1987

Synthesis and photochemical rearrangements of 1-tert-butyl-1,2-cyclooctadiene

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Synthesis and photochemical rearrangements of 1-tert-butyl-1,2-cyclooctadiene

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Iowa State University, 1987

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Synthesis and photochemical rearrangements of 1-tert-butyl-1,2-cyclooctadiene

by

John David Price

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Organic Chemistry

Approved

In Charge of Major Work

For the Major Department

For the Graduate College

Iowa State University
Ames, Iowa

1987

CONTENTS

Page

DEDICATION iii

INTRODUCTION 1

HISTORICAL SECTION 2

- Triplet Vapor Phase Reactions of Cyclic Allenes 2
- Triplet Solution Phase Reactions of Cyclic Allenes 10
- Singlet Reactions of Cyclic Allenes 13
- Strained Cyclic Allenes 20

RESULTS AND DISCUSSION 25

- Goals of This Research 25
- Synthesis of 1,2-Cyclooctadiene Derivatives 26
- Triplet Reactions of 1-tert-Butyl-1,2-cyclooctadiene 37
- Singlet Reactions of 1-tert-Butyl-1,2-cyclooctadiene 41
- Triplet Reaction Mechanisms 48
- Singlet Reaction Mechanisms 58

CONCLUSION 78

EXPERIMENTAL SECTION 80

- General Procedures 80

BIBLIOGRAPHY 109

ACKNOWLEDGMENTS 114

DEDICATION

This work is dedicated to my parents, Clarence and Lorna Price.

INTRODUCTION

Although the photochemistry of alkenes,[1] and 1,3-dienes[2] has been the subject of intensive investigation during the past three decades, allenes, or 1,2-dienes, have received little attention. This is despite their ready synthetic availability and well characterized ground state chemistry.[3]

The situation has changed significantly within the past few years, as a number of allenyl systems have been examined under diverse reaction conditions. It is now known that allenes undergo a rich assortment of fundamental photoreactions, many of which are analogous to those of simple alkenes. Among these are π-bond rotation,[4,5] hydrogen and carbon migration,[6-13] β-homolysis,[14] molecular rearrangements such as the di-π-methane[15,16] and Cope rearrangements,[17-19] cycloadditions,[20] and addition of polar solvents.[21-23] Two reviews are now available which survey many aspects of allene photochemistry.[24,25]

The photochemical reactions of 9- and 10-carbon cyclic allenes have played a prominent role in these studies. The present dissertation has two fundamental goals: (a) to synthesize a kinetically stable eight membered ring allene; (b) to explore the effects of diminished ring size and molecular strain in cyclic allene photoreactions.

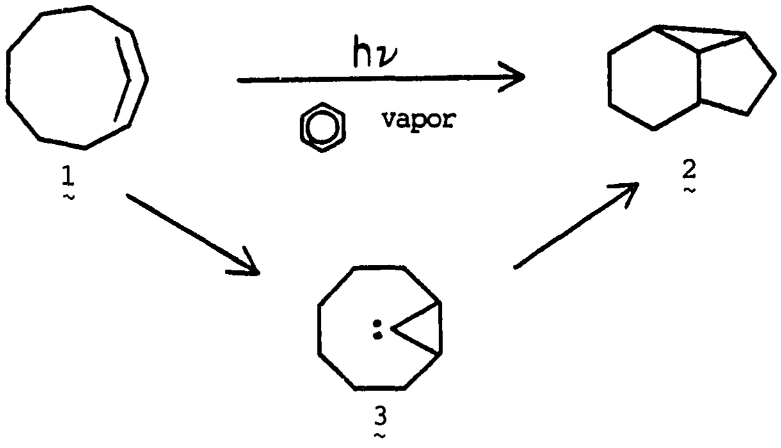
HISTORICAL SECTION

Triplet Vapor Phase Reactions of Cyclic Allenes

The first photochemical reaction of a cyclic allene was reported by Ward and Karafiath.[17] This remains a seminal paper in allene photochemistry, as the authors proposed mechanisms still central to interpretation of these reactions. The reactions studied involved the triplet state; such states were generated in solution as well as in the vapor phase.

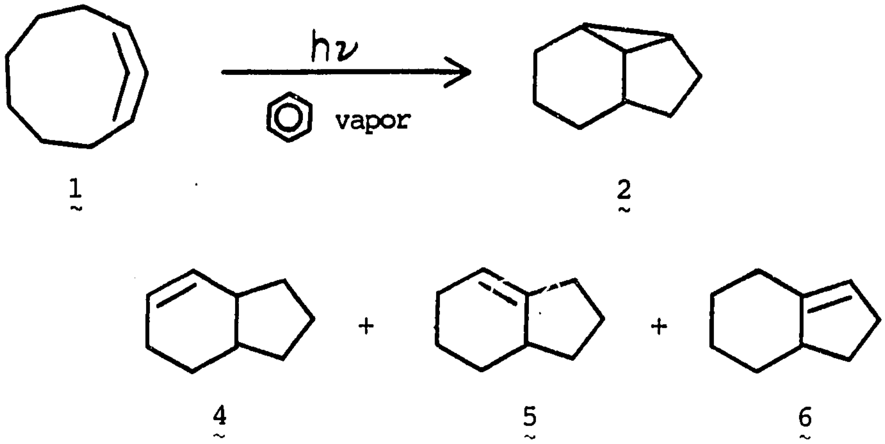
When 1,2-cyclononadiene **1** was irradiated with benzene in the vapor phase, the sole product reported was tricyclo-[4.3.0.$0^{2,9}$]nonane **2**. The reported quantum yield for formation of **2** is 0.17, and the tricyclononane was believed to be a primary product. The most economical mechanism for the isomerization of cyclononadiene to tricyclononane was proposed to be closure of the allene to a cyclopropylidene intermediate (**3**, Scheme 1), followed by stepwise insertion into a C-H bond.

Scheme 1



This reaction was later subjected to more careful scrutiny by Stierman and Johnson;[6] it was shown that in addition to tricyclononane 2, three minor primary products were also obtained.

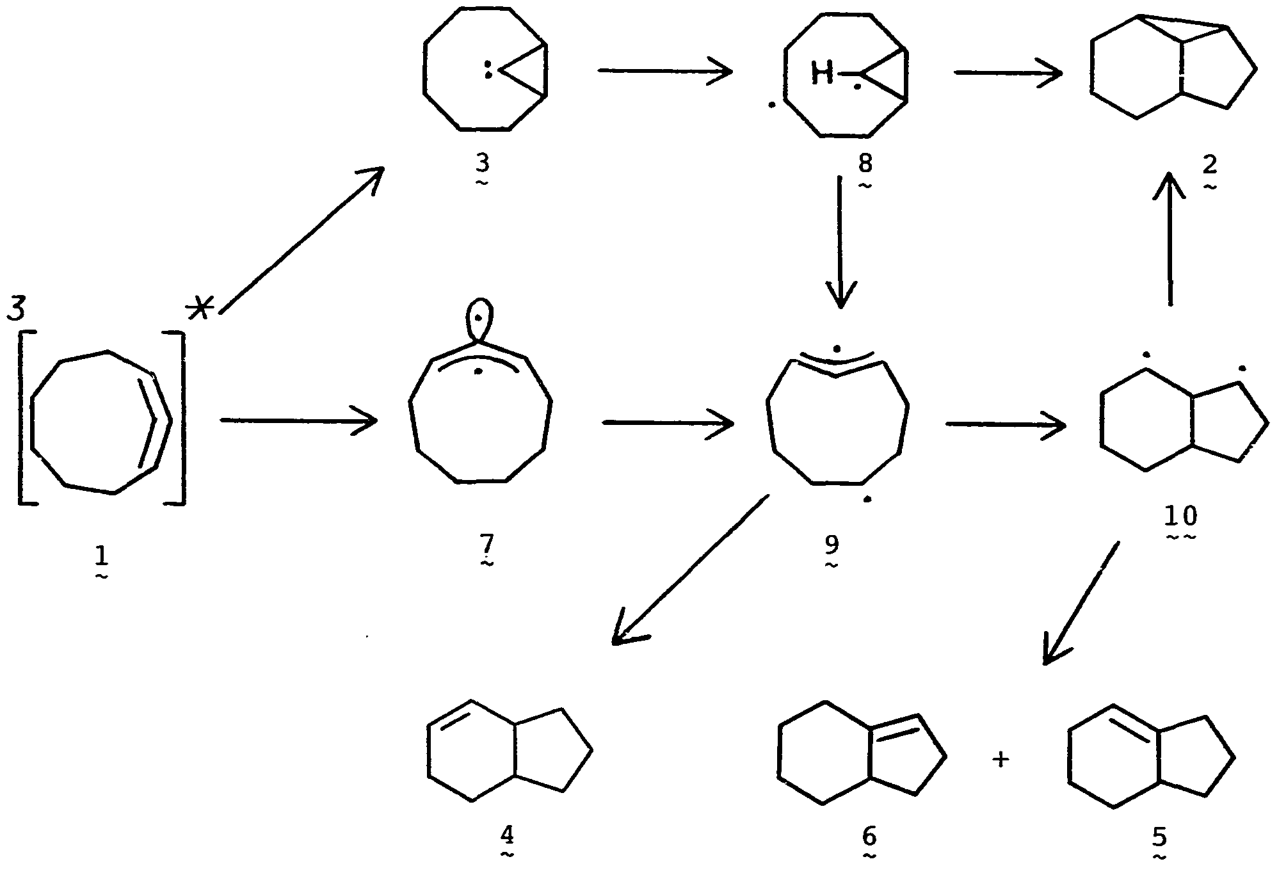
Scheme 2



To explain the formation of products 4, 5, and 6, it was proposed that two potential intermediates were accessible from the allene triplet excited state. These were triplet cyclopropylidene 3, and triplet planar allene 7, as shown below.

Formation of the minor bicyclic olefins could thus arise from two different pathways. In the mechanism which passes through cyclopropylidene 3, biradical 8, derived from hydrogen abstraction, could partition between closure to tricyclononane 2, and ring opening to allyl biradical 9. This biradical can close directly to 4, following spin inversion, or may undergo bridging to the central carbon of

Scheme 3



the allyl radical to afford 1,3-diradical **10**. From this intermediate, 1,2-hydrogen migration leads to the formation of the bridgehead olefins **5** and **6**. Direct three-membered ring closure from **10** could afford **2**.

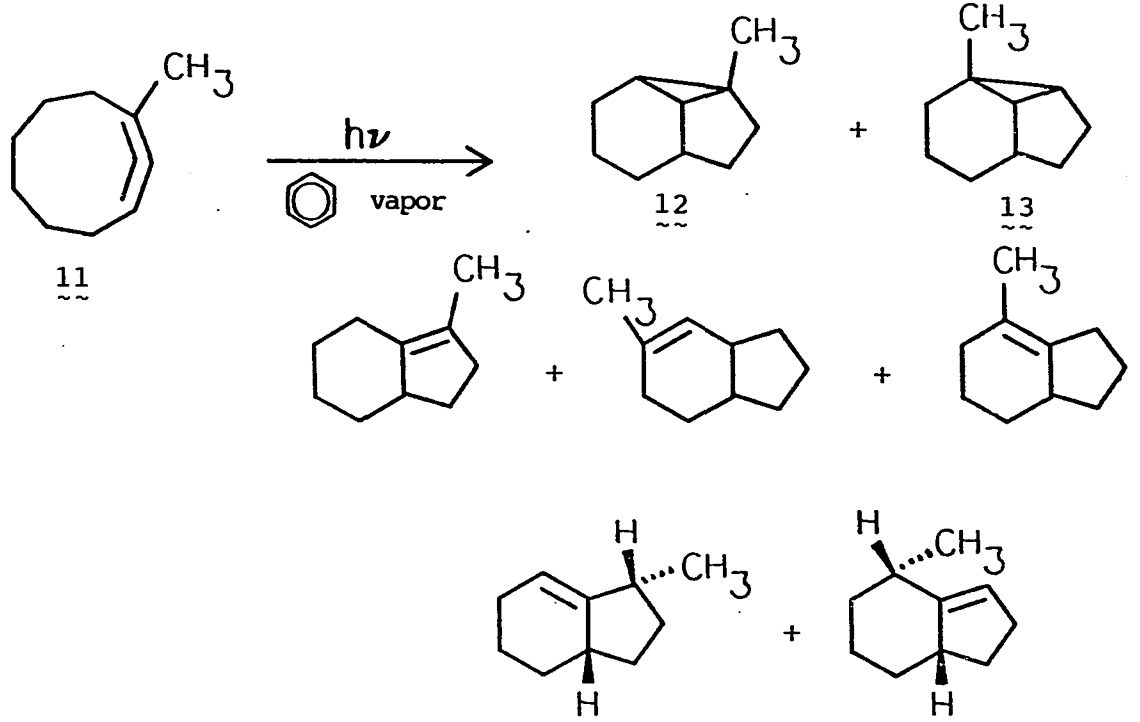
A triplet planar allene may also explain the observed photochemistry, as hydrogen extraction from **7** leads to formation of the allyl biradical **9**, from which all the observed products may be derived, as shown above. Discrimination between the two mechanisms is problematic, as both converge upon a common intermediate; allyl biradical **9**.

To further study this mechanism, Stierman and Johnson investigated the reaction of 1-methyl-1,2-cyclononadiene **11**.[26] As shown in Scheme 4, irradiation of **11** with benzene in the vapor phase resulted in the formation of two major products, identified as 9-methyltricyclo[4.3.0.0^{2,9}]nonane **12** and 2-methyltricyclo[4.3.0.0^{2,9}]nonane **13**.

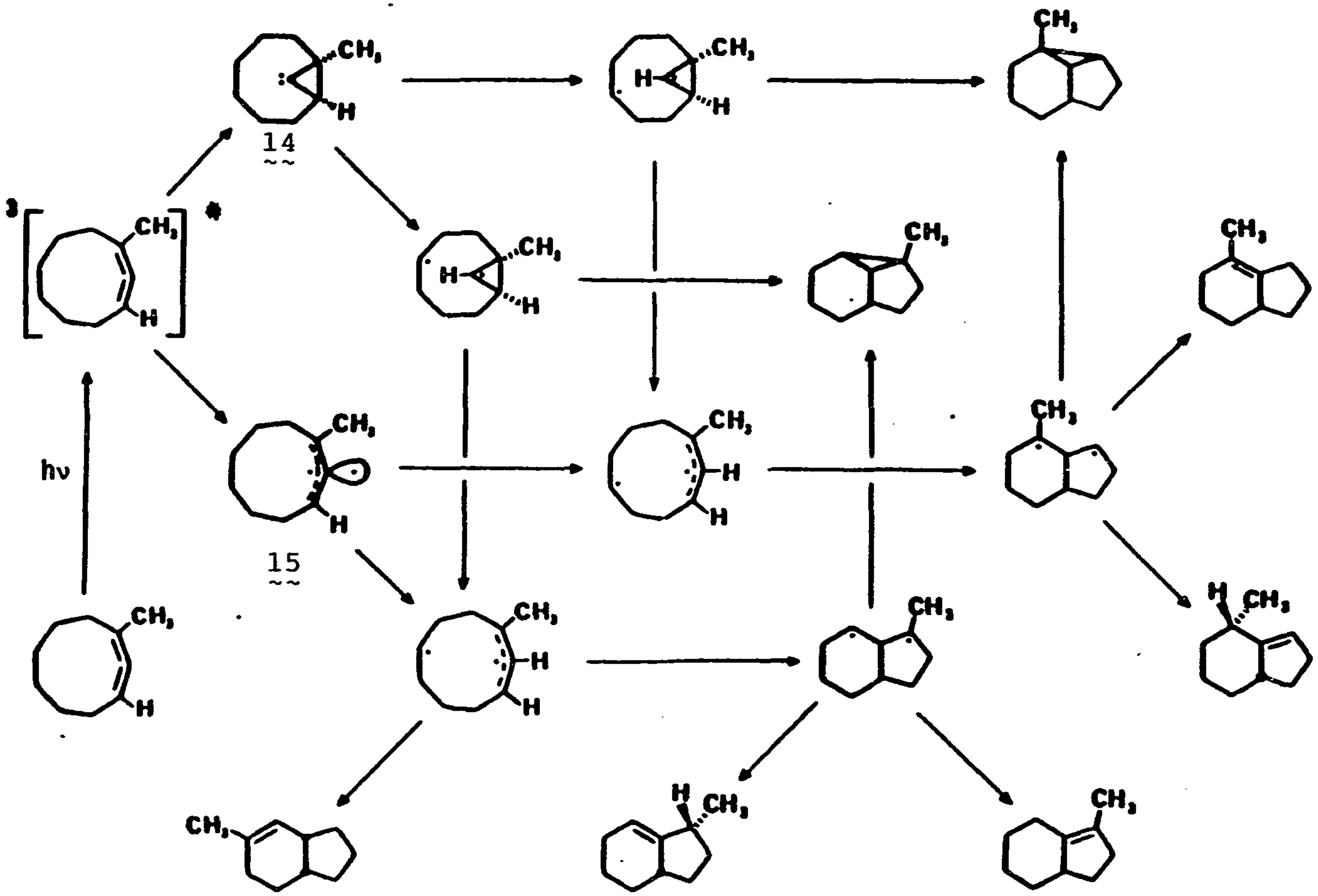
The tricyclic hydrocarbons constitute 87% of the product mixture. As with 1,2-cyclononadiene, several minor bicyclic olefins were also formed, and a similar mechanism, postulated to involve cyclopropylidene **14** and planar allene **15** is shown in Scheme 5.

Perhaps the most convincing evidence for the involvement of cyclopropylidenes in these reactions is due to investigation of 1,2-cyclodecadiene **16**. As has been reported by Price and Johnson, irradiation of **16** with

Scheme 4



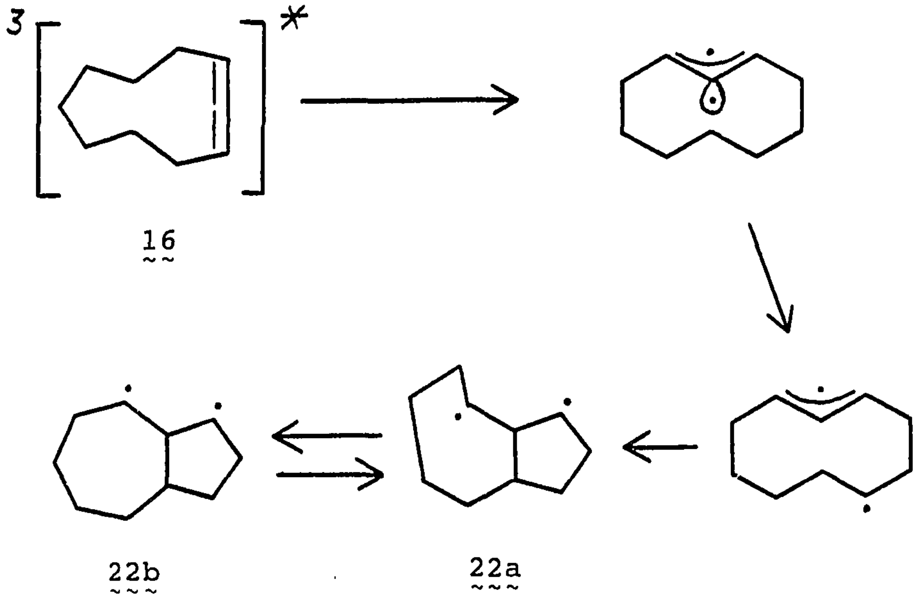
Scheme 5



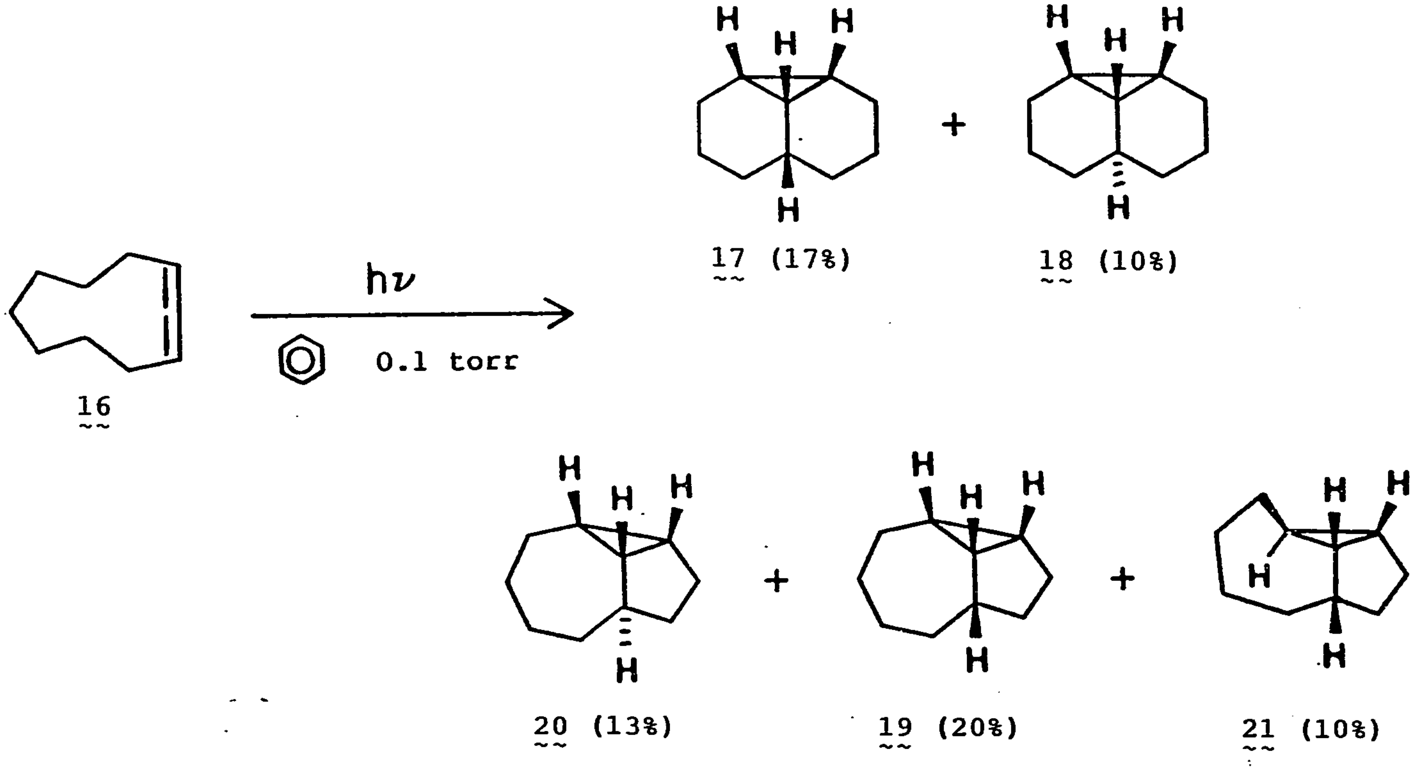
benzene in the vapor phase produces a complex mixture of tricyclodecanes 17-21.[13] Bridgehead olefins comprise only 4% of the product distribution (Scheme 6).

Of particular significance is formation of *trans*-fused-cyclopropane 21. It appears unlikely that the strained *trans*-bicyclo[5.1.0]octane moiety of 21 could result from closure of 1,3-biradical 22a, which could derive from a planar allene (Scheme 7). Instead, facile conformational interconversion between biradicals 22a and 22b would lead to almost exclusive formation of the more stable *cis*-bicyclo-[5.1.0]octane moiety of tricyclics 19 and 20, a result not observed. Pre-closure of the three membered ring is essential to formation of these strained tricyclics.

Scheme 7

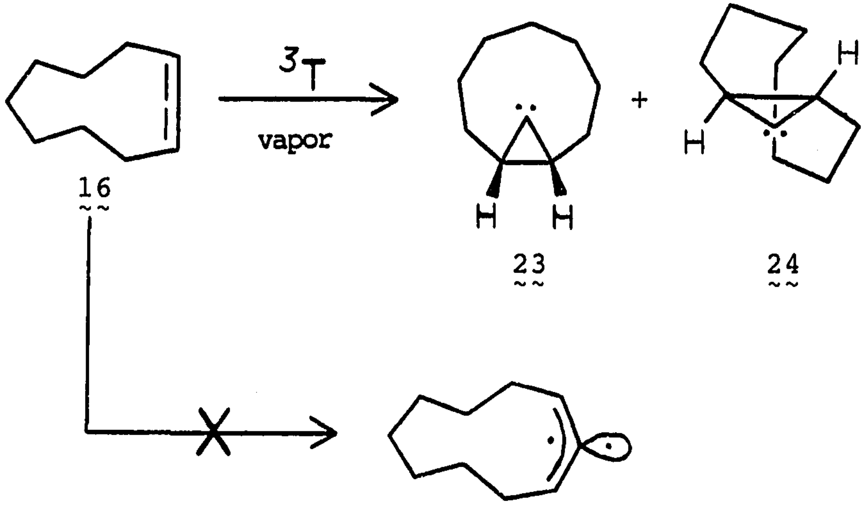


Scheme 6



A more plausible mechanism is shown in Scheme 8, where formation of cis- and trans-cyclopropylidenes, 23 and 24, are proposed as progenitors to tricyclics 17-21. The small amounts of bicyclic olefins could arise from a minor pathway due to opening of a cyclopropyl radical, as described earlier.

Scheme 8



Triplet Solution Phase Reactions of Cyclic Allenes

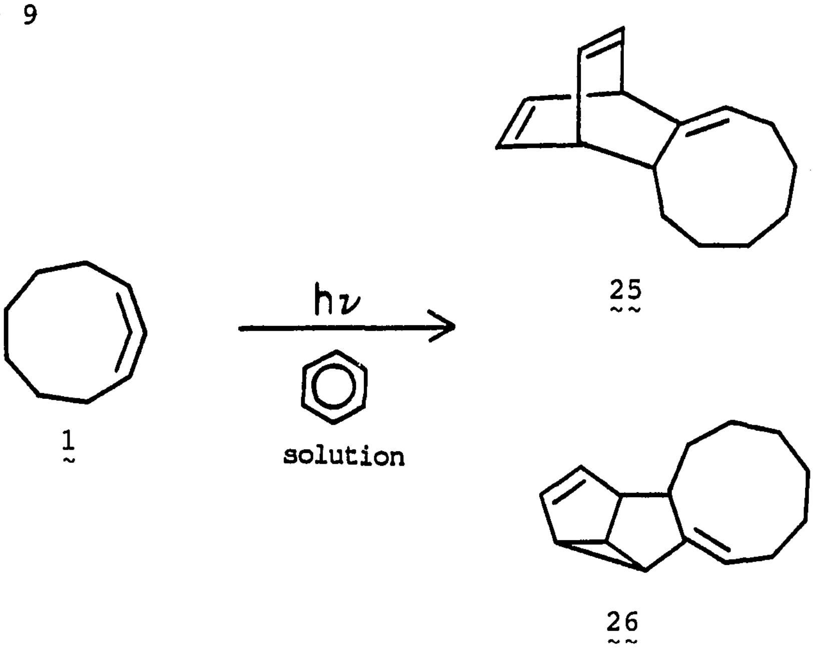
The solution phase cycloaddition of benzene with 1,2-cyclononadiene 1 has been studied by Berridge et al.[20] Since the π-systems of the two ethylenic units are orthogonal to one another in allenes, and thus do not interact appreciably, 1 was expected to react as a simple olefin.

The observed mode of cycloaddition of benzene with an olefin, i.e., ortho-, meta-, or para-, has been correlated empirically with the ionization potential of the olefin.

Olefins with an ionization potential greater than 9.6 eV or less than 8.7 eV tend to yield ortho- and para-cycloadducts. Molecules with an ionization potential between these values lead to meta-adducts.[27,28] The ionization potential of **1** has been determined by its photoelectron spectrum to be 8.87 eV.[29] These factors lead to the prediction that the predominant mode of cycloaddition for 1,2-cyclononadiene will be meta.

Irradiation of **1** in benzene was reported to give two adducts, **25** and **26**, in the ratio of 6:1 respectively (Scheme 9). This result is not as predicted, and has been questioned by Stierman and Johnson, who found that, although two major adducts were formed in the ratio of 6:1, the

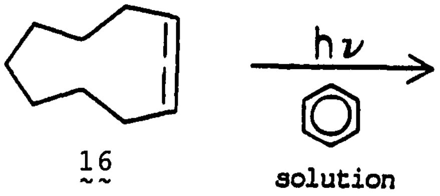
Scheme 9



structural assignments were reversed. Experiment thus agrees with prediction.

In dramatic contrast to the triplet solution phase behavior of 1, when 1,2-cyclodecadiene 16 is irradiated in benzene, there is no evidence for cycloadduct formation.[13] What is found instead, are the same tricyclics and alkenes as are obtained in the triplet vapor phase reaction (Scheme 10). An additional striking result is formation of the strained trans-cyclopropane 21 as the major product (41%).

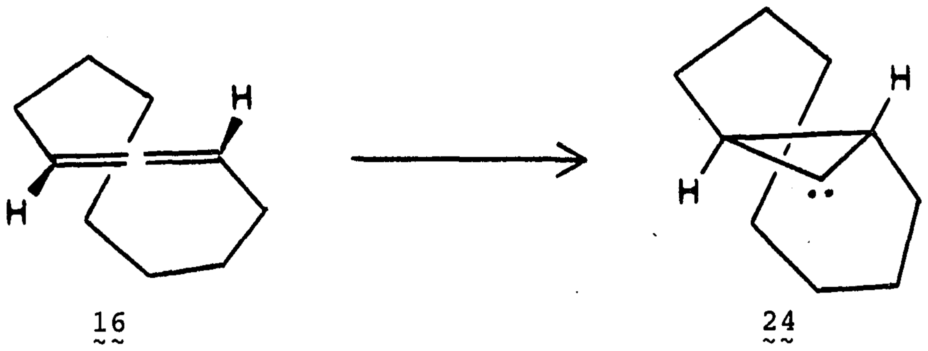
Scheme 10



21 (41%) 17 (26%)
19 (14%) 20 (10%)
18 (6%)

The failure of 16 to form cycloadducts with benzene has not been explained. However, preliminary experiments with 1,2-cycloundecadiene, suggest that the preferred reaction of cyclic allenes with benzene may be rearrangement to isomeric products, rather than cycloadduct formation.[30] Preference for formation of the trans-isomer 21 may be attributed to minimization of hydrogen motion and deformation of the methylene skeleton in three membered ring formation as suggested in Scheme 11.

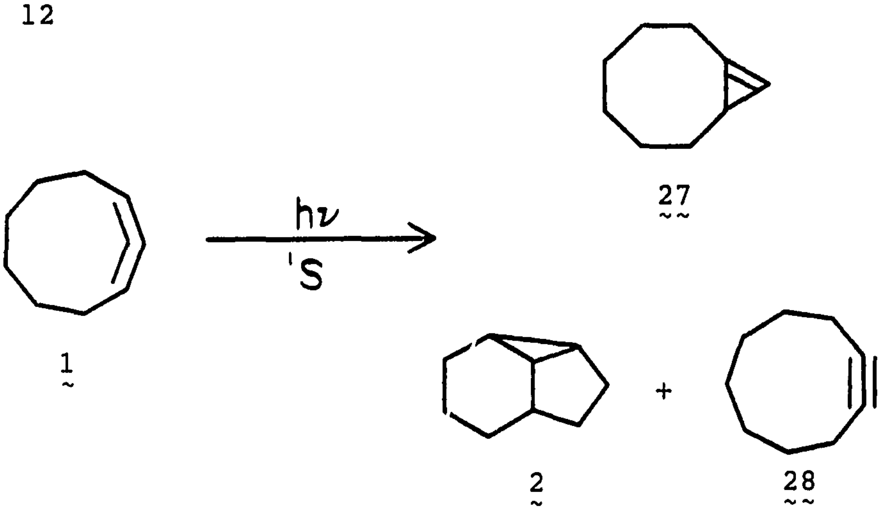
Scheme 11



Singlet Reactions of Cyclic Allenes

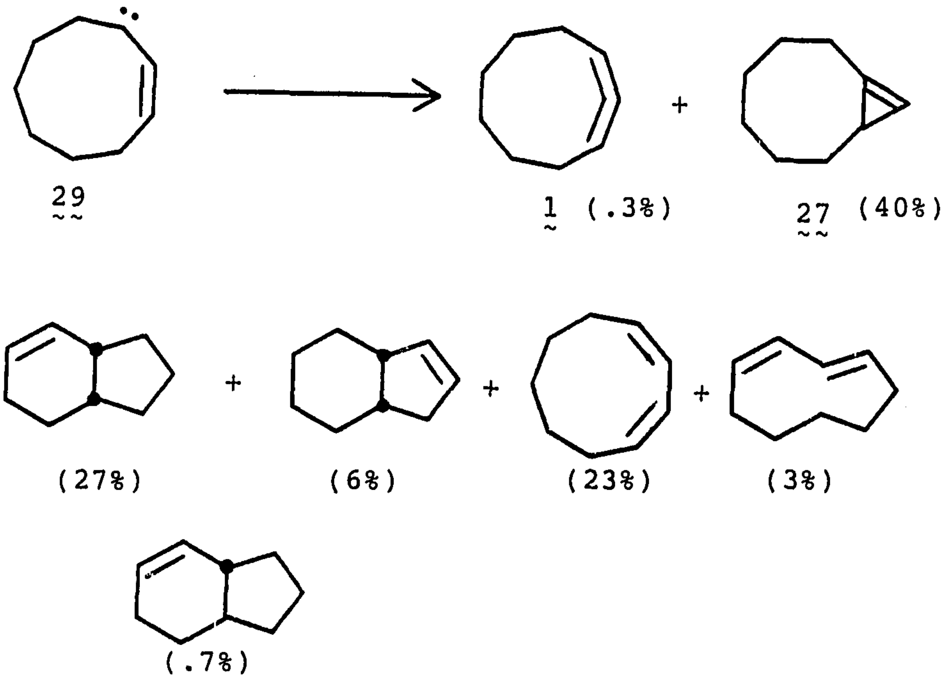
The first detailed studies of the singlet solution phase reactions of 1,2-cyclononadiene 1 were undertaken by Stierman and Johnson.[6,11,26] Direct irradiation of 1 yielded the three primary photoproducts shown in Scheme 12. These were identified as bicyclo[6.1.0]non-1(9)-ene 27, tricyclo[4.3.0.$0^{2,9}$]nonane 2, and cyclononyne 28, formed in the ratio of 94:3:3.

Scheme 12



When monodeuterated 1 was irradiated, a kinetic isotope effect of $k_H/k_D = 1.30$ was measured for the formation of cyclopropene 8. This implies that hydrogen, and not carbon is migrating. One intermediate that could arise from a hydrogen migration in 1,2-cyclononadiene is the vinylcarbene cyclononenylidene 29. This carbene was generated independently by the photolysis of the sodium salt of the corresponding tosylhydrazone. The results are shown in Scheme 13.

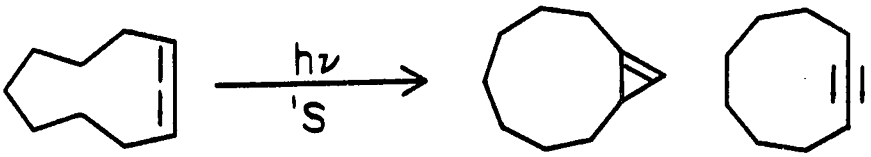
Scheme 13



Because cyclononenylidene yields substantial amounts of 1,3-cyclononadiene, and tranannular insertion products which are not observed upon irradiation of 1, its involvement as an intermediate in singlet reactions of 1 is unlikely.

In similar fashion, direct irradiation of 1,2-cyclodecadiene produces a mixture composed of two isomers which were identified as bicyclo[7.1.0]dec-1(10)-ene 30, and cyclodecyne 31.[13] The ratio of cyclopropene to alkyne is 5:1.

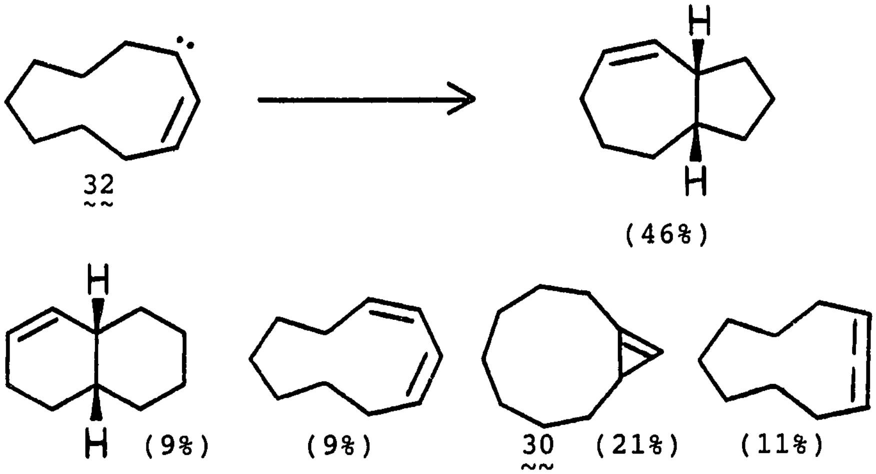
Scheme 14



16 30 31

The vinylcarbene 32, arising from a 1,2-hydrogen migration in 16 also, was generated as described above, and yielded a product mixture substantially different from that of the photoreaction as shown in Scheme 15.

Scheme 15



32

(46%)

(9%) (9%) 30 (21%) (11%)

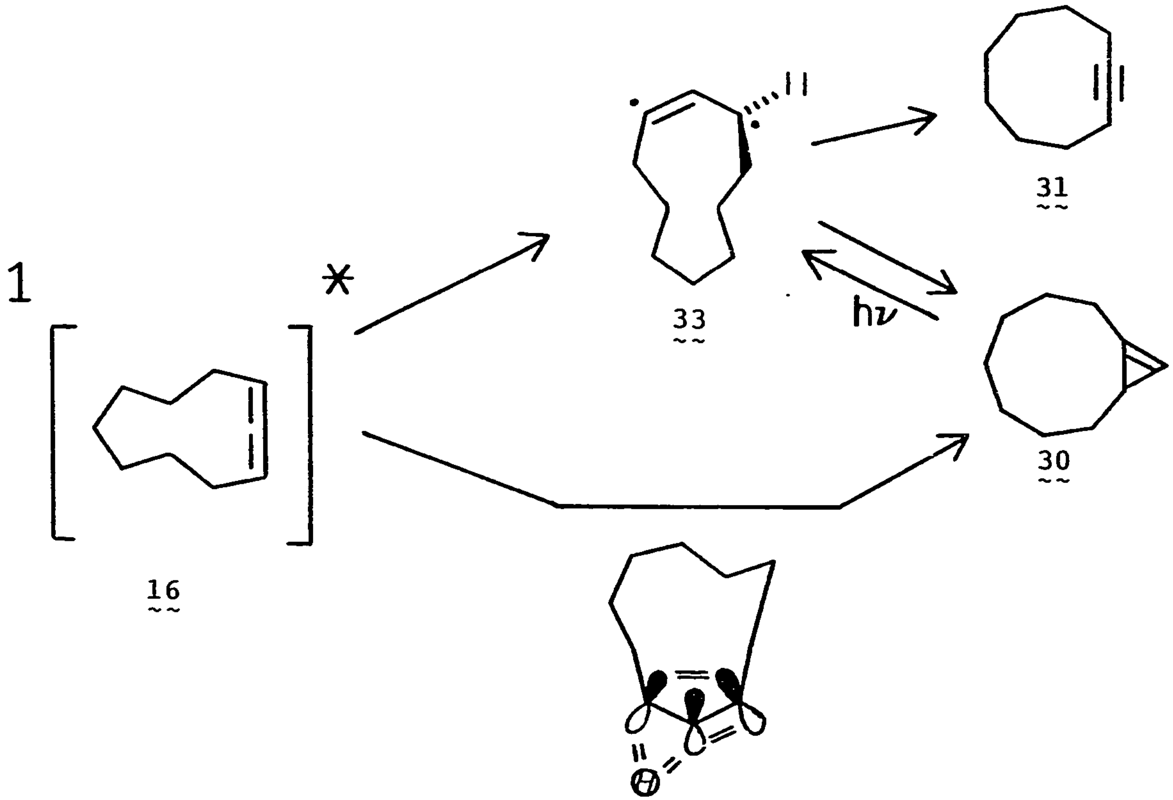
Potential mechanisms for the singlet photoreactions of 1,2-cyclonona- and 1,2-cyclodecadiene are shown in Scheme 16. The most economical mechanism for cyclopropene formation involves simultaneous 1,2-hydrogen migration and bond formation between terminal carbons of the allene moiety. The two pathways shown in Scheme 16 differ mainly in the timing of bond forming and breaking events.

As vinylcarbenes have been eliminated as discrete intermediates in these reactions, an alternative is a photochemically allowed concerted $[\sigma 2a + \pi 2a]$ mechanism. This mechanism involves simultaneous 1,2-hydrogen migration and C1-C3 bond formation. The Huckel transition state for this concerted process is shown in Scheme 16.

Details of these processes are derived from *ab initio* CI calculations for hydrogen migration in allene, reported by Klett and Johnson.[10] The geometry of the point on the potential surface corresponding to a pericyclic minimum is approximated by that of bent bisected biradical **33**, shown in Scheme 16. Internal conversion at this geometry could lead to cyclopropene formation via C1-C3 bonding, or alternately, through a second 1,2-hydrogen migration to cycloalkyne.

In an attempt to determine if the reaction was concerted, a sample of optically active **1** was irradiated. No optical rotation was detected in isolated samples of cyclopropene **27**. However, these experiments were not

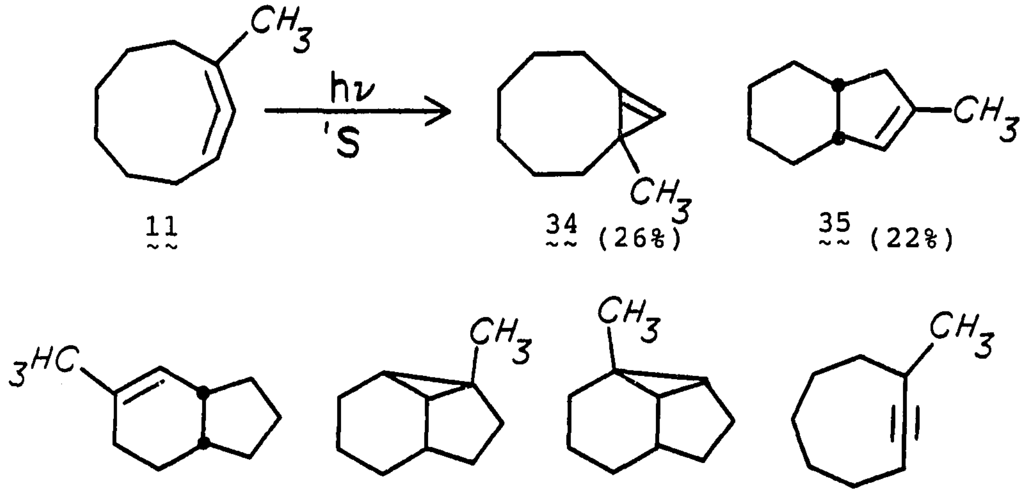
Scheme 16



definitive as it was determined that the rate of racemization is much greater than that of reaction; $k_{racemization}/k_{reaction} = 70$.

Direct irradiation of 1-methyl-1,2-cyclononadiene **11** afforded a complex mixture of isomeric hydrocarbons as shown in Scheme 17.[26] These were identified as cyclopropene **34**, bicyclics **35** and **36**, tricyclics **37** and **38**, and cycloalkyne **39**. The singlet reaction of **11** thus differs greatly from that of the unsubstituted allene.

Scheme 17

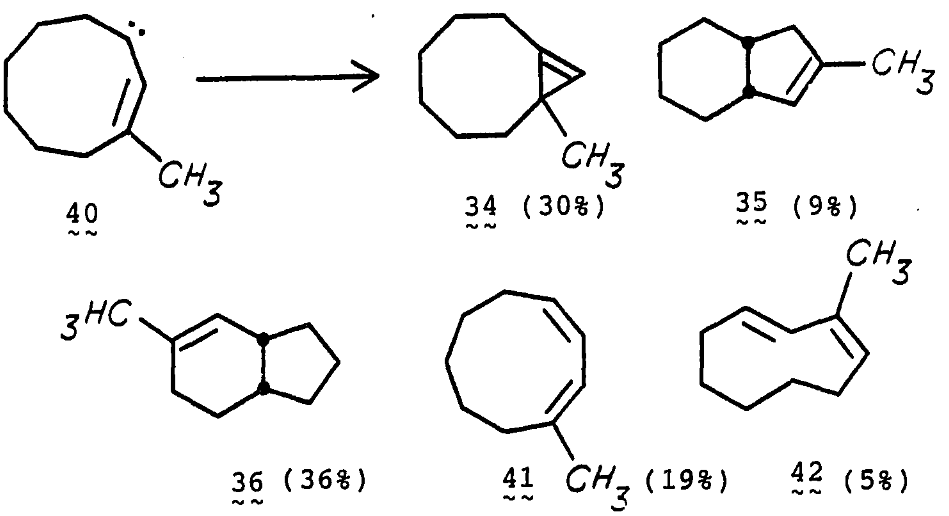


11 **34** (26%) **35** (22%)

36 (10%) **37** (3%) **38** (4%) **39** (24%)

3-Methylcyclonon-2-enylidene **40**, the vinyl carbene arising from a 1,2-hydrogen migration in **11**, was considered as a possible intermediate. Its generation by photolysis of the corresponding tosylhydrazone sodium salt yielded the hydrocarbon mixture shown in Scheme 18.

Scheme 18



In contrast to the singlet photoreactions of 1,2-cyclonona- and cyclodecadiene, the reactions of the methyl substituted derivative **11** appear to involve the intermediacy of a vinylcarbene. Three products derived from vinylcarbene **40**, cyclopropene **34**, and bicyclics **35** and **36**, are also obtained by irradiation of allene **11**. Furthermore, direct irradiation of 1,3-dienes **41** and **42** leads ultimately to cis,cis-2-methyl-1,3-cyclooctadiene **43**, a secondary product obtained by irradiation of allene **11**. It thus appears that all products obtained from vinyl carbene **40** are also formed by photolysis of 1-methyl-1,2-cyclononadiene **11**.

The tricyclic products **37** and **38** may arise from a triplet cyclopropylidene in a process analogous to that discussed for the photoreaction of 1,2-cyclononadiene **1**.

The mechanism proposed for the formation of 3-methylcyclononyne **39** is also analogous for the photoreaction of **1**.

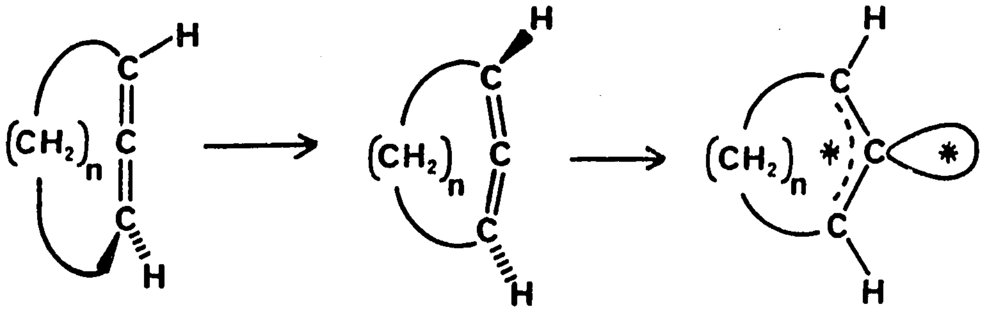
Strained Cyclic Allenes

The geometry of allene is linear, with the two π-systems orthogonal to one another. However, this situation changes if an allene moiety is incorporated into a ring of less than ten total carbons. In this case the allene is strained and distorted from its usual linear, orthogonal geometry. This deformation occurs in two ways: bending from linearity, and twisting from orthogonality (Scheme 19). Furthermore, it is believed that these two modes are coupled in allenes, such that bending leads to twisting and vice versa.[5]

Prior to the present work, the smallest isolable cyclic allene was 1,2-cyclononadiene. In smaller rings, twisting and bending are greater, which results in increased kinetic reactivity. The extreme case of twisting and bending should result in a planar structure as shown in Scheme 19. A very fundamental question is: at what point in the cyclic allene series, if any, does an allene fail to adopt a chiral geometry? In other words, can a point be reached where ring constraints enforce a planar geometry?

The limitations of cyclic allene chirality are remarkable. 1,2-Cyclohexadiene **44** may be prepared by a number of routes as shown in Scheme 20. In the absence of trapping agents, only dimers and tetramers are isolated.[31]

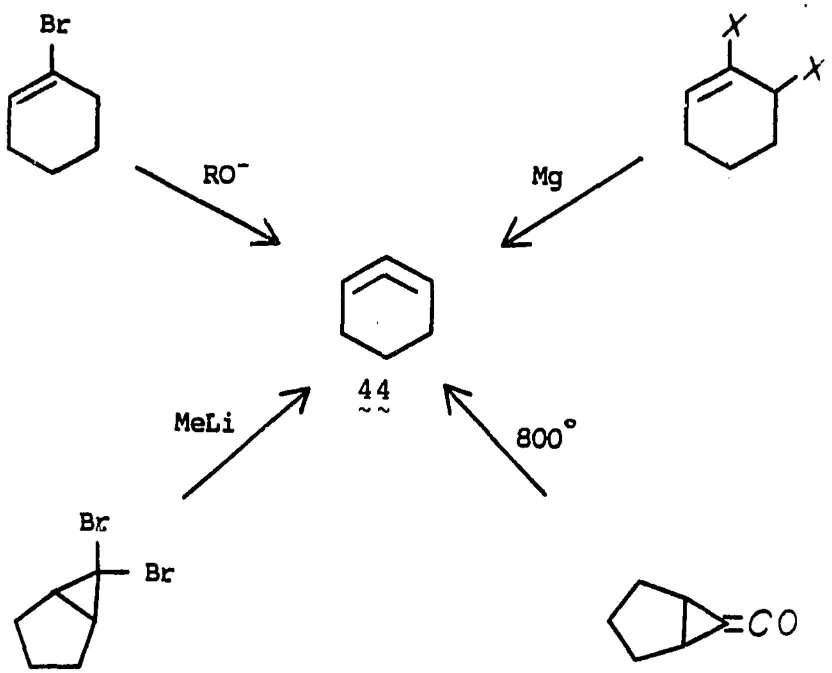
Scheme 19



(* = ·, +, -)

Most early workers appear to have been reluctant to consider that 44 exists as a chiral molecule.[31-36] The first experimental evidence that 1,2-cyclohexadiene does indeed exist as a chiral structure was presented by Balci and Jones.[37] Their experiments employed chiral vinyl bromide 45 as the allene precursor, and made clever use of an isotope effect; i.e., HBr is eliminated in preference to DBr. When 1,2-cyclohexadiene prepared in this manner was trapped with diphenylisobenzofuran, optically active cycloadducts were obtained, thus establishing that 1,2-cyclohexadiene exists as a chiral structure (Scheme 21).

Scheme 20

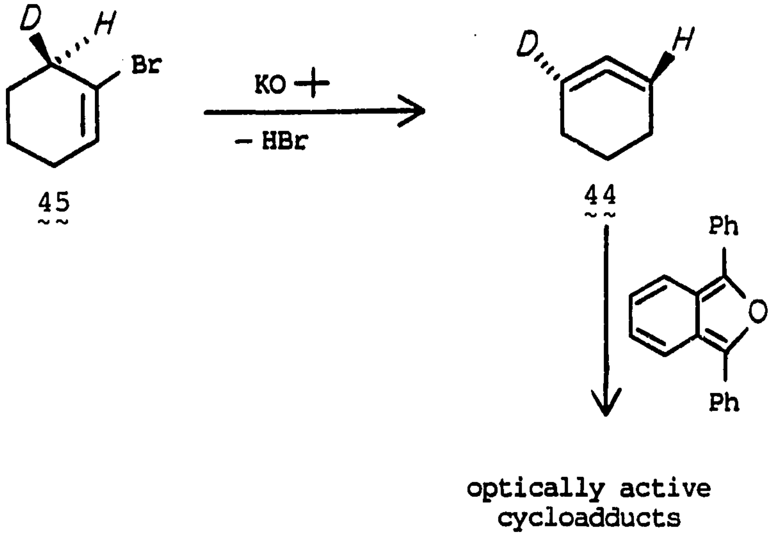


Unfortunately, insufficient experimental evidence exists to determine the structure of smaller cyclic allenes. Attempts at generating 1,2-cyclopentadiene in solution, instead gave evidence for the formation of its isomer, cyclopentyne.[38-40]

In light of the fact that 1,2-cyclohexadiene exists as a chiral structure, there is little doubt that higher homologs are also chiral. Nevertheless, Balci and Jones have generated optically active 1,2-cycloheptadiene by the same route employed for the 6-carbon allene, and found that optically active cycloadducts were obtained.[37]

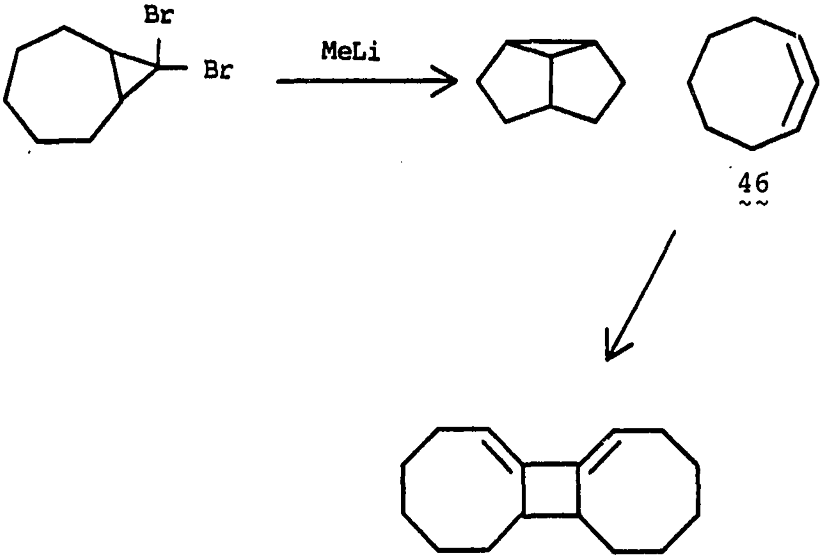
1,2-Cyclooctadiene 46 has been generated and observed spectroscopically at low temperature (-60°C) by ^{1}H NMR spectroscopy. The molecule is sufficiently stable that its dimerization kinetics may be studied, however at ambient temperatures, only dimers are isolable.[41-43] The route of Marquis and Gardner is shown below (Scheme 22).

Scheme 21



For a more complete summary of structural limitations in cyclic allenes, the reader is referred to a recent review.[44]

Scheme 22



RESULTS AND DISCUSSION

Goals of This Research

Interest in the synthesis and subsequent photochemical rearrangements of derivatives of 1,2-cyclooctadiene, grew out of the convergence of two different areas of research in our group. One was the continued interest in the synthesis of small-ring cyclic cumulenes. Efforts in this direction have culminated in the synthesis of the smallest isolable cyclic butatriene, 1,2,3-cyclononatriene.[45]

The second area of interest centered on ring size and substituent effects in cyclic allene photochemistry. As noted in the Historical Section, there are a number of fundamental mechanistic questions in the photochemical behavior of the cyclic allenes thus far studied. Specifically, what is the mode of reaction of triplet allenes in solution: rearrangement to cyclopropylidene derived products, or cycloaddition with benzene? Also, what is the mechanism of singlet rearrangements? Are the reactions concerted, as appears to be the case with 1,2-cyclonona- and decadiene, or do they involve the involvement of discrete intermediates as in the case of the alkyl substituted derivative, 1-methyl-1,2-cyclononadiene. Extending these studies to the next smaller ring, 1,2-cyclooctadiene, is problematic however, as this molecule rapidly dimerizes at ambient temperatures.

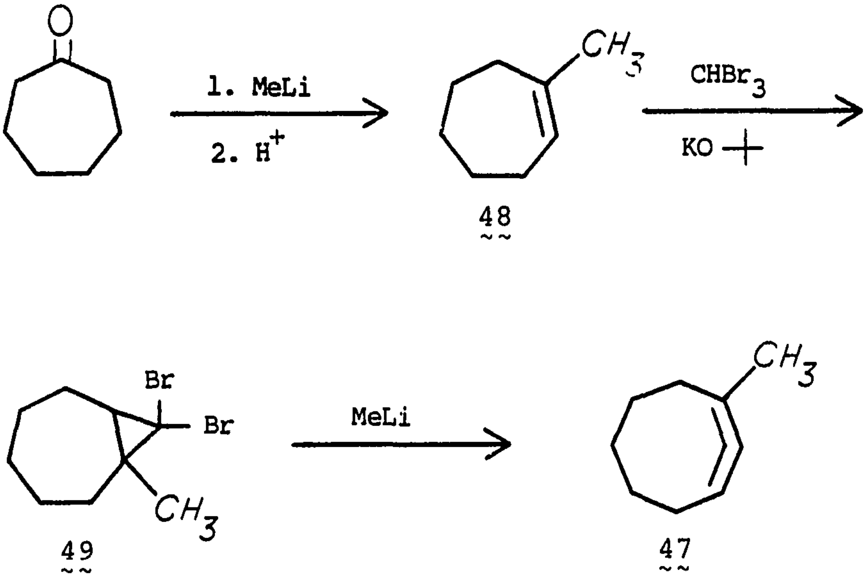
Thus, the question posed at the onset of this project was twofold: (a) can a suitable derivative of 1,2-cyclooctadiene be prepared such that the molecule is stable to dimerization; (b) if so, what new mechanistic insights will be provided regarding the photochemical reactions of cyclic allenes in general? Some answers to these questions are described in the following sections.

Synthesis of 1,2-Cyclooctadiene Derivatives

The smallest isolable cyclic allene is 1,2-cyclononadiene 1. The next smaller homologue, 1,2-cyclooctadiene 46, dimerizes rapidly at room temperature. Yet, recent MNDO calculations have suggested that the strain energy for this molecule is only 15 kcal/mol.[46,47] This should be compared with strain energies of 29 kcal/mol for cyclopropane, 56 kcal/mol for cyclopropene, and 26 kcal/mol for cyclobutane.[48] The instability of 46 and other strained allenes may be attributed to strain relief afforded by dimerization.[49] As this dimerization should be sensitive to steric hindrance,[44,50] it was proposed that alkyl substitution at C1 of 1,2-cyclooctadiene might lead to sufficient stabilization such that the molecule could prove isolable.

The first derivative prepared was 1-methyl-1,2-cyclooctadiene 47, as outlined in Scheme 23. Treatment of cycloheptanone with methyllithium, followed by acid catalyzed dehydration of the intermediate alcohol, afforded 1-methylcycloheptene **48**, in 70% overall yield. 8,8-Dibromo-1-methylbicyclo[5.1.0]octane **49** was obtained in 90% yield by treating **48** with potassium tert-butoxide and bromoform. Reaction of dibromide **49** with methyllithium afforded one major product (>90%) as determined by ^{1}H NMR analysis; this was identified as allene **47**. Compared to the unsubstituted allene, this molecule displayed enhanced stabilization to dimerization. The material was stable in solution at ambient temperature, and could be concentrated in $CDCl_3$ to obtain spectral data. When concentrated to dryness, however, it was rapidly converted to an insoluble yellow precipitate, making its use as a photochemical substrate

Scheme 23

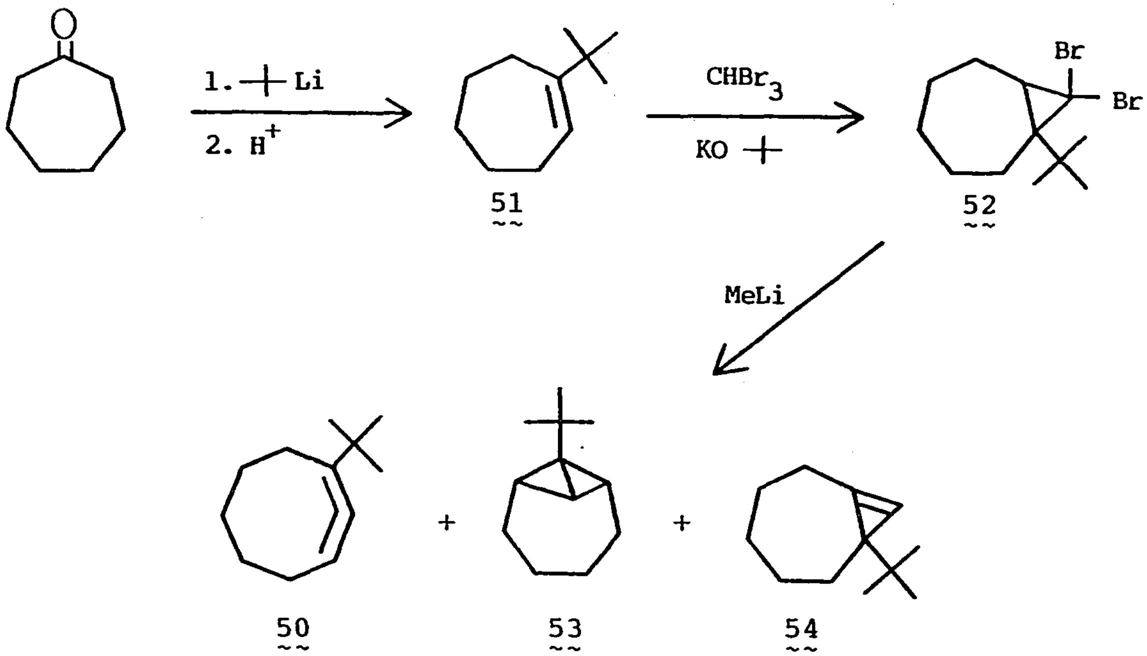


less than desirable. Efforts in this direction were thus shifted to a more hindered target molecule, 1-tert-butyl-1,2-cyclooctadiene **50**.

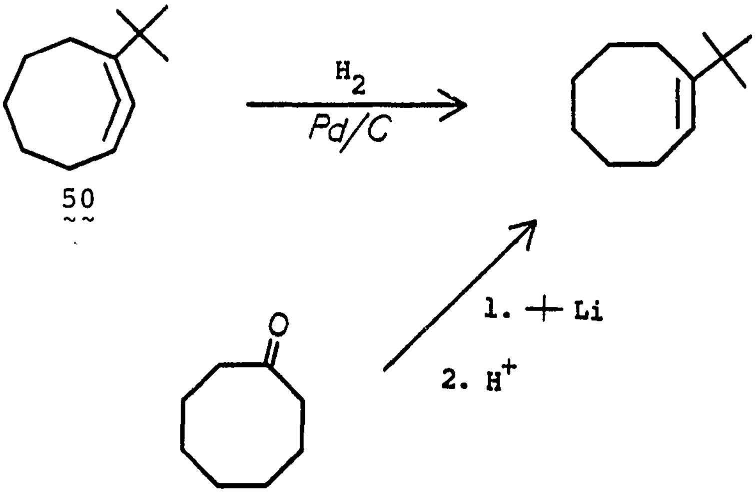
The synthesis of **50** is shown in Scheme 24. The preparation of 1-tert-butylcycloheptene **51** and 8,8-dibromo-1-tert-butylbicyclo[5.1.0]octane **52** proceeded as in the case of the methyl derivative in 48% and 37% yields respectively. Treatment of dibromide **52** with methyllithium, however, afforded a mixture of three isomeric hydrocarbons in 92% yield. These were isolated by preparative gas chromatography on glass columns, and identified as: 1-tert-butyl-1,2-cyclooctadiene **50**, 1-tert-butyltricyclo[5.1.0.0^{2,8}]-octane **53**, and 7-tert-butylbicyclo[5.1.0]oct-1(8)-ene **54**, in the ratio of 43:6:1.

Characterization of **50** as an allene follows from its IR and ^{13}C NMR data. These include a characteristic asymmetric C=C=C stretch at 1942 cm^{-1}, and ^{13}C NMR resonances at δ 202.2 (sp), 117.7 (sp^2), and 94.4 (sp^2) ppm. The ultraviolet spectrum of **50** showed a maximum at < 210 nm, but this band tailed to ca. 260 nm (ε_{254} = 1460). Additionally, hydrogenation of **50** leads smoothly to 1-tert-butylcyclooctene, identical to an authentic sample, prepared as shown below.

Scheme 24



Scheme 25



The structure of bicyclobutane 53 is assigned based upon ^{13}C and ^{1}H NMR data. Especially noteworthy is the ^{13}C NMR spectrum which shows seven aliphatic resonances, an observation indicative of molecular symmetry. This type of carbenoid insertion product is well precedented.[51]

The cyclopropene 54 displays a typical downfield ^{1}H NMR resonance at δ 6.45 ppm, as well as a strong IR absorption at 1765 cm^{-1}, corresponding to the C=C stretch of cyclopropenes.

Figure 1 shows the MNDO optimized structure for 50 plotted along the C1-C2-C3 plane. The allene moiety is predicted to be bent 22°, a value nearly identical to that predicted by MNDO calculations on the parent allene.[46] The heat of formation is calculated to be 24.6 kcal/mol.

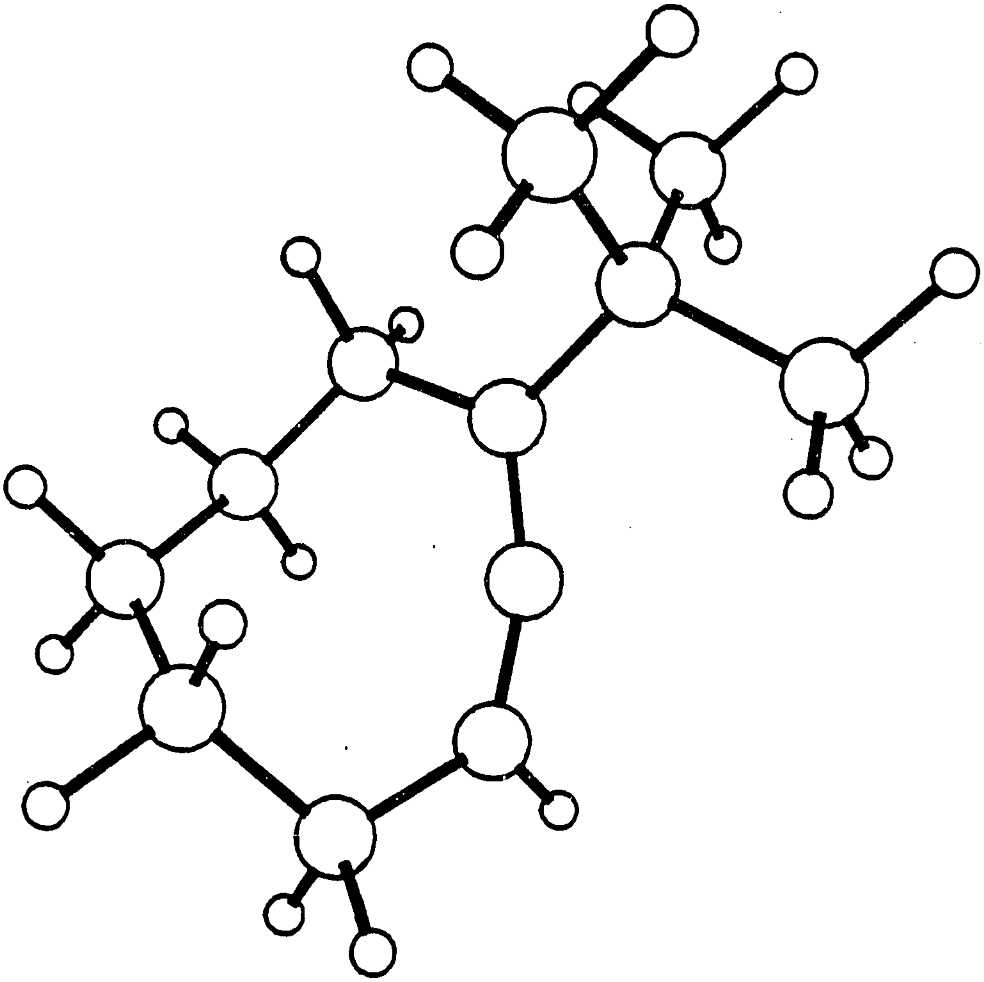
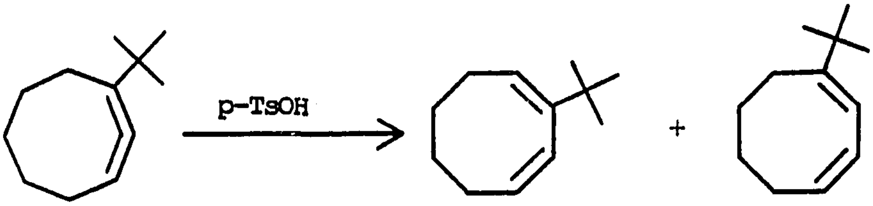


Figure 1. MNDO optimized geometry of 1-tert-butyl-1,2-cyclooctadiene

The stability of 1-tert-butyl-1,2-cyclooctadiene 50 is quite remarkable when compared to the unsubstituted allene. Not only can neat samples of 50 be stored at ambient temperature for extended periods with no sign of dimerization, but one step in the purification of 50 involves vacuum distillation.

The allene is, however, extremely sensitive to traces of acid. Brief treatment of 50 with para-toluenesulfonic acid results in rapid formation of 1,3-dienes 55 and 56 (Scheme 26). These dienes have previously been reported.[52] The same rearrangement occurs when 50 is treated with potassium tert-butoxide in DMSO, although the reaction is much slower.

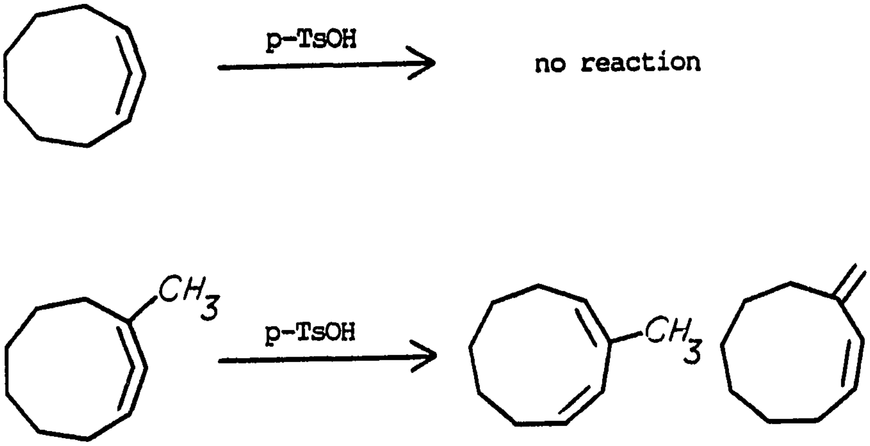
Scheme 26



50 55 56

Acid catalyzed rearrangement is undoubtedly facilitated by strain relief. Under identical conditions, 1,2-cyclononadiene did not react, while its 1-methyl derivative 47, rearranged slowly to 2-methyl-1,3-cyclooctadiene 57, and 3-methylene-1-cyclooctene 58 (Scheme 27).

Scheme 27

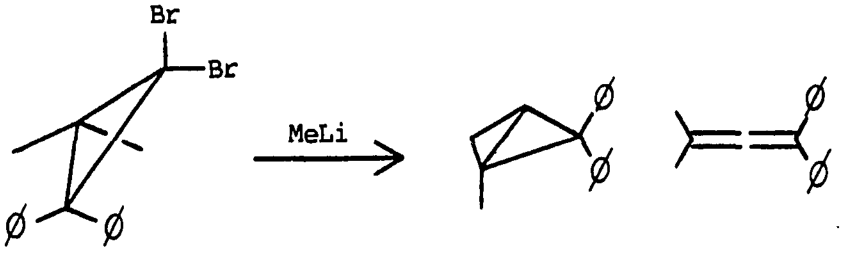


57 58

It was because of this sensitivity to acid, that initial purification of allene 50 required vacuum distillation. Traces of unreacted dibromide 52, or of incompletely reduced monobromide, when placed on a gas chromatography column at elevated temperatures, can act as acid generators, due to elimination of HBr. This appears to explain the observation that after a few preparative GLC injections, rather than isolating 50, only the 1,3-diene rearrangement products 55 and 56 were obtained. Once the crude material was distilled however, this ceased to be a problem, and separation of the allene from the other products in the reaction mixture was once more feasible.

Isolation of large quantities of material by preparative gas chromatography is tedious at best. Because significant bicyclobutane 53 are also formed in the reaction, an alternative route for the synthesis of 50 was proposed, where it was hoped that C-H insertion reactions might be minimized. This route employed the same dibromide precursor 52, but used magnesium metal to generate the cyclopropylidenoid precursor to 50. Such altered selectivity has precedent in work from our own research group. As shown in Scheme 28, treatment of dibromide 59 with methyllithium results in the formation of an allene and a bicyclobutane.[53] Carbon-hydrogen insertion greatly predominates. However, when 59 is treated with Mg in ethyl ether, only 1,1-diphenyl-3-methyl-1,2-butadiene is formed.

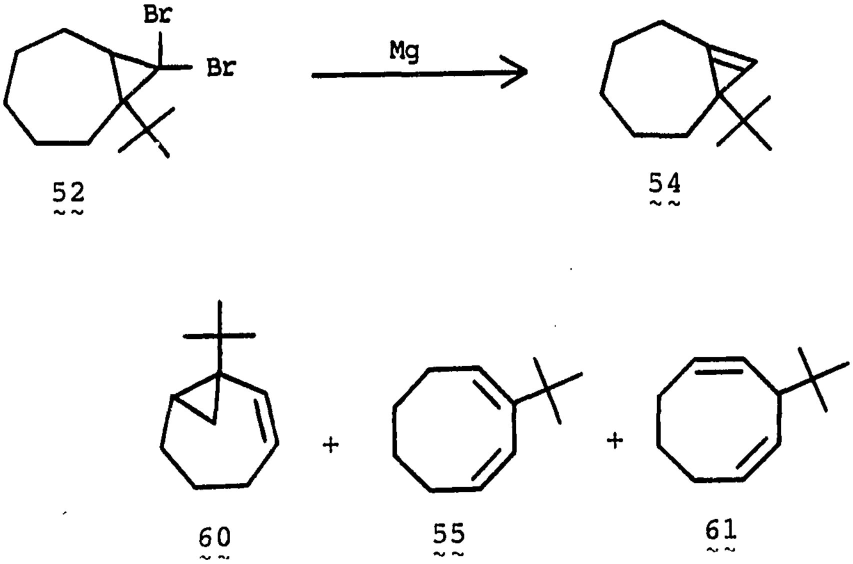
Scheme 28



59

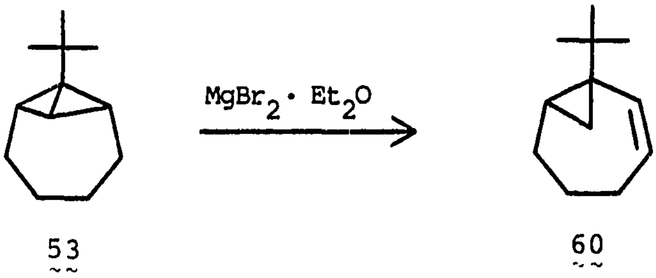
Unfortunately, such selectivity was not observed for the present system. When dibromide 52 was treated with magnesium metal, a mixture of four products was obtained, as shown in Scheme 29. Three of these isomers were isolable by preparative gas chromatography, and were identified as cyclopropene **54** (3%), 1-tert-butylbicyclo[5.1.0]oct-2-ene **60** (39%), and 1,3-diene **55** (37%).

Scheme 29



The structure of vinyl cyclopropane **60** was assigned based upon its ^{1}H NMR spectrum, as well as by its independent synthesis from bicyclobutane **53** (Scheme 30). Such ring opening reactions effected by magnesium bromide are well precedented for bicyclobutanes.[54]

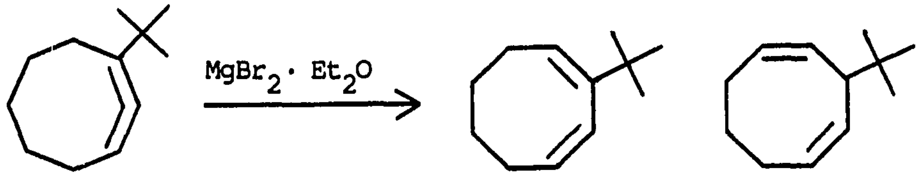
Scheme 30



The fourth isomer (21%) was not stable to a variety of preparative gas chromatography conditions and could not be isolated. Structure assignment was tentatively based upon the ^{1}H NMR spectrum of the crude reaction mixture; this showed a ratio of vinyl to tert-butyl protons of 4:9. Also noted was the facile rearrangement of 61 to 1,3-diene 55, when isolation was attempted by preparative thin layer chromatography (silica gel or florisil).

Formation of dienes 55 and 61 from the reaction of dibromide 52 with magnesium was unexpected. It seemed likely that these arose from a secondary reaction of initially formed allene 50 with magnesium bromide, acting as a Lewis acid. Although this reaction does not occur with other allenes, involvement of magnesium bromide was suggested by the large amount of vinyl cyclopropane 60 formed, once again, presumably through rearrangement of initially formed bicyclobutane 53. As a test of this hypothesis, allene 50 was treated with magnesium bromide; this yielded dienes 55 and 61 as shown in Scheme 31.

Scheme 31



50 55 61

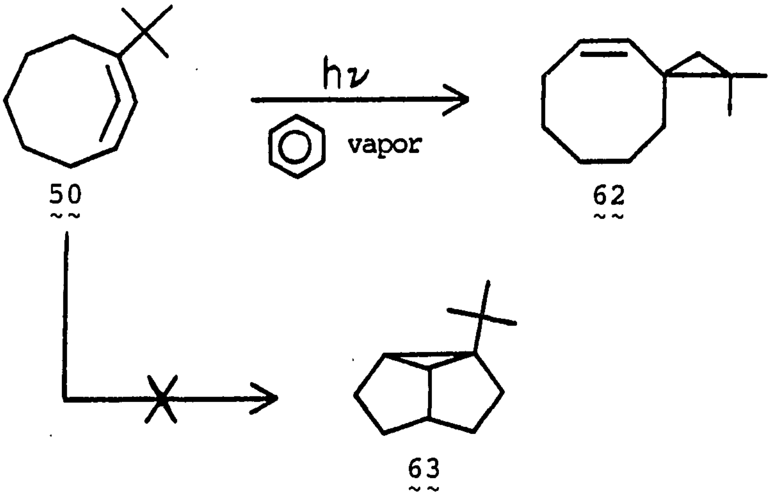
With the synthesis and isolation of this cyclic allene firmly in hand, attention was next directed toward its photochemical behavior.

Triplet Reactions of 1-tert-Butyl-1,2-cyclooctadiene

Based upon the triplet vapor phase behavior of other allenes, irradiation of 1-tert-butyl-1,2-cyclooctadiene with benzene in the vapor phase was expected to yield tricyclooctane 63 (Scheme 32). This is a known ring system.[41] However, such was not the observed result; the ^{1}H NMR spectrum of the sole photoproduct of this reaction displayed two olefinic protons (δ 5.61-5.47 ppm, m), two cyclopropyl protons (δ 0.36 ppm, d, J = 3.7 Hz; δ 0.29 ppm, d, J = 3.7 Hz), and two methyl groups (δ 1.16 ppm, s; δ 1.04 ppm, s). A geminal relationship of these two methyl groups was suggested by the IR data (gem-dimethyl C-H bending 1396, 1375 cm^{-1}). The high resolution mass spectrum showed the product to be isomeric with 50. Based upon these data, the structure of the photoproduct was tentatively assigned as 1,1-dimethylspiro[2,7]dec-4-ene 62.

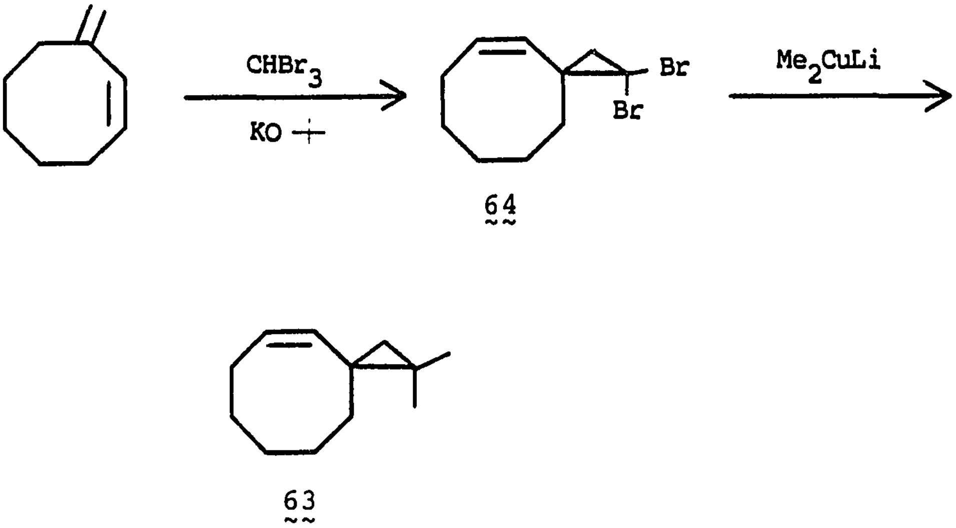
Confirmation of this structure was provided by the independent synthesis outlined in Scheme 33. Treatment of 3-methylene-1-cyclooctene with potassium tert-butoxide and bromoform afforded the dibromo carbene adduct 64 as a single

Scheme 32



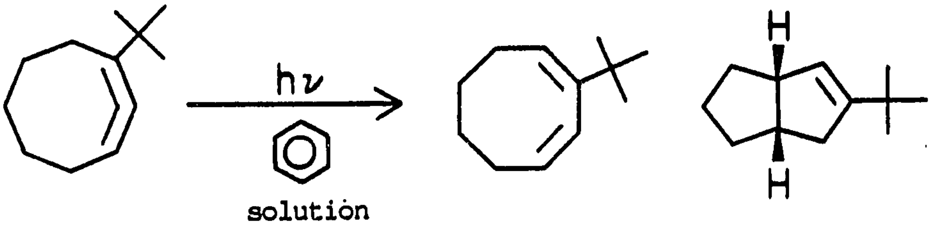
regioisomer. Reaction of this compound with lithiumdimethylcuprate afforded spirodecene 62 in 56% yield. This material was identical in all respects with that obtained from the triplet vapor phase reaction of 50.

Scheme 33



Irradiation of 1-tert-butyl-1,2-cyclooctadiene in benzene solution once again proved to be a departure from previous allene triplet behavior. Neither cycloadducts nor cyclopropylidene derived products were observed. At low conversions ($\leq$ 20%), two isomeric photoproducts were detected in the ratio of 1:1. These were isolated by preparative gas chromatography, and identified as 2-tert-butyl-1,3-cyclooctadiene 55, and 3-tert-butyl[3.3.0]oct-2-ene 65 (Scheme 34). The 1,3-diene has been prepared by the acid catalyzed rearrangement of 50 (Scheme 26). Structure assignment for bicyclooctene 65 will be discussed in the next section.

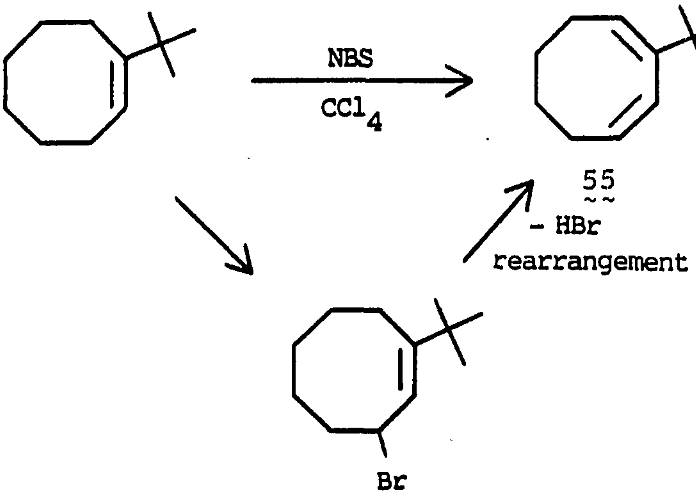
Scheme 34



50 55 65

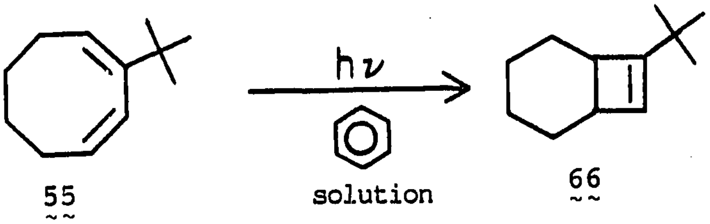
2-tert-Butyl-1,3-cyclooctadiene was also prepared by the reaction of 1-tert-butylcyclooctene with N-bromosuccinimide. Under the reaction conditions, the intermediate allylic bromide dehydrobrominated. 1,3-Diene 55 is formed in 82% yield (Scheme 35). This was an unfortunate result, since it was desired to use the allyl bromide as a precursor to diene 56.

Scheme 35



At higher conversions in the photoreactions of 50, a third product was observed; this was isolated and identified as 7-tert-butylbicyclo[4.2.0]oct-7-ene 66, based upon its ^1H NMR and IR spectra (cyclobutene C=C stretch, 1616 cm^{-1}). Cyclobutene 66 was believed to be a secondary product, as it was not observed at low conversions of 50, and it apparently arose at the expense of the 1,3-diene 55. This was confirmed by irradiation of a pure sample of 55 in benzene (Scheme 36). One product, cyclobutene 66, was formed. This results from a triplet sensitized electrocyclization, which has precedent in the triplet and singlet reactions of 1,3-cyclooctadiene.[55]

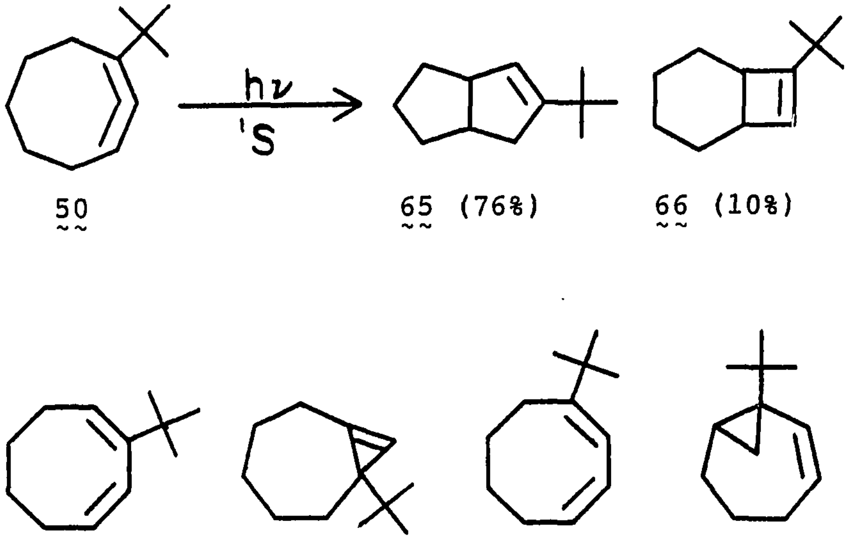
Scheme 36



Singlet Reactions of 1-tert-Butyl-1,2-cyclooctadiene

Direct irradiation of GLC purified 1-tert-butyl-1,2-cyclooctadiene in a dilute degassed cyclohexane solution at 254 nm led to the formation of five primary photoproducts (Scheme 37). The products were determined to be primary by their relative percentages at various conversions. Analysis of the crude reaction mixture by capillary GLC and ^{1}H NMR spectroscopy, with authentic product samples in hand, allowed the following assignments: 3-tert-butylbicyclo-[3.3.0]oct-2-ene (65, 76%), 7-tert-butylbicyclo[4.2.0]oct-7-ene (66, 10%), 2-tert-butyl-1,3-cyclooctadiene (55, 5%), 8-tert-butylbicyclo[5.1.0]oct-1(8)-ene (54, 4%), 1-tert-butyl-1,3-cyclooctadiene (56, 2%). A sixth product, 1-tert-butylbicyclo[5.1.0]oct-2-ene (60, <1%) was also observed; due to its low yield it could not be determined if this compound were primary or secondary.

Scheme 37



50 → **65** (76%) + **66** (10%)

55 (5%) **54** (4%) **56** (2%) **60** (t)

The above percentages represent ratios of photoproducts (excluding unreacted allene), and were determined by ^{1}H NMR integration. Quantitatively similar results were obtained by capillary GLC analysis.

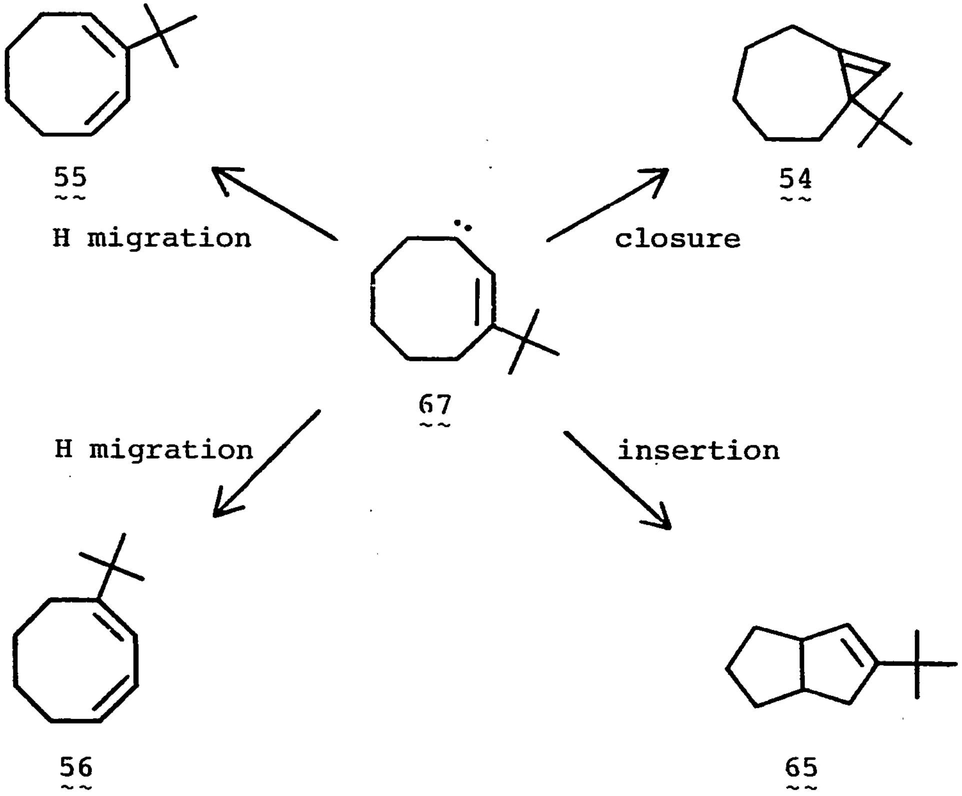
Of the isomers shown in Scheme 37, all except bicyclic olefin **65** have been previously characterized in this dissertation. Elucidation of this structure was problematic, as the spectral data alone were inconclusive. Evidence that the compound was a bicyclic olefin came from the ^{1}H NMR spectrum, which displayed a single vinyl resonance (δ 5.07, br s). The GC-mass spectrum indicated the material was indeed isomeric with starting allene ($C_{12}H_{20}$). The IR spectrum was unexceptional, displaying C-H stretching and C=C stretching vibrations at 3045 and 1653 cm^{-1}, respectively; these are typical for five or six ring carbon ring systems. The ^{13}C NMR spectrum displayed two olefinic resonances at δ 152.45 and 124.66 ppm.

One potential independent synthesis of **65** was suggested by the known behavior of cyclic vinylcarbenes. As noted in the Historical Section, these intermediates often undergo transannular insertion to form bicyclic olefins, with nearly exclusive cis-stereochemistry at the ring juncture. The unsubstituted vinylcarbene, cyclooct-2-enylidene, has been generated by Kirmse, by thermolysis of the sodium salt of the corresponding tosylhydrazone. The two major products obtained were cis-bicyclo[3.3.0]oct-2-ene and 1,3-cyclooctadiene, in the ratio of 60:40. Potential pathways for cyclooctenylidene **67** are shown in Scheme 38.

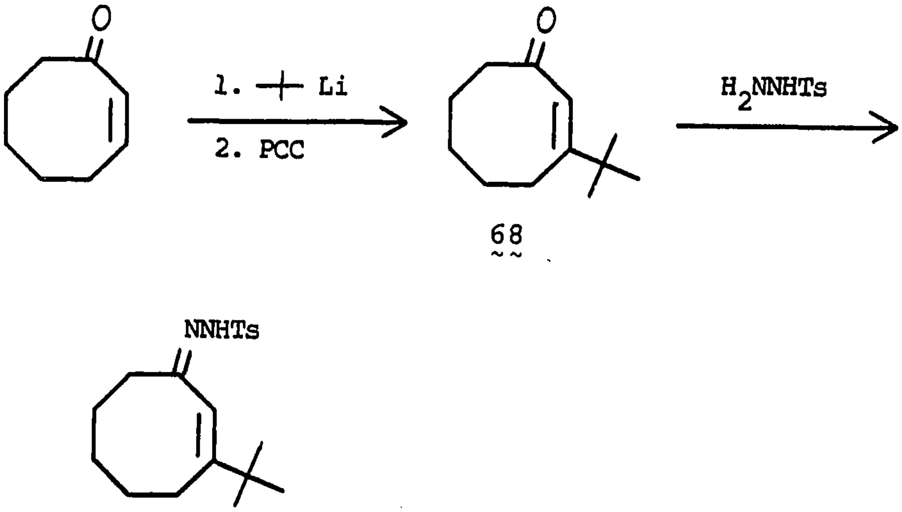
This experiment also provides valuable information about the mechanism of the singlet photorearrangement of allene **50**. Vinylcarbene **67** could arise from a 1,2-hydrogen migration from the singlet excited state of **50**. Indeed, at least three of the expected cyclooctenylidene derived products (**54**-**56**) are observed in the singlet reaction of allene **50**.

The precursor to vinylcarbene **67** is the α,β-unsaturated tosylhydrazone **69**, the preparation of which is shown in Scheme 39. Treatment of cyclooctenone with tert-butyl-

Scheme 38



Scheme 39



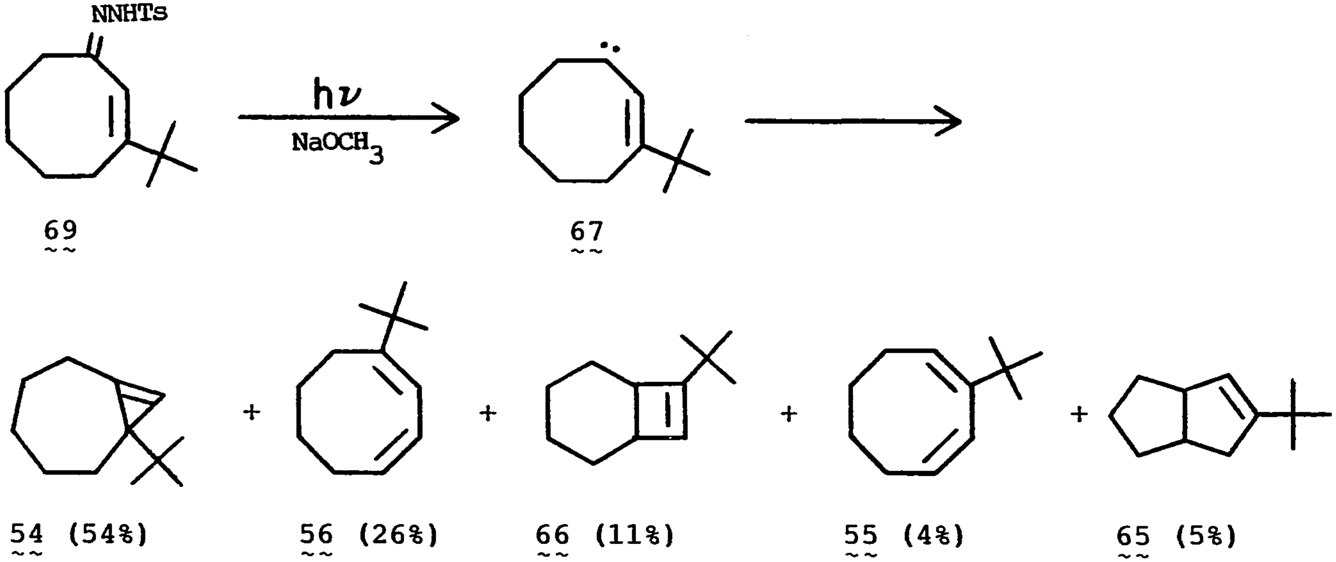
68

69

Photolysis of the sodium salt of **69** afforded a mixture of five isomers (Scheme 40). These were isolated by preparative gas chromatography and identified as cyclopropene **54** (54%), 1-tert-butyl-1,3-cyclooctadiene **56** (26%), cyclobutene **66**, (11%), 2-tert-butyl-1,3-cyclooctadiene **55** (4%). A fifth isomer, comprising 5% of the mixture was characterized as bicyclic olefin **65**; this was identical with material from the photochemical reactions of allene **50**.

Aside from the significance of the formation of **65** from this reaction, another noteworthy observation is the unexpected formation of a second transannular insertion product, cyclobutene **66**. In summary, 99% of the photoproducts obtained by direct irradiation of allene **50**, are

Scheme 40



69

67

54 (54%)

56 (26%)

66 (11%)

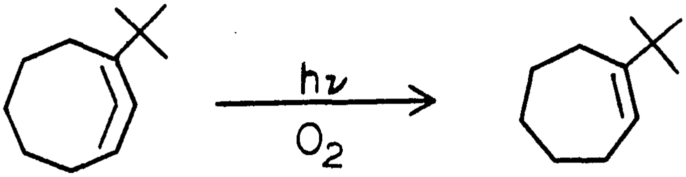
55 (4%)

65 (5%)

also found upon generation of vinylcarbene **67**, a result which will be discussed more fully in an ensuing section.

One final, and entirely unexpected result, should now be presented. When dilute (<0.015 M), incompletely argon degassed solutions of **50** were irradiated, only one product was obtained (Scheme 41). This was isolated by preparative gas chromatography and identified as 1-tert-butylcycloheptene **51**, a product arising from formal loss of a carbon atom! This result was serendipitous, since all solutions used in these photochemical experiments were degassed by bubbling with argon.

Scheme 41



50 **51**

Involvement of oxygen was established when the irradiations were performed using cyclohexene as solvent. No trapping products derived from reaction of atomic carbon with solvent were observed. However, significant amounts of cyclohexenone and cyclohexenol were obtained, in quantities approximately equal to the loss of allene **50**, or to formation of cycloheptene **51**. Prolonged degassing with

with solvent were observed. However, significant amounts of cyclohexenone and cyclohexenol were obtained, in quantities approximately equal to the loss of allene **50**, or to formation of cycloheptene **51**. Prolonged degassing with argon was necessary to observe the clean singlet rearrangements described earlier.

Triplet Reaction Mechanisms

Recent calculations and literature data allow the construction of a state correlation diagram for conversion of vertical triplet allene to either triplet cyclopropylidene or planar triplet allene.[10] Such diagrams in the past have been useful in understanding allene triplet reactions. Figure 2 shows a state correlation diagram for allene ground and excited states. Relative energies (eV) are plotted along the C_2 bending and twisting coordinates.

One important observation is that the two low-lying vertical triplet states of allene ($^3A_1$ and $^3B_2$) cannot be reached by benzene sensitization. The energies of 4.28 and 4.89 eV for allene T_1 and T_2 were determined experimentally from electron impact studies.[56] Energy transfer from benzene must be substantially nonvertical.

Geometries and energetics for the cyclopropylidene singlet and triplet states have been reported by Stierman and Johnson.[11] Cyclopropylidene was predicted to have a singlet ground state, approximately 0.6 eV below the

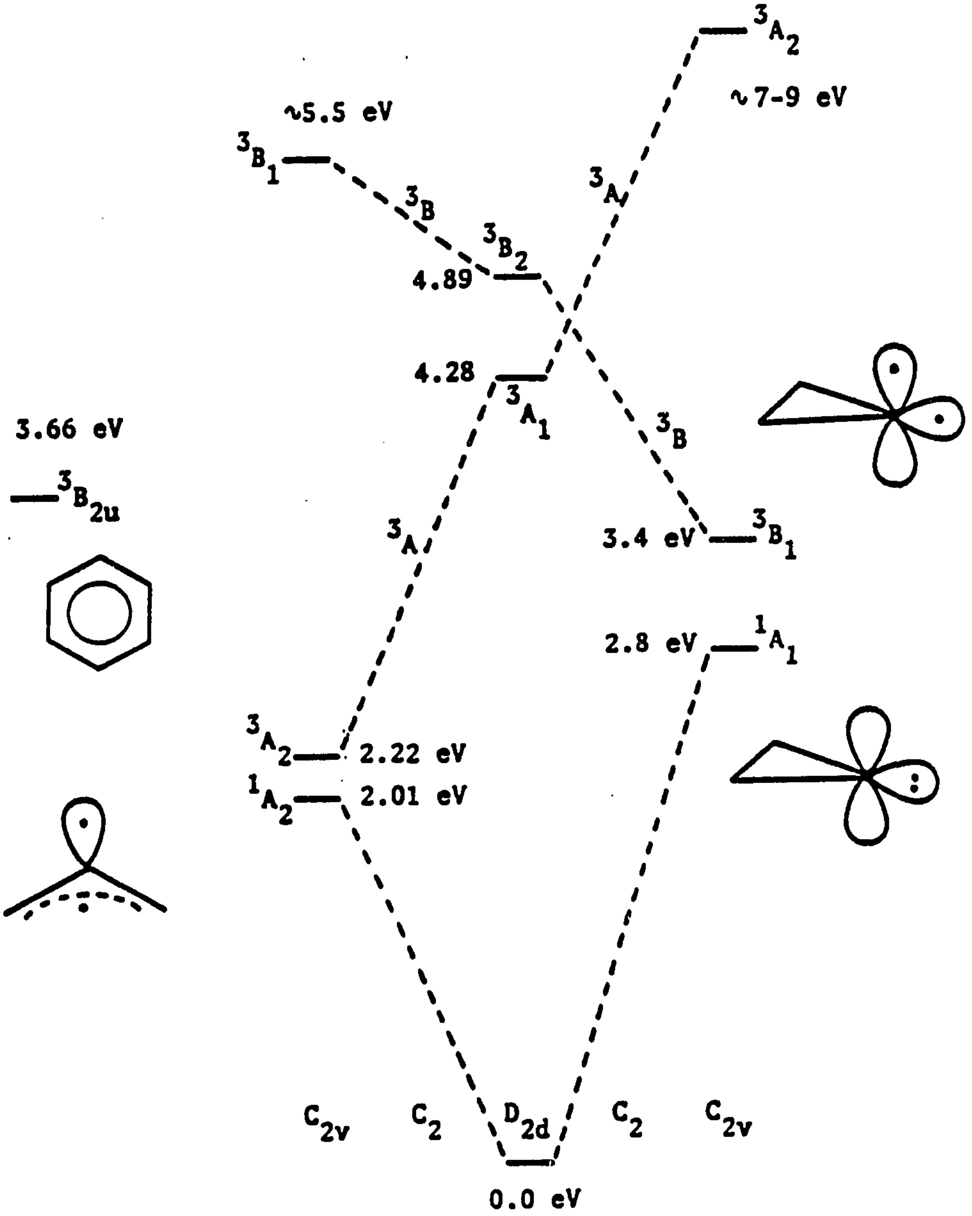


Figure 2. Allene correlation diagram

triplet. Energies for cyclopropylidene relative to allene are not available from experiment, but high level *ab initio* calculations predict the singlet to lie *ca*. 2.8 eV above ground state allene.[57,58]

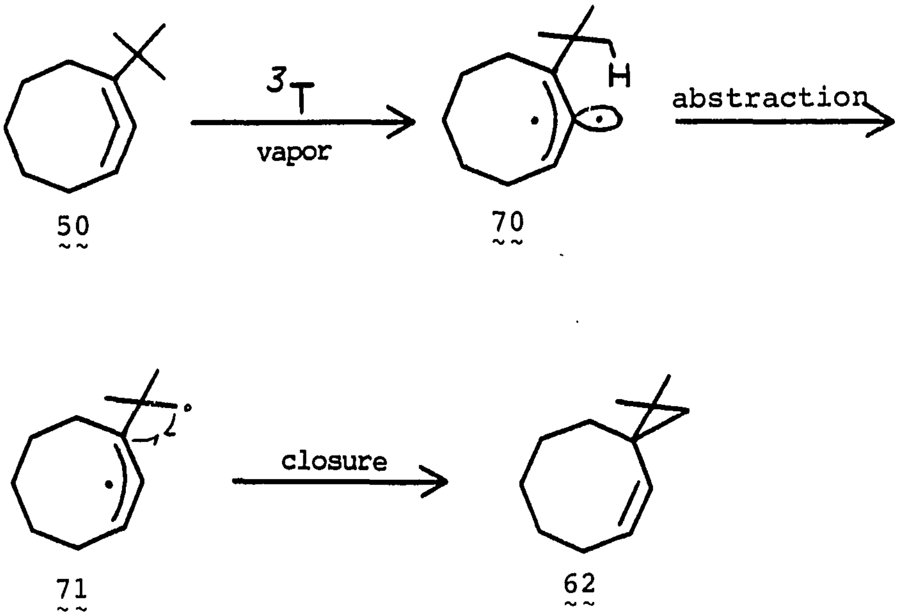
The energetics of planar C_{2v} allene have been determined by Angus et al. using *ab initio* MCSCF calculations.[46] As with cyclopropylidene, the singlet is predicted to be the ground state, with a singlet-triplet gap of 0.21 eV. The singlet is predicted to be 2.01 eV above ground state allene; this corresponds to the thermal rotational barrier in allene.

One particularly useful piece of information derived from Figure 2 is that energy transfer from triplet benzene (3.66 eV) may yield either triplet planar allene (2.22 eV) or triplet cyclopropylidene (3.4 eV). Thus from simple energetic considerations, either intermediate may be involved in allene triplet reactions. In either case, however, energy transfer from triplet benzene must be distinctly nonvertical.

Returning to the triplet vapor phase reaction of 1-tert-butyl-1,2-cyclooctadiene **50**, formation of spirodecene **62** can be most economically explained by the intermediacy of planar allene **70**, as shown in Scheme 42.

Hydrogen abstraction from a methyl group of the tert-butyl moiety leads to the allyl biradical **71** which, after

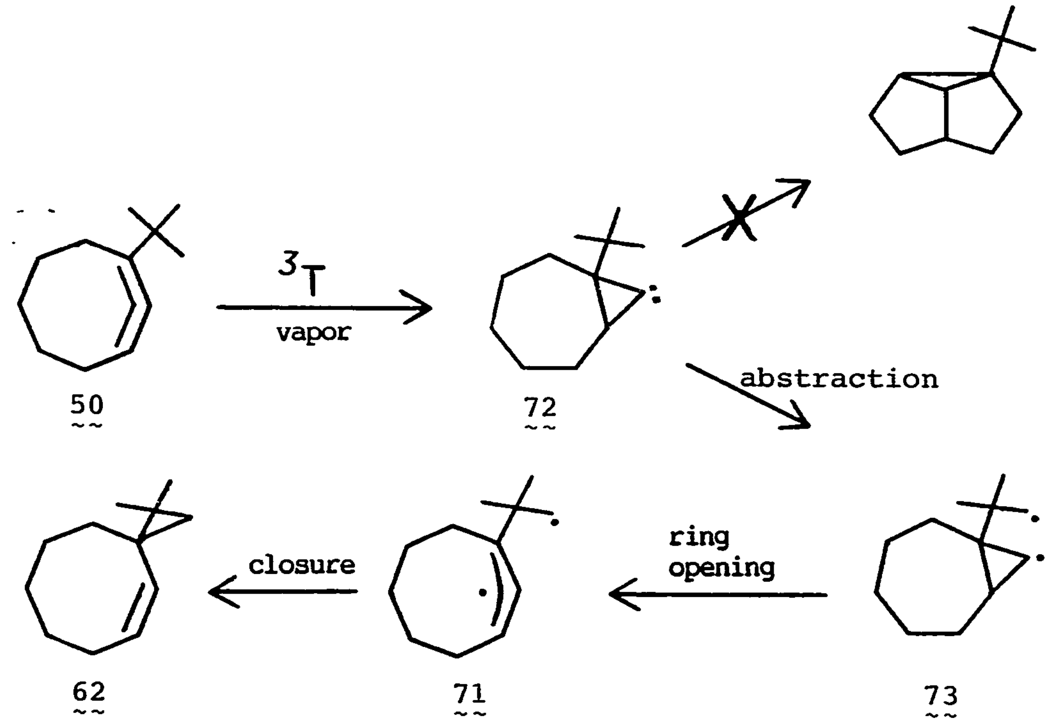
Scheme 42



spin inversion, may close directly to spirodecene 62. Molecular models indicate that the initial hydrogen abstraction should be facile due to proximity.

An alternative mechanism involves a cyclopropylidene; this is shown in Scheme 43. This mechanism requires hydrogen abstraction by cyclopropylidene 72, followed by ring opening of 73. This is problematic because of the absence of tricyclooctane 63, an expected product if this mechanism were operative. The tricyclic skeleton is known, and the cyclopropylidene 72 is certainly capable of adopting the required conformation which would lead to transannular product. More importantly, models show that the carbene in 72 may be too far from the tert-butyl group for hydrogen

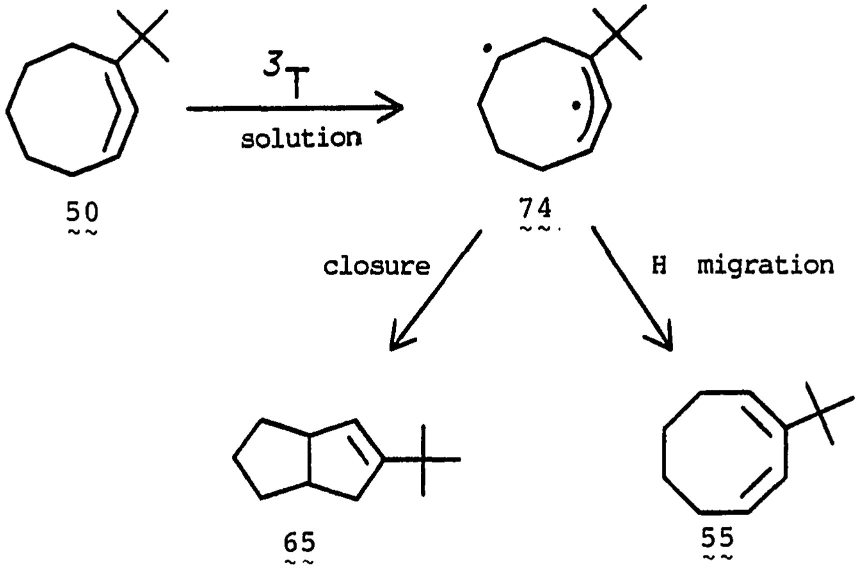
Scheme 43



abstraction to occur. We thus favor a mechanism which proceeds through hydrogen abstraction and recombination via a triplet planar allene.

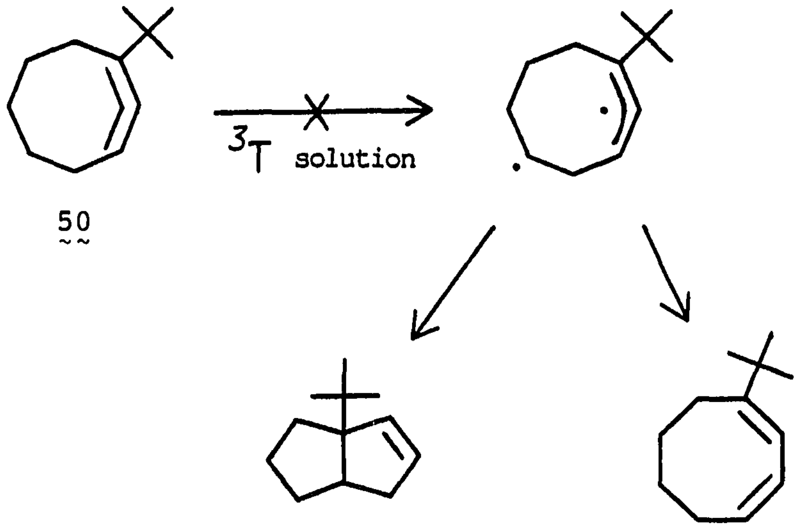
The products of the triplet solution phase irradiation of allene 50 also appear to derive from initial hydrogen abstraction by the central carbon of a triplet allene. In this case, however, abstraction must occur from the ring at C7, leading to allyl biradical 74, as outlined in Scheme 44. After spin inversion, this biradical may undergo closure through bonding between C3 and C7, forming bicyclooctene 65, or 1,2-hydrogen migration leading to 1,3-diene 55. As this mechanism involves transfer of hydrogen to the back face of the allenyl system, anti to the tert-butyl group, rotation about the allyl moiety is then required to obtain the cis-geometry observed in products 55 and 65.

Scheme 44



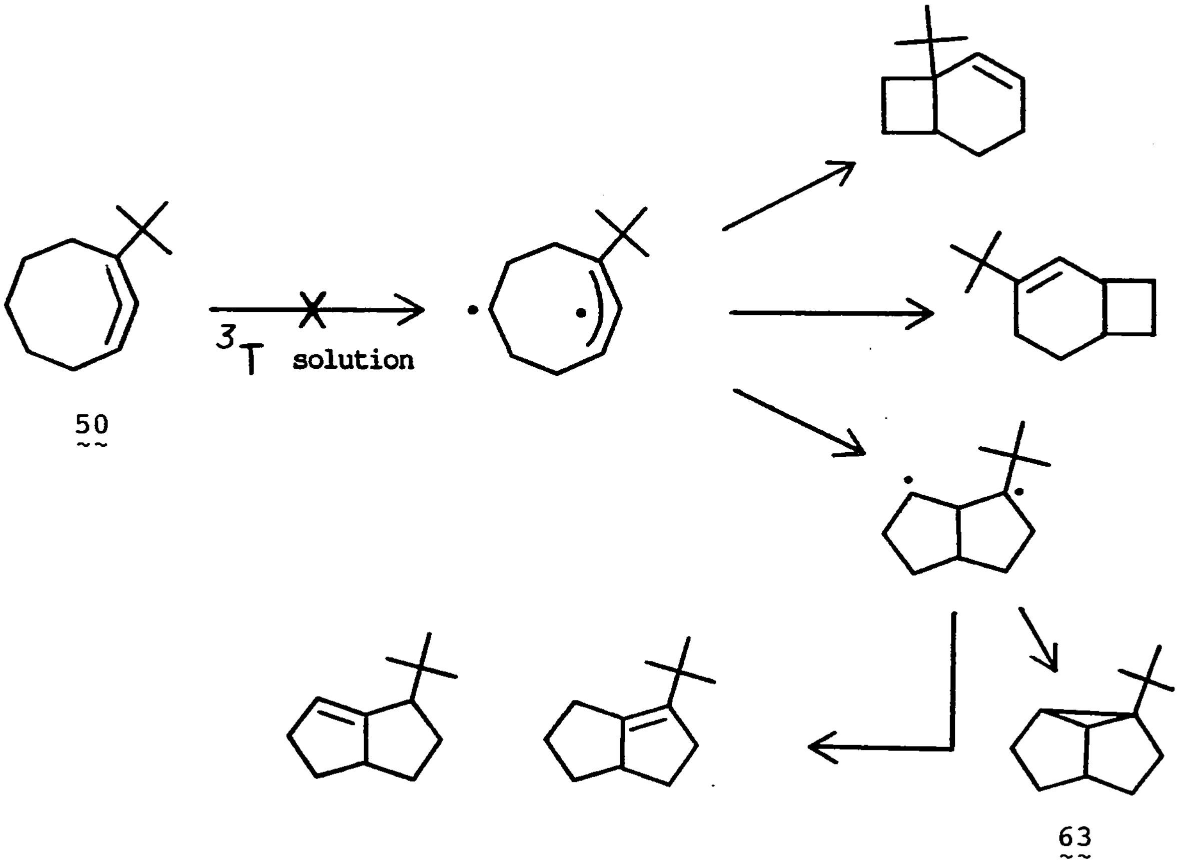
This observation raises a number of questions, however. Principal among these is why hydrogen abstraction occurs exclusively at C7 and not at C5 or C6. Reaction at these centers would doubtless lead to products which are not observed under these conditions (Schemes 45 and 46). Thus abstraction at C5 or C6 can be effectively excluded.

Scheme 45



50

One straightforward explanation for this remarkable selectivity comes from semiempirical MO calculations on 50. The geometry for triplet allene 50 was optimized with the MNDO method, starting from a geometry for the ground state. The optimized geometry (ΔH_f = 46.9 kcal/mol) has a nearly planar but still 18° bent allene moiety. In principle, those hydrogens which are closest to the central allene carbon should be selectively abstracted. Distances, in


50
^3T solution
63

Angstroms, from specific hydrogens to C2 are shown in parentheses in Figure 3. Closest approach is made by two tert-butyl hydrogens. As noted above, this is the site of abstraction in the vapor phase reaction. On the methylene skeleton, the hydrogens on C6, whose abstraction might lead to tricyclooctane 63 (Scheme 46) are directed away from the allene. Significantly, the tert-butyl group skews the methylene skeleton (which would otherwise have C_2 symmetry) such that an endo hydrogen on C7 is 0.15 Å closer than that on C5. This is entirely consistent with the observed regiochemistry.

We can only speculate as to the source of the difference between the triplet vapor and solution phase reactions. Although triplet biradical processes are proposed for both reactions, the site of reaction is rather dramatically dependent upon the phase. One possible explanation is that in the vapor phase, where rapid collisional deactivation with solvent molecules cannot occur, reaction proceeds through an intermediate with considerable excess vibrational energy. Such "hot" intermediates have been previously proposed in the interpretation of vapor phase photochemical reactions.[26] This high energy intermediate may exist in a conformation which facilitates methyl hydrogen abstraction. This may be an upper triplet state of a geometrically distorted allene.

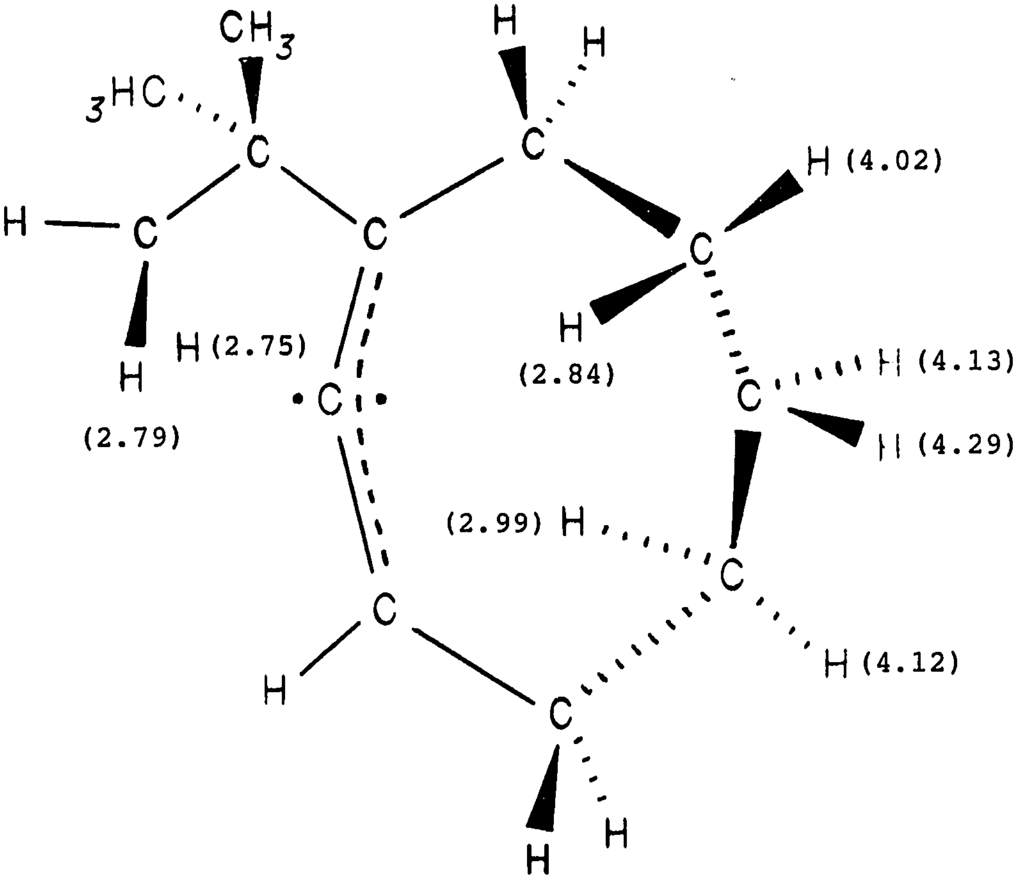


Figure 3. MNDO optimized geometry for triplet 1-tert-butyl-1,2-cyclooctadiene

Alternatively, a "hot" intermediate might be expected to display less selectivity in its reactions, thus resulting in abstraction of the most proximate hydrogen, despite formation of a relatively unstable primary radical. In solution, reaction occurs from a vibrationally "relaxed" intermediate. Hydrogen abstraction from the ring might then be favored due to formation of a more stable secondary radical.

Finally, the lack of cyclopropylidene derived products in the triplet reactions of 50 may be due to a ring size effect. Strained molecules, such as trans-cyclooctene, are often conformationally rigid. This rigidity, coupled with the availability of proximate hydrogens, may explain why abstraction from a planar triplet occurs before the allene moiety can undergo the twisting and bending motions necessary for cyclopropylidene formation. In larger systems, such as 1,2-cyclodecadiene, twisting and bending to a cyclopropylidene may more easily occur due to increased conformational mobility.

Singlet Reaction Mechanisms

Generation of 3-tert-butylcyclooct-2-enylidene 67 leads to formation of the same isomers which result from irradiation of allene 50. This is strongly suggestive evidence that the singlet photoreaction of 50 involves the intermediacy of a vinylcarbene. This is consistent with the singlet photoreactions of 1-methyl-1,2-cyclononadiene 11, where another vinylcarbene, 3-methylcyclonon-2-enylidene 40, appears to be involved. Both of these results are thus in clear contrast with the singlet photochemical rearrangements of the unsubstituted cyclic allenes 1 and 16, for which concerted pathways have been proposed. One explanation for this result, is that stabilization of vinylcarbenes 67 and 40 afforded by alkyl substitution, may favor this pathway. Alternatively, alkyl substitution may effect changes of the allene excited state surface, such that the minimum on the excited surface may be geometrically closer to a ground transition state leading to carbene formation.

The vinylcarbene pathway which is proposed for the reactions of 11 and 50, and the concerted pathway proposed for the reactions of 1 and 16, are undoubtedly closely related. This is implied by the substantial changes in reactivity which are induced by simple alkyl substitution.

As previously mentioned, *ab initio* CI calculations for hydrogen migration in allene have been reported by Klett and Johnson. Their results are shown in Figure 4. The potential surfaces show the expected pericyclic minimum, which results in an approach of ground and excited states. The geometry at this point approximates that of a bent bisected biradical 75. Internal conversion at this geometry could then lead to cyclopropene formation via C1-C3 bonding,

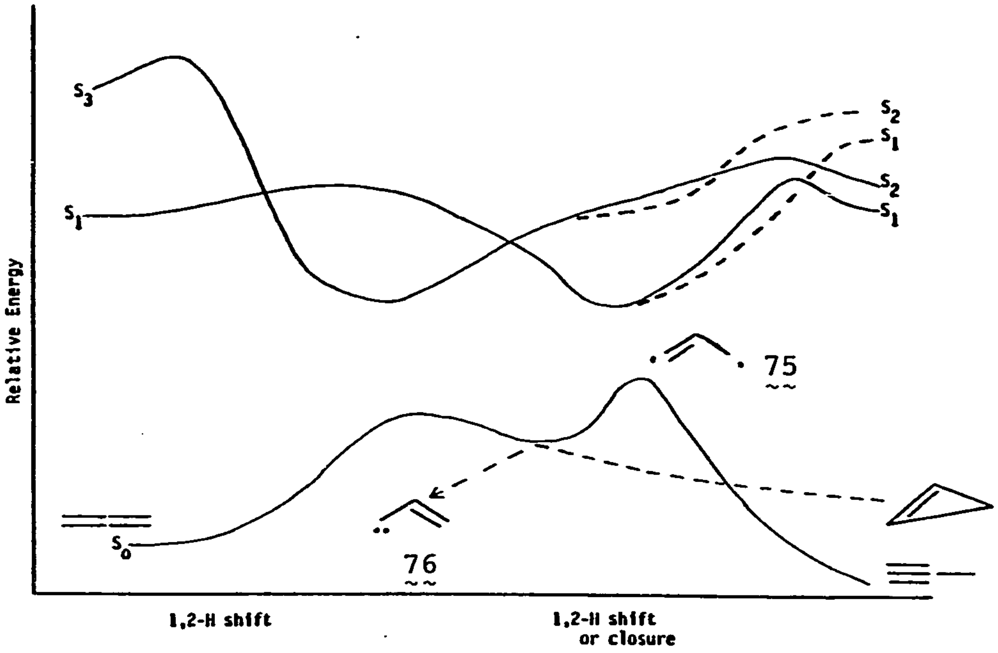


Figure 4. STO-3G CI potential surfaces

as appears to occur in the case of unsubstituted allenes, or alternatively, it may lead to formation of vinylcarbene 76, via π-bond rotation, in a process analogous to that proposed for alkyl substituted allenes.

A perplexing aspect of these results is why generation of vinylcarbene 67 from allene 50 and from tosylhydrazone 69 should yield such different product distributions. These are summarized in Figure 5. Either these two reactions generate altogether different species, or more likely in our opinion, there is incomplete equilibration among different conformations of 67. This assumes a competition among processes which have low activation barriers (commonly observed for highly exothermic carbene reactions) but very specific geometric requirements.

Closure to bicyclic olefin 65, probably requires a folded structure such as 67a (Figure 6), which is relatively close to the product geometry. This geometry, which is easily attainable, provides maximum overlap of the vacant (singlet) carbene orbital and the endo C7 hydrogen, which should be a requisite for insertion.

Inspection of models for the ground state of allene 50 shows that the endo hydrogen of C7 is already skewed towards C3, the incipient carbene site. A photochemical 1,2-hydrogen migration (C3 to C2) and further C1-C2-C3 bending and twisting can, with minimal motion of the remaining

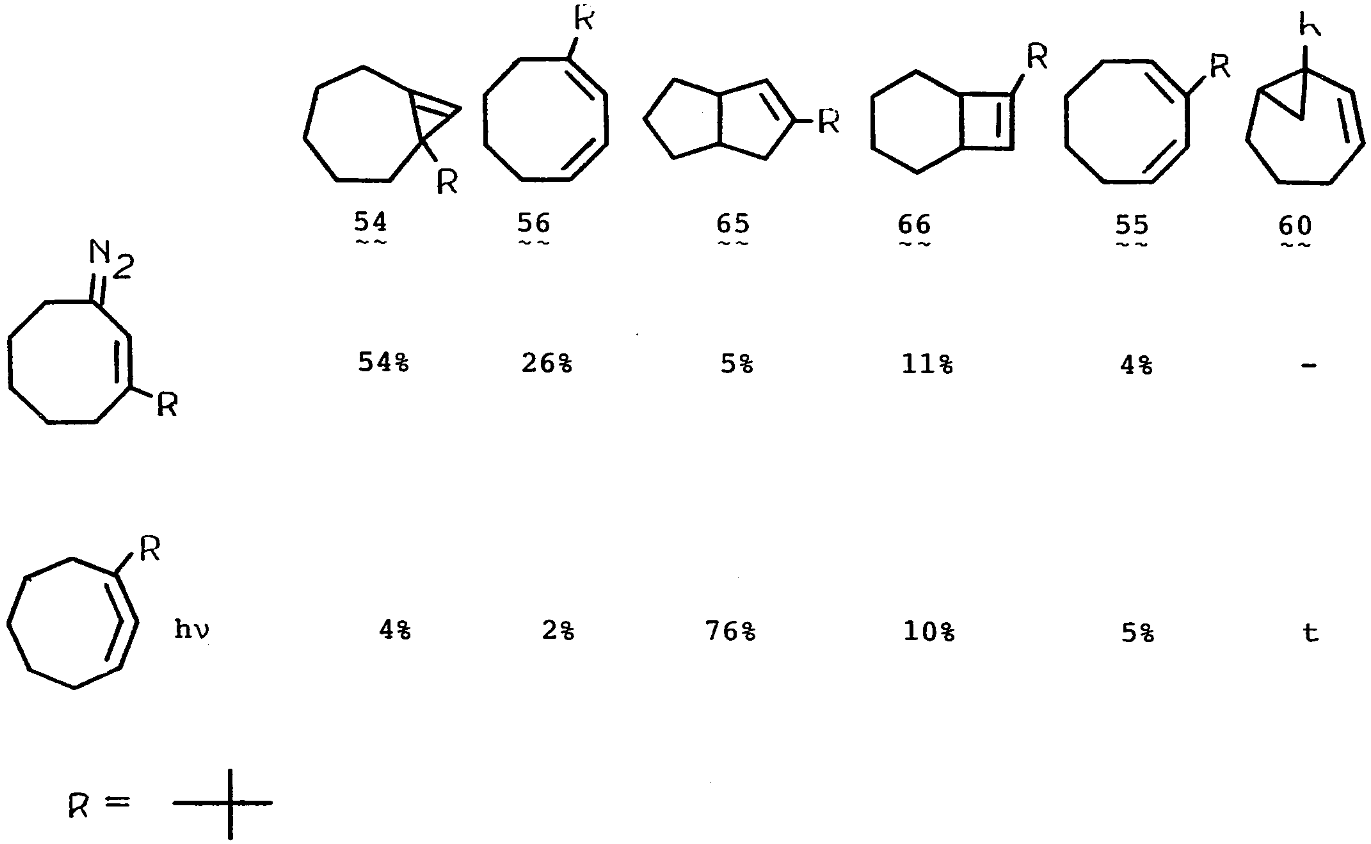
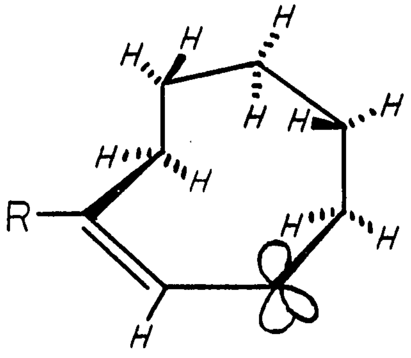


Figure 5. Vinylcarbene 67 product distribution

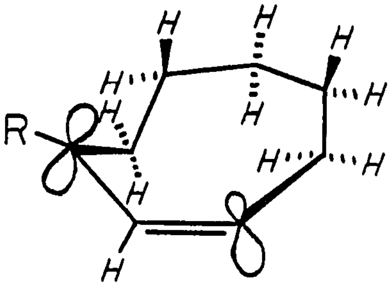
carbon skeleton, deliver the molecule to the conformation represented by 67a. Formation of this conformation may be facilitated by the molecular rigidity inherent in this strained cyclic system. If we assume a low barrier to transannular insertion, then conformational equilibration may not be competitive. This would explain predominant formation of 65 from irradiation of 50.

Photolysis of the diazo precursor to 67 (from tosylhydrazone 69) should initially lead to a quite different conformation. This initial conformation, which might be approximated by the MM2 optimized geometry for 3-tert-butylcyclooctenone (Figure 7), is depicted in Figure 6 as 67b. The cyclooctenone has a nearly planar enone moiety (dihedral angle 178°). This geometry is favorably aligned for 1,2-hydrogen migration to afford 1,3-diene 56. Closure to cyclopropene 54 also requires a specific geometry, approximated by 67c, in which the C1-C2 π bond is broken, and bonding between C1 and C3 is possible. This geometry may be obtained from 67b with minimal skeletal motion, by rotation of the p orbital of C1 towards the sp^2 orbital of C3. This explains predominant formation of 54 and 56 from the diazo precursor to vinylcarbene 67.

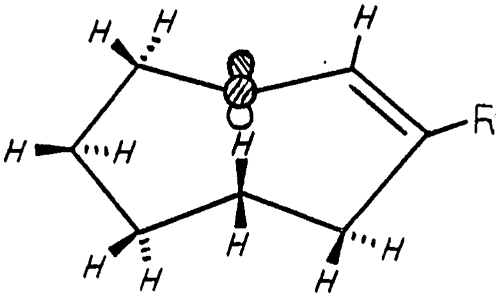
Generation of vinylcarbene 67, either from allene 50 or tosylhydrazone 69, also yields cyclobutene 66 (10%) and 1,3-diene 55 (4-5%). These result from a C-H insertion and



67b



67c



67a

Figure 6. Conformations of vinylcarbene 67

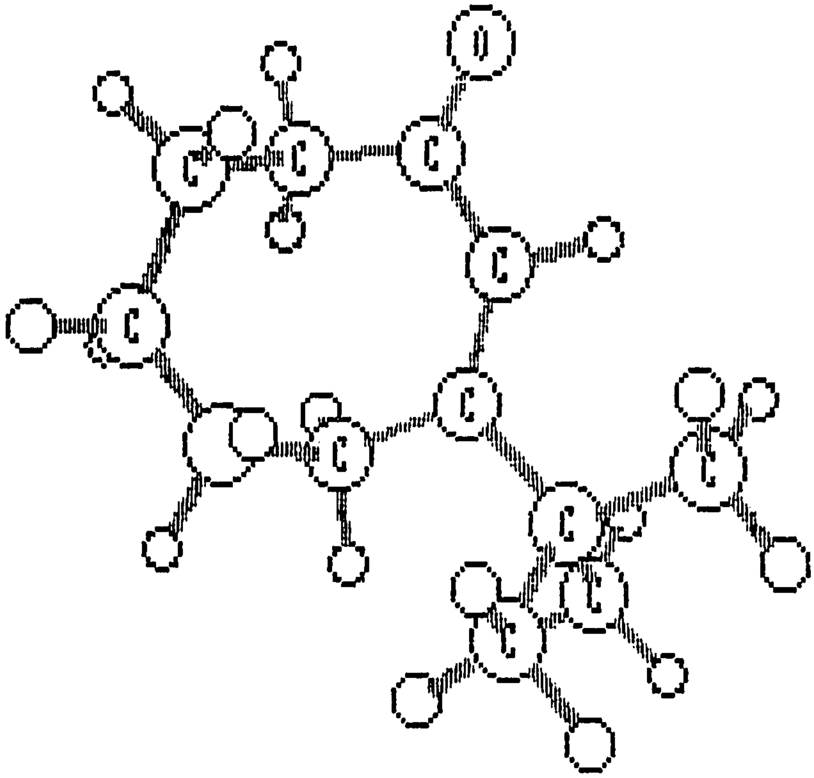
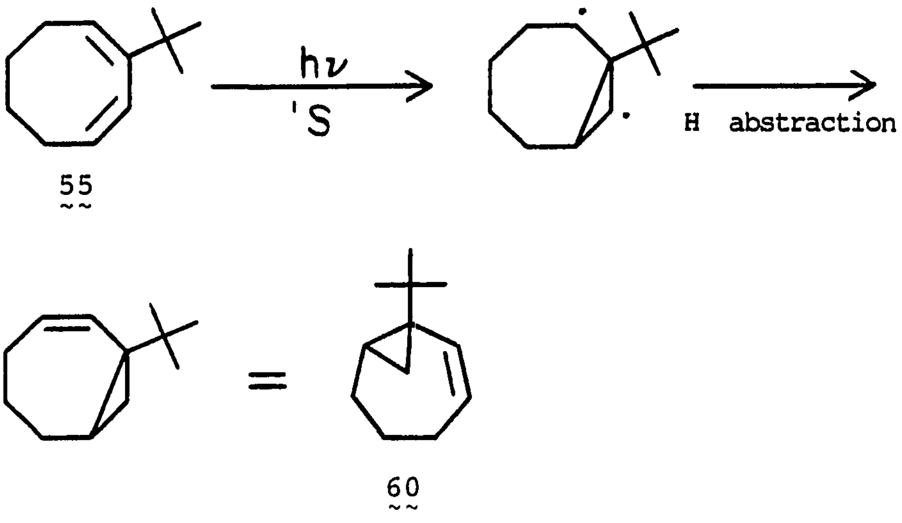


Figure 7. MM2 optimized geometry for 3-tert-butylcyclooctenone

1,4-hydrogen migration, respectively. Formation of these isomers as minor products is consistent with our contention that incomplete equilibration occurs among the conformations of **67**. Reaction from **67a** or **67b** occurs before equilibration to conformations yielding **66** and **55** is observed.

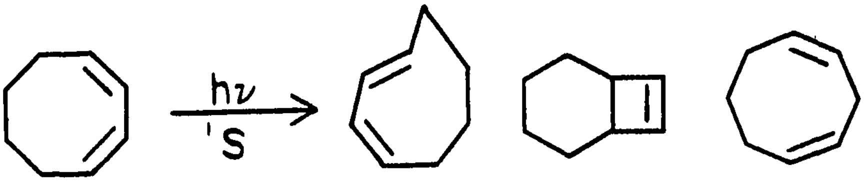
Isolation and identification of the minor products of a reaction often provide important mechanistic insight. A minor product, 1-tert-butylbicyclo[5.1.0]oct-2-ene **60**, was observed upon direct irradiation of allene **50**. Because of its low yield, it proved impossible to determine whether **60** was a primary or secondary product. One possible source was from a secondary reaction of 1,3-diene **55**, as outlined below.

Scheme 47



The singlet photochemical reactions of cis,cis-1,3-cyclooctadiene have been reported;[55] results are shown in Scheme 48. At low conversions, the major product is cis,trans-1,3-cyclooctadiene; this is accompanied by smaller amounts of cyclobutene. At higher conversions, a small amount of cis,cis-1,4-cyclooctadiene is observed; this results from a 1,3-sigmatropic hydrogen migration.

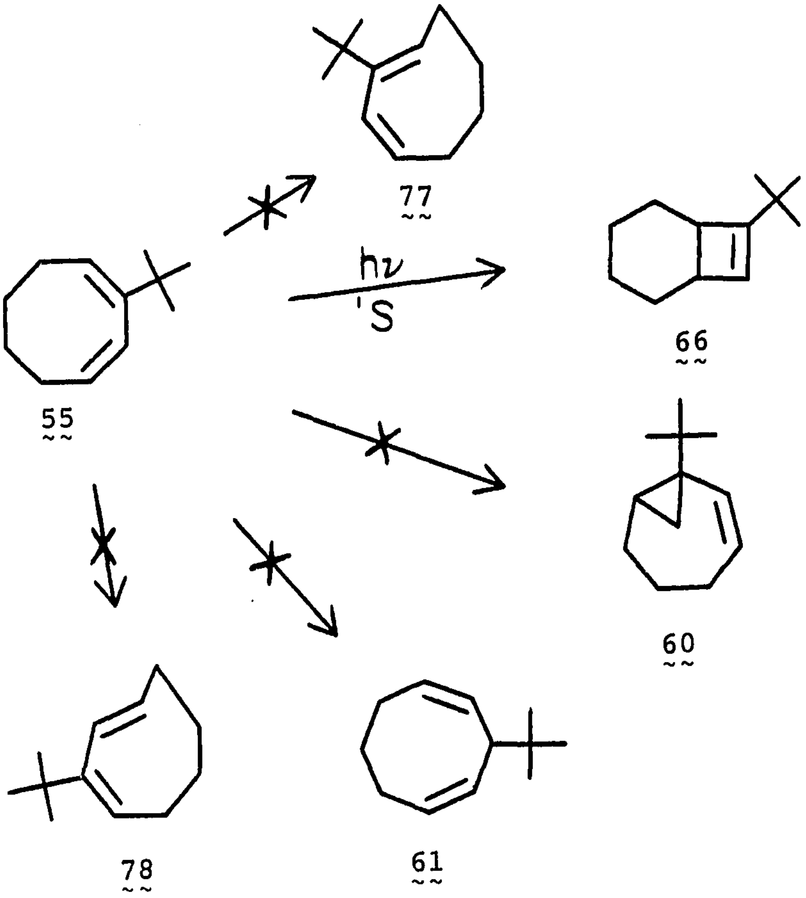
Scheme 48



The results of the direct irradiation of 1,3-diene 55 are shown in Scheme 49. Two products were obtained in the ratio of 12:1. The major isomer was isolable by preparative GLC, and was identified as the cyclobutene 66, which results from an expected disrotatory ring closure. The minor product was not isolated, but a partial ^{1}H NMR spectrum could be obtained by analysis of the crude reaction mixture. This spectrum displayed two vinyl resonances in the ratio of 1:1 (δ 6.15, d, J = 3.2 Hz; δ 6.00, d, J = 3.2 Hz). Structure 60 is immediately eliminated, as are cis,trans-dienes 77 and 78, and 1,4-diene 61.

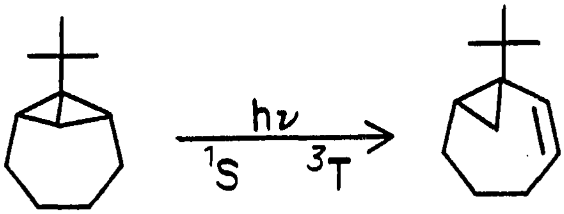
Another possible mechanism for the formation of vinyl cyclopropane 60 was suggested by a rather serendipitous

Scheme 49



result. During early studies of the triplet solution phase reactions of allene 50, the unseparated mixture of bicyclobutane 53 and allene was employed to ascertain the gross features of the allene reaction. It was not expected that 53 would react under these conditions. However, it did react, and at a rate faster than that of the allene. When pure samples of 53 were irradiated in benzene solution, a clean rearrangement to one isomer, vinyl cyclopropane 60, was observed (Scheme 50). As this bicyclobutane displays weak ultraviolet absorption beyond 254 nm, the direct irradiation was studied. Although this presumably singlet reaction was slower than the triplet, rearrangement to a single isomer, 60, also was obtained.

Scheme 50



53 60

It appears unlikely however, that 60 arises from a secondary reaction of bicyclobutane 53, as 53 is never observed as a product in the photochemical reactions of allene 50. This is despite careful efforts at detection.

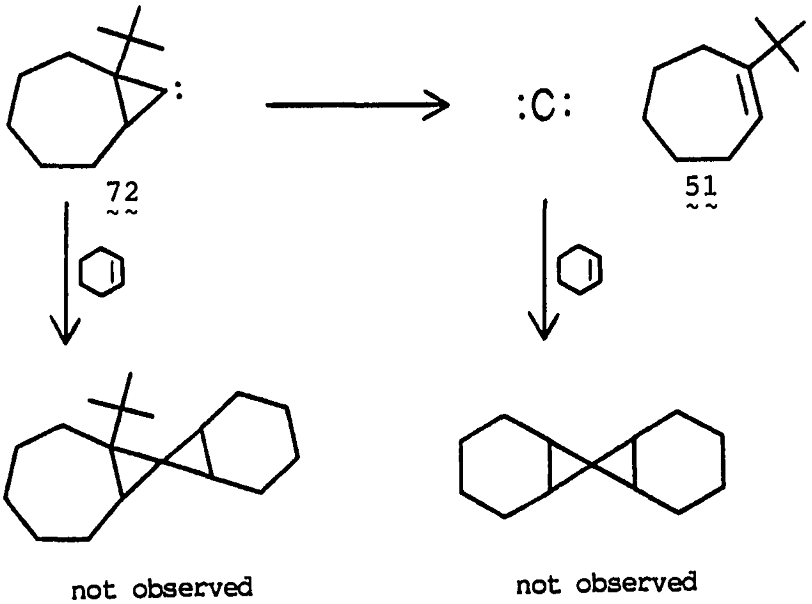
Although electron transfer induced rearrangements of bicyclobutanes to vinylcyclopropanes have been previously reported,[59] this is the first example of rearrangement proceeding via direct irradiation or triplet sensitization. The generality of this reaction is currently under investigation.

In many ways, the photoreactions of 1-tert-butyl-1,2-cyclooctadiene have proceeded rather unexpectedly. Yet no result was more surprising than the observation that irradiation of this allene in the presence of oxygen, led to the exclusive formation of a product resulting from formal carbon loss.

One very simplistic mechanism is loss of atomic carbon from cyclopropylidene **72**. A crude calculation however, indicates that extrusion of carbon from an electronically excited cyclopropylidene produced by excitation of ground state allene with 254 nm radiation, is endothermic by 50 kcal/mol. Ab initio SCF calculations have placed singlet cyclopropylidene 74 kcal/mol above allene.[60] This places the ΔH_f^o of cyclopropylidene at 120 kcal/mol (74 + 46 kcal/mol) in agreement with the thermochemical estimate of 116 kcal/mol.[61] The extrusion step itself is calculated to be endothermic by 92 kcal/mol if heats of formation for cyclopropylidene (120 kcal/mol), ^1D carbon (200 kcal/mol,[62]), and ethylene (12 kcal/mol) are considered. Irradiation of ground state allene with 254 nm (116 kcal/mol) light could produce an excited state cyclopropylidene with no more than 42 kcal/mol of excess energy (116 - 74 kcal/mol), far short of the required 92 kcal/mol.

This mechanism was further discounted, when the irradiation was carried out in cyclohexene solvent. No carbon trapped products were obtained, nor was the cyclopropylidene **72** trapped with solvent (Scheme 51). However, the intermediacy of oxygen in these reactions was established when formation of cyclohexenone and cyclohexenol

Scheme 51

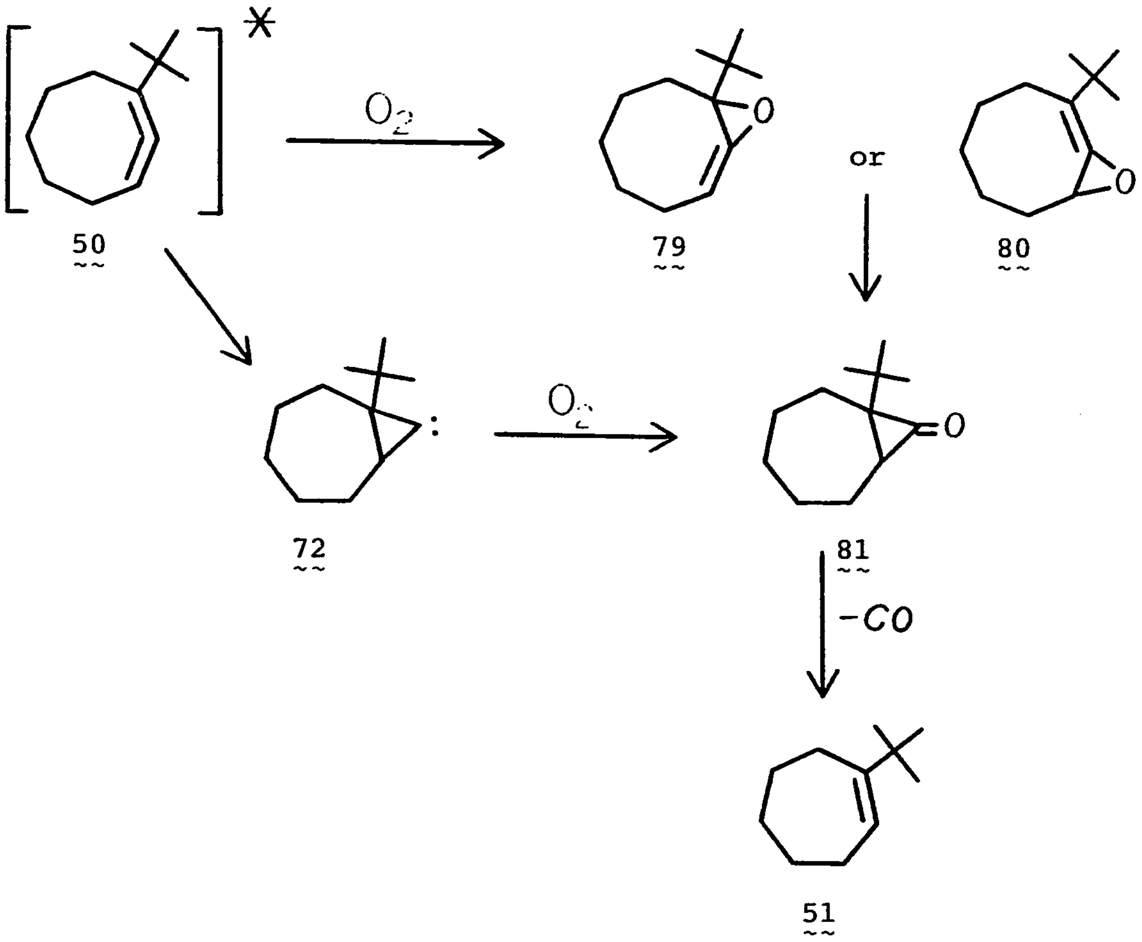


was observed. Cyclohexene alone does not react with oxygen under the conditions of the irradiation.

Two other mechanisms are outlined in Scheme 52. One mechanism proposes that oxygen is acting as a quencher of singlet excited allene, forming allene oxides 79 and/or 80. Thermal rearrangement of allene oxides to cyclopropanones is well precedented,[61] and in this case may be facilitated by relief of strain. Thermal or photochemical extrusion of carbon monoxide, also well precedented, would then yield cycloheptene 51.[61]

In support of this mechanism, it is well established that oxygen is a general and efficient quencher of the S_1 and T_1 states of organic molecules.[63-64] Usually the rate

Scheme 52



constant for quenching is within an order of magnitude of the diffusional quenching constant.

The mechanism for quenching may be physical or chemical in nature; i.e., it may or may not yield photoproducts. The two most commonly proposed chemical mechanisms are electron transfer, and diradical formation via addition (Scheme 53). Physical quenching mechanisms include exciplex formation and energy transfer.

Scheme 53

electron transfer

$$M^{*} + \underset{\bullet}{O}-\underset{\bullet}{O} \longrightarrow M^{\dot{+}} + O_2^{\dot{-}}$$

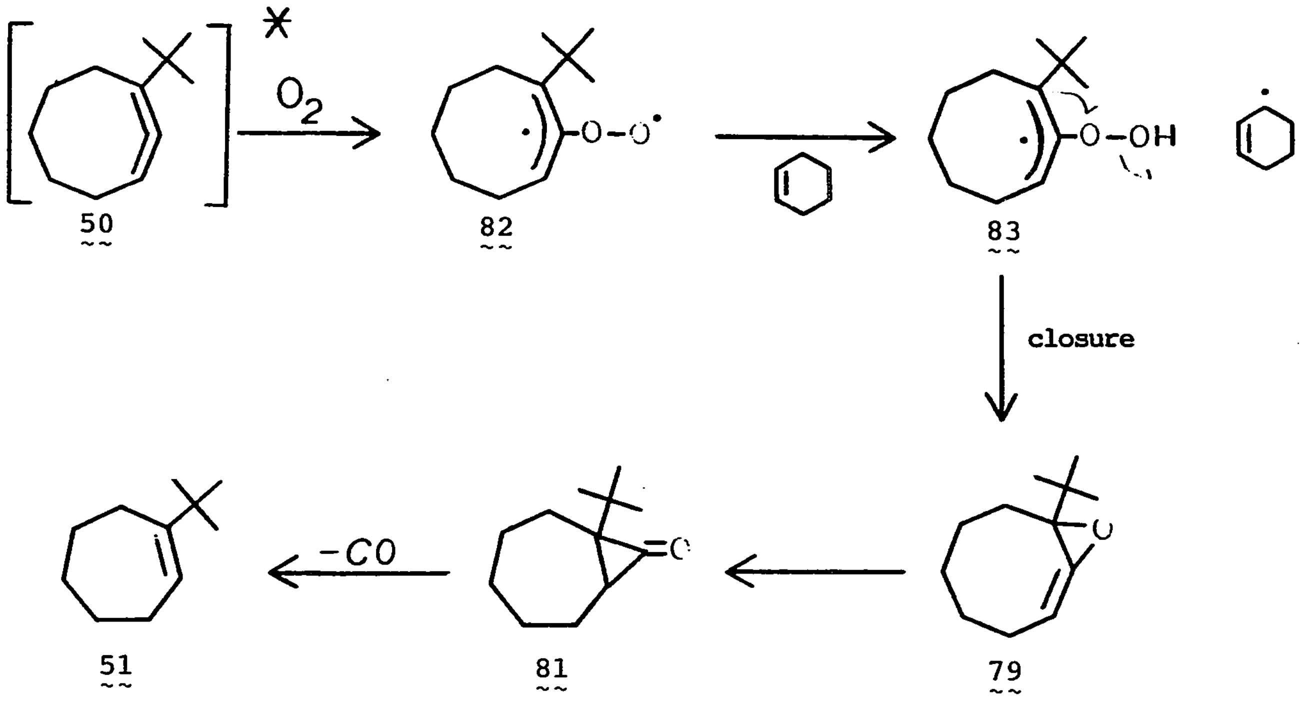
diradical formation

$$M^{*} + \underset{\bullet}{O}-\underset{\bullet}{O} \longrightarrow {}^{\cdot}M-O-O^{\cdot}$$

Quenching of excited singlet allene with molecular oxygen via diradical formation is shown in Scheme 54. Hydrogen abstraction by biradical 82 leads to formation of peroxide 83, which may close to allene oxides 79 (shown in Scheme 54) and/or 80, with subsequent loss of hydroxyl radical. Reaction of hydroxyl radical with solvent may explain formation of cyclohexenol and cyclohexenone.

This mechanism requires that quenching is an efficient process, since it effectively suppresses unimolecular product formation. One factor affecting the efficiency of

Scheme 54



diffusional quenching by molecular oxygen, is that oxygen diffuses considerably faster than organic molecules.[65] However, the solubility of oxygen is low in organic solvents (ca. 10^{-2} M at 760 mm O_2). If $k_q \sim 10^{10}\ M^{-1}\ s^{-1}$,[66,67] then $k_q[O_2] \lesssim 10^8\ s^{-1}$ at ordinary pressures. Thus singlet states with decay rates on the order of $10^8 - 10^9\ s^{-1}$ will not be efficiently quenched, even in air saturated solutions. For this mechanism to be operative then, the singlet lifetime of allene **50** must be greater than $10^{-8}\ s^{-1}$. Alternatively, some preassociation of $^3O_2$ and allene might be occurring.

As triplet states are substantially longer lived than singlets, and as they are also efficiently quenched with molecular oxygen, a sample of allene **50** in non-degassed benzene was irradiated. Consistent with the above mechanism, the sole product obtained was cycloheptene **51**. Under the reaction conditions (254 nm irradiation), benzene would absorb virtually all of the light, assuring that the reaction is occurring from the triplet state.

Additional evidence for the intermediacy of allene oxide **79** was provided by its independent generation. Allenes are known to form allene oxides when treated with meta-chloroperbenzoic acid (MCPBA).[68] Treatment of allene **50** with one equivalent of MCPBA, affords cycloheptene **51** in 86% yield. If the reaction is monitored by ^1H NMR spectroscopy, a vinyl resonance corresponding to allene oxide **79** is initially observed (δ 5.97 ppm, dd, J = 5.9 Hz, 3.5 Hz). Similar resonances are observed when 1,2-cyclonona- and cyclodecadiene are treated with meta-chloroperbenzoic acid. In the reaction of **50**, this resonance disappears with time, as the vinyl resonance for cycloheptene **51** increases (δ 5.67 ppm, t, J = 6.1 Hz). Thus an allene oxide derived from **50** does undergo elimination of carbon monoxide at ambient temperature to afford a cycloheptene.

The second mechanism depicted in Scheme 52 proposes that cyclopropanone **81** is formed when ground state cyclopropylidene **72** is trapped with oxygen. Molecular oxygen is known to efficiently trap carbenes to form ketones, and has frequently been employed as a scavenger of such intermediates.[69] The most effective argument against this mechanism is its requirement that trapping of cyclopropylidene leads to product suppression. Since it now appears that >99% of the photoproducts of **50** derive from a vinylcarbene, and that vinylcarbenes are not obtained from cyclopropylidenes, this mechanism seems unlikely.

Ring contraction arising from the singlet and triplet reactions of allene **50** is a novel and unexpected result. Further studies are clearly in order. The most important question is whether this reaction is general with other allenes. Also, quantitative studies to determine the rate of quenching, and of the singlet lifetime of **50** could help determine if this particular mechanism were operative.

CONCLUSION

1-tert-Butyl-1,2-cyclooctadiene has been synthesized and found to be stable to dimerization. This is the first example of a kinetically stable allene incorporated into an eight carbon ring. The molecule is, however, sensitive to acid, rapidly rearranging to 1,3-dienes.

1-tert-Butyl-1,2-cyclooctadiene undergoes a rich variety of fundamental photochemical reactions. Triplet reactions lead to hydrogen abstraction via planar allene, although the site of abstraction is highly dependent upon phase. In solution, abstraction occurs from the ring, exclusively at C_7, a result in accord with MNDO calculations on the equilibrium triplet state geometry. In the vapor phase, abstraction occurs from the tert-butyl moiety. No cyclopropylidene derived products are observed in either reaction, a departure from the triplet reactions of other cyclic allenes.

The singlet solution phase photoreactions of 1-tert-butyl-1,2-cyclooctadiene involve the intermediacy of a vinylcarbene, 3-tert-butylcyclooct-2-enylidene. Independent generation of this carbene affords the same products as singlet reaction of the allene, but in different ratios. This is consistent with results in other systems, where alkyl substitution apparently leads to formation of vinylcarbene intermediates in the singlet reactions of cyclic allenes.

Singlet and triplet photoreactions of 1-tert-butyl-1,2-cyclooctadiene in the presence of oxygen lead to exclusive formation of 1-tert-butylcycloheptene. It is proposed that this occurs by efficient trapping of excited state allene with molecular oxygen, leading to formation of an allene oxide, which after thermal rearrangement to a cyclopropanone, eliminates carbon monoxide. Independent generation of the corresponding allene oxide indicates this elimination readily occurs at ambient temperature.

EXPERIMENTAL SECTION

General Procedures

All ^1H (^{13}C) NMR spectra were measured on a Nicolet 300 (74) MHz spectrometer, with $CDCl_3$ as solvent and TMS as reference. Infrared spectra were recorded on an IBM Fourier transform IR/98 spectrometer. GC-mass spectra were obtained with a Hewlett Packard 5970 series mass selective detector, coupled to a HP 5890 series gas chromatograph. High resolution mass spectra were obtained using a Kratos Model MS 50 mass spectrometer. Ultraviolet spectra were recorded on a Perkin Elmer Model 320 spectrophotometer.

Gas chromatographic analyses were performed with a HP 5890 series gas chromatograph, with attached HP 3390A integrator. A 15 m methyl phenyl siloxane capillary glass column was used for all analyses. Preparative separations were performed on a Varian 920 gas chromatograph with glass lined injector, and glass columns. Melting points are uncorrected.

In all singlet solution phase photochemical experiments, spectroquality solvents were used. In triplet reactions, freshly distilled benzene was employed. Argon was bubbled through all solutions prior to irradiation. The light source used was a Rayonett RPR-100 reactor, fitted with 254 nm lamps. All photochemical substrates were purified by preparative GLC, to a purity greater than 99%.

All molecular orbital and molecular mechanics calculations were performed by Dr. Richard Johnson at the Juniversity of New Hampshire.

Preparation of 1-methylcycloheptene **48**

To a stirred solution of cycloheptanone (11.8 mL, 11.2 g, 100 mmol) in 100 mL of ethyl ether at 0°C was added dropwise 69 mL (2.75 g, 125 mmol) of a 1.8 M solution of methyllithium in ethyl ether. The solution was stirred at room temperature for 6 hours. Excess methyllithium was quenched by the addition of water. The organic fraction was washed with brine (3 x 100 mL), and dried over magnesium sulfate. Solvent was removed under reduced pressure leaving a clear yellow oil.

The crude 1-methyl-1-cycloheptanol and phosphoric acid (3 mL) were placed in a flask equipped with Vigreaux column (4") and short path distillation apparatus. The mixture was heated to reflux, and product was collected at 30-45°C (25 torr). The crude 1-methylcycloheptene was taken up in pentane (25 mL), washed with water (3 x 50 mL), and dried over magnesium sulfate. Solvent was removed under reduced pressure leaving a clear colorless oil. Analysis by capillary GLC (60°C) indicated the major component (>97%) to be 1-methylcycloheptene. The yield for the two step process was 7.72 g (70 mmol) or 70%. Spectral data were in agreement with literature values.[70]

^{1}H NMR ($CDCl_3$) δ 5.53 (t, J = 6.4 Hz, 1 H), 2.11-2.00 (m, 4 H), 1.71 (s, 3 H), 1.54-1.41 (m, 6 H).

Preparation of 8,8-dibromo-1-methylbicyclo[5.1.0]octane **49**

To a stirred suspension of 1-methylcycloheptene (7.72 g, 70 mmol) and potassium tert-butoxide (11.2 g, 100 mmol) in 100 mL of pentane at 0°C was added dropwise 8.0 mL (23 g, 91 mmol) of bromoform. The mixture was stirred at room temperature for 10 hours. Excess potassium tert-butoxide was quenched by the addition of water. The organic fraction was washed with water (3 x 100 mL), dried over magnesium sulfate, and concentrated under reduced pressure. Purification by fractional distillation afforded 16.9 g (63 mmol, 90%) of 8,8-dibromo-1-methylbicyclo[5.1.0]octane, boiling at 80-92°C (0.10 torr).

^{1}H NMR ($CDCl_3$) δ 2.32-2.21 (m, 1 H), 1.91-1.76 (m, 4 H), 1.66 (t, J = 12.5 Hz, 1 H), 1.52-1.42 (m, 1 H), 1.40 (s, 3 H), 1.36-1.11 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 51.37, 40.79, 35.21, 32.52, 32.16, 30.12, 27.83, 27.08, 25.20; IR (neat) 2984, 2955, 2924, 2854, 1462 cm^{-1}; mass spectrum, m/e (relative intensity) 282 (M+2, 1.1), 280 (M^+, 1.1), 203 (25), 202 (18), 201 (24), 200 (15), 121 (100), 105 (51), 93 (79), 79 (95), 67 (65), 55 (39); exact mass, measured 279.94616 calculated 279.94622, error -0.2 ppm.

Treatment of 8,8-dibromo-1-methylbicyclo[5.1.0]octane with methyllithium

To a solution of the dibromide (240 mg, 0.85 mmol) in 35 mL of pentane at 0°C was added 0.50 mL (19.8 mg, 0.90 mmol) of a 1.8 M solution of methyllithium in ethyl ether. The solution was stirred at room temperature for 0.5 hour. Subsequent work-up was done under a nitrogen atmosphere. Excess methyllithium was quenched by the addition of water (5 mL), and the organic fraction was dried over magnesium sulfate. Deuterochloroform (5 mL) was added and the solution was concentrated under reduced pressure to ca. 5 mL. An additional aliquot of deuterochloroform (5 mL) was added, and the solution concentrated. This procedure was repeated once more, and a ^{1}H NMR was obtained indicating complete conversion to one major component identified as 1-methyl-1,2-cyclooctadiene.

^{1}H NMR ($CDCl_3$) δ 4.93 (br s, 1 H), 1.99 (t, J = 15 Hz, 2 H), 1.65-1.52 (m, 2 H), 1.47 (s, 3 H), 1.36-1.13 (m, 6 H).

When concentrated to dryness, however, an insoluble yellow precipitate rapidly formed.

Preparation of 1-tert-butylcycloheptene 51

To a stirred solution of cycloheptanone (18.0 mL, 17.1 g, 153 mmol) in 150 mL of pentane at 0°C was added dropwise 90 mL (10 g, 153 mmol) of a 1.7 M pentane solution of tert-butyllithium. The mixture was stirred at room temperature for 8 hours. Excess tert-butyllithium was quenched by the addition of isopropanol at 0°C, followed by water. The organic fraction was washed with water (3 x 150 mL), dried over magnesium sulfate, and concentrated under reduced pressure leaving a clear yellow oil.

A solution of the crude alcohol in 75 mL of benzene was mixed with 100 mg of para-toluenesulfonic acid. The reaction flask was fitted with a Dean-Stark trap, and the solution was heated to reflux for 8 hours. Solvent was removed under reduced pressure leaving a clear yellow oil. Purification by column chromatography (silica gel, 50 x 3 cm, eluting with hexanes) afforded 11.3 g (74.3 mmol, 48%) of 1-tert-butylcycloheptene as a clear colorless oil. Spectral data were in agreement with literature values.[71]

^{1}H NMR ($CDCl_3$) δ 5.62 (t, J = 7.5 Hz, 1 H), 2.19-2.13 (m, 2 H), 2.13-2.04 (m, 2 H), 1.79-1.69 (m, 2 H), 1.45-1.35 (m, 2 H), 0.99 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 153.19, 122.04, 36.40, 33.29, 28.92, 28.63, 28.28, 27.53, 27.21; IR (neat) 3055, 2966, 2920, 2868, 1479, 1466, 1477, 1391, 1360 cm^{-1}; mass spectrum, m/e (relative intensity) 152 (M^+, 27), 137 (44), 109 (49), 95 (75), 81 (100), 67 (62), 57 (82).

Preparation of 8,8-dibromo-1-tert-butylbicyclo[5.1.0]-octane 52

To a stirred suspension of 1-tert-butylcycloheptene (10.6 g, 69.7 mmol) and potassium tert-butoxide (15.7 g, 140 mmol) in 150 mL of pentane at 0°C, was added dropwise 11.4 mL (32.9 g, 130 mmol) of bromoform. The mixture was stirred at room temperature for 8 hours. Excess potassium tert-butoxide was quenched by the addition of water. The organic fraction was washed with water (3 x 150 mL), dried over magnesium sulfate, and concentrated under reduced pressure. Unreacted bromoform and olefin were removed by vacuum distillation (35-40°C, 0.10 torr) leaving an orange oil, which was purified by column chromatography (silica gel, 50 x 3 cm, eluting with hexanes). The clear colorless oil obtained was taken up in 15 mL of pentane and stored overnight at -20°C to induce crystallization. 8,8-Dibromo-1-tert-butylbicyclo[5.1.0]octane (8.26 g, 25.5 mmol, 37%) was obtained as white crystals melting at 46-47°C.

^{1}H NMR ($CDCl_3$) δ 2.47-2.34 (m, 1 H), 2.34-2.22 (m, 1 H), 1.90 (t, J = 8.5 Hz, 1 H), 1.80-1.61 (m, 6 H), 1.51-1.33 (m, 1 H), 1.27 (t, J = 12.4 Hz, 1 H), 1.20 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 52.03, 42.22, 36.82, 36.66, 34.23, 32.48, 31.19, 29.41, 29.25, 28.34; IR (neat) 2945, 2920, 2843, 1445, 1364 cm^{-1}; mass spectrum, m/e (relative intensity) 326 (M+2, 10), 324 (M^+, 10), 309 (15), 267 (10), 212 (17), 199 (15), 187 (15), 163 (81), 123 (25), 109 (100); exact mass, measured 323.9917, calculated 323.9912, error 1.5 ppm.

<u>Treatment of 8,8-dibromo-1-tert-butylbicyclo[5.1.0]octane with methyllithium</u>

To a stirred solution of the dibromide (4.91 g, 15.2 mmol) in 25 mL of pentane at 0°C was added 10.0 mL of a 1.8 M solution of methyllithium (396 mg, 18.0 mmol) in ethyl ether. The solution was stirred at room temperature for 2 hours. Excess methyllithium was quenched by the addition of water. The organic fraction was washed with water (3 x 50 mL), dried over magnesium sulfate, and concentrated under reduced pressure. Purification by vacuum distillation through a micro still (0.05 torr, pot temperature kept below 60°C), afforded 2.29 g (14.0 mmol, 92%) of hydrocarbon product as a clear colorless oil. Capillary GLC analysis (80°C) indicated formation of three major products. These were isolated on a preparative scale (25% Carbowax on Chromosorb W, 5' x 0.25", 110°C) and identified as:

1-tert-Butyl-1,2-cyclooctadiene (**50**, 85%); a colorless oil; ^{1}H NMR ($CDCl_3$) δ 5.30-5.22 (m, 1 H), 2.25-2.12 (m, 2 H), 2.00-1.77 (m, 2 H), 1.66-1.30 (m, 6 H), 1.07 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 202.21, 117.73, 94.44 (J_{CH} = 166 Hz), 33.23, 29.28 (double intensity), 28.79, 28.24, 27.60, 27.24; IR (neat) 2979, 2928, 2862, 1942, 1475, 1448, 1394, 1361, 1315, 1259 cm^{-1}; mass spectrum, m/e (relative intensity) 164 (M^+, 5), 149 (15), 136 (4), 121 (36), 107 (60), 93 (87), 79 (100), 67 (58), 57 (61); exact mass, measured 164.1565, calculated 164.1565, error 0.0 ppm; ultraviolet spectrum (cyclohexane), shoulder 235 nm (ε 9780), (ε_{254} = 1460).

7-tert-Butylbicyclo[5.1.0]oct-1(8)-ene (**54**, 2%). Spectral data are given elsewhere.

1-tert-Butyltricyclo[5.1.0.0^{2,8}]octane (**53**, 12%); a colorless oil; ^{1}H NMR ($CDCl_3$) δ 2.66-2.61 (m, 2 H), 1.73-1.66 (br s, 4 H), 1.31 (pentet, J = 2.9 Hz, 4 H), 1.04 (t, J = 3.4 Hz, 1 H), 0.96 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 48.98, 33.25, 32.00, 29.44, 29.08, 27.30, 14.62; IR (neat) 2933, 2869, 1479, 1458, 1394, 1365, 1319 cm^{-1}; mass spectrum, m/e (relative intensity) 164 (M^+, 6), 149 (13), 121 (20), 107 (39), 93 (61), 79 (97), 67 (34), 57 (100); exact mass, measured 164.1568, calculated 164.1565, error 1.6 ppm; ultraviolet spectrum (cyclohexane), tail end absorption (ε_{254} = 30).

Hydrogenation of 1-tert-butyl-1,2-cyclooctadiene

To a solution of GLC purified 1-tert-butyl-1,2-cyclooctadiene (25 mg, 0.15 mmol) in 5 mL of pentane was added a catalytic amount of palladium on carbon (10%). A balloon containing hydrogen was attached for 30 minutes, after which the catalyst was filtered off, and the pentane removed under reduced pressure, leaving 22 mg (88%) of a clear colorless oil. Capillary GLC (80°C) indicated formation of one component identified as 1-tert-butylcyclooctene. Spectral data are in agreement with literature values.[72]

^{1}H NMR ($CDCl_3$) δ 5.42 (t, J = 8.3 Hz, 1 H), 2.43-2.37 (m, 2 H), 2.11-2.03 (m, 2 H), 1.57-1.49 (m, 3 H), 1.45 (br s, 5 H), 1.04 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 148.17, 120.81, 36.55, 31.06, 29.67, 29.31, 26.69, 26.50, 26.33, 26.04; IR (neat) 3047, 2926, 2851, 1474, 1448, 1391, 1360 cm^{-1}.

Preparation of 1-tert-butylcyclooctene

To a stirred solution of cyclooctanone (19.7 mL, 18.9 g, 150 mmol) in 150 mL of pentane at 0°C was added dropwise 90 mL (10.0 g, 153 mmol) of a 1.7 M pentane solution of tert-butyllithium. The solution was stirred at room temperature for 8 hours. Excess tert-butyllithium was quenched by the addition of isopropanol at 0°C, followed by water. The organic fraction was washed with water (3 x 150 mL), and dried over magnesium sulfate. Solvent was removed under reduced pressure leaving a clear yellow oil.

The crude 1-tert-butylcyclooctanol in 100 mL of benzene was treated with para-toluenesulfonic acid (200 mg). The reaction flask was fitted with a Dean-Stark trap, and the solution was heated to reflux for 8 hours. Purification by column chromatography (50 x 3 cm, silica gel, eluting with hexanes) afforded 9.42 g (57.5 mmol, 38%) of 1-tert-butylcyclooctene.

Treatment of 1-tert-butyl-1,2-cyclooctadiene with para-toluenesulfonic acid

To a stirred solution of 55 mg (0.34 mmol) of GLC purified allene in 15 mL of benzene was added 10 mg of para-toluenesulfonic acid. The solution was stirred for 4 hours at room temperature. The acid was removed by passing the solution through a short (2") alumina column, and solvent was removed under reduced pressure leaving 49 mg (0.30 mmol, 88%) of a clear colorless oil. Analysis by capillary GLC indicated complete conversion to two major isomers, which were isolated on a preparative scale (10' x 0.25", 15% SE-30 on Chromosorb W, 140°C) and identified as:

2-tert-Butyl-1,3-cyclooctadiene (**55**, 87%); a colorless oil; ^{1}H NMR ($CDCl_3$) δ 5.95 (d, J = 11.2 Hz, 1 H), 5.75 (dt, J = 11.2 Hz, 7.3 Hz, 1 H), 5.49 (t, J = 8.1 Hz, 1 H), 2.02 (br s, 4 H), 1.36 (br s, 4 H), 1.04 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 145.80, 131.76, 126.07, 122.28, 34.93, 29.39, 28.26, 27.84, 27.70, 22.73; IR (neat) 3011, 2964, 2926, 2854, 1506, 1477, 1447, 1391, 1360 cm^{-1}; mass spectrum m/e (relative intensity) 164 (M^+, 11), 149 (4), 121 (11), 108 (23), 93 (33), 79 (61), 57 (100); ultraviolet spectrum (cyclohexane), λ_{max} 220 nm ($\varepsilon = 1.12 \times 10^5$), ($\varepsilon_{254} = 6.12 \times 10^3$).

1-tert-Butyl-1,3-cyclooctadiene (**56**, 13%); a colorless oil; ^{1}H NMR ($CDCl_3$) δ 5.79 (d, J = 4.4 Hz, 1 H), 5.71 (dd, J

= 11.7 Hz, 4.4 Hz, 1 H), 5.59 (dt, J = 11.7 Hz, 5.9 Hz, 1 H), 2.31-2.25 (m, 2 H), 2.13 (dd, J = 10.7 Hz, 5.9 Hz, 2 H), 1.60-1.42 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 149.09, 130.48, 126.40, 119.74, 36.85, 29.99, 29.76, 27.24, 26.24, 22.71; IR (neat) 3005, 2964, 2937, 2868, 1479, 1468, 1391, 1362, 1281 cm^{-1}; mass spectrum, m/e (relative intensity) 164 (M^+, 17), 149 (6), 121 (17), 108 (37), 93 (54), 79 (100); ultraviolet spectrum (cyclohexane), λ_{max} 234 nm (ε = 5950), ε_{254} = 2230.

Reaction of 1,2-cyclononadiene with para-toluenesulfonic acid

To a solution of 1,2-cyclononadiene (110 mg, 0.90 mmol) in 10 mL of benzene was added para-toluenesulfonic acid (19 mg, 0.10 mmol). The solution was stirred for 12 hours at room temperature. The acid was removed by passing the solution through a short (2") column of alumina. Concentration at reduced pressure left a clear yellow oil. Analysis by capillary GLC (60°C) and by ^1H NMR indicated only starting material.

Reaction of 1-methyl-1,2-cyclononadiene with para-toluenesulfonic acid

To a solution of 1-methyl-1,2-cyclononadiene (111 mg, 0.82 mmol) in 10 mL of benzene was added para-toluenesulfonic acid (20 mg, 0.10 mmol). The solution was stirred for 12 hours at room temperature. Acid was removed by passing the solution through a short (2") alumina column. Solvent was removed on a rotorap leaving a clear yellow oil. Analysis by capillary GLC (70°C) indicated starting allene and two other components. These were isolated on a preparative scale (10' x 0.25", 15% SE-30 on Chromosorb W, 140°C) and identified as:

cis,cis-2-Methyl-1,3-cyclononadiene (**57**, 9%)[73]; a colorless oil; ^{1}H NMR (CDCl$_3$) δ 5.82 (d, J = 10.7 Hz, 1 H), 5.61 (dt, J = 10.7 Hz, 8.3 Hz, 1 H), 5.37 (t, J = 8.3 Hz, 1 H), 2.09-2.00 (m, 4 H), 1.70 (s, 3 H), 1.65-1.55 (m, 2 H), 1.47-1.37 (m, 4 H).

1-Methyl-1,2-cyclononadiene (**47**, 74%)[74]; a colorless oil; ^{1}H NMR (CDCl$_3$) δ 5.17 (br s, 1 H), 2.35-2.10 (m, 2 H), 1.82-1.73 (m, 1 H), 1.69 (d, J = 2.8 Hz, 3 H), 1.65-1.45 (m, 7 H), 1.45-1.25 (m, 2 H).

3-Methylene-1-cyclononene (**58**, 17%)[26]; a colorless oil; ^{1}H NMR (CDCl$_3$) δ 6.08 (d, J = 12.1 Hz, 1 H), 5.44 (dd, J = 12.1 Hz, 9.3 Hz, 1 H), 4.90 (br s, 2 H), 2.56-2.48 (m, 2 H), 2.41-2.32 (m, 2 H), 1.67-1.40 (m, 8 H).

Treatment of 1-tert-butyl-1,2-cyclooctadiene with potassium tert-butoxide

The GLC purified allene (50 mg, 0.30 mmol) in 5 mL of dimethylsulfoxide was treated with potassium tert-butoxide (110 mg, 1.00 mmol) for 12 hours at room temperature, after the method of Vaidyanathaswamy and Devaprabhakara.[75] Water

(50 mL) was added, and the solution was extracted with pentane (3 x 25 mL). The combined organic fractions were dried over magnesium sulfate, filtered, and concentrated under reduced pressure leaving 42 mg (84%) of a colorless oil. Capillary GLC and ^{1}H NMR analysis indicated three major components, identified as:

2-tert-Butyl-1,3-cyclooctadiene (**55**, 10%), 1-tert-butyl-1,2-cyclooctadiene (**50**, 71%), and 1-tert-butyl-1,3-cyclooctadiene (**56**, 11%).

Reaction of 8,8-dibromo-1-tert-butylbicyclo[5.1.0]octane with magnesium

To a stirred suspension of magnesium dust (610 mg, 25.3 mmol) in 5 mL of ethyl ether was added 1.33 g (4.10 mmol) of the dibromide in 5 mL of ethyl ether. An exothermic reaction ensued. The reaction mixture was diluted with an additional 10 mL of ethyl ether, and stirred at room temperature for 10 hours. The solution was decanted away from unreacted magnesium, washed with water (3 x 50 mL), and dried over magnesium sulfate. Solvent was removed on a rotovap leaving 586 mg (87%) of a pale yellow oil. Analysis by ^{1}H NMR indicated formation of four major products, three of which were isolable by preparative GLC (15% SE-30 on Chromosorb W, 10' x 0.25", 100°C) and identified as:

7-tert-Butylbicyclo[5.1.0]oct-1(8)-ene (**54**, 3%).

1-tert-Butylbicyclo[5.1.0]oct-2-ene (**60**, 39%); a colorless oil; ^{1}H NMR (CDCl$_3$) δ 5.67 (d, J = 11.2 Hz, 1 H), 5.36 (ddd, J = 11.2 Hz, 6.4 Hz, 4.4 Hz, 1 H), 2.48-2.34 (m, 1 H), 2.14-2.03 (m, 1 H), 1.99 (dd, J = 16.9 Hz, 7.2 Hz, 1 H), 1.62-1.52 (m, 1 H), 1.17-0.94 (m, 1 H), 0.84 (s, 9 H), 0.70 (dd, J = 8.3 Hz, 3.9 Hz, 1 H), -0.047 (dd, J = 5.3 Hz, 3.9 Hz, 1 H); ^{13}C NMR (CDCl$_3$) δ 131.20, 127.13, 33.22, 30.68, 29.61, 28.51, 27.25, 23.39, 21.33, 17.03; IR (neat) 3067, 3007, 2953, 2930, 2866, 1458, 1391, 1362 cm^{-1}; mass spectrum, m/e (relative intensity) 164 (M^{+}, 23), 149 (100), 121 (32), 107 (66), 93 (46), 79 (54), 67 (20), 57 (76); exact mass, measured 164.1567, calculated 164.1565, error 1.15 ppm.

2-tert-Butyl-1,3-cyclooctadiene (**55**, 37%).

The fourth isomer was not stable to a variety of preparative GLC conditions and was not isolated. A tentative structure based upon analysis of the ^{1}H NMR of the crude reaction mixture is proposed as:

3-tert-Butyl-1,4-cyclooctadiene (**61**, 21%) partial ^{1}H NMR (CDCl$_3$) δ 5.65 (d, J = 9.3 Hz, 2 H), 4.98-4.88 (m, 2 H), 1.27 (s, 9 H).

<u>Reaction of 1-tert-butyl-1,2-cyclooctadiene with magnesium bromide</u>

To neat GLC purified allene (40 mg, 0.24 mmol) was added 3 mL of a 0.14 M solution of magnesium bromide in ethyl ether, prepared by the method of Bachman et al.[76] The solution was stirred for 2 hours at room temperature. The organic fraction was washed with water (3 x 50 mL), and dried over magnesium sulfate.

Solvent was removed under reduced pressure leaving 33 mg (83%) of a clear colorless oil. Analysis by ^{1}H NMR indicated three components, which were identified as:

2-tert-Butyl-1,3-cyclooctadiene (**55**, 64%), 1-tert-butyl-1,2-cyclooctadiene (**50**, 23%), and 3-tert-butyl-1,4-cyclooctadiene (**61**, 13%).

Reaction of 1-tert-butyltricyclo[5.1.0.$0^{2,8}$]octane with magnesium bromide

To neat GLC purified tricyclooctane (5 mg, 0.03 mmol) was added 0.5 mL of a 0.14 M solution of magnesium bromide in ethyl ether.[76] The solution was stirred at room temperature for 0.5 hour. Pentane was added (5 mL), and the solution was washed with water (2 x 5 mL), and dried over magnesium sulfate. Solvent was removed under reduced pressure leaving a clear colorless oil. Analysis by ^{1}H NMR indicated complete conversion to 1-tert-butylbicyclo[5.1.0]-oct-2-ene **60**.

Benzene sensitized vapor phase irradiation of 1-tert-butyl-1,2-cyclooctadiene

1-tert-Butyl-1,2-cyclooctadiene (125 mg, 0.76 mmol, GLC purified) and benzene (0.20 mL, 170 mg, 2.2 mmol) were placed in a 3.7 L Vycor tube. The bottom portion of the tube was cooled to -78°C, and the system was evacuated to *ca*. 0.15 torr and backflushed with nitrogen three times. After the final evacuation, the tube was allowed to warm to room temperature and was placed in a Rayonett reactor fitted with 254 nm lamps. The irradiation was carried out during 64 hours. 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 neutral alumina, and concentrated under reduced pressure to give 92 mg (74%) of a colorless oil. Analysis by capillary GLC (80°C) and ^{1}H NMR indicated 66% conversion to one photoproduct identified as 1,1-dimethylspiro[2,7]dec-4-ene **62**. The remainder of the reaction mixture was unreacted allene.

Preparation of 1,1-dibromospiro[2,7]dec-4-ene **64**

To a stirred suspension of potassium tert-butoxide (5.60 g, 50.0 mmol) and 3-methylene-1-cyclooctene (5.00 g, 40.9 mmol) in 100 mL of pentane was added 3.60 mL (10.4 g, 41.4 mmol) of bromoform at 0°C. The mixture was stirred at room temperature for 10 hours. Excess potassium tert-butoxide was quenched by the addition of water. The organic fraction was washed with water (3 x 100 mL), and dried over magnesium sulfate. Solvent was removed under reduced pressure leaving a brown oil. Purification was by fractional distillation. 1,1-Dibromospiro[2,7]dec-4-ene was collected as a clear, colorless oil boiling at 95-102°C (0.05 torr). The yield of the reaction was 9.41 g (32 mmol) or 78%.

^{1}H NMR ($CDCl_3$) δ 5.77 (dt, J = 10.3 Hz, 8.2 Hz, 1 H), 5.60 (d, J = 10.3 Hz, 1 H), 2.26-2.18 (m, 2 H), 1.88-1.52 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 133.94, 131.06, 39.86, 37.08, 32.68, 27.84, 26.14, 25.66, 24.99; IR (neat) 3018, 2930, 2854, 1450 cm^{-1}; mass spectrum, m/e (relative intensity) 296 (M+2) 294 (M^+, 0.8), 215 (7), 213 (7), 133 (44), 105 (40), 91 (100), 79 (57), 67 (35), 51 (21); exact mass, measured 293.94427, calculated 293.94418, error 0.3 ppm.

Preparation of 1,1-dimethylspiro[2,7]dec-4-ene **62**

Dimethyl cuprate was prepared by the method of Corey and Posner.[77] To a suspension of copper(I) iodide (2.23 g, 11.7 mmol) in 5 mL of ethyl ether at 0°C was added 13.0 mL of a 1.8 M solution of methyllithium (515 mg, 23.4 mmol) in ethyl ether. The mixture was stirred for 8 hours, and 560 mg (1.93 mmol) of 1,1-dibromospiro[2,7]dec-4-ene was added. The reaction was stirred for 24 hours at room temperature. Excess methyllithium was quenched by the addition of water. The organic fraction was washed with saturated aqueous ammonium chloride (2 x 100 mL), followed by water (100 mL), and dried over magnesium sulfate. Solvent was removed under reduced pressure leaving a yellow oil which was taken up in pentane and passed through a short (2") alumina column. After removal of solvent, 214 mg (1.30 mmol, 56%) of a clear colorless oil was obtained. Analytically pure samples were obtained by preparative GLC (15% Carbowax on Chromosorb W, 10' x 0.25", 130°C).

^{1}H NMR ($CDCl_3$) δ 5.61-5.47 (m, 2 H), 2.30-2.11 (m, 2 H), 1.65-1.42 (m, 8 H), 1.16 (s, 3 H), 1.04 (s, 3 H), 0.36 (d, J = 3.7 Hz, 1 H), 0.29 (d, J = 3.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 134.30, 131.28, 36.74, 29.14, 28.39, 27.59, 25.94, 25.64 (double intensity), 24.06, 21.79, 21.54; IR (neat) 3047, 3005, 2980, 2924, 2864, 1452, 1396, 1375 cm^{-1}; mass spectrum, m/e (relative intensity) 164 (M^+, 59), 149 (35), 121 (49), 107 (66), 93 (76), 79 (100), 67 (82); exact mass, measured 164.15644, calculated 164.15650, error 0.3 ppm.

Benzene sensitized solution phase irradiation of 1-tert-butyl-1,2-cyclooctadiene

A solution of GLC purified 1-tert-butyl-1,2-cyclooctadiene (66 mg, 0.40 mmol) in 20 mL of benzene was placed in a quartz tube and degassed for 3 hours with argon. The solution was irradiated in a Rayonett reactor using 254 nm lamps. The reaction was monitored at different conversions by capillary GLC (80°C). At low conversions (<20%), two primary photoproducts were observed in the ratio of 1:1.

These were isolated by preparative GLC (20% Carbowax on Chromosorb W, 5' x 0.25", 100°C) and identified as:

cis-3-tert-Butylbicyclo[3.3.0]oct-2-ene (65, 11%); a colorless oil; ^{1}H NMR (CDCl$_3$) δ 5.07 (s, 1 H), 3.14-3.04 (m, 1 H), 2.68-2.52 (m, 2 H), 2.00 (d, J = 13.7 Hz, 1 H), 1.73-1.56 (m, 2 H), 1.48-1.38 (m, 2 H), 1.38-1.21 (m, 2 H), 1.02 (s, 9 H); ^{13}C NMR (CDCl$_3$) δ 152.45, 124.66, 50.24, 40.51, 39.76, 35.75, 32.74, 29.34, 25.17; IR (neat) 3045, 2949, 2903, 2862, 1653, 1477, 1458, 1447, 1389, 1362 cm^{-1}; mass spectrum, m/e (relative intensity) 164 (M$^+$, 15), 149 (5), 121 (12), 108 (24), 93 (29), 79 (46), 69 (27), 57 (100); exact mass, measured 164.1559, calculated 164.1565, error 3.7 ppm.

2-tert-Butyl-1,3-cyclooctadiene (55, 10%). The remaining 79% of the reaction mixture is unreacted allene.

At higher conversions, a new product was observed, which increased with time at the expense of 2-tert-butyl-1,3-cyclooctadiene. This compound was not isolable by preparative GLC due to its similar retention time with 3-tert-butylbicyclo[3.3.0]oct-2-ene, but was identified in the next experiment as 7-tert-butylbicyclo[4.2.0]oct-7-ene, 66.

Benzene sensitized solution phase irradiation of 2-tert-butyl-1,3-cyclooctadiene

A solution of GLC purified 2-tert-butyl-1,3-cyclooctadiene (44 mg, 0.27 mmol) in 20 mL of benzene was degassed for 3 hours with argon. The solution was irradiated in a Rayonett reactor using 254 nm lamps. The reaction was monitored at different conversions by capillary GLC (80°C). At all conversions, only one major photoproduct was observed, comprising greater than 96% of the product mixture at a conversion of 46%. This compound was isolable by preparative GLC (10% SE-30 on Chromosorb W, 10' x 0.25", 100°C) and identified as:

7-tert-Butylbicyclo[4.2.0]oct-7-ene **66**; a colorless oil; ^{1}H NMR ($CDCl_3$) δ 5.69 (s, 1 H), 2.77 (dd, J = 11.0 Hz, 6.2 Hz, 1 H), 2.51 (dd, J = 11.0 Hz, 5.4 Hz, 1 H), 1.72-1.49 (m, 5 H), 1.42-1.31 (m, 3 H), 1.02 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 162.19, 127.50, 40.32, 36.30, 33.26, 28.40, 25.27, 24.78, 19.05, 18.96; IR (neat) 3030, 2961, 2934, 2864, 1616, 1475, 1462, 1389, 1360 cm^{-1}; mass spectrum, m/e (relative intensity) 164 (M^+, 15), 149 (19), 121 (20), 108 (48), 93 (38), 79 (53), 67 (27), 57 (100); exact mass, measured 164.1565, calculated 164.1565, error 0.0 ppm.

Preparation of 2-tert-butyl-1,3-cyclooctadiene **55**

A mixture of 1-tert-butylcyclooctene (1.037 g, 6.25 mmol), N-bromosuccinimide (1.668 g, 9.337 mmol) and benzoyl peroxide (30 mg) in 15 mL of carbontetrachloride was heated to reflux for 30 minutes. Succinimide was removed by filtration, and solvent was removed on a rotorap leaving a yellow oil. Purification by column chromatography (silica gel, 50 x 3 cm, eluting with hexanes) afforded 850 mg (5.18 mmol, 83%) of 2-tert-butyl-1,3-cyclooctadiene.

Benzene sensitized solution phase irradiation of 1-tert-butyltricyclo[5.1.0.0^{2,8}]octane

A solution of GLC purified 1-tert-butyltricyclo-[5.1.0.0^{2,8}]octane (12 mg, 0.073 mmol) in 8 mL of benzene was degassed with argon for 2 hours. The solution was irradiated in a Rayonett reactor with 254 nm lamps, and was monitored at different conversions by capillary GLC (80°C). At all conversions, only one major photoproduct was observed, comprising greater than 90% of the product mixture at a conversion of 82%. Analysis of the crude reaction mixture indicated this product to be 1-tert-butylbicyclo-[5.1.0]oct-2-ene, **60**.

Singlet solution phase irradiation of 1-tert-butyl-1,2-cyclooctadiene

A solution of GLC purified 1-tert-butyl-1,2-cyclooctadiene (41 mg, 0.25 mmol) in 20 mL of spectral grade cyclohexane was degassed with argon for 12 hours. The solution was placed in a Rayonett reactor equipped with 254 nm lamps and irradiated for 8 hours. Analysis by capillary GLC (80°C) and ^{1}H NMR indicated the formation of 6 photoproducts at a conversion of 38%, which were identified as:

3-tert-Butylbicyclo[3.3.0]oct-2-ene (**65**, 76%), 7-tert-butylbicyclo[4.2.0]oct-7-ene (**66**, 10%), 2-tert-butyl-1,3-cyclooctadiene (**55**, 5%), 8-tert-butylbicyclo[5.1.0]oct-1(8)-ene (**54**, 4%), 1-tert-butyl-1,3-cyclooctadiene (**56**, 2%), and 1-tert-butylbicyclo[5.1.0]oct-2-ene (**60**, 1%).

Percentages refer to the ratios of photoproducts (excluding unreacted allene) and were determined by ^{1}H NMR integration. Similar results were obtained by capillary GLC analysis. At different conversions (12, 29, 51, and 71%) the reaction composition remained unchanged. These products constituted greater than 97% of the photoproduct mixture.

Singlet solution phase irradiation of 1-tert-butyl-1,2-cyclooctadiene. Irradiation in cyclohexene

A solution of GLC purified 1-tert-butyl-1,2-cyclooctadiene (14.5 mg, 0.088 mmol) and n-dodecane (7.5 mg, 0.044 mmol) as an internal standard in 2 mL of cyclohexene was degassed with argon for 1 hour. The solution was placed in a Rayonett reactor and irradiated with 254 nm lamps. The reaction was monitored by capillary GLC (80°C), and was stopped after 48 hours at a conversion of 10%. Analysis by gas chromatography-mass spectroscopy indicated the reaction mixture to be composed of:

2-Cyclohexenol (7.9%), 2-cyclohexenone (1.4%), 1-tert-butylcycloheptene (**51**, 9.4%), 1-tert-butyl-1,2-cyclooctadiene (**50**, 81.1%).

Preparation of 3-tert-butyl-2-cycloocten-1-one **68**

The general procedure of Dauben and Michno was employed.[78] To a solution of 2-cycloocten-1-one (13.9 g, 81 mmol) in 150 mL of pentane at 0°C was added 10.0 g (156 mmol) of tert-butyllithium in pentane. The reaction was stirred for 8 hours at room temperature. Excess tert-butyllithium was quenched by the addition of isopropanol at 0°C, followed by water. The organic fraction was washed with water (3 x 150 mL), and dried over magnesium sulfate. Solvent was removed under reduced pressure leaving a clear yellow oil.

The crude 1-tert-butyl-2-cycloocten-1-ol in 50 mL of methylene chloride was added to a stirring slurry of pyridinium chlorochromate (51.8 g, 240 mmol) in 500 mL of methylene chloride, and the mixture was stirred for 8 hours at room temperature. The mixture was diluted with 500 mL of ethyl ether, the solution was decanted from the black residue, and the residue was washed with ethyl ether (2 x 100 mL). The combined ether fractions were washed with 5% aqueous hydrochloric acid (5 x 250 mL) and water (2 x 250 mL). The solution was dried over magnesium sulfate, and concentrated under reduced pressure leaving a clear yellow oil. Purification was by column chromatography (silica gel, 70 x 2 cm, eluting with 20% ethyl ether/hexanes). Fractions were collected in 200 mL increments. Fractions 4-6 contained material with greater than 98% purity as determined by capillary GLC (100°C). The fractions were combined, concentrated under reduced pressure, and distilled to give 3-tert-butyl-2-cycloocten-1-one (860 mg, 4.77 mmol, 5.9%) as a clear oil, boiling at 75-78°C (0.10 torr).

^{1}H NMR ($CDCl_3$) δ 6.16 (s, 1 H), 2.75 (t, J = 7.1 Hz, 2 H), 2.69 (t, J = 6.8 Hz, 2 H), 1.78-1.68 (m, 2 H), 1.68-1.57 (m, 2 H), 1.56-1.47 (m, 2 H), 1.10 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 204.67, 162.83, 128.41, 42.28, 38.56, 28.73, 28.02, 25.59, 23.55, 23.33; IR (neat) 3046, 2959, 2932, 2868, 1649, 1610, 1487, 1456, 1394, 1364, 1350, 1335, 1301, 1286, 1261, 1250 cm^{-1}; mass spectrum, m/e (relative intensity) 180 (M^+, 15), 137 (66), 123 (71), 109 (41), 95 (35), 81 (40), 67 (55), 55 (69), 41 (100); exact mass, measured 180.15131, calculated 180.15142, error 0.6 ppm.

Preparation of 3-tert-butyl-2-cycloocten-1-one para-toluenesulfonhydrazone 69

To a solution of 3-tert-butyl-2-cycloocten-1-one (440 mg, 2.44 mmol) in 10 mL of benzene was added 470 mg (2.50 mmol) of para-toluenesulfonhydrazide. The solution was stirred at room temperature for 8 hours. Pentane (10 mL) was added and the cloudy solution was stored at -20°C for 48 hours to induce crystallization. The precipitate was collected by filtration, washed with pentane, and dried under vacuum. 3-tert-Butyl-2-cycloocten-1-one para-toluenesulfonhydrazone (436 mg, 1.25 mmol, 51%) was obtained as white crystals melting at 98-101°C.

^{1}H NMR ($CDCl_3$) δ 7.80 (d, J = 7.8 Hz, 2 H), 7.35 (s, 1 H), 7.29 (d, J = 7.8 Hz, 2 H), 5.42 (s, 1 H), 2.41 (s, 3 H), 2.35 (t, J = 5.9 Hz, 2 H), 1.80 (m, 2 H), 1.58 (br s, 3 H), 1.43-1.30 (m, 3 H), 1.09 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 160.27, 158.36, 143.67, 129.37, 128.30, 127.91, 113.32, 37.71, 37.29, 29.56, 28.13, 27.16, 26.97, 24.74, 21.50; IR (KBr) 3207, 3030, 2932, 2870, 1636, 1597, 1468, 1450, 1379, 1366, 1337, 1167 cm^{-1}; elemental analysis, calculated for $C_{15}H_{26}N_2O_2S$: C, 65.48, H, 8.10, N, 8.04; found: C, 66.09, H, 8.17, N, 7.65.

Photolysis of the sodium salt of 3-tert-butyl-2-cycloocten-1-one para-toluenesulfonhydrazone

A solution of the tosylhydrazone (360 mg, 1.03 mmol) and 40 mL of freshly distilled tetrahydrofuran, in a Pyrex flask, was degassed with argon for 2 hours. Sodium methoxide (301 mg, 5.10 mmol) was added, and the solution was irradiated in a Rayonett reactor using 300 nm lamps until all trace of the red diazo intermediate had disappeared (6 hours). The solution was poured into 100 mL of pentane, and washed with water (5 x 100 mL). The pentane fraction was dried over magnesium sulfate. Solvent was removed under reduced pressure, leaving a yellow oil, which was passed through a short (2") plug of alumina. A clear colorless oil was obtained. The yield of hydrocarbon product was 74 mg (0.41 mmol), or 44%. Analysis by capillary GLC (80°C) indicated formation of 5 products which were isolated by preparative GLC (15% SE-30 on Chromosorb W, 10' x 0.25", 140°C) and identified as:

7-tert-Butylbicyclo[5.1.0]oct-1(8)-ene (**54**, 54%); a colorless oil; ^{1}H NMR (CDCl$_3$) δ 6.45 (s, 1 H), 2.70 (dt, J = 13.5 Hz, 4.4 Hz, 1 H), 2.38 (td, J = 11.5 Hz, 6.3 Hz, 1 H), 1.92-1.85 (m, 1 H), 1.78 (td, J = 11.5 Hz, 3.9 Hz, 1 H), 1.68 (dd, J = 14.4 Hz, 6.6 Hz, 1 H), 1.53 (dt, J = 13.6 Hz, 3.9 Hz, 1 H), 1.40 (dt, J = 13.6 Hz, 3.9 Hz, 1 H), 1.29 (dd, J = 12.2 Hz, 5.9 Hz, 1 H), 1.14 (q, J = 11.6 Hz, 1 H), 0.95-0.84 (m, 1 H), 0.81 (s, 9 H); ^{13}C NMR (CDCl$_3$) δ 129.34, 104.16, 35.12, 33.70, 33.18, 29.75, 29.20, 29.07, 27.65, 25.70; IR (neat) 2961, 2930, 2854, 1765, 1464, 1418, 1389, 1362, mass spectrum, m/e (relative intensity) 164 (M$^+$, 17), 149 (100), 107 (26), 93 (22), 81 (19), 79 (14); exact mass, measured 164.15668, calculated 164.15650, error 1.1 ppm.

1-tert-Butyl-1,3-cyclooctadiene (**56**, 26%).

7-tert-Butylbicyclo[4.2.0]oct-7-ene (**66**, 11%).

3-tert-Butylbicyclo[3.3.0]oct-2-ene (65, 5%).

2-tert-Butyl-1,3-cyclooctadiene (55, 4%).

Singlet solution phase irradiation of 2-tert-butyl-1,3-cyclooctadiene

A solution of GLC purified 2-tert-butyl-1,3-cyclooctadiene (37 mg, 0.21 mmol) in 20 mL of cyclohexane was degassed with argon for 2 hours. The solution was placed in a Rayonett reactor and irradiated at 254 nm. The reaction was monitored by capillary GLC (80°C), and was stopped after 8 hours at a conversion of 56%. Analysis by capillary GLC and ^{1}H NMR indicated formation of two photoproducts in the ratio of 12:1. The major product was identified as 7-tert-butylbicyclo[4.2.0]oct-7-ene (66, 60%). The minor component (5%) although not isolated, was determined not to be 1-tert-butyl-1,3-cyclooctadiene by analysis of the ^{1}H NMR of the crude reaction mixture. The remainder of the reaction mixture was unreacted allene.

Singlet solution phase irradiation of 1-tert-butyltricyclo[5.1.0.0^{2,8}]octane

A solution of GLC purified tricyclo[5.1.0.0^{2,8}]octane (12 mg, 0.073 mmol) in 12 mL of cyclohexane was degassed with argon for 2 hours. The solution was placed in a Rayonett reactor and irradiated with 254 nm lamps. The reaction was monitored by capillary GLC (80°C), and was stopped after 16 hours at a conversion of 30%. Analysis by capillary GLC and ^{1}H NMR indicated formation of one product identified as 1-tert-butylbicyclo[5.1.0]oct-2-ene (**60**, 30%).

Reaction of 1-tert-butyl-1,2-cyclooctadiene with meta-chloroperbenzoic acid

A solution of GLC purified 1-tert-butyl-1,2-cyclooctadiene (7.0 mg, 0.043 mmol) in 0.5 mL of deuterochloroform was placed in a NMR tube, and 7.4 mg (0.043 mmol) of meta-chloroperbenzoic acid was added. The solution was allowed to stand at room temperature for 45 minutes, and a ^{1}H NMR spectrum was obtained. Two vinyl resonances were observed in the approximate ratio of 1:1, which were assigned to:

1-tert-Butyl-1,2-cyclooctadieneoxide (**86**); partial ^{1}H NMR ($CDCl_3$) δ 5.97 (dd, J = 5.9 Hz, 3.5 Hz).

1-tert-Butylcycloheptene (**51**); partial ^{1}H NMR ($CDCl_3$) δ 5.67 (t, J = 6.1 Hz).

After standing for an additional 5 hours, another ^{1}H NMR spectrum was obtained indicating 1-tert-butyl-1-cycloheptene as the major component present.

Reaction of 1,2-cyclononadiene and 1,2-cyclodecadiene with meta-chloroperbenzoic acid

The above procedure was repeated with 1,2-cyclononadiene (14.0 mg, 0.115 mmol) and meta-chloroperbenzoic acid (19.9

mg, 0.115 mmol) in 0.5 mL of deuterochloroform. After standing for 2 hours at room temperature no starting material remained. Two downfield resonances were observed in the ratio of 1:1 and were assigned to:

1,2-Cyclononadiene oxide; partial ^{1}H NMR ($CDCl_3$) δ 5.31 (dd, J = 10.7 Hz, 2.9 Hz, 1 H), 4.53 (dd, J = 7.1 Hz, 2.2 Hz, 1 H).

The same procedure was repeated with 1,2-cyclodecadiene (12.0 mg, 0.088 mmol) and meta-chloroperbenzoic acid (15.3 mg, 0.088 mmol) in 0.5 mL of deuterochloroform. Analysis of the ^{1}H NMR indicated two downfield resonances in the ratio of 1:1 assigned to:

1,2-Cyclodecadiene oxide; partial ^{1}H NMR ($CDCl_3$) δ 5.97 (dd, J = 8.3 Hz, 4.4 Hz, 1 H), 4.53 (dd, J = 7.1 Hz, 2.2 Hz, 1 H).

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ACKNOWLEDGMENTS

I would like to acknowledge my major professor, Dr. Richard Johnson, for his encouragement and support of this work. I would also like to thank Dr. Thomas Barton for his generous contribution of both time and material during the final stages of this project.

I owe a special debt of gratitude to Dr. Thomas Waddell of the University of Tennessee at Chattanooga. His exceptional qualities as a scientist and educator inspired my career in chemistry.

This work would have been difficult to complete without the assistance and close friendship of my colleagues, Dr. James Macias and Dr. Babu Srinivasan. Without the love and support of my mother, father, and brother, Tom, and of my family in Ames, Michael and Barbara Klett, it would have been impossible.