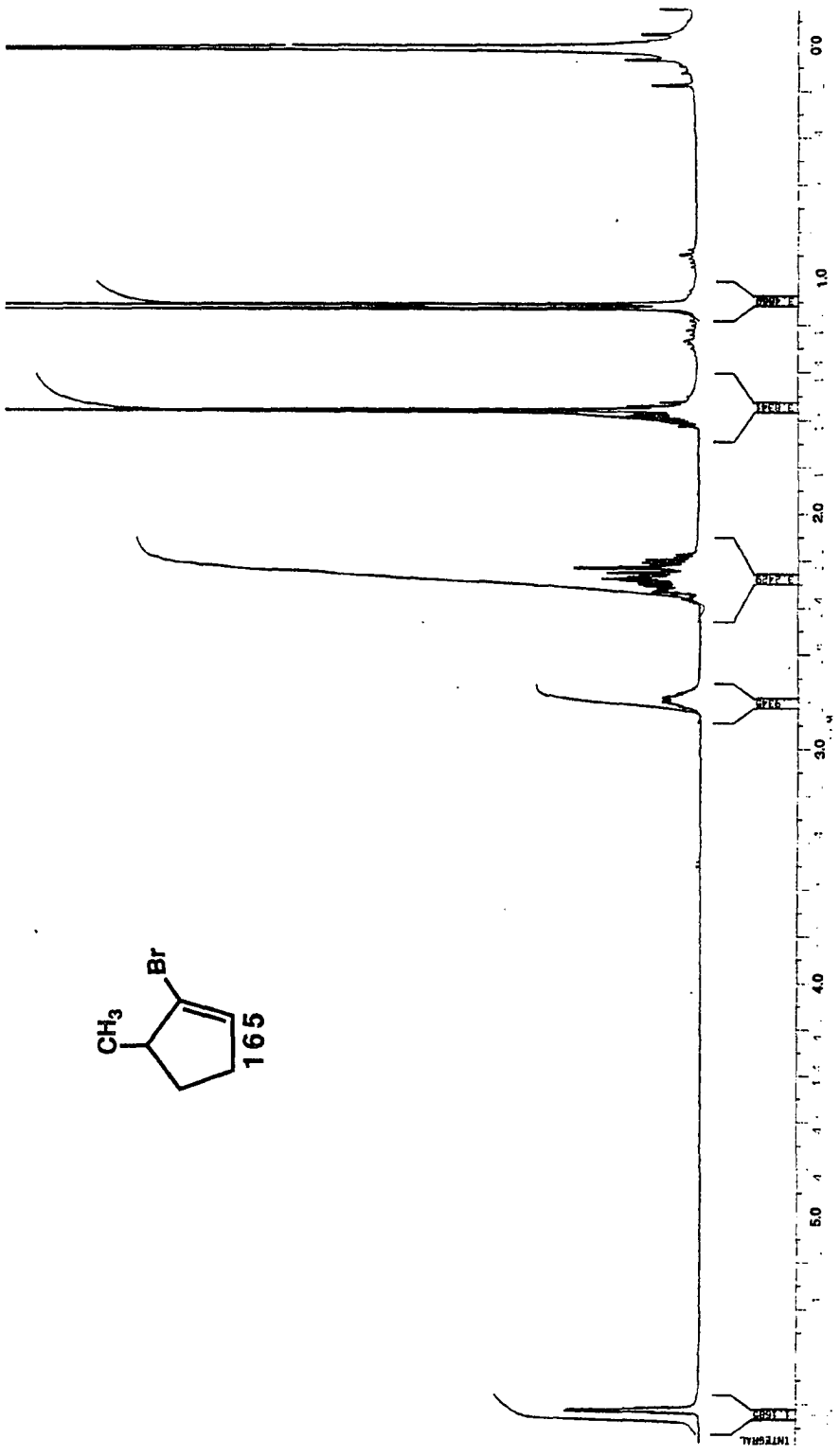

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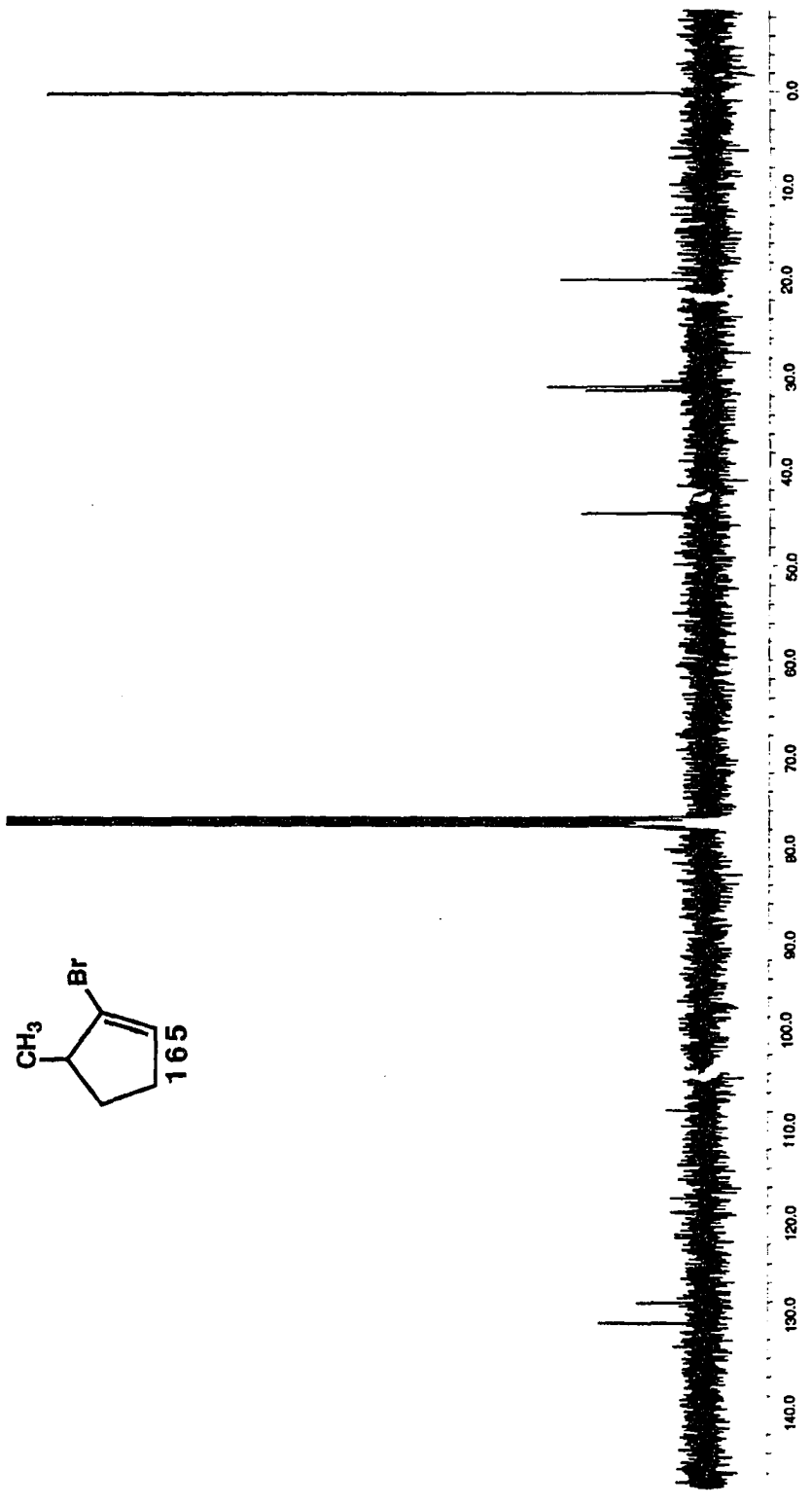

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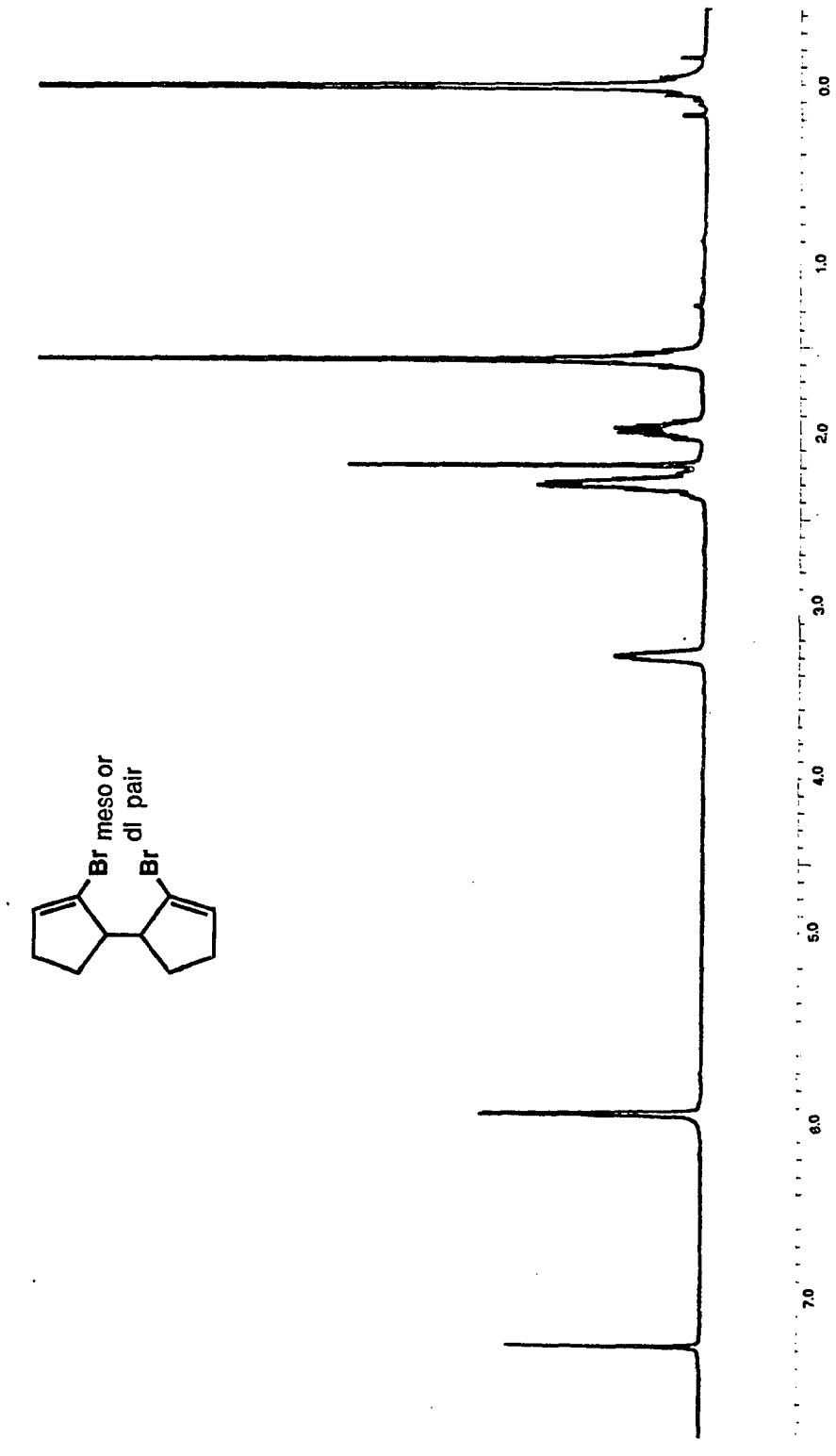

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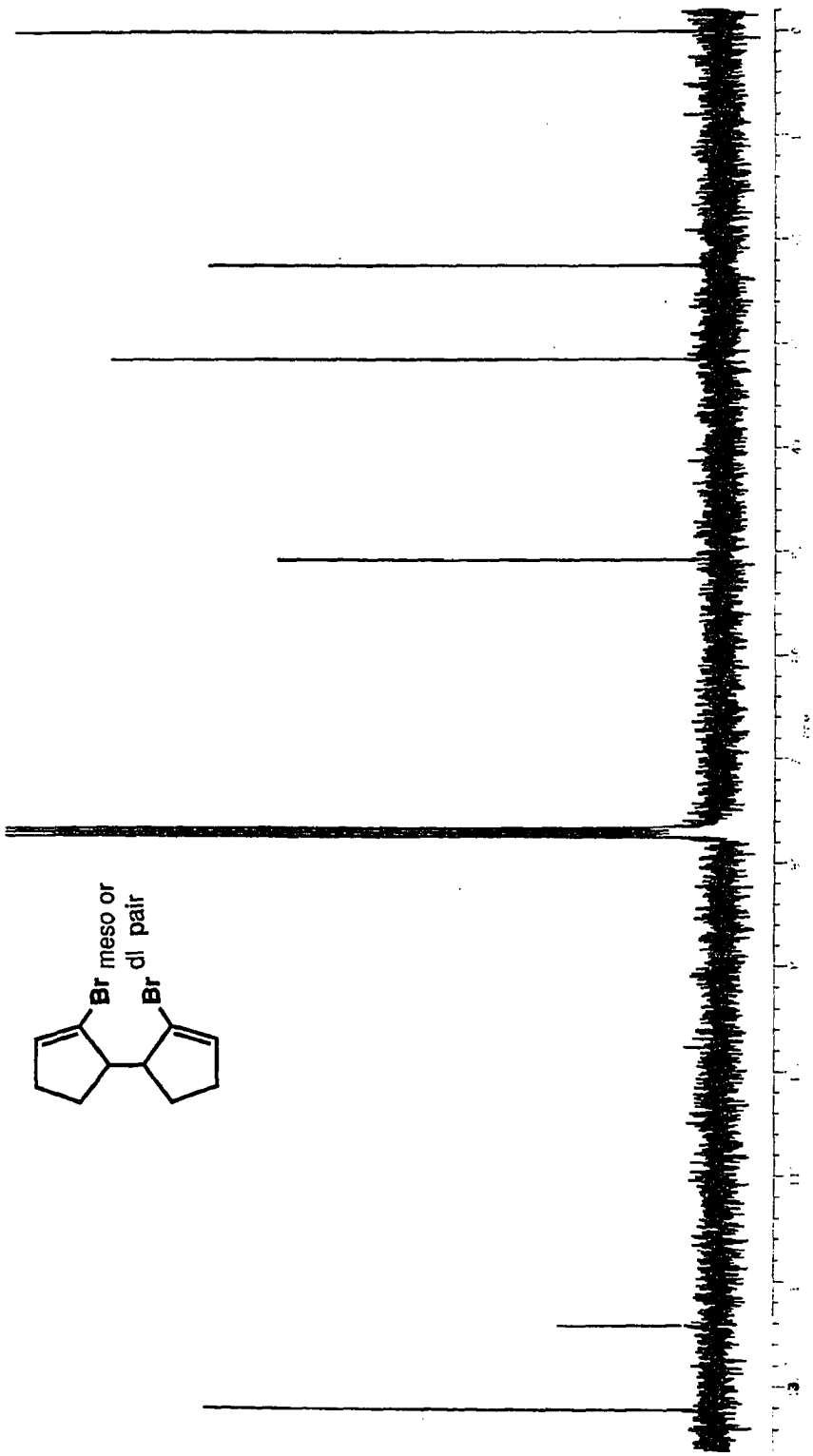

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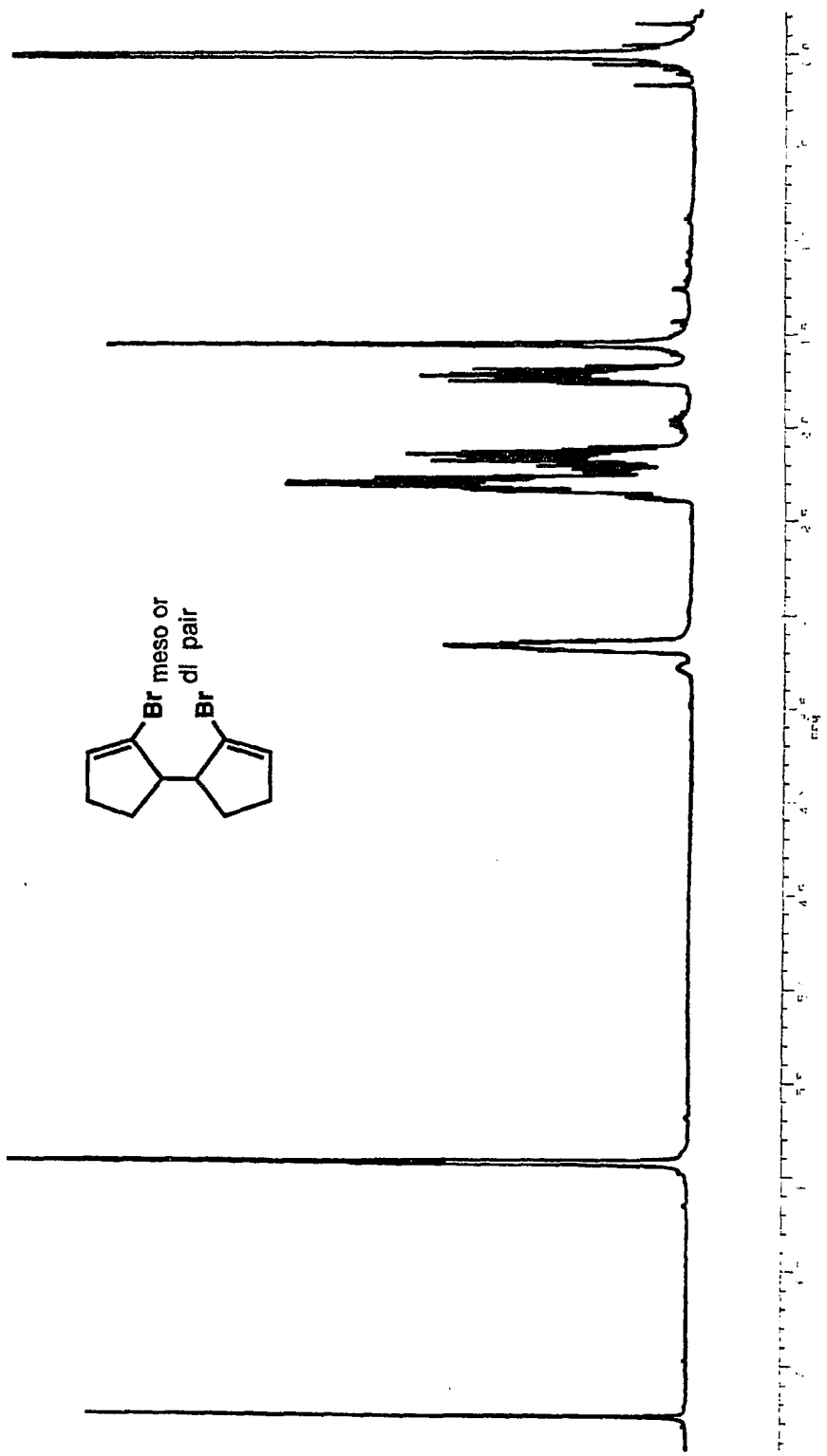

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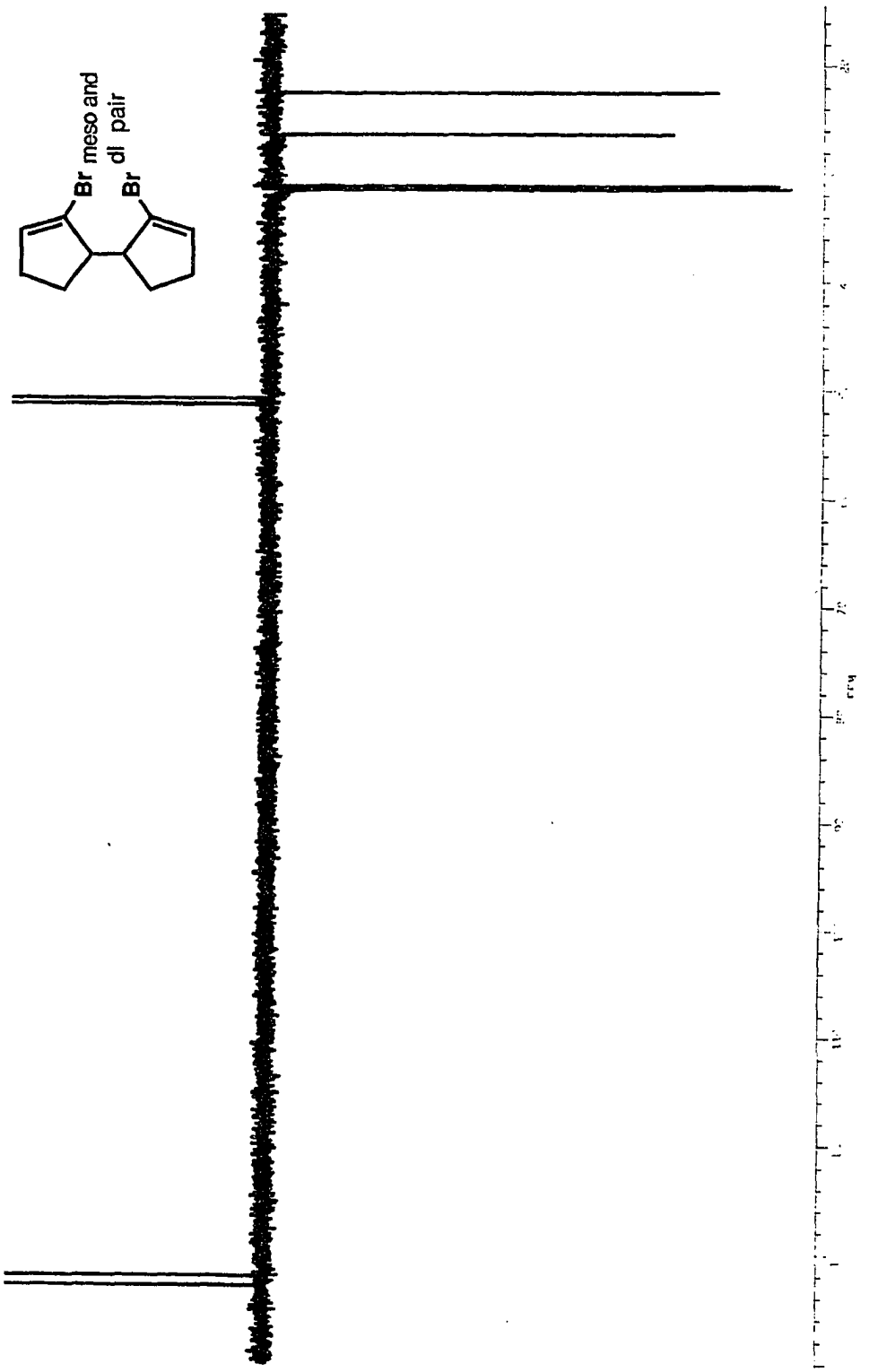

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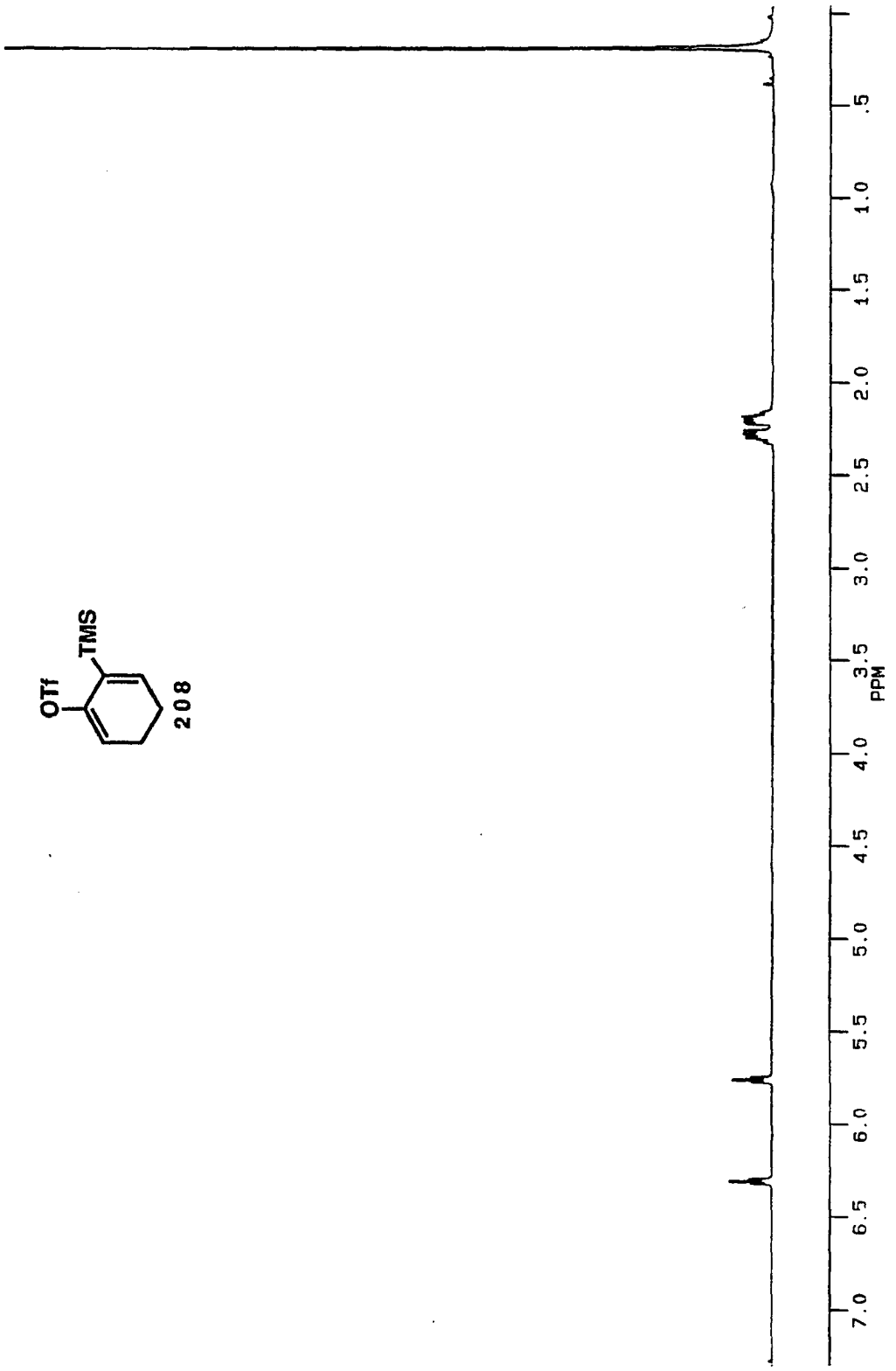

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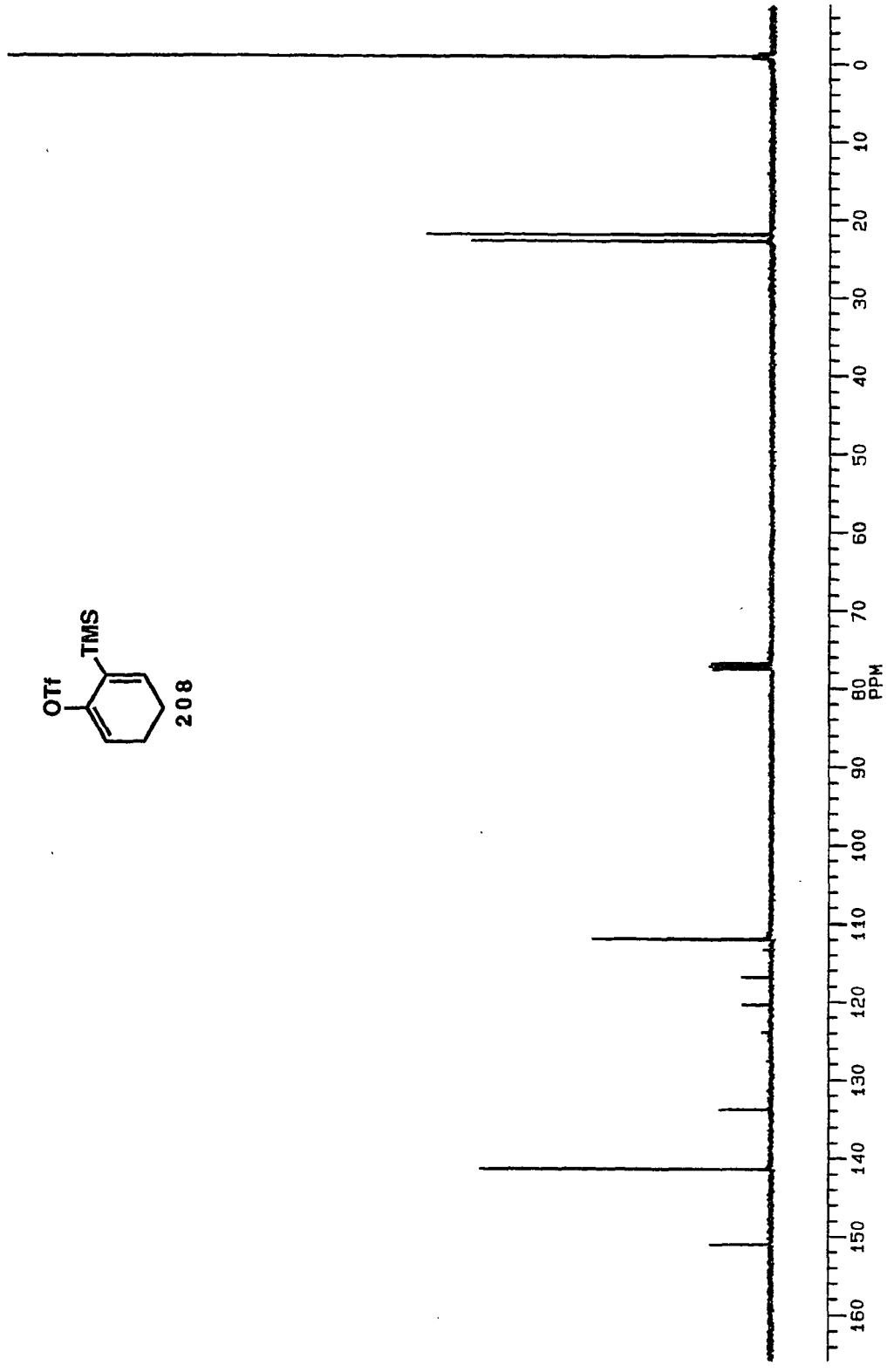

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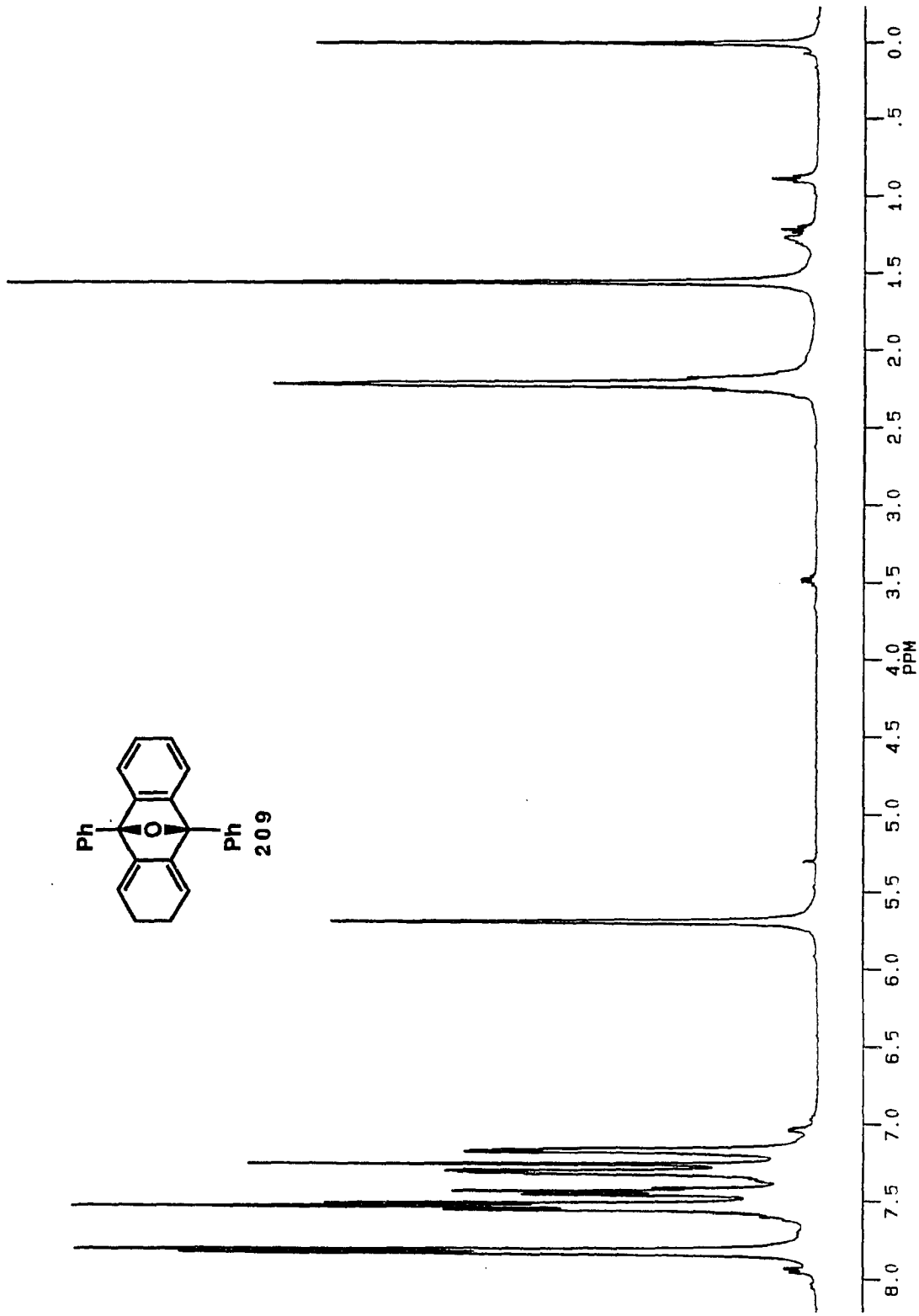

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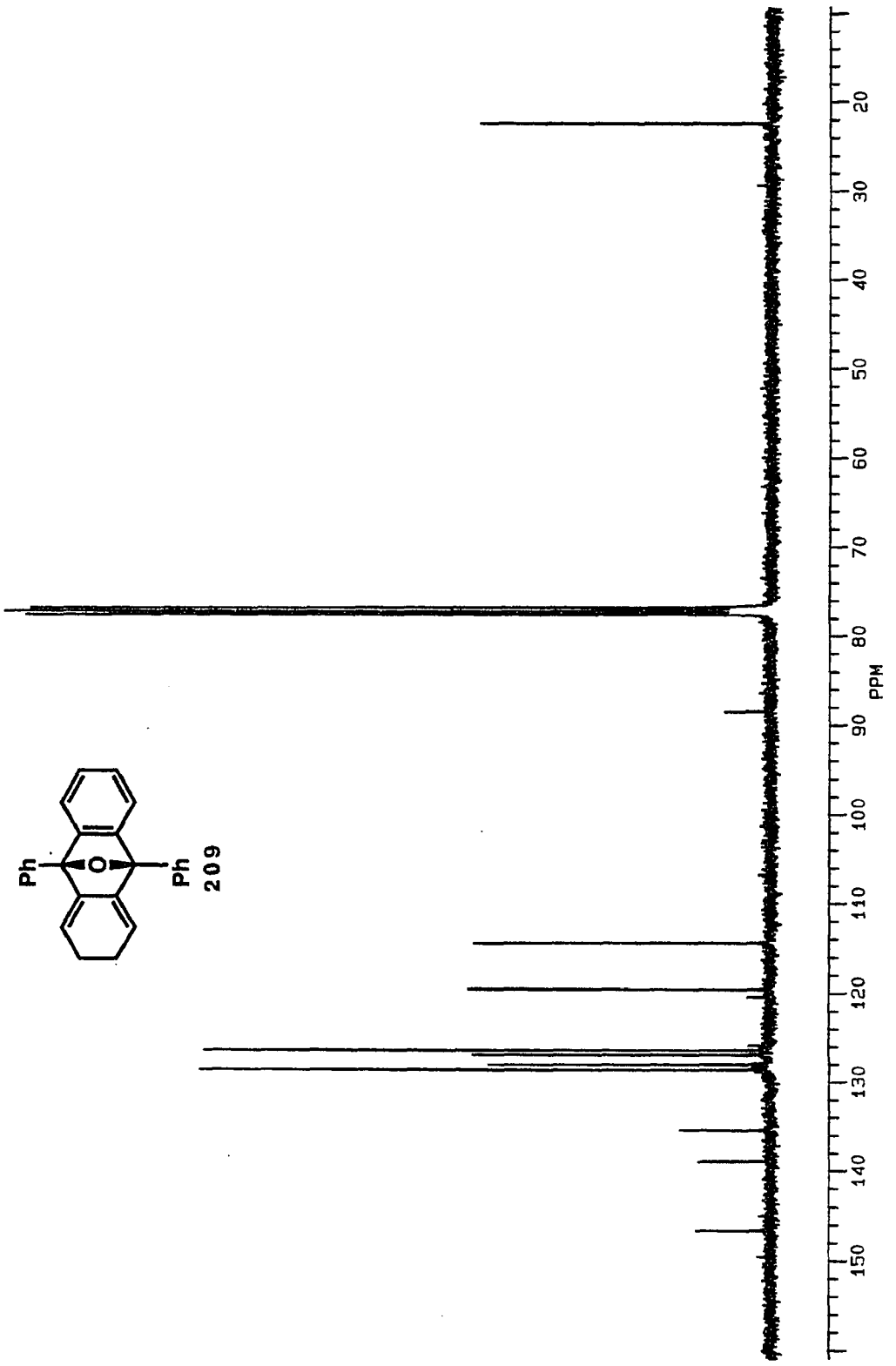

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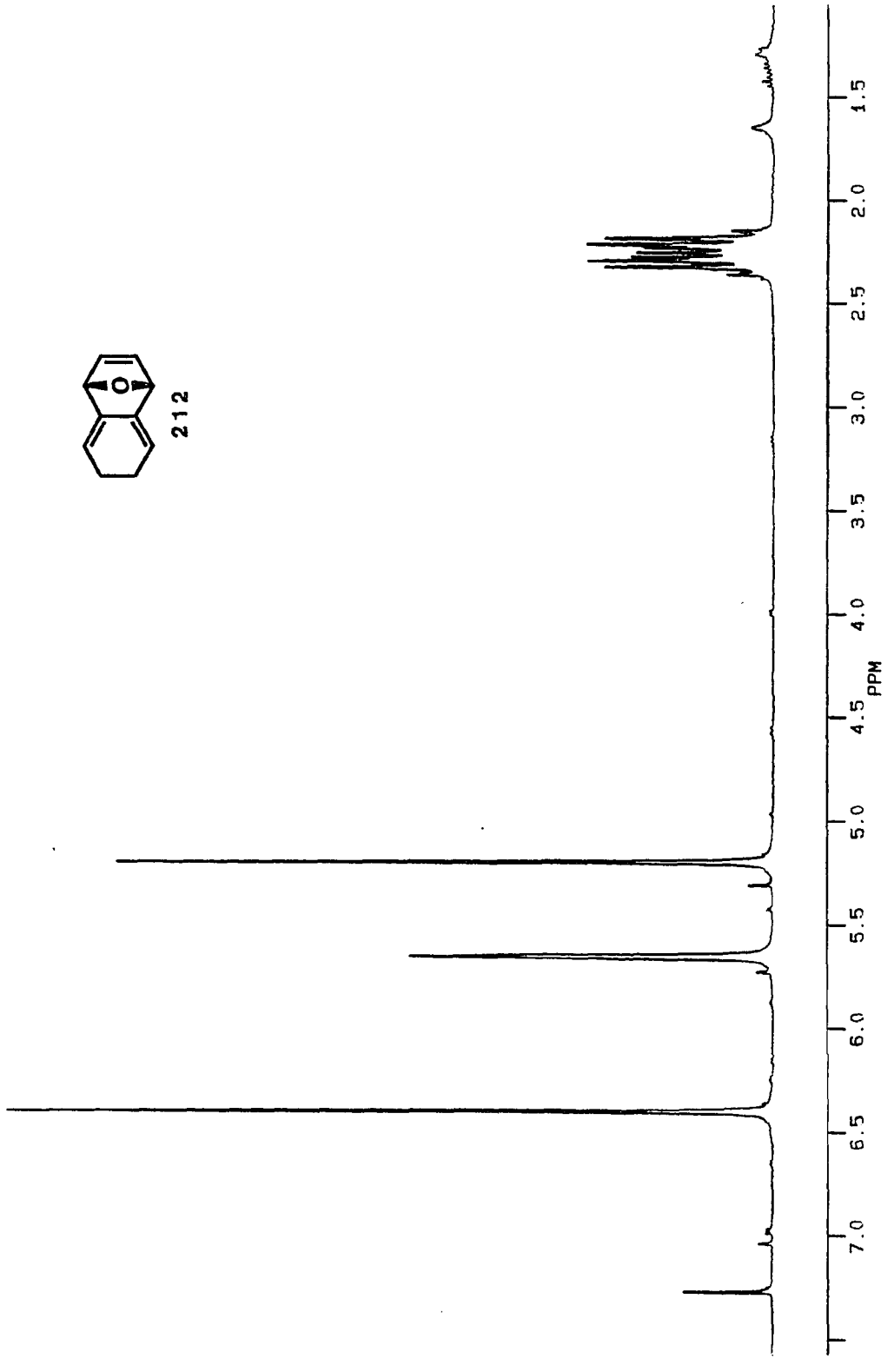

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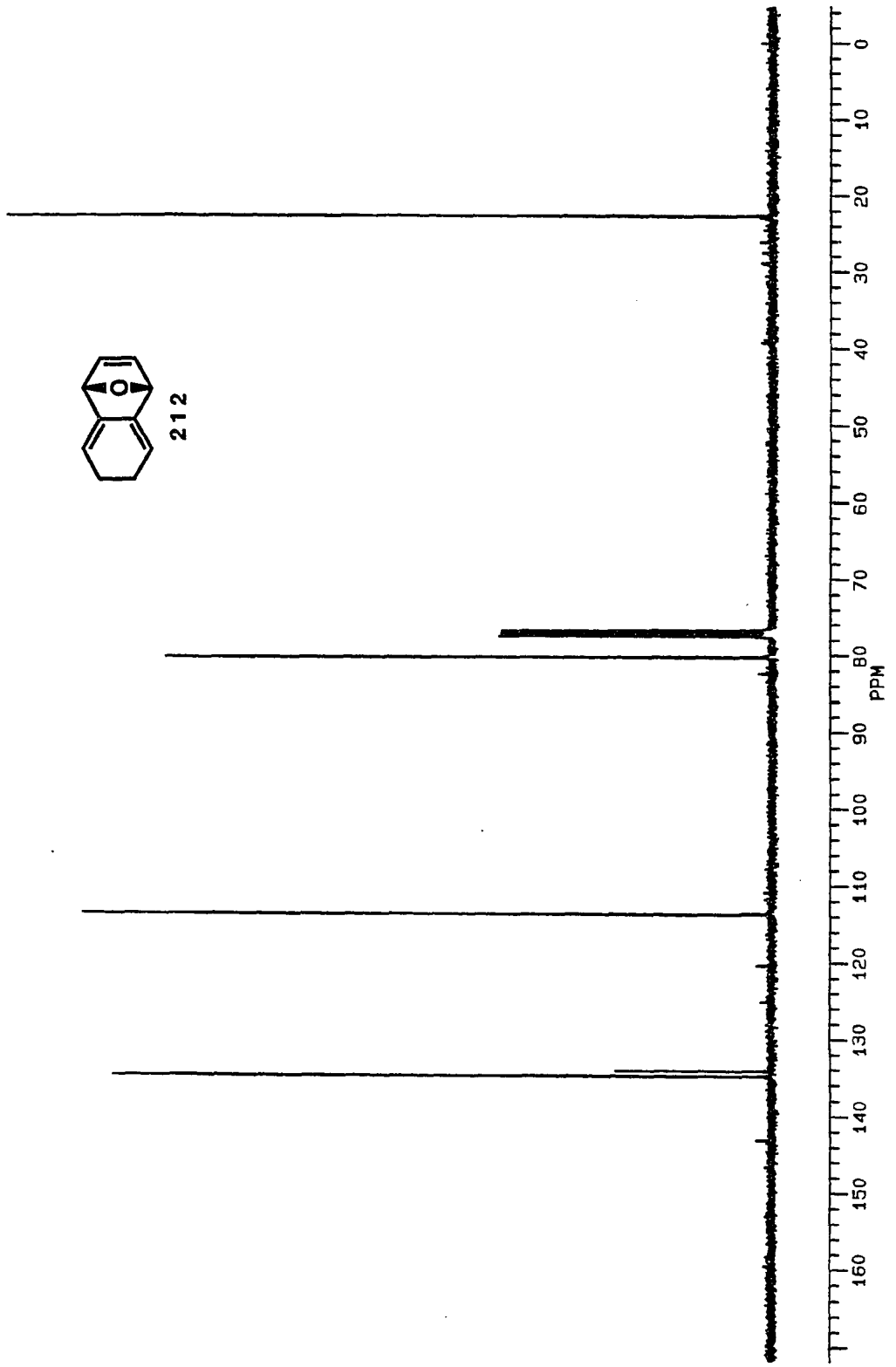

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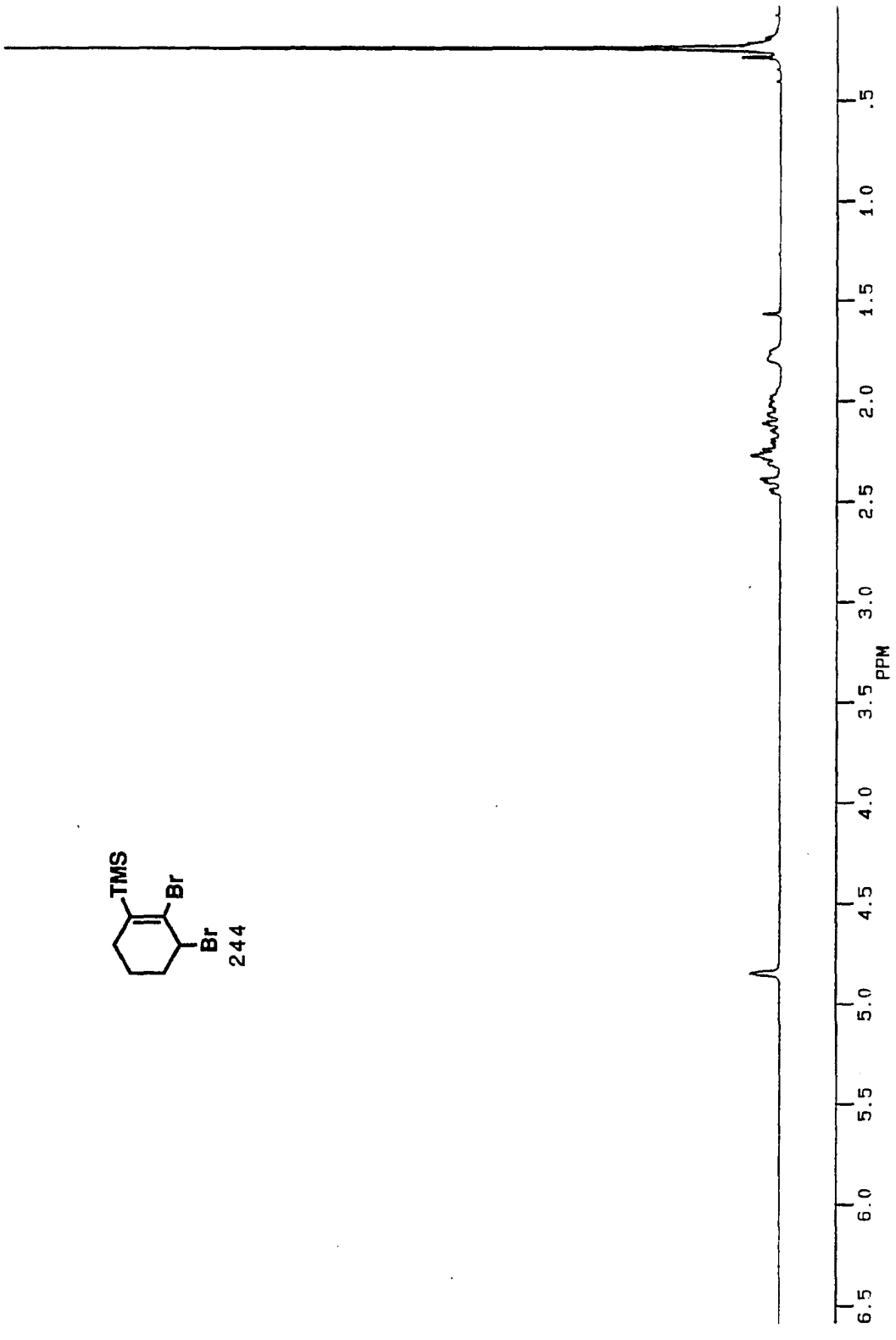

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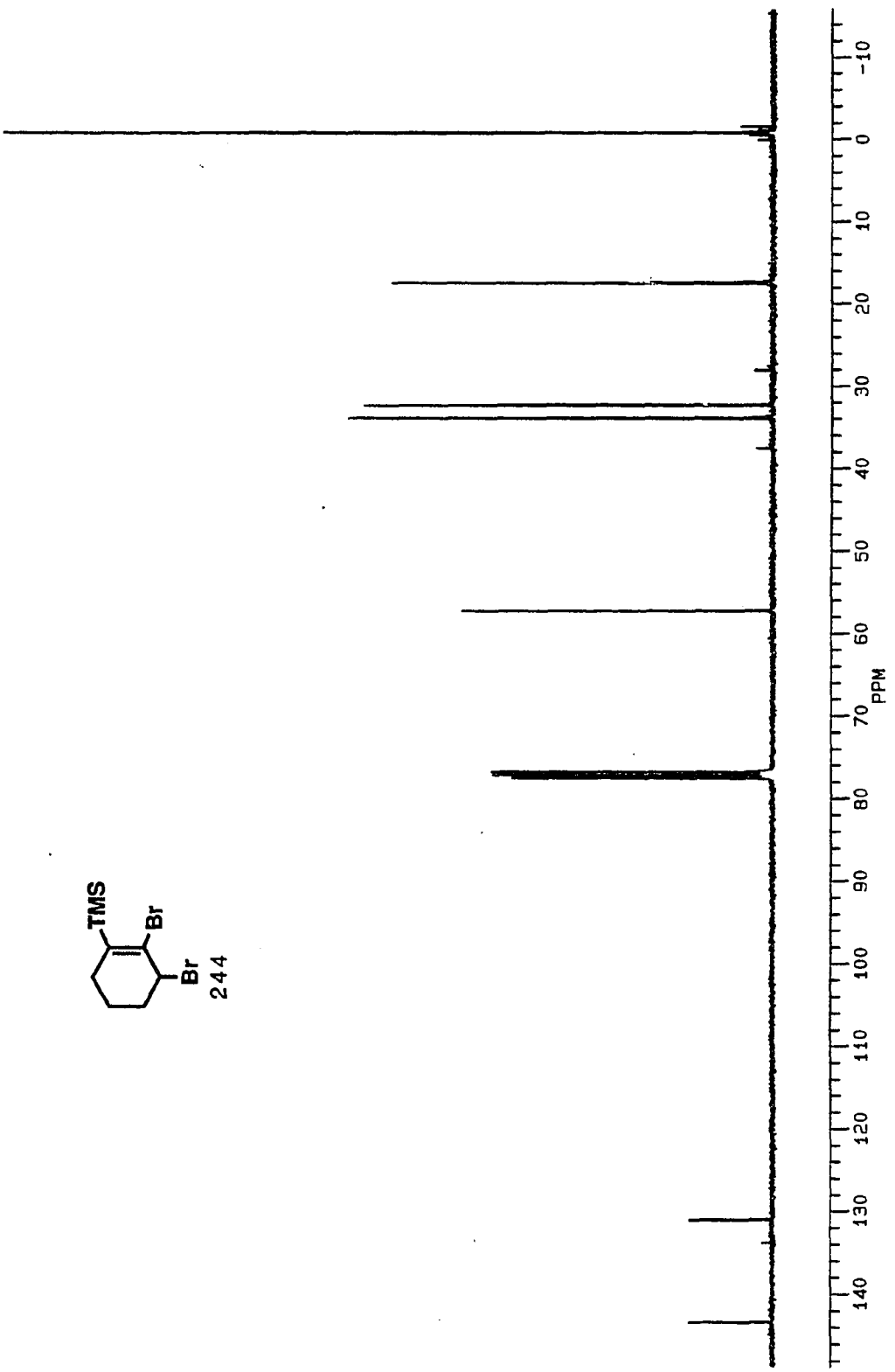

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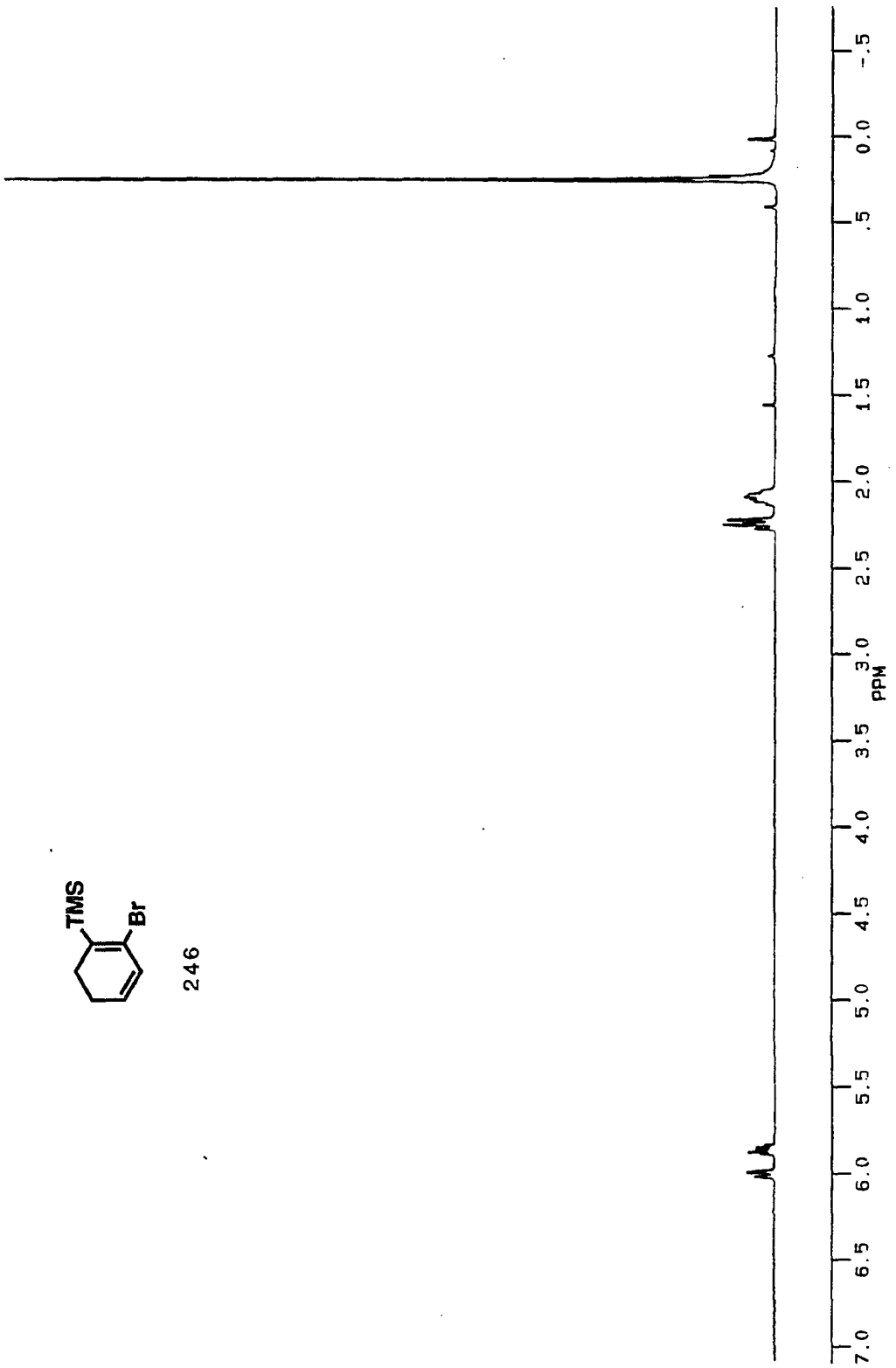

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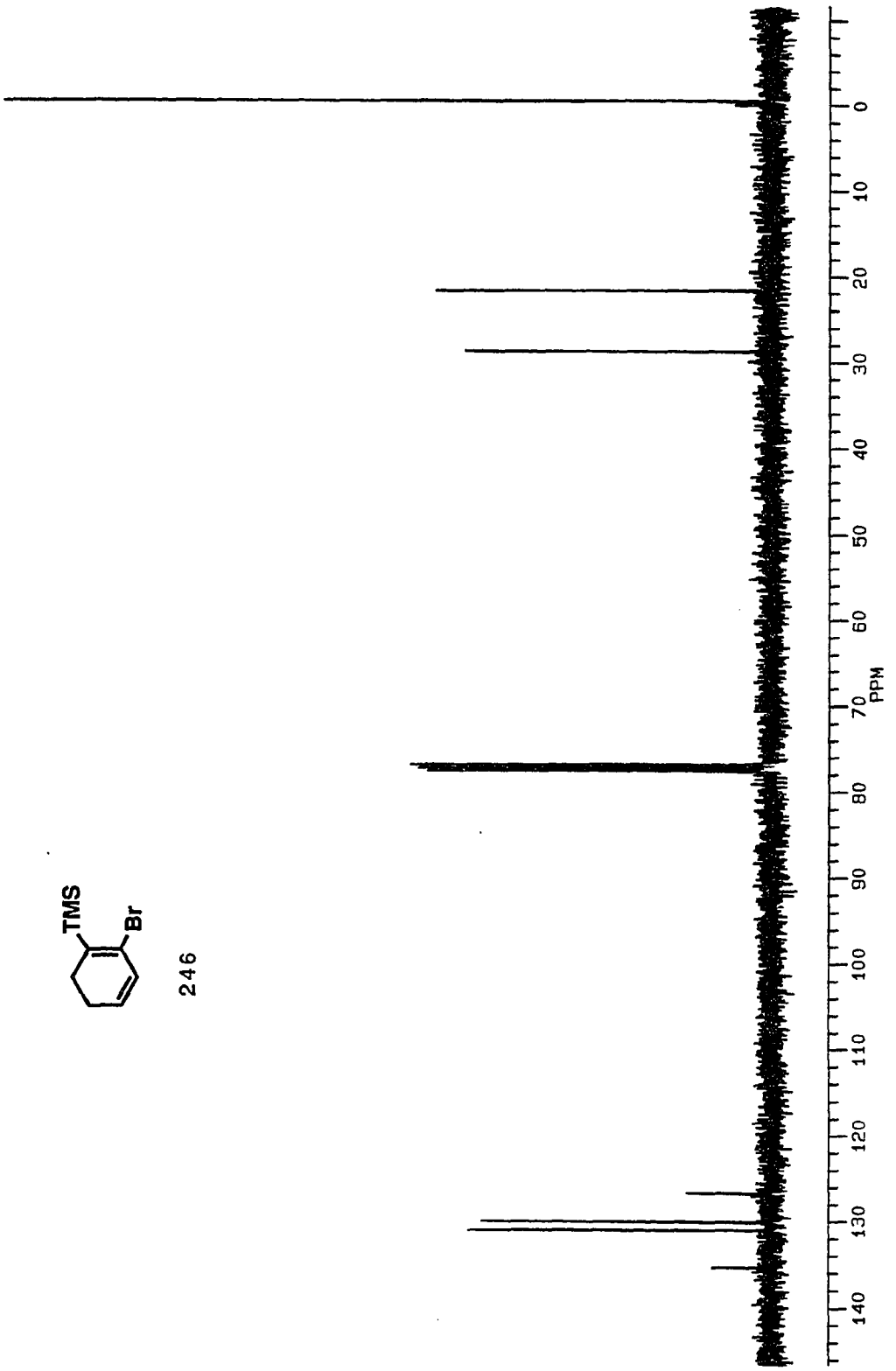

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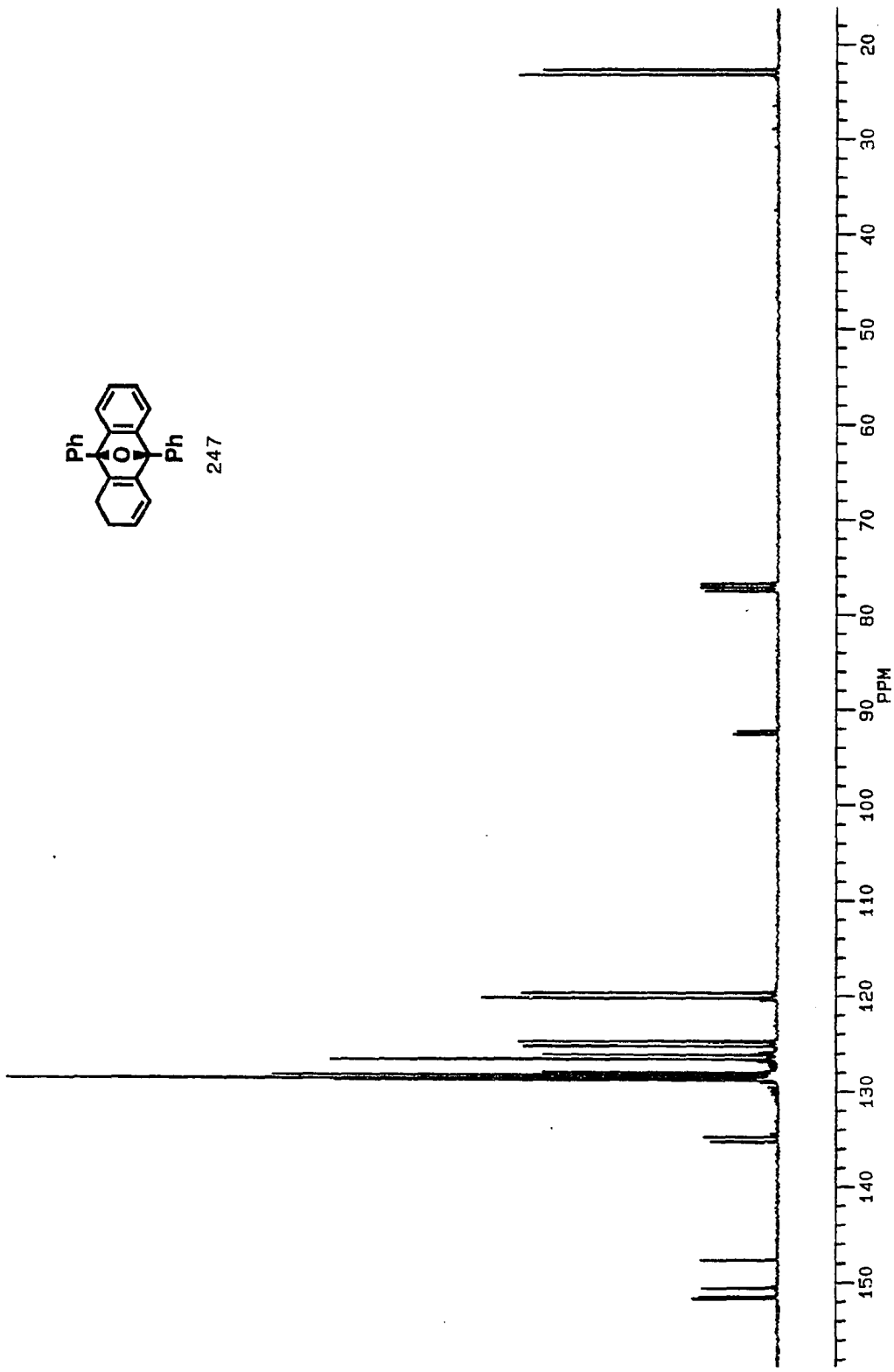

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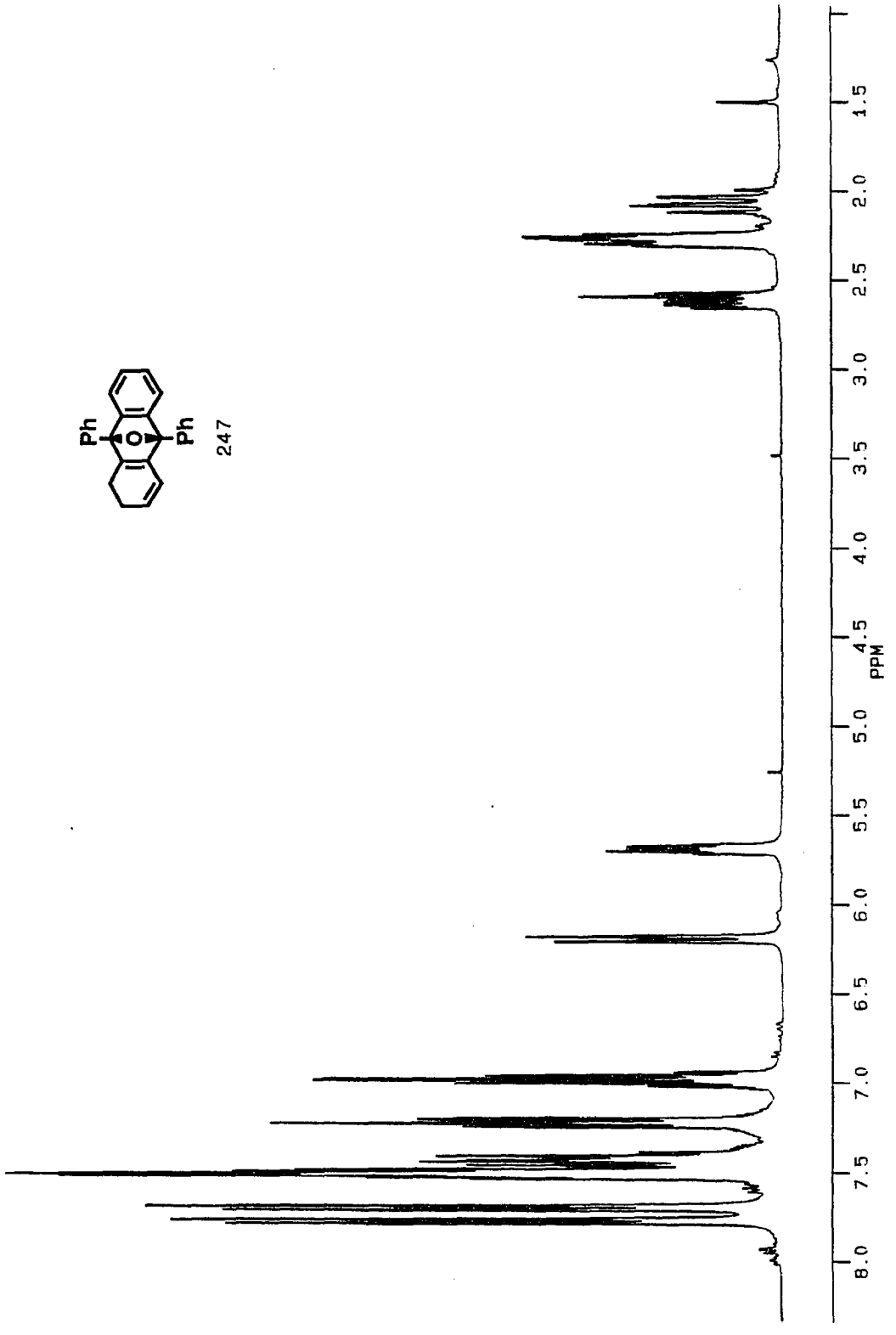

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REFERENCES

(1) Tolbert, L. M.; Ali, M. B. *J. Am. Chem. Soc.* **1982**, *104*, 1742.

(2) Demuth, M.; Mikahail, G. *Synthesis* **1989**, *3*, 145.

(3) Evans, S. V.; Garcia-Garibay, M.; Omkaram, N.; Scheffer, J. R., Trotter, J.; Wireko, F. *J. Am. Chem. Soc.* **1986**, *108*, 5648.

(4) Rau, H. *Chem. Rev.* **1983**, *83*, 535 and references therein.

(5) Förster, T. "Fluoreszenz Organischer Verbindungen"; Vandenhoeck und Ruprecht: Göttingen, 1951; pp 83 ff.

(6) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836.

(7) Hammond, G. S.; Cole, R. S. *J. Am. Chem. Soc.* **1965**, *87*, 3256.

(8) Murov, S. L.; Cole, R. S.; Hammond, G. S. *J. Am. Chem. Soc.* **1968**, *90*, 2957.

(9) Balavoine, G.; Jugé, S., Kagan, H. B. *Tetrahedron Lett.* **1973**, 4159.

(10) Ouannès, C.; Beugelmans, R. R. *J. Am. Chem. Soc.* **1983**, *95*, 8472.

(11) Drucker, C. S.; Toscano, V. G.; Weiss, R. G. *J. Am. Chem. Soc.* **1973**, *95*, 6482.

(12) (a) Inoue, Y.; Kunitomi, Y.; Takamuku, S.; Sakurai, H. *J. Chem. Soc., Chem. Commun.* **1978**, 1024. (b) Inoue, Y.; Yokoyama, T.; Yamasaki, N.; Tai, A. *J. Am. Chem. Soc.* **1989**, *111*, 6480.

(13) Demuth, M.; Raghavan, P. R.; Carter, C.; Nakano, K.; Schaffner, K. *Helv. Chim. Acta* **1980**, *63*, 2434.

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(14) Hoshi, N.; Furukawa, Y.; Hagiwara, H.; Sato, K. *Chem. Lett.* **1980**, 47.

(15) Simpson, J. E.; Daub, G. H.; Hayes, F. N. *J. Org. Chem.* **1973**, *38*, 1771.

(16) Tétreau, C.; Lavalette, D.; Cabaret, D.; Geraghty, N.; Welvart, Z. *Nouveau Journal De Chemie* **1982**, *6*, 461.

(17) (a) Jacobs, T. L.; Danker, D. *J. Org. Chem.* **1957**, *22*, 1424. (b) Jones, W. M.; Wilson, J. W.; Tutweiler, F. B. *J. Am. Chem. Soc.* **1963**, *85*, 3309. (c) Mason, S. F.; Vane, G. W. *Tetrahedron Lett.* **1965**, 1593. (d) Rossi, R.; Diversi, P. *Synthesis* **1973**, 25.

(18) (a) Cope, A. C.; Bumgardner, C. L. *J. Am. Chem. Soc.* **1956**, *78*, 2812. (b) Liu, R. S. H. *J. Am. Chem. Soc.* **1967**, *87*, 3996.

(19) Isaksson, R.; Roschester, J.; Sandström, Wistrand, L-G. *J. Am. Chem. Soc.* **1985**, *107*, 4074.

(20) Inoue, Y.; Daino, Y.; Hagiwara, S.; Nakamura, H.; Hakushi, T. *J. Chem. Soc., Chem. Commun.* **1985**, 804.

(21) Becker, R. S.; Edwards, L.; Bost, M. E.; Griffin, G. *J. Am. Chem. Soc.* **1972**, *90*, 2957.

(22) Kirchhoff, M. Experimental work conducted at the University of New Hampshire.

(23) (a) Schuster, H.F.; Coppola, G.M., "Allenes in Organic Synthesis", John Wiley & Sons, **1984**. (b) Houben-Weyl, "Methoden der Organischen Chemie", E. Müller, ed., Band IV/5, Parts I and II. Georg Thieme Verlag, Stuggart, 1975-76. (c) S. Patai, ed., "The Chemistry of Ketenes, Allenes, and Related Compounds", Wiley, 1980, Parts 1 and 2.

(24) Johnson, R.P., *Org. Photochem.*, **1985**, *7*, 75.

(25) Stierman, T. J.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 3971.

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(26) Chapman, O. L. *Pure Appl. Chem.* **1975**, *40*, 511.

(27) (a) Steinmetz, M. G.; Stark, E. J.; Yen, Y-P.; Mayes, R. T. *J. Am. Chem. Soc.* **1983**, *105*, 7209. (b) Steinmetz, M. G.; Strinivasan, R.; Leigh, W. J. *Rev. Chem. Intermed.* **1984**, *5*, 57.

(28) (a) Ward, H. R.; Karafiath, E. *J. Am. Chem. Soc.* **1969**, *91*, 7475. (b) Ward, H. R.; Karafiath, E. *J. Am. Chem. So9c.* **1969**, *91*, 522. (c) Ward, H. R.; Karafiath, E. *J. Am. Chem. Soc.* **1969**, *90*, 2193.

(29) Price, J. D.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 2187.

(30) Berridge, J. C.; Forrester, J.; Foulger, B. E.; Gilbert, A. *J. Chem. Soc., Perkin Trans.I* **1980**, 2425.

(31) Price, J. D.; Johnson, R. P. Submitted to *J. Org. Chem.*

(32) (a) Lewina, R. J.; Trachtenberg, D. H. *Zh. Obsch. Khim.* **1936**, *6*, 764. (b) Zweifel, G.; Horng, A.; Snow, J. T. *J. Am. Chem. Soc.* **1970**, *92*, 1427.

(33) Salomon, R. G.; Sinha, A.; Salomon, M. F. *J. Am. Chem. Soc.* **1978**, *100*, 520.

(34) (a) Ginzburg, Ya. I. *J. Gen. Chem.* (USSR) **1940**, *10*, 513. (b) Hennion, G. F.; Sheenan, J. J.; *J. Am. Chem. Soc.* **1949**, *71*, 1964. (c) Bertrand, M. *Bull Soc. Chim. France,* **1956**, 461. (d) Jones, E. R. H.; Lee, H. H.; Whiting, M. C. *J. Chem. Soc.* **1960**, 341.

(35) Moore, W. R.; Ward, H. R.; Merritt, R. F. *J. Am. Chem. Soc.* **1961**, *83*, 2019.

(36) Paquette, L. A. *Synthesis* **1975**, *6*, 347.

(37) Stierman, T. J. Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1985.

(38) Padwa, A. *Org. Photochemistry* **1979**, *4*, 1, and references therein.

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(39) (a) Pasto, D. J.; Haley, M.; Chapman, D. M. *J. Am. Chem. Soc.* **1978**, *100*, 5272. (b) Walborsky, H. M. *Tetrahedron* **1981**, *37*, 1625.

(40) (a) Günther, H.; Herrig, W.; Seel, H.; Tobias, S. *J. Org. Chem.* **1980**, *45*, 4329. (b) Baird, M. S. *J. Chem. Soc. Perkin I* **1979**, 1020.

(41) Korth, H-G.; Lommes, P.; Sustmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 663.

(42) Price, J. D.; Johnson, R. P. *Tetrahedron Lett.* **1985**, *26*, 2499.

(43) Hopf, H.; Dietmar, G.; Lenk, W. *Isr. J. Chem.* **1985**, *26*, 79.

(44) Lam, B.; Johnson, R. P. *J. Am. Chem. Soc.* **1983**, *105*, 7479.

(45) For reviews and leading references, see: (a) Platz, M. S. *Acc. Chem. Res.* **1988**, *21*, 241. (b) Tedder, J. M. *Tetrahedron* **1982**, *38*, 313. (c) Wentrup, C., "Reactive Molecules: The Neutral reactive Intermediates in Organic Chemistry", John Wiley and Sons, Inc., **1984**.

(46) For other theoretical studies on hydrogen abstraction reactions, see: (a) Wildman, T. A. *Chem. Phys. Lett.* **1986**, *126*, 325. (b) Severance, D.; Pandey, B.; Morrison, H. *J. Am. Chem. Soc.* **1987**, *109*, 3231. (c) Gordon, M. S.; Gano, D. R.; Boatz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5771. (d) Gordon, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 4054. (e) Bauschlicher Jr., C. W.; Bender, C. F.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1976**, *98*, 3072. (g) Carr, R.W. *J. Phys. Chem.* **1972**, *76*, 1581. (h) Bodor, N.; Dewar, M. J. S.; Wasson, J. S. *J. Am. Chem. Soc.* **1972**, *94*, 9095.

(47) Karan, H. I. *J. Org. Chem.* **1981**, *46*, 2186.

(48) Stierman, T.J.; Shakespeare, W. C.; Johnson, R.P. *J. Org. Chem.* **1990**, *55*, 1043.

(49) Mosher, O. A.; Flicker, W.M.; Kupperman, A. *J. Chem. Phys.* **1975**, *62*, 2600.

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(50) (a) Schmidt, M. W.; Lee, E. K. C. *J. Am. Chem. Soc.* **1970**, *92*, 3579. (b) Rodriguez, O.; Morrison, H. *J. Chem. Soc. Chem. Commun.* **1971**, 679.

(51) Jones Jr., M.; Moss, R. A. "Carbenes", Vols. I and II, John Wiley & Sons, **1973**, 1975.

(52) (a) Valazanos, P.; Elbert, S. T.; Ruedenberg, K. *J. Am. Chem. Soc.* **1985**, *107*, 3780. (b) Rauk, A.; Bouma, W. J.; Radon, L. *J. Am. Chem. Soc.* **1985**, *107*, 3780. (c) Honjou, N.; Pacansky, J.; Yoshimine, M. *J. Am. Chem. Soc.*, **1985**, *107*, 5332. See also ref. 25 for earlier calculations on cyclopropylidene.

(53) (a) Seeger, R.; Krishnan, R.; Pople, J. A.; Von R. Schleyer, P. *J. Am. Chem. Soc.*, **1977**, *99*, 7103. (b) Krogh-Jespersen, K. *J. Comput. Chem.* **1982**, *3*, 571.

(54) Angus Jr., R. O.; Schimidt, M. W.; Johnson, R. P. *J. Am. Chem. Soc.*, **1985**, *107*, 532.

(55) Binkley, J. S.; Frisch, M.; Roghavachari, K.; DeFrees, D. J.; Schlegel, H. B.; Whiteside, R.; Fluder, E.; Seeger, R.; Pople, J. A. GAUSSIAN 82, Carnegie-Mellon University, Pittsburgh, PA.

(56) Hehre, W. J.; Radom, L.; von R. Schleyer, P.; Pople, J. A. "Ab Initio Molecular Orbital Theory", Wiley Interscience, **1986**.

(57) Dupuis, M.; Spangler, D.; Wendoloski, J. J. NRCC Software Catalog, Vol. 1, program CG01, GAMESS, **1980**, modified by Schmidt, M. W.; Elbert, S. T. and Lam, B., **1987**.

(58) (a) Dupuis, M.; Pacansky, J. *J. Chem. Phys.* **1982**, *76*, 2511. (b) Gordon, M. S.; Gano, D. R.; Boatz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5771.

(59) Rauk, A.; Drake, A. F.; Mason, Stephen F. *J. Am. Chem. Soc.* **1979**, *101*, 2284.

(60) Martin, P. S.; Yates, K.; Csizmadia, I. G. *J. Mol. Struct. (Theochem.)* **1988**, *170*, 107.

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(61) (a) Pascal, R. A., Jr.; Baum, M. W.; Wagner, C. K.; Rodgers, L. R. *J. Amer. Chem. Soc.* **1984**, *106*, 5377. (b) Pascal, R. A., Jr.; Baum, M. W.; Wagner, C. K.; Rodgers, L. R. *J. Amer. Chem. Soc.* **1986**, *108*, 6477.

(62) Andro, T. M. Experimental work conducted at the University of New Hampshire. Shakespeare, W. C. Spectroscopic conducted at the University of New Hampshire.

(63) Paquette, L. A.; Aravamuthan, V.; Burke, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 8032.

(64) Moore O', F. *J. Chem. Soc. B.* **1970**, 785.

(65) Lewis, E. S.; Symons, M. C. R. *Quart. Rev.* **1958**, *12*, 230.

(66) Corey, E. J.; Pasto, D. J.; Mock, W. L. *J. Am. Chem. Soc.* **1961**, *83*, 2957.

(67) (a) von Baeyer, A. *Ber. Dtsch. Chem. Ges..* **1885**, *18*, 2278. (b) Perkin, W., Jr. *Ber. Dtsch. Chem. Ges..* **1884**, *17*, 323.

(68) Wiberg, K. B. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 312 and references therein.

(69) Leibman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311 and references therein.

(70) Wiberg, K. B.; *Acc. Chem. Res.* **1982**, *104*, 5239. (b) Wiberg, K. B. *Chem Rev.* **1989**, *89*, 975.

(71) (a) Maier, G. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 309. (b) Maier, G.; Pfriem, S.; Schäfer, U.; Malsch, K. -D.; Matusch, R. *Chem. Ber.* **1981**, *36*, 350.

(72) Venepalli, B. R.; Agosta, W. C. *Chem. Rev.* **1987**, *87*, 399 and references therein.

(73) Traetteberg, M. *Acta Chem. Scand. B* **1975**, *29*, 29.

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(74) Inoue, Y.; Ueoka, T.; Kuroda, T.; Hakushi, T. *J. Chem. Soc., Perkin Trans. 2* **1983**, 983 and references therein.

(75) Evers, J. T. M.; Mackor, A. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 423.

(76) Verbeek, J.; van Lenthe, J. H.; Timmermans, P. J. J. A.; Mackor, A.; Budzelaar, P. H. M. *J. Org. Chem.* **1987**, *52*, 2955.

(77) (a) Warner, P. M. *Chem. Rev.* **1989**, *89*, 1067. (b) Borden, W. T. *Chem. Rev.* **1989**, *89*, 1095. (c) Billups, W. E.; Haley, M. M.; Lee, G-A. *Chem. Rev.* **1989**, *89*, 1147.

(78) Dünker, A.; Szeimies, G. *Tetrahedron Lett.* **1985**, *26*, 3555.

(79) (a) Zoch, H-G.; Szeimies, G.; Römer, R.; Schmitt, R. *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 877. (b) Schlüter, A-D.; Belzner, J.; Heywang, U.; Szeimies, G. *Tetrahedron Lett.* **1983**, *24*, 891. (c) Zoch, H-G.; Szeimies, G.; Römer, R.; Germain, G.; Declercq, J.-P. *Chem Ber.* **1983**, *116*, 2285.

(80) (a) Angus Jr., R. O. Ph.D. Dissertation, Iowa State University, Ames, Iowa, **1985**. (b) Andres, J.; Cardenas, R.; Tapia, O. *J. Chem. Soc. Perkin II*, **1985**, 363.

(81) Angus Jr., R. O.; Schmidt, M. W.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 532.

(82) Moore, W. R.; Moser, W. R. *J. Am. Chem. Soc.* **1970**, *92*, 5469.

(83) Dillon, P. W.; Underwood, G. R. *J. Am. Chem. Soc.* **1974**, *96*, 779.

(84) Balci, M.; Jones, W. M. *J. Am. Chem. Soc.* **1980**, *102*, 7607.

(85) Seeger, R.; Krishnan, R.; Pople, J. A.; von R. Schleyer, P. *J. Am. Chem. Soc.* **1977**, *99*, 7103.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

(86) (a) Traetteberg, M.; Bakken, P.; Almenningen, A. *J. Mol. Struct.* **1981**, *70*, 287. (b) Luche, J. L.; Damiano, J. C.; Crabbe, P.; Cohen-Addad, C.; Lajzerowicz, J. *Tetrahedron*, **1977**, *33*, 961.

(87) Skattebol, L. *Tetrahedron Letters,* **1961**, 167. See also: Skattebol, L.; Solomon, S. *Org. Synth.*, **1969**, *49,* 35.

(88) Wisser, J. P.; Ramakers, J. E., *J. Chem. Soc. Chem. Commun.* **1972**, 178.

(89) (a) Wittig, G.; Meske-Schuller, J. *Leibigs Ann. Chem.* **1968**, *76*, 711. (b) Visser, J. P.; Ramakers, J. E. *J. Chem. Soc. Chem. Commun.* **1972**, 178.

(90) Johnson, R. P. *Chem. Rev,* **1989**, *89*, 1111 and references therein.

(91) Wentrup, C.; Gross, G.; Maquestiau, A.; Flammang, R. *Angew. Chem. Int. Ed. Engl.* **1983**, *27*, 542.

(92) Runge, A.; Sander, W. *Tetrahedron Lett.* **1986**, *27*, 5835.

(93) Price, J. P.; Shakespeare, W. C.; Johnson, R. P. unpublished results.

(94) Loiselle, P. M. B.S. Thesis, The University of New Hampshire, Durham, NH, 1987.

(95) Tolbert, L. M.; Islam, Md. N.; Johnson, R. P.; Loiselle, P. M.; Shakespeare, W. C. *J. Am. Chem. Soc.* **1990**, *112*, 6416.

(96) Christl, M.; Schreck, M. *Chem. Ber.* **1987**, *120*, 915.

(97) (a) Houk, K. N.; Lin, Y.-T.; Brown, F. K. *J. Am. Chem. Soc.* **1986**, *108*, 554. (b) Dewar, M. J. S.; Pierini, A. B. *J. Am. Chem. Soc.* **1984**, *106*, 203. (c) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 209. (d) Dewar, M. J. S.; Olivella, S.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1986**, *108*, 5771. (e) Tolbert, L. M.; Ali, M. B. *J. Am. Chem. Soc.* **1984**, *106*, 3806. (f) Tolbert, L. M; Ali, M. B. *J. Am. Chem. Soc.* **1981**, *103*, 2104.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

(98) (a) Favorski, A. E. *J. Gen.Che m. USSR,* **1936**, *6*, 720. (b) Favorski, A. E. *Bull. Soc. Chim. France,* **1936**, *5*, 1727.

(99) Wittig, G.; Heyn, J. *Liebigs Ann. Chem.* **1972**, *756*, 1.

(100) Chapman, O. L. *Pure Appl. Chem.* **1979**, *51*, 331.

(101) Wasserman, E.; Barash, L.; Trozzolo, A. M.; Murray, R. W.; Yager, W. A. *J. Am. Chem. Soc.* **1964**, *86*, 2304.

(102) Bofill, J. M.; Bru, N.; Ferras, J.; Olivella, S.; Sole, A.; Vilarrasa, J. *J. Am. Chem. Soc.* **1988**, *110*, 3740.

(103) Tolbert, L. M.; Siddiqui, S. *J. Am. Chem. Soc.* **1984**, *106*, 5538.

(104) Salaün, J.; Fadel, A. *Organic Syntheses* **1985**, *64*, 50.

(105) Christiansen, W. G. (E.R. Squibb & Sons) U.S. 2,146,720. Feb. 14, **1936**.

(106) Dehmlow, E. V.; Franke, K. *Liebigs Ann. Chem.* **1979**, 1456.

(107) Mousseron, M.; Winternitz, F.; Jacquier, R. *Compt. Rend.* **1947**, *224*, 1062.

(108) Crandall, J. K.; Clark, A. C. *J. Org. Chem.* **1972**, *37*, 4236.

(109) Rieke, R. D.; Hudnall, P. M. *J. Am. Chem. Soc.* **1972**, *94*, 7178.

(110) (a) Chan, T. H.; Chang, E.; Vinokur, E. *Tetrahedron Lett.* **1970**, 1137. (b) Chan, T. H.; Chang, E. *J. Org. Chem.* **1974**, *39*, 3264.

(111) (a) Cunico, R. F.; Dexheimer, E. M. *J. Am. Chem. Soc.* **1972**, *94*, 2868. (b) Cunico, R. F.; Dexheimer, E. M. *J. Organometallic Chem.* **1973**, *59*, 153.

(112) Chan, T. H.; Massuda, D. *J. Am. Chem. Soc.* **1977**, *99*, 936.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

(113) (a) Chan, T. H.; Massuda, D. *Tetrahedron Lett.* **1975**, 3383. (b) Arney, B. E., Jr. Ph.D. Thesis, Rice University, **1986.**

(114) Chan, T. H.; Mychajlowskij, W.; Ong, B. S.; Harpp, D. N. *J. Org. Chem.* **1978**, *43*, 1526.

(115) Denmark, S. E.; Klix, R. C.; *Tetrahedron*, **1988**, *44*, 4043.

(116) (a) Smith, J. G.; Quinn, N. R.; Viswanathan, M. *Synth. Commun.* **1983,** *13*, 1. (b) Smith, J. G.; Quinn, N. R.; Viswanathan, M. *Synth. Commun.* **1983,** *13*, 773. (c) Smith, J. G.; Drozda, S. E.; Petraglia, S. P; Quinn, N. R.; Rice, E. M.; Taylor, B. S.; Viswanathan, M. *J. Org. Chem.* **1984**, *49*, 4112.

(117) (a) Wittig, G.; Fritze, P. *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 846; (b) *Leibigs Ann. Chem.* **1968**, *711*, 82.

(118) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry", Verlag Chimie, 1971, pp

(119) Shih, C.; Fritzen, E. L.; Swenton, J. S. *J. Org. Chem.* **1980,** *45*, 4462.

(120) Angus Jr., R. O.; Johnson, R. P. *J. Org. Chem.* **1984**, *49*, 2880.

(121) Moore, W. R.; Ozretich, T. M. *Tetrahedron Lett.* **1967**, 3205.

(122) Banerjee, S.; Engel, R.; Axelrad, G. *Phosphorus and Sulfur* **1983**, *15*, 15.

(123) McMurry, J. G.; Scott, W. J. *Tetrahedron Lett.* **1983**, *24*, 979.

(124) (a) Wittig, G.; Krauss, E.; Wiethammer, K. *Justus Leibigs Ann. Chem.* **1960**, *630*, 10. (b) Whitney, S. E.; Winters, M.; Rickborn, B. J. *J. Org. Chem.* **1990**, *55*, 929.

(125) "The Aldrich Library of NMR Spectra," **1983**, 2(1), 865A.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

(126) (a) Iyoda, M.; Otani, H.; Oda, M.; Kai, Y.; Baba, Y.; Kasai, N.; *J. Chem. Soc. Chem. Commun.* **1986**, 1794. (b) Iyoda, M.; Mizusuna, A.; Kurata, H.; Oda, M. *J. Chem. Soc. Chem. Commun.* **1989**, 1690 and references therein.

(127) Bloomquist, A. T.; Liu, L. H. *J. Am. Chem. Soc.* **1953**, *75*, 2153.

(128) Reviews: (a) Hoffman, R. W. *Dehydrobenzene and Cycloalkynes*; Academic: New York, **1967**. (b) Krebs, A., Wilke, J. *Top. Curr. Chem.* **1984**, *109*, 189. (c) Nakagawa, M. *The Chemistry of the Carbon-Carbon Triple Bond;* Patai, S., Ed.; Wiley, Chichester, England, **1978**; pp 635-712.

(129) Hasse, J.; Krebs, A. *Z. Naturforsch., A*, **1971**, *26a*, 1190.

(130) Wittig, G.; Meske-Schüller, J. *Leibigs Ann. Chem.* **1968**, *711*, 65.

(131) (a) Krebs, A.; Kimling, H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 509. (b) Krebs, A.; Kimling, H. *Tetrahedron Lett.* **1970**, 761.

(132) Olivella, S.; Pericàs, M. A.; Riera, A.; Solé, A. *J. Org. Chem.* **1987**, *52*, 4160 and references therein.

(133) (a) Olivella, S.; Pericàs, M. A.; Riera, A.; Solé, A. *J. Chem. Research* **1985**, 328. (b) Olivella, S.; Pericàs, M. A.; Riera, A.; Solé, A. *J. Amer. Chem. Soc.* **1986**, *108*, 6884.

(134) Fitzgerald, G.; Saxe, P.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1983**, *105*, 690.

(135) Montgomery, L. K.; Roberts, J. D. *J. Am. Chem. Soc.* **1960**, *82*, 4750.

(136) Wittig, G.; Wilson, E. R. *Chem. Ber.* **1965**, 451.

(137) Fitzgerald, G.; Schaefer III, H. F. *Isr. J. Chem.* **1983**, *23*, 93.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

(138) Magnus, P.; Fortt, S.; Pitterna, T.; Snyder, J. P. *J. Am. Chem. Soc.* **1990**, *112*, 4986 and references therein.

(139) Meier, H.; Hanold, N.; Molz, T.; Bissinger, H. J.; Kolshorn, H.; Zountsas, J. *Tetrahedron* **1986**, *42*, 1711 and references therein.

(140) Nagendrappa, G. *Synthesis* **1980**, 704.

(141) (a) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 1685. (b) Köhler, H. -J.; Fruwert, J.; Jenichen, A. *J. Mol. Struct. (Theochem)* **1984**, *108*, 299.

(142) (a) Dewar, M. J. S.; Ford, G. P.; McKee, M. L; Rzepa, H. S.; Thiel, W.; Yamaguchi, Y. *J. Mol. Struct. (Theochem)* **1978**, *43*, 135. (b) Dewar, M. J. S.; Ford, G. P.; Rzepa, H. S. *J. Mol. Struct. (Theochem)* **1979**, *51*, 275. (c) Radziszewski, J. G.; Downing, J. W.; Jawdosiuk, M.; Kovacic, P.; Michl, J. *J. Am. Chem. Soc.* **1985**, *107*, 594. (d) Jenichen, A. *J. Mol. Struct. (Theochem)* **1988**, *167*, 227.

(143) Kazmutza, K.; Pulay, P. *Theor. Chim. Acta.* **1975**, *37*, 67.

(144) Nelander, B.; Ribbegärd, G. *J. Mol. Struct.* **1974**, *20*, 325.

(145) (a) Wotiz, J. H.; Celmer, W. D. *J. Am. Chem. Soc.* **1952**, *74*, 1860. (b) Wotiz, J. H.; Mancuso, D. E. *J. Org. Chem.* **1957**, *22*, 207 and refefences therein.

(146) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(147) Durig, J. R.; Li, Y. S.; Witt, J. D.; Zens, A. P.; Ellis, P. D. *Spectrochimica Acta* **1977**, *33A*, 529.

(148) McMahon, R. J.; Abelt, C. J.; Chapman, O. L.; Johnson, J. W.; Kreil, C. L.; LeRoux, J-P.; Mooring, A. M.; West, P. R. *J. Am. Chem. Soc.* **1987**, *109*, 2456.

(149) Aldrich, **1988/1989** p. 174.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

(150) Horák, M.; Smejkal, J.; Farkas, J. *Czech. Chem. Commun.* **1963**, *28*, 2280.

(151) Backer, H. J.; Vander, J. R. *Rec. Trav. Chim.* **1943**, *62*, 561.

(152) (a) Bolster, J. M.; Kellog, R. M. *J. Am. Chem. Soc.* **1981**, *103*, 2868. (b) Gassman, P. G.; Valcho, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4768. (c) Chapman, O. L.; Gano, J.; West, P. R.; Regitz, M.; Maas, G. *J. Am. Chem. Soc.* **1981**, *103*, 7033.

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