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Exploratory and mechanistic studies of cycle allene photochemistry

Thomas James Stierman
Iowa State University

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EXPLORATORY AND MECHANISTIC STUDIES OF CYCLIC ALLENE PHOTOCHEMISTRY

Iowa State University PH.D. 1985

Exploratory and mechanistic studies of cyclic allene photochemistry

by

Thomas James Stierman

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For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa
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INTRODUCTION

The synthesis and ground state chemistry of allenes have been the focus of much research and a wide variety of allenes are readily prepared. Additionally, the photochemistry of many olefinic substrates, including simple alkenes, 1,3-dienes, and 1,4-dienes, has been intensively studied during the past three decades. In light of this, it is surprising to find that, until recently, there has been relatively few and scattered reports of the photoreactions of allenes (i.e., 1,2-dienes).

Within the past few years, however, there has been a significant effort devoted to the characterization and understanding of the photoreactions of allenes. A number of systems have now been examined under a variety of conditions and a rich assortment of fundamental photoreactions have been observed. As a result of these studies, our knowledge of the photoreactions of allenes has been greatly enhanced.

The purpose of this manuscript is to present the results of our studies focusing on the photoreactions of various 9-carbon ring cyclic allenes and to briefly summarize the previous literature which is of direct significance. For a comprehensive survey of allene photochemistry the reader is referred to two recent reviews.[1,2]

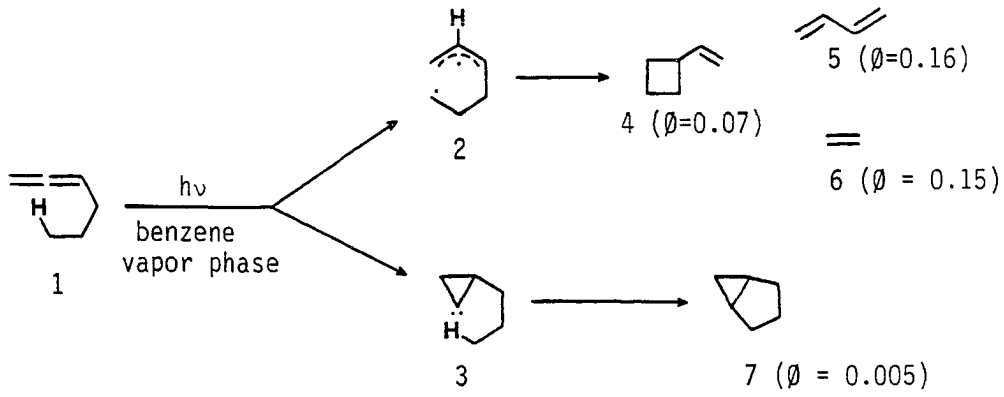
HISTORICAL

Allene Triplet Reactions

Much of the early work in the area of allene photochemistry was conducted on vapor phase samples and with benzene sensitization. In 1969, Ward and Karafiath reported the most comprehensive early photochemical study of allenes. These authors described the benzene sensitized vapor phase reactions of 1,2-hexadiene (**1**), 1,2-cyclononadiene (**8**), 1,2,6-heptatriene (**11**), and 1,2,6-cyclononatriene (**13**).[3] The reactions observed are presumably due to triplet states.

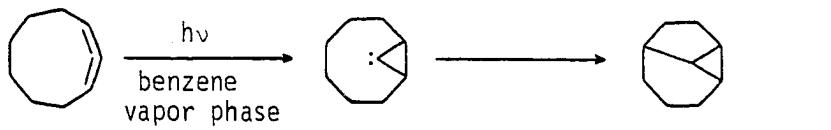
The benzene sensitized vapor phase photolysis of 1,2-hexadiene (**1**) led to the formation of four products (Scheme 1). Biradical **2** was considered to be a potential intermediate leading to the formation of **4** (via ring closure) and **5** and **6** (via fragmentation). That no cyclohexene was observed, however, led the authors to question this and arguments supporting a concerted mechanism were also presented. Bicyclohexane **7** was believed to be formed via cyclopropylidene **3**.

Scheme 1



Irradiation of 1,2-cyclononadiene (8) under similar conditions led to the formation of tricyclo[4.3.0.$0^{2,9}$]nonane (10) as the sole reported product (Scheme 2).[3,4] As in the reaction of 1, a cyclopropylidene intermediate (i.e., 9) was proposed as the precursor to 10.

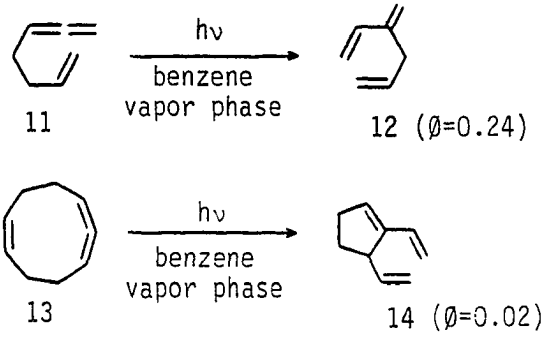
Scheme 2



8 9 10 (Ø=0.17)

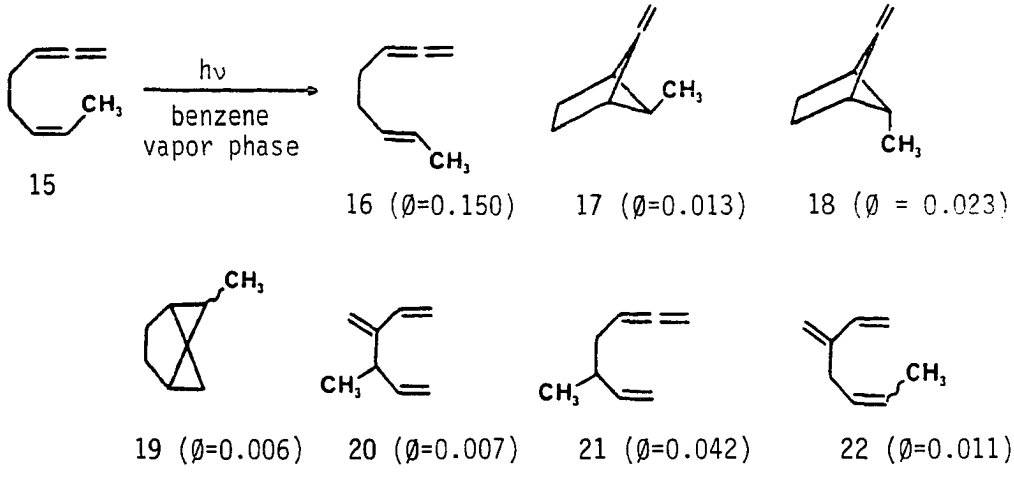
The photochemical behavior of unsaturated allenes 11 and 13 was significantly different from that of saturated analogs 1 and 8.[3,5] In these reactions, no evidence was found which would suggest the formation of a cyclopropylidene intermediate. The benzene sensitized vapor phase irradiation of 1,2,6-heptatriene (11) led to the formation of triene 12 as the sole reported primary product. Similarly, irradiation of 1,2,6-cyclononatriene (13) resulted in the formation of triene 14 as the sole reported primary product (Scheme 3). A concerted photo-Cope rearrangement was considered to be the most likely pathway to the observed products, although a biradical mechanism seems more consistent with the triplet multiplicity.

Scheme 3



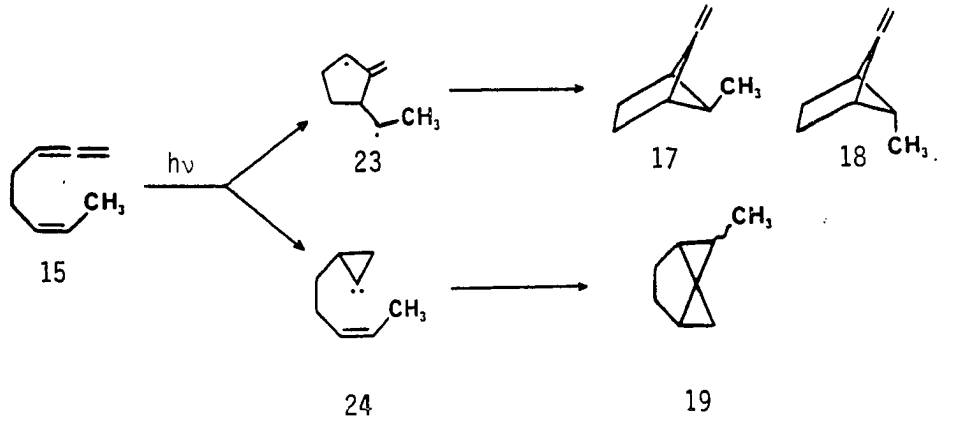
In 1981, Karan described the benzene sensitized vapor phase photolysis of cis-1,2,6-octatriene (**15**), a methyl-substituted derivative of **11**.[6] The photochemistry was considerably more complex than that reported for **11**. Photolysis of cis-1,2,6-octatriene (**15**) led to the formation of trans isomer **16**, along with six other primary products (Scheme 4).

Scheme 4



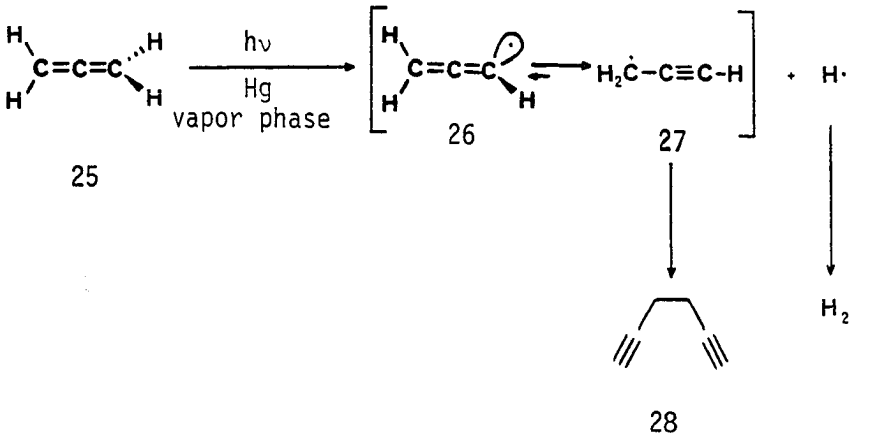
The major primary photoprocess was cis-trans isomerization to **16**. Bicyclics **17** and **18** were viewed as arising via diradical **23** in a stepwise manner, and tricyclic **19** formation was attributed to the intermediacy of cyclopropylidene **24** (Scheme 5). The isomerization of **15** to **20** corresponds to a Cope rearrangement, in which a biradical process seems most likely to be involved. The formation of **21** and **22** can be explained either by a stepwise process involving σ-homolysis or by 1,3-sigmatropic shifts.

Scheme 5



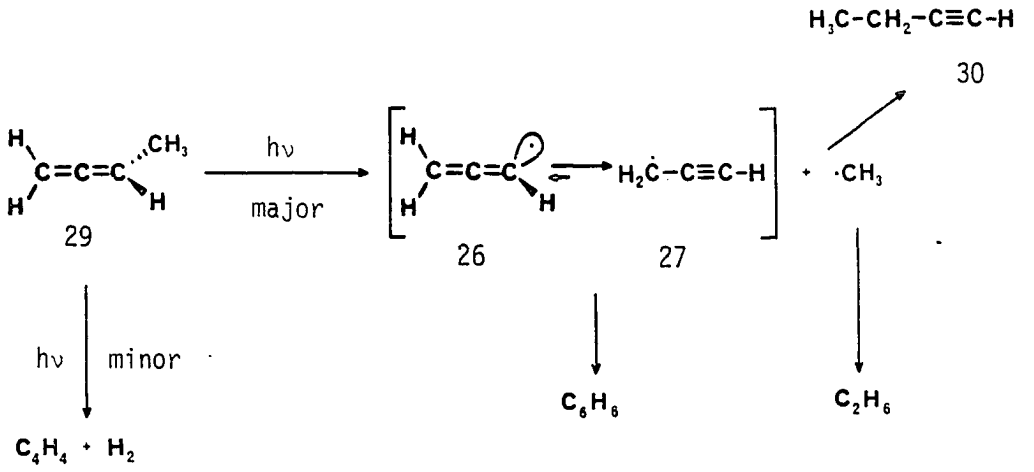
The first report of an allene photolysis was by Collin and Lossing in 1957.[7] Mercury photosensitized vapor phase decompositions of allene (**25**) and 1,2-butadiene (**29**) were reported. Irradiation of allene (**25**) led to the formation of hydrogen, a C_3H_3 radical, and what was believed to be 1,5-hexadiyne (**28**). Thus, the sole photoprocess appeared to be C-H bond homolysis, which leads to the generation of a hydrogen atom and a C_3H_3 radical species (Scheme 6). The latter is believed to favor the propargyl structure (**27**).

Scheme 6



The major photoprocess observed in the irradiation of 1,2-butadiene (29) was C-C bond homolysis, which leads to the formation of methyl radicals and a C_3H_3 radical species (Scheme 7). No evidence for the formation of a C_4H_5 radical, via potential C-H bond homolysis, could be found. Loss of hydrogen was observed as a minor process.

Scheme 7

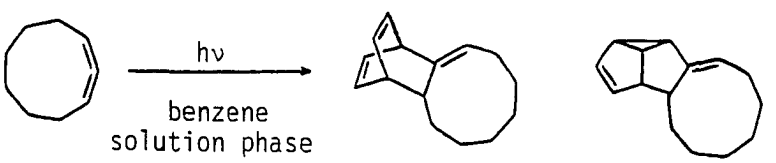


The phase dependence of allene triplet reactions is of interest. There are two previous reports of benzene sensitized solution phase irradiations of allenes. Both describe the photolysis of 1,2-cyclononadiene (8), however, the two sources report vastly differing chemistry.

Irradiation of 1,2-cyclononadiene (8) in benzene solution at 254 nm, as reported by Ward and Karafiath in 1969, resulted in the formation of tricyclic 10 along with three other products in slightly lesser amounts.[3] Tricyclic 10 was the sole photoproduct reported in the benzene sensitized vapor phase irradiation and was believed to be formed via a cyclopropylidene intermediate (Scheme 2).[3] The three other products observed in the solution phase irradiation were not identified.

Irradiation of 1,2-cyclononadiene (8) in benzene solution, as reported by Bryce-Smith et al.[8] and Berridge et al.[9], resulted in the formation of two benzene cycloadducts in a ratio of 6:1 (Scheme 8). The major component was assigned the para-structure 31, while the minor component was assigned the meta-structure 32. No isomeric products were reported by the authors, although it is not clear that they searched for these.

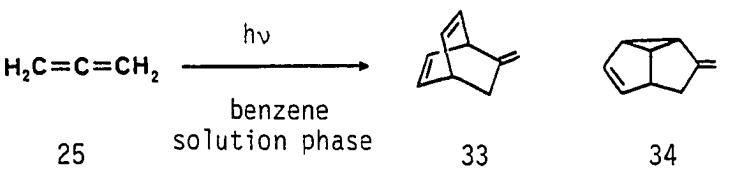
Scheme 8



8 31 32

Similar reactions of parent allene **25** in benzene solution also were reported by Bryce-Smith et al.[8] and Berridge et al.[9] As in the irradiation of **8**, the product mixture contained two major components in a ratio of 2:1; these were identified as para-cycloadduct **33** and meta-cycloadduct **34**, respectively (Scheme 9).

Scheme 9



25 33 34

It should be noted, however, that the observed cycloaddition reactions most likely do not involve triplet allene species. Indeed, numerous studies of benzene cycloadditions with ethylenic systems suggest that these reactions arise from the S_1 state of benzene and that exciplexes are involved as adduct precursors.[10,11,12]

Allene Singlet Reactions

As with the triplet sensitized reactions, most of the early investigations of allene direct irradiations involved vapor phase reactions. These irradiations typically resulted in the formation of complex mixtures and mechanistic interpretation was difficult due to incomplete product identification and the abundance of primary and secondary processes observed.

Doepker and Hill[13] first reported the vapor phase direct irradiation of 1,2-butadiene in 1969, and later, Diaz and Doepker[14] reported a reinvestigation of the reaction. The identified products included isomers 1-butyne and 1,3-butadiene, as well as numerous fragmentation products. The reaction was significantly affected by changes in wavelength and pressure of the substrate and also by the presence of other gases.

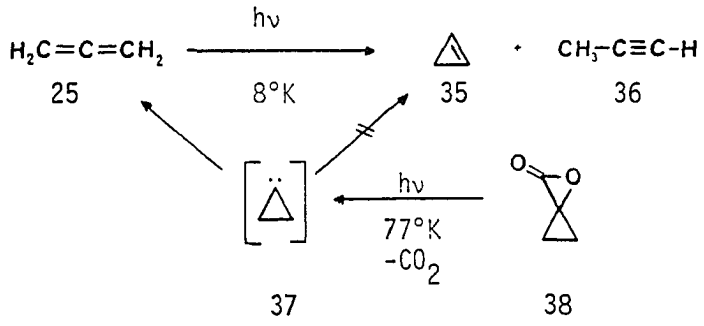
Ward and Karafiath briefly described the vapor phase direct irradiation of allenes **1**, **8**, and **11**.[3] The products which were identified generally corresponded to those observed in the benzene sensitized vapor phase reactions. Fragmentation products were noted in the reaction of **11**, in addition to the photo-Cope product **12**.

Steinmetz et al. has reported that the direct photolysis of 1,2-hexadiene (**1**) in pentane results in the formation of 1-hexyne as the major product and that the vapor phase fragmentation and bicyclic products are not observed in the solution phase reaction.[1] The direct irradiation of 3-methyl-1,2-pentadiene in pentane also was mentioned; major products observed were 3-ethyl-3-methyl-cyclopropene and 3-methyl-1-pentyne.

The matrix-isolated irradiation of allene (**25**) at 8°K was reported by Chapman in 1975, although only in very preliminary form. Cyclopropene (**35**) and methylacetylene (**36**) were observed as photoproducts (Scheme 10).[15] Cyclopropylidene (**37**) was presumed to be an intermediate in the formation of cyclopropene (**35**), however, its independent generation from spirolactone **38** gave only allene (**25**). In

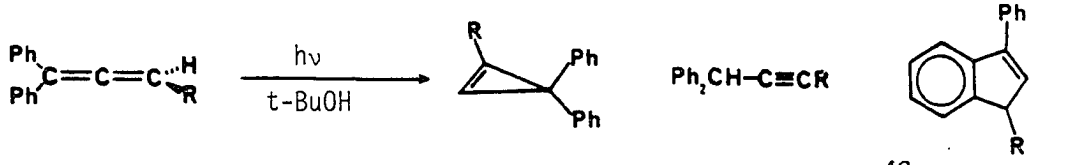
other experiments, irradiation of matrix-isolated vinylmethylene gave allene (25), cyclopropene (35), and methylacetylene (36).

Scheme 10



A number of recent studies have focused on the singlet photorearrangements of various phenyl-substituted allenes. In 1982, Steinmetz et al. described the direct irradiation of 1,1-diphenyl-3-alkylallenes 39a and 39b in t-butanol.[16] The primary photoproducts observed were cyclopropenes 40, propynes 41, and indenes 42 (Scheme 11). The reactive excited state multiplicity was demonstrated to be singlet as attempts to sensitize the reaction failed to give any of the observed products.

Scheme 11

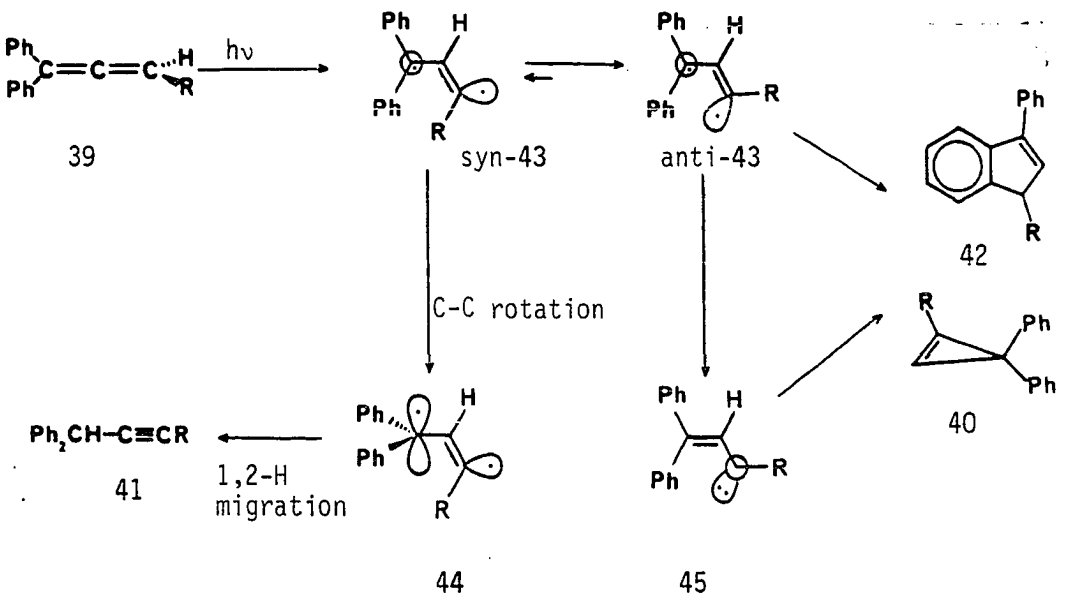


39a, R=n-Pr — 40a — 41a — 42a

39b, R=t-Bu — 40b (Ø=0.006) — 41b (Ø=0.005) — 42b (Ø=0.010)

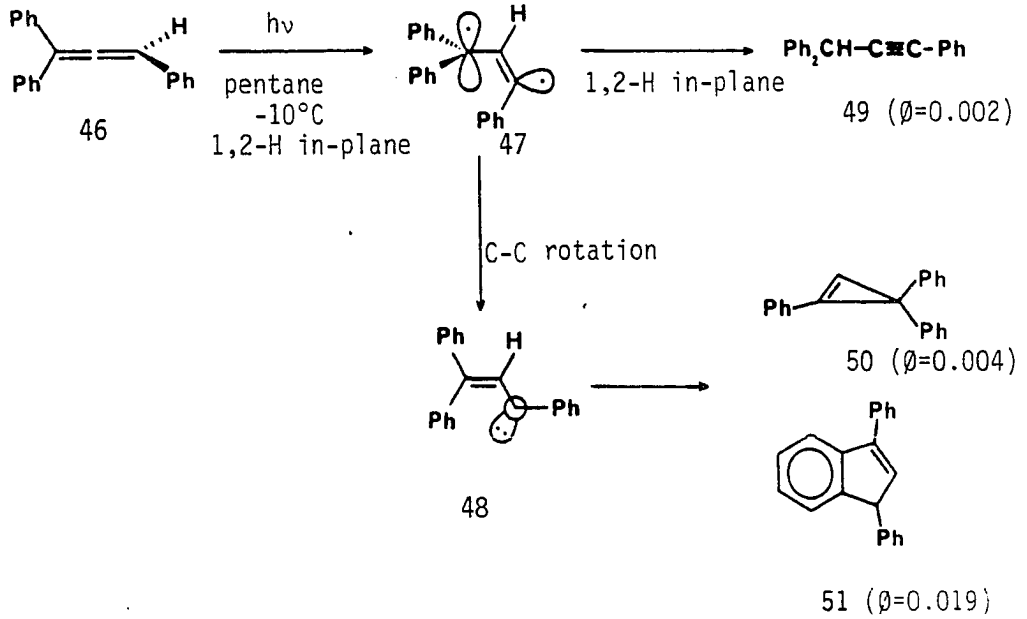
The authors proposed a mechanism for the photorearrangements which involves various electronic states and isomers (syn and anti) of a vinylmethylene species (Scheme 12). Vinylmethylene diradical anti-43 and vinylcarbene 45 were considered to be potential intermediates in the photoisomerization to the cyclopropene and indene products. Vinylcarbene 45 (R = t-Bu) was generated independently and 39b, 40b, and 42b were observed as products, consistent with its proposed intermediacy. No alkyne product, however, was observed and this mitigated against the sole intermediacy of vinylcarbene 45. Thus, vinylmethylene diradical syn-43 was proposed as leading to the alkyne product, via initial C-C bond rotation to a bisected vinylbiradical geometry (44), followed by a 1,2-hydrogen shift.

Scheme 12



Parallel studies were conducted by Klett and Johnson, who reported the direct irradiation of triphenylallene (**46**) and tetraphenylallene (**52**) in 1983.[17] Direct irradiation of triphenylallene (**46**) in pentane at -10°C afforded as primary photoproducts cyclopropene **50**, indene **51**, and propyne **49** (Scheme 13). Triplet sensitization proved ineffective and demonstrated that the observed rearrangements were from the singlet excited state.

Scheme 13



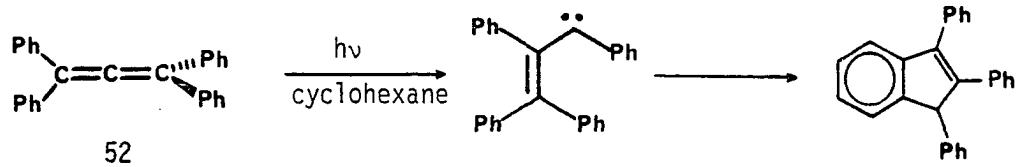
Three potential vinylcarbene intermediates, arising from either 1,2-hydrogen or 1,2-phenyl migrations, were generated independently and the results indicated that vinylcarbene **48** intermediacy was consistent with the formation of **50** and **51** in the photolysis. The absence of propyne **49** in the independent generation of **48** led the

authors to propose the initial formation of bisected biradical **47** from irradiation of **46**, with 1,2-hydrogen migration giving **49** and C-C bond rotation leading to **48**.

Consistent with this proposed pathway, Klett and Johnson, in a subsequent report, described the deuterium isotope effect on these rearrangements.[18] An isotope effect in the range of ca. 1.1-1.4 was observed for **50** and **51** formation, while an isotope effect of ca. 3.7 was observed for the formation of **49**. This is what might be expected for a single 1,2-hydrogen migration leading to the vinylcarbene derived products and for two sequential 1,2-hydrogen migrations leading to propyne formation.

Direct irradiation of tetraphenylallene (**52**) in cyclohexane very slowly yielded indene **54** as the sole reported primary photoproduct (Scheme 14). Sensitization experiments again showed the reactive excited state to be singlet. Vinylcarbene **53** is most likely an intermediate in this reaction, however, attempts to generate suitable precursors to **53** were unsuccessful. This reaction demonstrates that 1,2-phenyl migration, although much slower than 1,2-hydrogen migration, may occur.

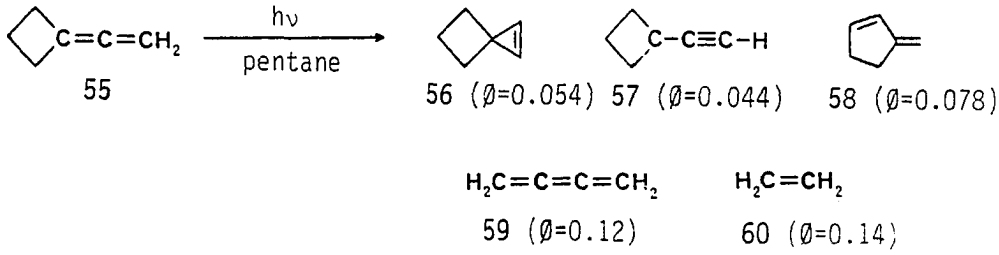
Scheme 14



52 53 54

Steinmetz et al. have reported an allene photolysis which appears to involve both 1,2-carbon and 1,2-hydrogen migrations.[19] Direct irradiation of vinylidenecyclobutane (**55**) in pentane at 185 nm led to the formation of five primary photoproducts (Scheme 15).

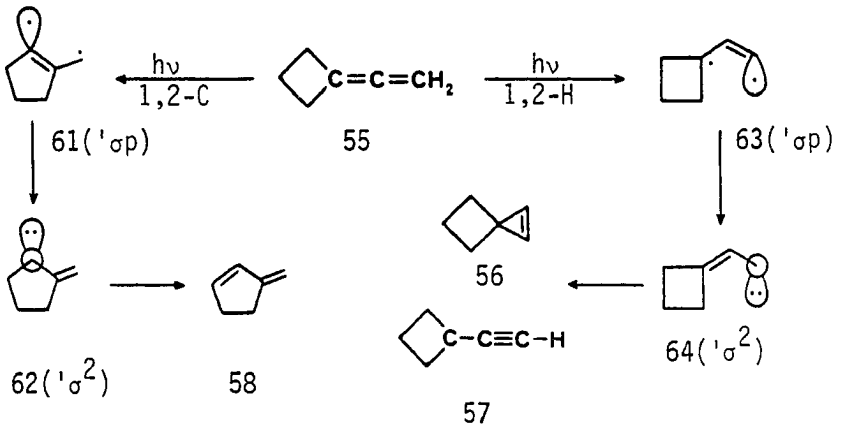
Scheme 15



55 → **56** (Ø=0.054) + **57** (Ø=0.044) + **58** (Ø=0.078) + **59** (Ø=0.12) + **60** (Ø=0.14)

The most efficient photoprocess observed was fragmentation to afford 1,2,3-butatriene (**59**) and ethylene (**60**). Both concerted and stepwise [2 + 2] cycloreversion mechanisms were considered. The proposed mechanism for the photoisomerization processes involves vinylcarbene intermediates **62** and **64** (Scheme 16). Neither of these vinylcarbenes, however, were generated independently. Furthermore, alkyne formation was attributed to vinylcarbene **64** ($^1\sigma^2$ state), which appears to be inconsistent with an earlier report by the same author,[16] and contrary to the experimental observation that alkyne products have not been obtained in previous independent generations of potential vinylcarbene intermediates.

Scheme 16

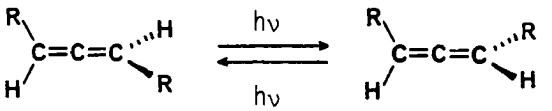


Steinmetz et al. also have reported the photochemistry of the homologs vinylidenecyclopentane and vinylidenecyclohexane.[1] These systems demonstrate that 1,2-carbon migration is only able to compete significantly with 1,2-hydrogen migration when it is accompanied by the relief of ring strain.

Allene π-Bond Rotation

The photochemical cis-trans isomerization of olefins by simple π-bond rotation is a well-known process which generally occurs with high efficiency. By analogy, one might expect that π-bond rotation in allenes, leading to the interconversion of enantiomers, should be a facile photoprocess (Scheme 17). There are only a few reported experimental studies, however, of the photoracemization of allenes.

Scheme 17



65 66

Borden examined the irradiation of partially resolved 1,3-di-t-butylallene in benzene at 300 nm and observed slow racemization, however, the results were not quantitatively reproducible.[20]

Rodriguez and Morrison reported in 1971 that toluene photosensitizes the rapid racemization of optically active penta-2,3-diene, in what was proposed to be a triplet process.[21] No attempt to quantify this reaction, however, appears to have been made.

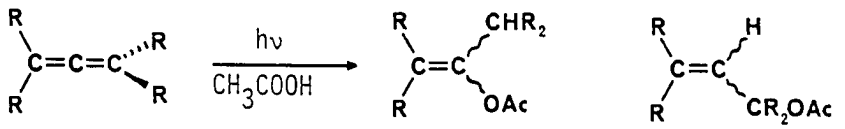
Hornback has examined the direct irradiation of optically active 1,3-diphenylallene and, as expected, observed racemization.[22] The observed quantum efficiency, however, varied from 0.38-0.96.

Protic Solvent Additions to Allenes

The photoaddition of protic solvents across π-bonds has been the subject of numerous investigations. A variety of mechanisms have been proposed, including the involvement of polarized nonvertical twisted excited states in some systems. A few studies examining the photoaddition of protic solvents to allenes have been reported.

Fujita et al. studied the photoassisted addition of acetic acid to a variety of allenes and reported the exclusive formation of vinyl acetates (68) in all but one system (Scheme 18).[23] The allylic acetate (69) was obtained only from the irradiation of 1,2-cyclononadiene (8). A triplet mechanism was proposed for these reactions based upon sensitization experiments.

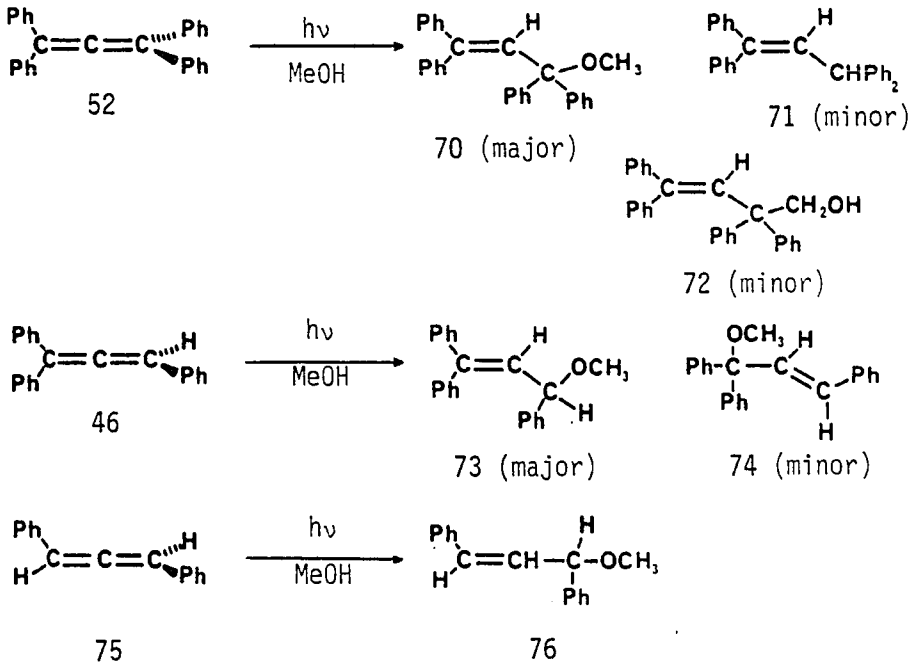
Scheme 18



67 68 69

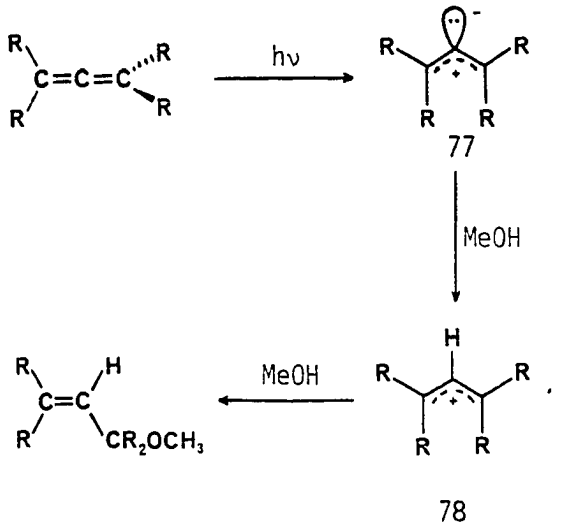
In contrast to this report, Klett and Johnson have observed that allylic ethers are formed from the irradiation of tetraphenylallene (52), triphenylallene (46), and 1,3-diphenylallene (75) in methanol (Scheme 19).[24] Sensitization experiments implicated the involvement of singlet excited states in these reactions and further suggested that the formation of vinyl ethers in other reactions may correspond to a radical cation process.

Scheme 19



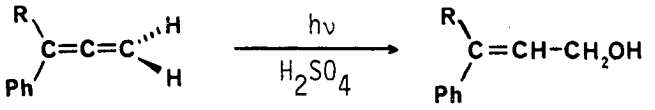
The mechanism proposed for these reactions involved initial twisting of the excited singlet allene to a highly polarized species (77). Protonation by the solvent yields a ground state allyl cation (78), which leads to the observed products (Scheme 20). The minor amounts of 71 and 72 which are obtained may result from a competitive homolytic hydrogen abstraction from solvent.

Scheme 20



Similar results have been subsequently reported by Rafizadeh and Yates for the photochemical hydration of phenylallene (79) and 1-methyl-1-phenylallene (80).[25] Irradiation of allenes 79 and 80 in 20% aqueous sulfuric acid-acetonitrile yielded the cinnamyl alcohols 81 and 82 in what was believed to be a singlet process (Scheme 21). The proposed mechanism for this reaction was similar to that reported by Klett and Johnson.

Scheme 21



79, R=H
80, R=Me

81, R=H
82, R=Me

The photohydration of nitro derivatives of **79** was also examined and a dramatic change in regiochemistry was observed. These substrates gave nitro-phenylacetones as products and appeared to arise via triplet excited states.

RESULTS AND DISCUSSION

Goals of This Research

Recent investigations of acyclic phenylallene photoreactions,[16,17,18] and an earlier report by Chapman,[15] have suggested that 1,2-hydrogen migration might be an important singlet photoreaction of allenes. Vinylcarbene intermediates have been implicated in these reactions.

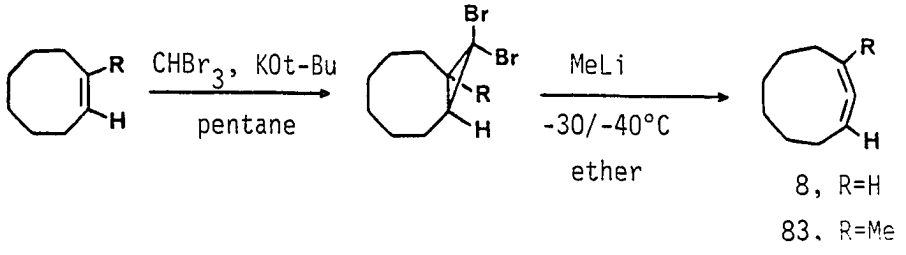
1,2-Cyclononadiene (**8**) is perhaps the archetypal cyclic allene. The singlet photoreaction of **8**, as first described in 1969 by Ward and Karafiath,[3] appeared to contrast with results for allene and phenylallenes. The only identified photoproduct was tricyclo-[4.3.0.$0^{2,9}$]nonane (**10**), and a bicyclic cyclopropylidene seemed the most likely intermediate. An initial goal of the present study was to carefully reexamine the singlet photochemistry of **8**, to determine if the singlet reactivity was indeed different from that of acyclic allenes. This eventually led to a thorough exploratory and mechanistic study of cyclic allene photoreactions.

Synthesis of Cyclic Allenes

The cyclic allenes examined in this study, 1,2-cyclononadiene (**8**) and 1-methyl-1,2-cyclononadiene (**83**), were efficiently prepared via the classic Doering-Moore-Skattebol route (Scheme 22). The first step involved addition of dibromocarbene to the cyclic olefin precursor. The resulting adduct was then opened to the corresponding allene by

treatment with methyllithium at reduced temperature. Allenes 8 and 83 were obtained in good yields (ca. 70% overall) and were determined to be of high purity (> 99%) by capillary GLC analysis. Further purification was accomplished by preparative scale GLC for material used in all analytical irradiations.

Scheme 22



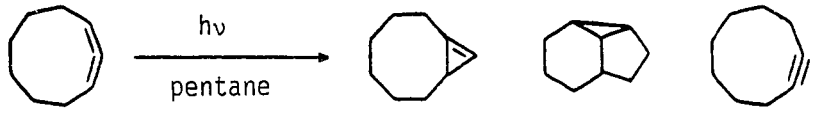
Singlet Photochemistry of 1,2-Cyclononadiene

Direct irradiation of 1,2-cyclononadiene in pentane

Direct irradiation of dilute solutions of 1,2-cyclononadiene (8) in pentane at $\lambda > 220$ nm (Vycor filter) to low conversions (0.25-2%) indicated bicyclo[6.1.0]non-1(9)-ene (84), tricyclo[4.3.0.$0^{2,9}$]nonane (10), and cyclononyne (85) (ratio 94:3:3) were primary photoproducts (Scheme 23). At these conversions, capillary GLC analysis showed 84, 10, and 85 to constitute greater than 95% of the photoproducts. Examination of product ratios as a function of conversion also demonstrated the primary nature of these products.

The possibility of solution phase wavelength effects was explored through irradiation of pentane solutions of 8 with 185/254 nm light. No difference was observed in the low conversion photoproducts.

Scheme 23



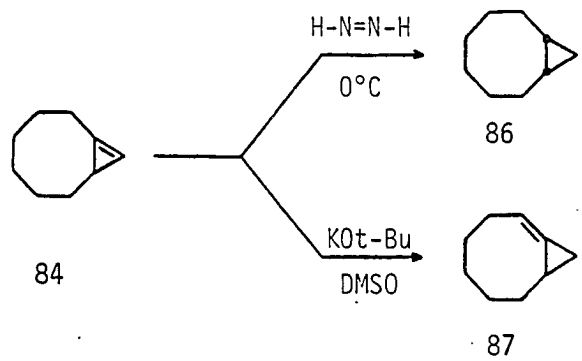
8 84 (94%) 10 (3%) 85 (3%)

Extended irradiation of 8 in pentane at > 220 nm yielded a complex mixture composed of 11 products, as determined by capillary GLC analysis. The additional products which were observed at higher conversions appeared to be arising from secondary photoreactions of **84**, as indicated by the change in product ratios as a function of conversion. This was verified by the irradiation of a pure sample of **84** in pentane. A similar mixture of products was obtained. The photochemistry of cyclopropene **84** will be described in a subsequent section.

The novel bicyclic cyclopropene **84** is of fundamental interest as an anti-Bredt olefin and its formation in the photochemical isomerization of **8** is its first reported synthesis. Cyclopropene **84** is surprisingly stable and was readily isolated pure by preparative scale GLC, using a glass column and a glass-lined injector. Spectral data for **84** included a singlet in the ^{1}H NMR at δ 6.47 and a strong infrared adsorption at 1780 cm^{-1}, both indicative of a cyclopropene moiety. Diimide reduction of **84** gave cis-bicyclo[6.1.0]nonane (**86**), identical with an authentic sample, while brief treatment with

potassium t-butoxide in DMSO afforded bicyclo[6.1.0]non-1(2)-ene (87) (Scheme 24). The latter reaction is consistent with the proposed intermediacy of 84 in the dehydrobromination of cis-9-bromo-bicyclo[6.1.0]nonane under similar conditions to afford 87.[26] There are two previous reports of derivatives of 84.[27]

Scheme 24



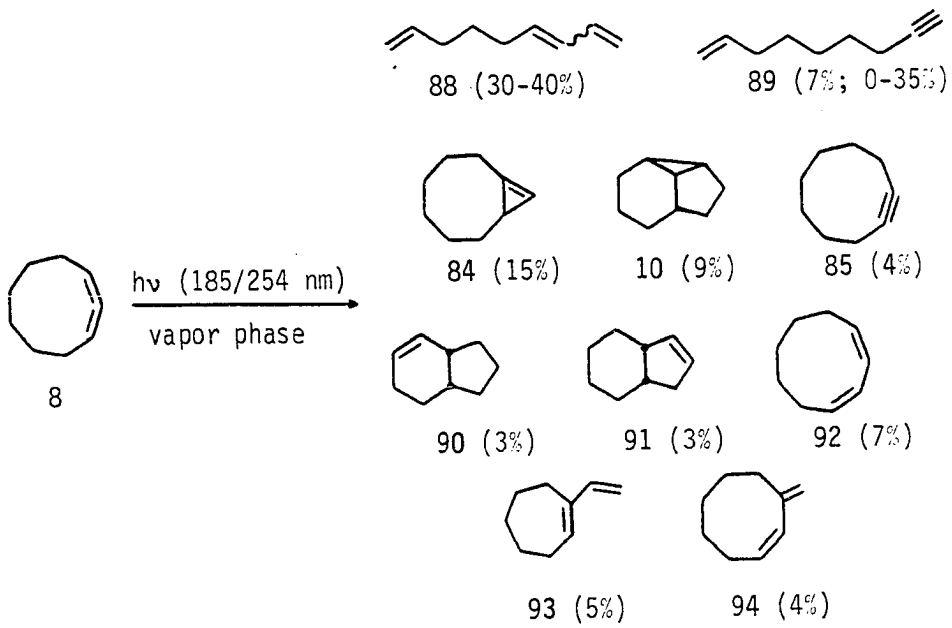
Tricyclo[4.3.0.$0^{2,9}$]nonane (10) and cyclononyne (85) were isolated by preparative scale GLC and identified by comparison of their capillary GLC retention times and 300 MHz ^{1}H NMR spectra with those of authentic samples, whose syntheses are described in the experimental section.

Direct irradiation of 1,2-cyclononadiene in the vapor phase

Direct irradiation of 1,2-cyclononadiene (8) in the vapor-phase at λ = 185(+254) nm to moderate conversions (ca. 10-20%) afforded a complex mixture composed of over 12 products, as determined by

capillary GLC analysis. Lower conversion irradiations (ca. 1-5%) under these conditions yielded similar results and provide evidence that these products may all be primary. Product ratios in these experiments were somewhat variable and typical product distributions are given in Scheme 25. These reactions were done on very small scale (5-10 mg), which precluded isolation of individual components. All identifications are based upon comparison of capillary GLC retention times and the 300 MHz ^{1}H NMR spectrum of the crude mixture with those of authentic samples, whose syntheses are described in the experimental section.

Scheme 25



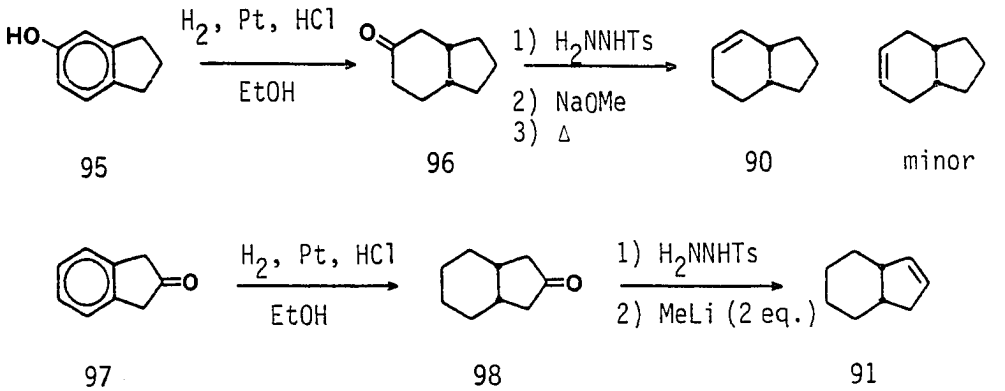
1,3,8-Nonatriene (88) was reproducibly the major product (30-40%) and was observed as a mixture of the trans and cis isomers (ratio

3:1). An authentic sample was obtained by a Wittig reaction using allyltriphenylphosphonium bromide and 5-hexen-1-al, affording the trans and cis isomers in the ratio 57:43 (300 MHz ^{1}H NMR analysis).

The amount of non-1-en-8-yne (**89**) which was observed varied considerably, ranging from 0 to 35% of the product mixture. An explanation for this variation will be presented later. An authentic sample was obtained by the thermolysis of **8**, as previously described by Crandall and Watkins.[28]

The cis-bicyclics **90** and **91** were independently synthesized from the cis-bicyclic ketones **96** and **98**, which were obtained from 5-indanol (**95**) and 2-indanone (**97**), as shown in Scheme 26. A previous assignment for **91** as a product of the thermolysis of **8** is incorrect.[28] The correct structure is the isomeric bicyclic **90**.

Scheme 26



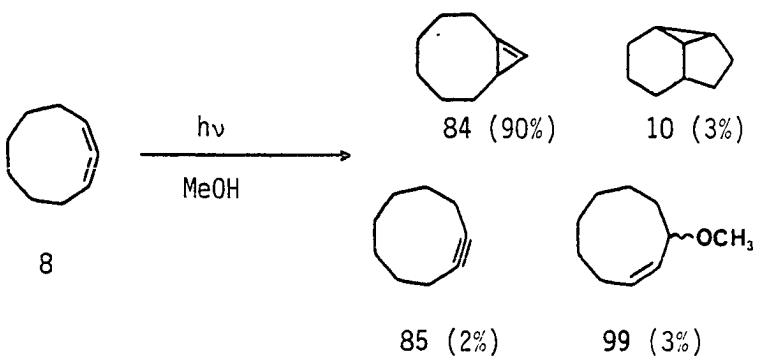
An authentic sample of cis-cis-1,3-cyclononadiene (**92**) was obtained by the base catalyzed isomerization of **8**.[29] Authentic samples of 1-vinylcycloheptene (**93**) and 3-methylenecyclooctene (**94**)

were obtained by Wittig reactions, using methyltriphenyl-phosphonium bromide, with cycloheptene-1-carboxaldehyde and cyclooct-2-en-1-one.

Direct irradiation of 1,2-cyclononadiene in methanol

Direct irradiation of dilute solutions of 1,2-cyclononadiene (8) in methanol at $\lambda > 220$ nm to low conversion (< 2%) indicated bicyclo[6.1.0]non-1(9)-ene (84), cyclononyne (85), tricyclo[4.3.0.$0^{2,9}$]nonene (10), and cis-3-methoxycyclononene (99) (ratio 90:2:3:3) were primary photoproducts (Scheme 27). At this conversion 84, 10, 85, and 99 constituted greater than 95% of the photoproducts. That these products were indeed primary was demonstrated by the examination of product ratios at varying conversions.

Scheme 27

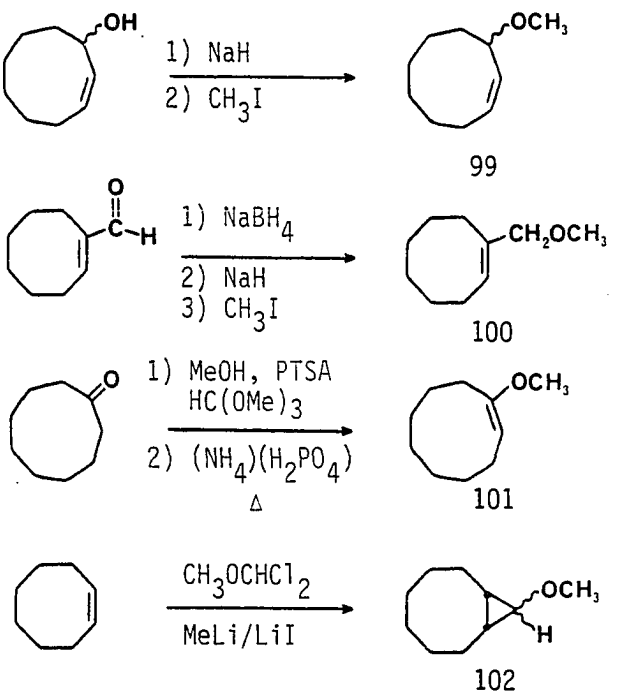


Upon extended irradiation of 8 in methanol, secondary reactions of cyclopropene 84 were observed. This led to an increasing percentage of 99 along with the formation of 1-(methoxymethyl)-cyclooctene (100). Careful analysis of the reaction mixture, as described in the experimental section, showed that exo-9-methoxy-

bicyclo[6.1.0]nonane (exo-102) and cis-1-methoxy-cyclononane (101) were not present (detection limit 0.1%). Ether product formation, from the irradiation of 8 in methanol, was found to be inefficient relative to the observed isomerization processes. Indeed, from 2-20% conversion, the total amount of ether products constitute less than 5% of the product mixture.

All identifications are based upon comparison of capillary GLC retention times and the 300 MHz ^1H NMR spectrum of the crude reaction mixture with those of authentic samples. Authentic samples of the potential ether products **99**, **100**, **101** and **102** were prepared as outlined in Scheme 28.

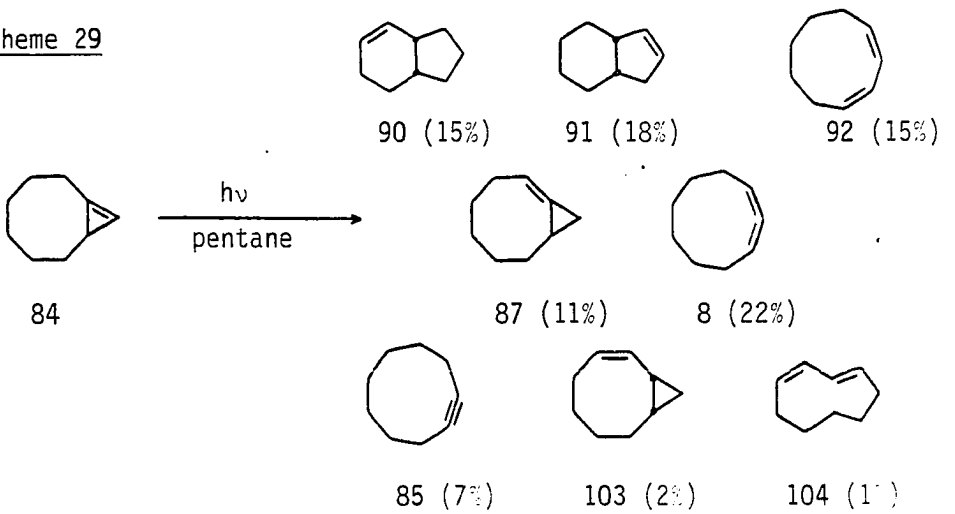
Scheme 28



Direct irradiation of bicyclo[6.1.0]non-1(9)-ene in pentane

Direct irradiation of dilute solutions of bicyclo[6.1.0]non-1(9)-ene (**84**) in pentane at $\lambda > 220$ nm to low conversion (ca. 2%) yielded a mixture composed of 8 products, as determined by capillary GLC analysis (Scheme 29). These products were found to be primary by the examination of product ratios at varying conversions. All identifications are based upon comparison of capillary GLC retention times and the 300 MHz ^{1}H NMR spectrum of the crude reaction mixture with those of authentic samples, whose syntheses are described in the experimental section.

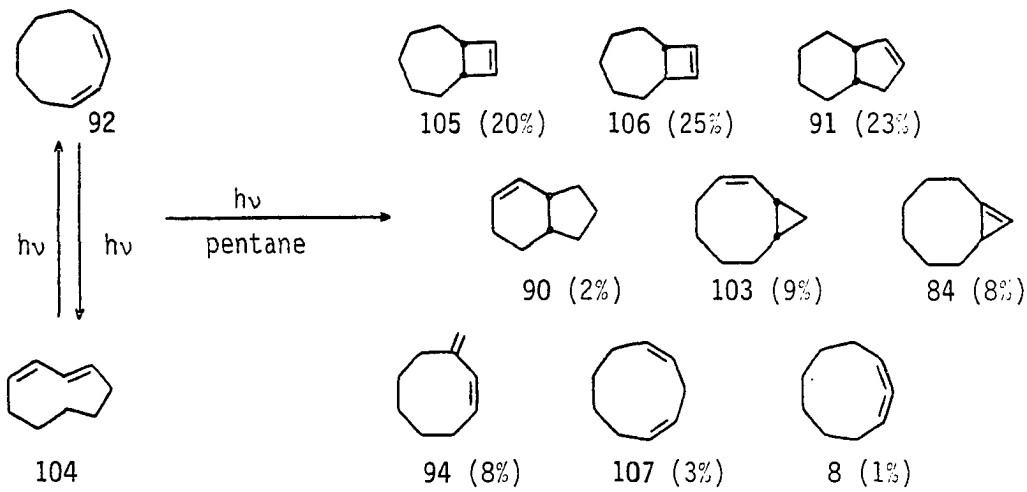
Scheme 29



Especially noteworthy in the photochemical reactions of **84** is the formation of allene **8**, effectively reversing the **8** → **84** transformation. The formation of cyclononyne (**85**) as a primary photoproduct is also of special interest. Although thermal cyclopropene-propyne conversions are well-known,[1] we believe this is the first reported example of an analogous photochemical reaction.[30]

At higher conversions of **84**, secondary photoreactions of cis-cis-1,3-cyclononadiene (**92**) were observed. This was demonstrated by the irradiation of a pure sample of **92** in pentane at 254 nm. Rapid cis-trans isomerization was initially observed, leading to a photoequilibrium mixture of **92** and **104** (ratio ca. 11:1). This was followed by the formation of a mixture composed of 9 additional products, as determined by capillary GLC analysis (Scheme 30). These products were isolated by preparative scale GLC and identified (with the exception of isomers **105** and **106**) by comparison of their capillary GLC retention times and 300 MHz ^{1}H NMR spectra with those of authentic samples, whose syntheses are described in the experimental section. The cis and trans-bicyclo[5.2.0]non-8-enes, **105** and **106**, were identified by comparison of their ^{1}H NMR spectra with those reported in the literature.[31]

Scheme 30



The photochemistry of 1,3-cyclononadiene was first described by Shumate and Fonken in 1966.[31b] Their results were similar, however, they did not report observing isomers **84**, **103**, and **94**. The ratios for the products they did report match fairly closely with those observed here.

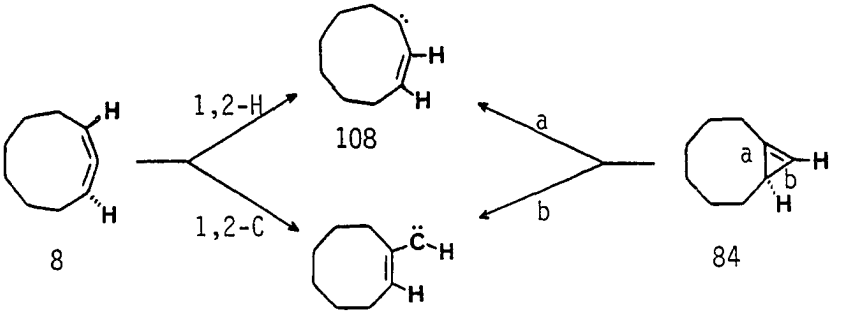
Authentic samples of the bicyclo[6.1.0]nonenes, **87** and **103**, were obtained by the dehydrobromination and subsequent isomerization of cis-9-bromo-bicyclo[6.1.0]nonane.[26] cis-cis-1,4-Cyclononadiene (**107**) was obtained by the base catalyzed isomerization of **8**.[29] A sample of cis-trans-1,3-cyclononadiene (**104**) was obtained by the irradiation of **92**, stopping the reaction after the rapid photoequilibrium was reached, and isolating the minor component of the equilibrium mixture by preparative scale GLC.

Independent generation of potential vinylcarbene intermediates

Vinylcarbenes have been suggested as intermediates in the thermal interconversions of cyclopropenes, allenes, and alkynes.[1] They have also been proposed as intermediates in the photorearrangements of phenyl-substituted allenes.[16,17,18] We, therefore, considered vinylcarbenes **108** and **109** to be potential intermediates in the photoreactions of allene **8** and cyclopropene **84** (Scheme 31).

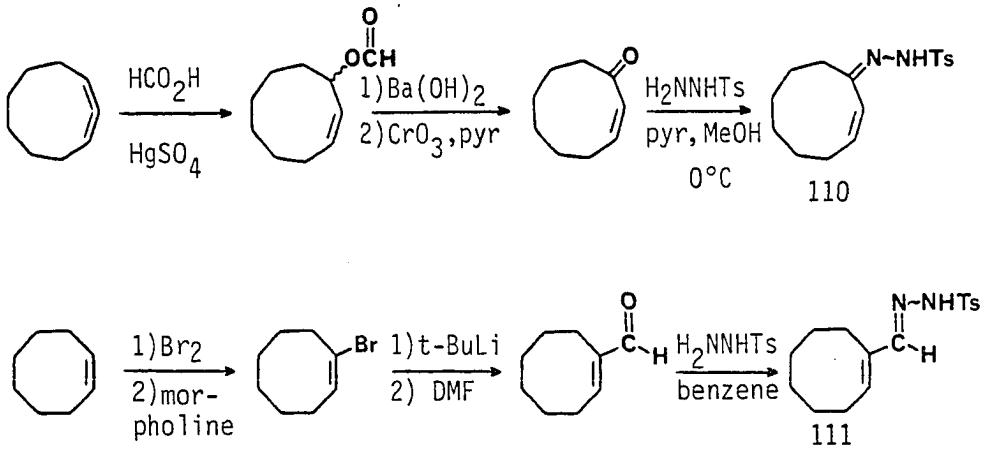
From allene **8**, a 1,2-hydrogen shift would afford **108**, while a 1,2-carbon shift would give **109**. Cleavage of bond (a) in cyclopropene **84** would afford **108**, while cleavage of bond (b) would give **109**. Both vinylcarbenes **108** and **109** were generated independently via photolysis and thermolysis of the corresponding tosylhydrazone sodium salts.

Scheme 31



The tosylhydrazone precursors to vinylcarbenes 108 and 109 were prepared as shown in Scheme 32. Both had been reported previously,[32] but were not used for carbene generation.

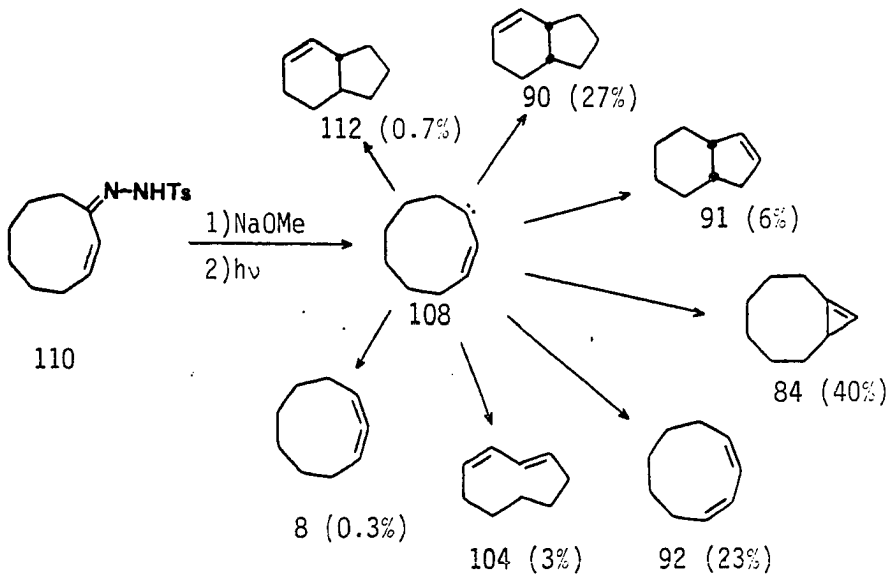
Scheme 32



Treatment of cyclonon-2-en-1-one tosylhydrazone (110) in THF with sodium methoxide, followed by irradiation through Pyrex, led in 70% yield to a mixture composed of 7 isomeric hydrocarbon products (m/e 122), as determined by GC-MS. The 5 major components (90, 91, 84, 92,

and 104) were isolated by preparative scale GLC and identified by comparison of their capillary GLC retention times and 300 MHz ^1H NMR spectra with those of authentic samples. The two minor (8 and 112) components were assigned based upon comparison of their capillary GLC retention times with those of authentic samples.

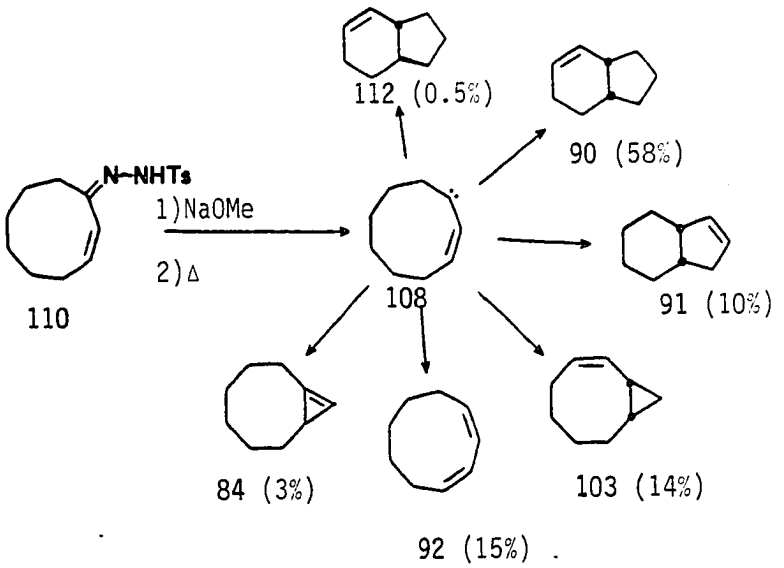
Scheme 33



Treatment of cyclonon-2-en-1-one tosylhydrazone (110) in diglyme with sodium methoxide, followed by heating (to ca. 120°C), led in 33% yield to a mixture composed of 6 isomeric hydrocarbon products (m/e 122), as determined by GC-MS. A similar mixture was obtained in 70% yield when 1 equivalent of n-butyllithium was used in place of the sodium methoxide. All identifications (with the exception of 112) are based upon comparison of capillary GLC retention times and the 300 MHz

^{1}H NMR spectrum of the crude reaction mixture with those of authentic samples. Assignment of **112** is based upon comparison of only the capillary GLC retention time with that of an authentic sample.

Scheme 34

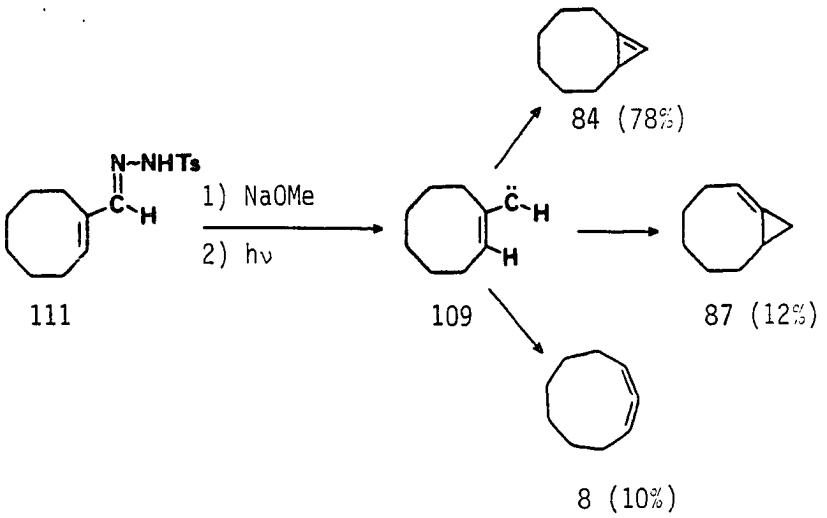


Both thermal and photochemical generation of vinylcarbene **108** afforded relatively similar products. In the thermal reaction, however, **8** and **104** were absent and the percentage of **84** was greatly reduced. This may be due to their thermal sensitivity. Additionally, isomer **103** is only observed in the thermal reaction. The reason for this is unclear, however, it may be arising from thermolysis of cyclopropene **84**. It does not appear to be arising from a base catalyzed (excess sodium methoxide) isomerization of **84**, as the reaction using slightly less than 1 equivalent of n-butyllithium as base gave similar results.

Importantly, the nearly exclusive cis stereoselectivity observed in the formation of the transannular insertion products (**90**, **91**, **103**, and **112**) accords with reaction from a singlet vinylcarbene. A stepwise triplet process presumably would yield more trans product.

Treatment of cyclooctene-1-carboxaldehyde tosylhydrazone (**111**) in THF with sodium methoxide, followed by irradiation through Pyrex, led in 44% yield to a mixture composed of 3 isomeric hydrocarbon products (m/e 122), as determined by GC-MS. These were isolated by preparative scale GLC and identified by comparison of their capillary GLC retention times and 300 MHz ^{1}H NMR spectra with those of authentic samples.

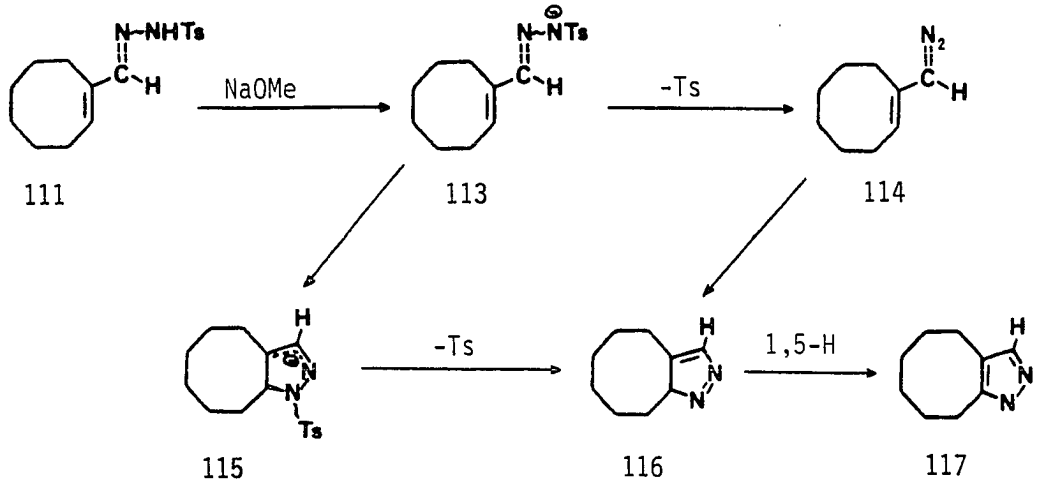
Scheme 35



Cyclopropene **84** is formed in good yield (78% of products, ca. 20% isolated yield after preparation GLC) from this reaction, and we believe this to be the best source of this interesting and previously unknown hydrocarbon. Also worth noting, is the significant amount of allene **8** (10%) formed from **109**. This is in contrast to the seemingly general belief that vinylcarbenes do not rearrange to allenes.

Treatment of cyclooctene-1-carboxaldehyde tosylhydrazone (**111**) in diglyme with sodium methoxide, followed by heating (to ca. 160°C), yielded only 3,4-hexamethylenepyrazole **117**. Capillary GLC analysis and 300 MHz ^{1}H NMR analysis of the crude product showed that no C_9H_{14} products were present. Identification of **117** is based upon comparison of its 300 MHz ^{1}H NMR spectrum and melting point with those reported in the literature.[32a]

Scheme 36

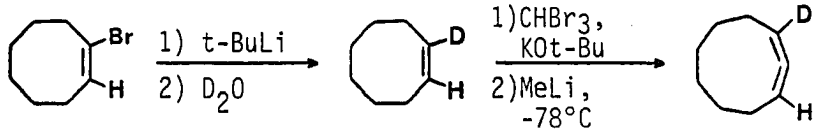


Pyrazole 117 may arise via cyclization of either the initially formed tosylhydrazone sodium salt (113) or, potentially, via the vinyldiazo intermediate 114 (Scheme 36). If vinyldiazo 114 is leading to pyrazole 117, then the rate of cyclization of 114 must be much faster than the rate of tosyl loss from 113, as no pink coloration of the reaction solution (expected for a vinyldiazo intermediate) is observed throughout the course of the reaction. All other reactions reported previously here, resulting in vinylcarbene generation via a vinyldiazo intermediate, displayed a transient pink coloration which dissipated as the reaction proceeded to completion.

Deuterium kinetic isotope effect on the singlet photorearrangement of 1,2-cyclononadiene

1-Deuterio-1-2,cyclononadiene (8-d) was prepared (Scheme 37) to probe the mechanism of the allene 8 to cyclopropene 84 photorearrangement. 1-Deuteriocyclooctene (118) was first obtained by treating 1-bromocyclooctene with t-butyllithium and quenching the resulting lithio-derivative with D_2O. ^2H NMR analysis of 118 showed that the deuterium was incorporated solely in the vinyl position, while ^1H NMR analysis indicated that there was ca. 100% deuterium incorporation at that site. This material was converted to the deuterium-substituted allene 8-d by the standard method as described previously (Scheme 37). ^2H NMR analysis of 8-d showed that the deuterium was incorporated solely in the allenic position, while ^1H NMR analysis indicated that there was ca. 100% deuterium incorporation at that site.

Scheme 37

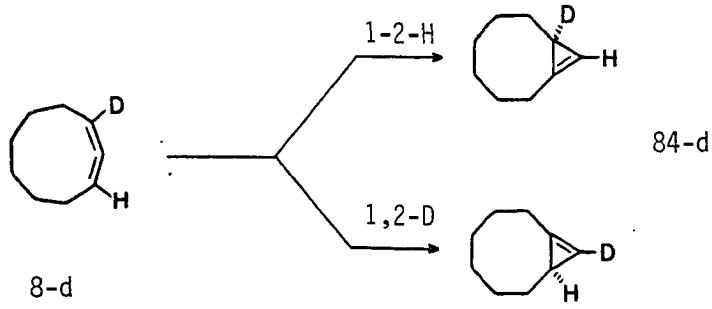


118 8-d

1-Deuterio-1,2-cyclononadiene (8-d) in pentane was irradiated at $\lambda > 220$ nm to low conversions (ca. 3-12%) and the crude reaction product mixtures were analyzed by ^2H NMR. The deuterium isotope effect in each case was measured by taking the ratio of the area of the allylic cyclopropenyl signal (δ 1.43) to that of the vinylic signal (δ 6.45). No variation as a function of conversion could be observed, as the error in the measurements exceeded any noticeable change. Thus, the deuterium isotope effect was calculated as the mean of the values obtained. As expected, preference for hydrogen migration was observed, with $k_H/k_D = 1.30 \pm 0.06$ (Scheme 38).

These experiments also demonstrate that both cyclopropene hydrogens arise uniquely from the allenic hydrogens, thus eliminating the possibility of more complicated transpositions.

Scheme 38



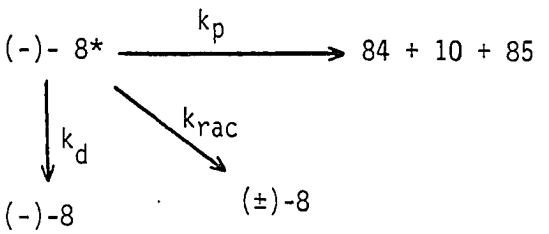
Direct irradiation of optically active 1,2-cyclononadiene in pentane

Optically active 1,2-cyclononadiene (**8**) was prepared and irradiated in order to further probe the mechanism of the allene **8** to cyclopropene **84** photorearrangement. Both are inherently chiral. In principle, a concerted reaction might transform optically active **8** into active **84**. The procedure of Byrd and Caserio,[33] involving partial hydroboration with a chiral reagent, was employed to obtain optically active **8** with $[\alpha]_D$ = -24° (1.35, $CHCl_3$) and an optical purity of ca. 15%.

Direct irradiation of optically active **8** in pentane at $\lambda > 220$ nm to low conversions (ca. 1-4%) was followed by preparative scale GLC isolation of **8** and **84**. As expected, recovered **8** was substantially racemized (ca. 50-75%) even at these low conversions. Additionally, in all cases, isolated cyclopropene **84** was found to be inactive, within detection limits at the sodium D line or by measurement of the optical rotatory dispersion (ORD) spectrum.

In other experiments, the rate of racemization relative to that of product formation was determined by monitoring the optical rotation (α) of the solution and the disappearance of allene **8**. Equation 1, derived by Wagner et al.[34] for a kinetic scheme similar to that shown in Scheme 39, allows the calculation of the relative rates of racemization and product formation from the data obtained.

Scheme 39



Equation 1

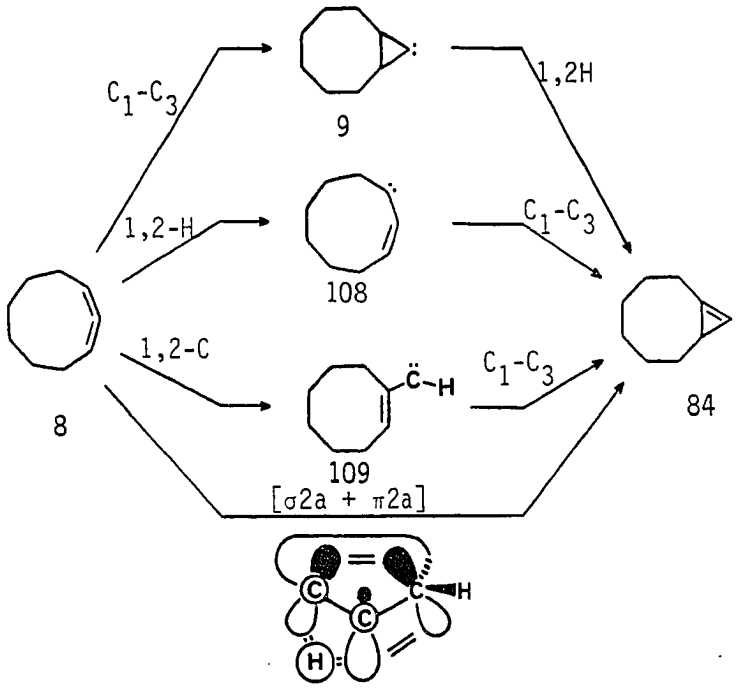
$$\log(\alpha_i/\alpha) = (1 + k_{rac}/k_p)\log([8]_i/[8])$$

The plot of $\log(\alpha_i/\alpha)$ vs. $\log([8]_i/[8])$ at varying conversions (< 3%) was linear (correlation coefficient 0.99) and gave $k_{rac}/k_p = 70$. Thus, as expected, racemization is far more efficient than rearrangement to cyclopropene **84**. This experiment is the first reported example of an allene singlet racemization and, additionally, provides the first direct comparison of the efficiency of allene π-bond rotation to other types of photoisomerization.

Discussion of 1,2-cyclononadiene singlet solution phase reaction mechanisms

The conversion of racemic 1,2-cyclononadiene (**8**) to bicyclo[6.1.0]non-1(9)-ene (**84**) was observed to be the predominant singlet solution-phase photoisomerization process. The most economical pathways for this conversion involve 1,2-hydrogen (or carbon) migration, and bond formation between terminal carbons of the allene moiety. These pathways, depicted in Scheme 40, differ mainly in the timing of bond forming and breaking events.

Scheme 40



In principle, cyclopropene 84 may be formed via singlet cyclopropylidene 9 if C_1-C_3 bond formation occurs first. However, several independent results provide argument against cyclopropylidenes as precursors to cyclopropenes. Kirmse and Hellwig have previously generated cyclopropylidene 9 (presumably singlet) in methanol;[35] 1,2-cyclononadiene (8) was the sole hydrocarbon product reported. Similarly, Chapman has generated parent cyclopropylidene (37) at 77°K and observed only allene (25) formation.[15] Consistent with these results, Honjou et al. have reported high level ab initio calculations, which predict that the barrier to 1,2-hydrogen migration in singlet cyclopropylidene is larger than that for opening to allene.[36]

While these data strongly suggest that the transformation of 8 to 84 via cyclopropylidene 9 is unlikely, they do not exclude the potential formation of 9 from singlet excited 8. This is because if singlet 9 were formed, it would be expected to revert primarily to ground state 8, and its formation might escape detection. The small amount (3%) of tricyclic 10 which is observed from direct irradiation of 8 is noteworthy in this regard.

One possibility for the origin of 10 is that transannular C-H insertion in photogenerated singlet 9 is able to compete to some degree with ring opening. The generation of 9 in methanol by Kirmse and Hellwig, however, did not lead to any formation of tricyclic 10 (detection limit 0.1%); 1,2-cyclononadiene (8) and exo-9-methoxybicyclo[6.1.0]nonane (exo-102) were the sole products reported as deriving from 9. That no exo-9-methoxybicyclo[6.1.0]nonane (exo-102) was observed upon the irradiation of 8 in methanol, provides strong evidence that singlet 9 is not obtained in the photoreaction of 8. An alternative route to tricyclic 10 is via intersystem crossing of singlet excited 8 to yield triplet cyclopropylidene 9, which has been proposed as an intermediate in the benzene sensitized vapor-phase photoisomerization of 8 to 10.[3]

Vinylcarbene intermediates provide another potential route to cyclopropene photoproducts. Initial 1,2-hydrogen migration could yield cyclopropene 84 via singlet vinylcarbene 108, while initial 1,2-carbon migration would give 84 via singlet vinylcarbene 109. These vinylcarbenes do not appear to be intermediates in the formation of

cyclopropene **84**, because their independent generation afforded significant amounts of other products, which were not observed as primary products in the solution phase photoreactions of **8**. Additionally, the observed deuterium isotope effect for formation of **84**, k_H/k_D = 1.3, provides argument that hydrogen rather than carbon is migrating; this mitigates against vinylcarbene **109**.

It has been suggested by Steinmetz et al. that different electronic states of the vinylcarbene may lead to distinctly different chemistry, which would further complicate the situation.[1,16,37] Such state selective reactivity is unlikely, however, as GVB calculations by Davis et al. predict that the two lowest singlet states of vinylmethylene lie within a few kcal/mol of each other.[38] Thus, facile internal conversion would be expected.

Vinylcarbene **108** can exist as four discrete isomers (Figure 1), which may also exhibit distinctly different chemistry. The calculations by Davis et al., however, predict a low barrier to syn-anti interconversion (ca. 4 kcal/mol), via S_2 of vinylmethylene.[38] Interconversion of the cis and trans isomers, perhaps, may be more problematic. The ab initio calculations reported by Honjou et al. predict a substantial barrier to π bond rotation in vinylmethylene.[36] This is of the same magnitude as the barrier to formation of allene from vinylmethylene (ca. 12 kcal/mol), and is significantly larger than the barrier calculated for cyclopropene formation (< 5 kcal/mol). Thus, it is unclear whether π bond rotation will be able to compete with other reactions of the vinylcarbene.

cis-anti-108 cis-syn-108 trans-syn-108 trans-syn-108

Figure 1. Cyclonon-2-enylidene Isomers

An attractive alternative to the discrete intermediates considered above is a photochemically allowed concerted [σ2a + π2a] mechanism. This would involve simultaneous 1,2-hydrogen (or carbon) migration and C_1-C_3 bond formation. As noted above, the deuterium isotope effect observed for the rearrangement of **8** to **84**, k_H/k_D = 1.3, provides argument that hydrogen is migrating. The Hückel four electron transition state for a concerted process is depicted in Scheme 40.

Recent ab initio CI calculations for hydrogen migration in allene have been reported by Klett and Johnson. The potential surfaces show the expected pericyclic minimum, which exists due to approach of ground and excited states (Figure 2).[18] The geometry at this point approximates that of a bent bisected biradical **119**. Internal conversion at this geometry might lead to cyclopropene via C_1-C_3 bond formation or, alternatively, to vinylcarbene via π bond rotation. Constraints imposed by the carbocyclic ring may be crucial in preventing rotation to vinylcarbene **108** in the photoreaction of **8**. Indeed, in the acyclic phenylallenes which were previously

examined,[16,17,18] rotation to discrete vinylcarbene intermediates appears to predominate.

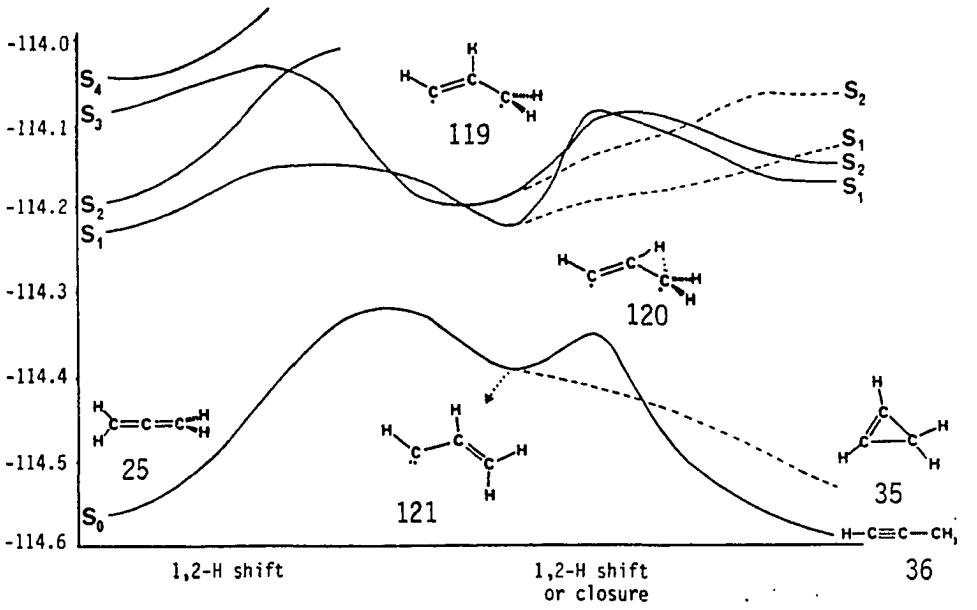


Figure 2. Singlet Potential Energy Surface

The geometry of bisected biradical **119** is also close to that of the ground transition state, **120**, which leads to alkyne through an in-plane 1,2-hydrogen migration. Thus, the small amount of cyclononyne (**85**) observed in the singlet photoreaction of 8 may also be explained by internal conversion at this geometry. Partitioning among the various pathways which are depicted in Figure 2 would be expected to be highly structure dependent.

The irradiation of 1,2-cyclononadiene (**8**) in methanol does not resolve the vinylcarbene *vs.* concerted mechanistic question, since the efficiency of carbene trapping is unknown. Indeed, we note that

secondary reactions of cyclopropene **84**, which almost certainly involve vinylcarbenes, did not change dramatically in methanol. Similarly, cyclopropylidene **9** is not trapped efficiently by methanol (ca. 4%).[35]

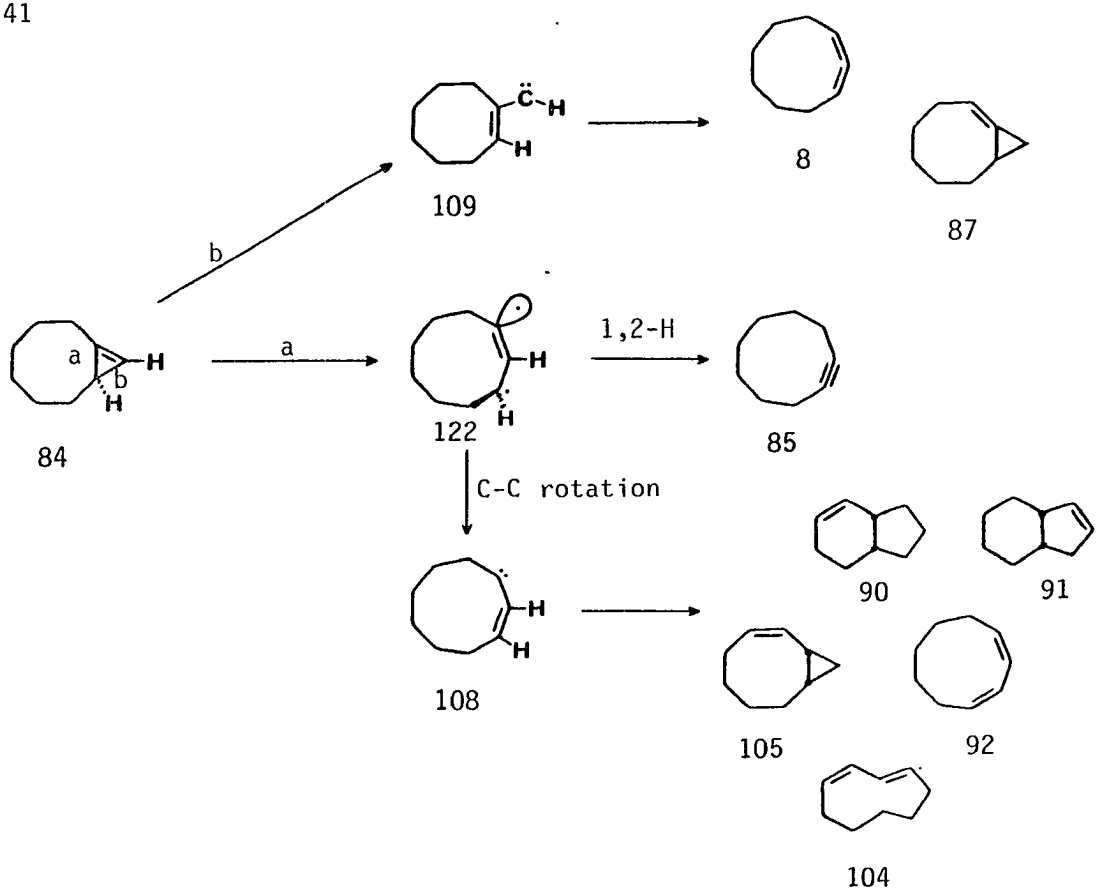
While the irradiation of optically active 1,2-cyclononadiene (**8**) offered the potential to differentiate between the possible pathways, the results for these experiments were not definitive. The failure to detect any optical rotation in the isolated samples of cyclopropene 84 does not necessarily mitigate against concerted rearrangement. This is because the facile competitive photo racemization of allene **8** would result in **84** of low optical purity. Additional factors to be considered are the small amounts of **84** which are isolable at low conversions of **8**, and the potential for an inherently low rotation in optically pure **84**. Thus, even if cyclopropene **84** was formed stereospecifically, its rotation may be below our detection limit.

Discussion of bicyclo[6.1.0]non-(9)-ene singlet reaction mechanisms

Vinylcarbenes are commonly believed to be intermediates in the photolysis of cyclopropenes.[39] Independent generation of vinylcarbenes **108** and **109** demonstrates that they are intermediates in the photoreactions of cyclopropene **84**, since all of the products observed in the irradiation of **84**, with the exception of cyclononyne (**85**), also were observed from vinylcarbene generation.

Cyclononyne (**85**) may be formed from a geometry corresponding to bisected biradical **122**, arising from cleavage of the cyclopropene

Scheme 41



internal C-C bond. This bisected biradical may undergo either a 1,2-hydrogen shift to give cyclononyne 85, or rotation about the C-C single bond to give vinylcarbene 108 and its characteristic products. This mechanism for alkyne formation from cyclopropene 84 is closely related to that proposed earlier for its formation from allene 8. Indeed, ab initio calculations show that both allene and cyclopropene excited states can arrive at an excited state bisected biradical geometry through in-plane H-migration, or in-plane ring opening, respectively (Figure 2).[18] Internal conversion and hydrogen migration will yield the alkyne product. Thus, in principle, common products may be observed in allene and cyclopropene photochemistry. This was the first reported example of a photochemical cyclopropene to alkyne conversion.

Dicsussion of 1,2-cyclononadiene singlet vapor phase reaction mechanisms

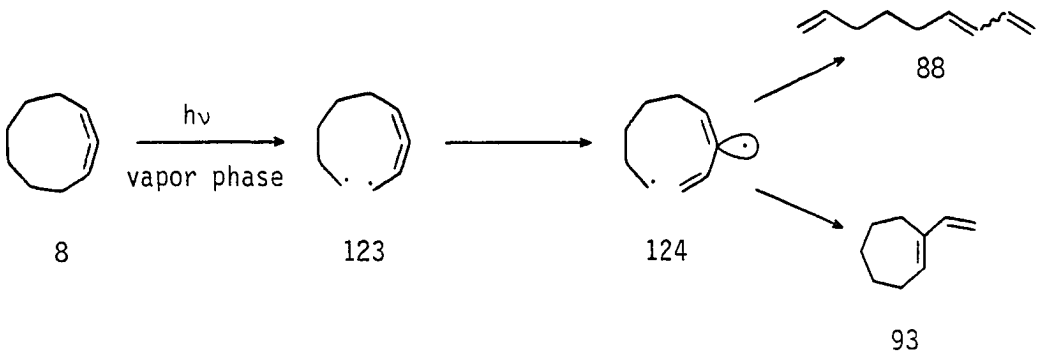
The vapor phase photoreaction of 1,2-cyclononadiene (8) proved to be considerably more complex than that observed in the solution phase. Product ratios in these experiments were somewhat variable, which suggested that careful control of reaction conditions (e.g. pressure) would be necessary in future studies. Nevertheless, consideration of mechanisms of the observed transformations is of interest.

Enyne 89 is the major product from the vapor phase thermolysis of 8,[28,40] and may simply result from a "hot ground state" of 8. This

pathway would be consistent with the large variation in the amount of **89** observed for different runs. Pressure in the reaction vessel was difficult to control, and variations would be expected to result in a change in the amount of observed "hot ground state" reaction. Increased pressure would presumably lead to less "hot ground state" reaction, as the collisional deactivation probability would increase. Doepker and coworkers have previously noted that the vapor phase reactions of 1,2-butadiene were significantly affected by changes in the pressure of the substrate, and also by the pressure of other gases.[13,14] Further experiments with more careful control of pressure and wavelength, in the vapor phase reactions of **8**, would undoubtedly help to clarify the situation.

1,3,8-Nonatriene (**88**) was reproducibly the major vapor phase product. This isomer may derive from cleavage of the σ-bond β to the allene chromophore, via butadienyl radical **124** (Scheme 42). This process would also explain the formation of 1-vinylcycloheptene (**93**). These products are not observed in solution and are minimized by irradiation at longer wavelengths in the vapor phase. Both observations argue that this cleavage is characteristic of an upper excited state of **8**.

Scheme 42



1,3,8-Nonatriene (88) also is formed in the vapor phase thermolysis of 8.[40] This suggests that an alternative pathway to 88 may be via a "hot ground state", as was proposed for enyne 89. This is considered to be unlikely, however, as the observed amounts of 88 and 93 remained fairly constant from run to run, while the amount of enyne 89 varied considerably.

Cyclopropene 84, cycloalkyne 85, and tricyclic 10 were observed in the solution phase photoreactions of 8 and their formation in the vapor may follow similar pathways. Contrary to the solution-phase photolyses, however, significant amounts of 1,3-cyclononadiene (92) and transannular insertion products (90 and 91) were observed in the vapor phase reaction; these appeared to be primary photoproducts. This result strongly suggests that cyclononenylidene 108 is involved in the vapor phase photoreaction of 8.

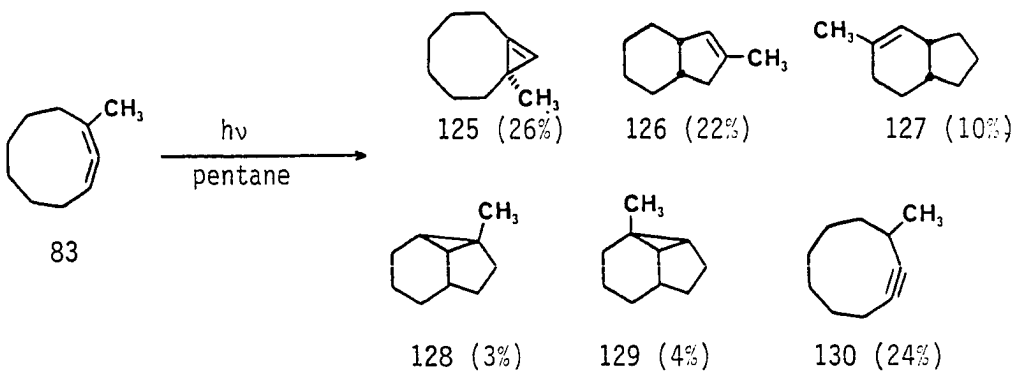
The mechanism for the formation of diene 94 is not clear. This product may be secondary.

Singlet Photochemistry of 1-Methyl-1,2-cyclononadiene

Direct irradiation of 1-methyl-1,2-cyclononadiene in pentane

Direct irradiation of dilute solutions of 1-methyl-1,2-cyclononadiene (**83**) in pentane at $\lambda > 220$ nm (Vycor filter) to low conversions (ca. 0.4-6%) led to cyclopropene **125**, cycloalkyne **130**, cis-bicyclics **126** and **127**, and tricyclics **128** and **129** as primary photoproducts (Scheme 43). These products make up ca. 90% of the primary photoproduct mixture. That these products were primary was demonstrated by the examination of product ratios at varying conversions.

Scheme 43



An additional component observed in the reaction mixture, cis-cis-2-methyl-1,3-cyclononadiene (**135**), was shown to be secondary by the examination of product ratios at varying conversions.

The singlet solution phase photoreaction of 1-methyl-1,2-cyclononadiene (**83**) thus contrasts substantially with that of the unsubstituted allene **8**. The cyclopropene product comprises a much

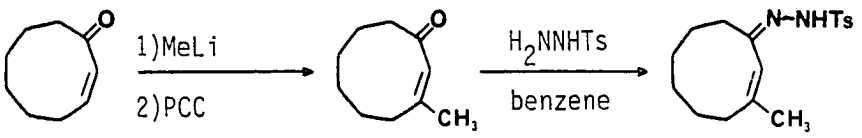
smaller portion (26% vs. 94%) of the mixture in the photoreaction of **83**, while the amount of alkyne product is significantly increased (from 3% to 24%). Bicyclic olefins were observed as primary photoproducts in the reaction of **83**, whereas, they were not observed as primary photoproducts in the solution phase reaction of **8**. Tricyclic product formation remains relatively constant in the two substrates.

8-Methylbicyclo[6.1.0]non-1(9)-ene (**125**) and 3-methylcyclononyne (**130**) have not been reported previously; these were identified by their characteristic spectral data (IR, ^{1}H and ^{13}C NMR). Tricyclics **128** and **129** are also new compounds, and were characterized by their spectral data and thermolysis (which will be described later). The 300 MHz ^{1}H NMR spectra were quite similar to those of the parent compound. Bicyclic olefins **126** and **127** were identified by comparison with authentic samples, independently synthesized as described in the experimental section.

Independent generation of 3-methylcyclonon-2-enylidene

3-Methylcyclonon-2-enylidene (**132**) was considered to be a potential intermediate in the photoreaction of 1-methyl-1,2-cyclononadiene (**83**). This vinylcarbene may arise via a 1,2-hydrogen shift in **83**. To explore this possibility, vinylcarbene **132** was independently generated by photolysis of the corresponding tosylhydrazone sodium salt. The tosylhydrazone precursor (**131**) was prepared in three steps from cyclononenone, as shown in Scheme 44.

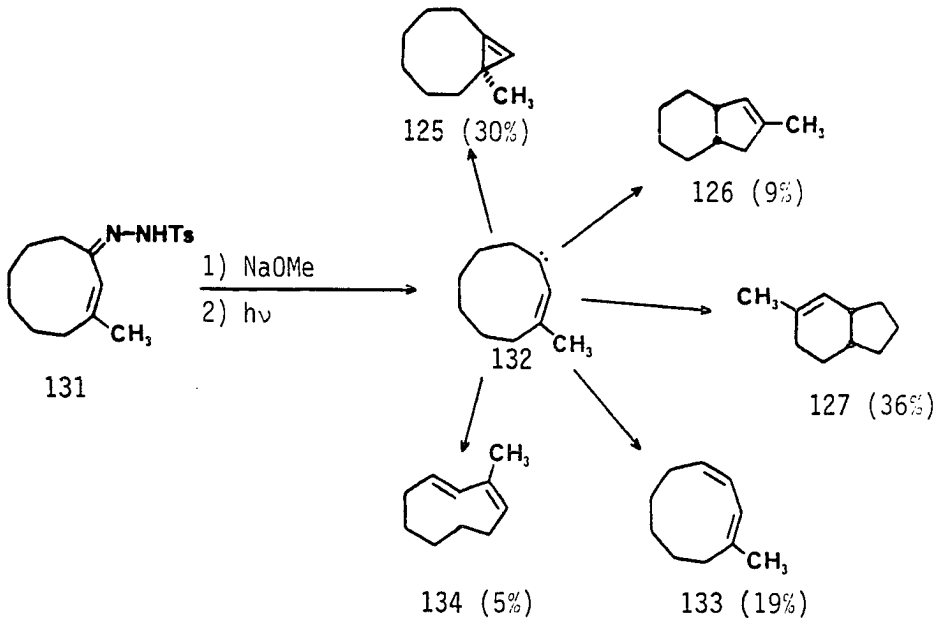
Scheme 44



131

Treatment of 3-methylcyclonon-2-en-1-one tosylhydrazone (131) in THF with sodium methoxide, followed by irradiation through Pyrex, led in 82% yield to a mixture composed of 5 isomeric hydrocarbons (m/e 136), as determined by GC-MS. These were all isolated by preparative scale GLC and were identified as shown in Scheme 45.

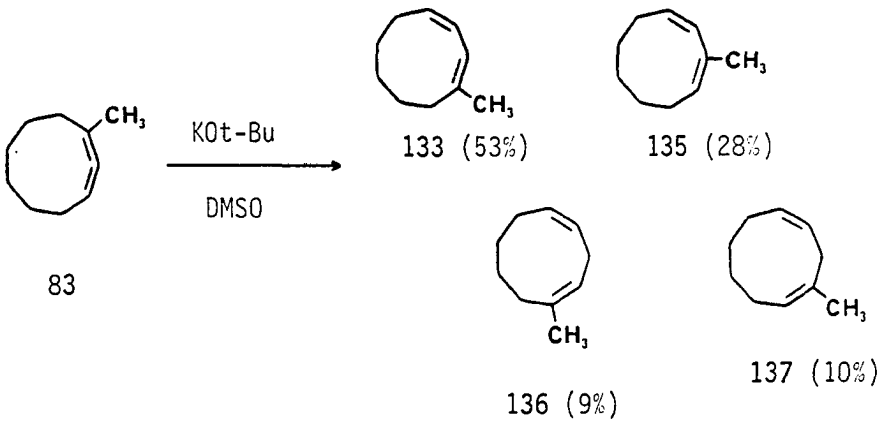
Scheme 45



The behavior of 3-methyl-cyclonon-2-enylidene (**132**) thus appears to be similar to that of the parent vinylcarbene, cyclonon-2-enylidene (**108**). Ring closure to afford cyclopropene products is a major process in each vinylcarbene. Additionally, the exclusive cis stereoselectivity observed in the formation of transannular insertion products (**126** and **127**) again accords with reaction from a singlet vinylcarbene. Both cis-cis and cis-trans 1,3-dienes result from each vinylcarbene, however, methyl substitution in **132** allows some interesting mechanistic insight. The cis-cis-1,3-cyclononadiene observed in the reaction of **132** is methyl substituted solely in the 1 position, while the cis-trans-1,3-cyclononadiene is methyl substituted exclusively in the 2 position. This demonstrates that the cis-cis diene arises via a 1,2-hydrogen shift, while the cis-trans diene arises via a 1,4-hydrogen shift. Examination of molecular models indicates that the favored conformations for each process may dictate the resultant stereochemistry.

An authentic sample of cis-cis-1-methyl-1,3-cyclononadiene (**133**) was prepared by the base catalyzed isomerization of 1-methyl-1,2-cyclononadiene (**83**), using the procedure described by Vaidyanathaswamy and Devaprabhakara for the similar isomerization of 1,2-cyclononadiene (**8**).[29] Treatment of **83** with potassium t-butoxide in DMSO led to a mixture composed of 4 isomeric products. These were isolated by preparative scale GLC and were identified as the methyl-substituted 1,3-dienes **133** and **135**, and 1,4-dienes **136** and **137** (Scheme 46).

Scheme 46



The 1,3-dienes **133** and **135** are both known compounds, and were identified by comparison of their 300 MHz ^{1}H NMR spectra with those reported.[41] The 1,4-dienes **136** and **137** were characterized primarily by their 300 MHz ^{1}H NMR spectral data. The assigned cis-cis stereochemistry in all 4 compounds is based upon the observed disubstituted double bond coupling constants and by analogy with reaction of the parent system, where only cis-cis isomers were observed.

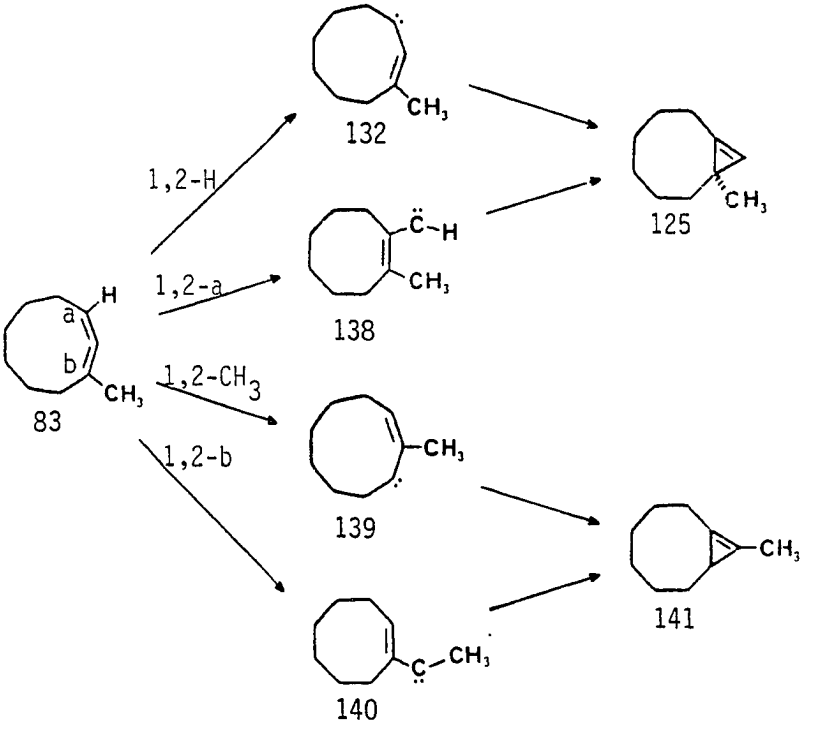
cis-trans-2-Methyl-1,3-cyclononadiene (**134**), observed in the reaction of vinylcarbene **132**, was identified by spectral and chemical data. The 300 MHz ^{1}H NMR spectrum suggested a methyl substituted 1,3-diene moiety was present, and the trans configuration in the disubstituted double bond was indicated by the observed 16 Hz coupling constant. The chemical shift for the methyl group, δ 1.78, verified its substitution on the diene moiety. Methyl substitution at C_2 of the diene was deduced by the absence of a characteristic broad singlet

observed in the vinyl region for the proton at the 2 position in 1-methyl substituted-1,3-cyclononadienes. Finally, the proposed structure was confirmed by the facile photochemical isomerization of **134** to the known cis-cis-2-methyl-1,3-cyclononadiene (135), an authentic sample of which was in hand.

Synthesis of 9-methylbicyclo[6.1.0]non-1(9)-ene and the chemistry of 1-cyclooctenyl-1-ethylidene

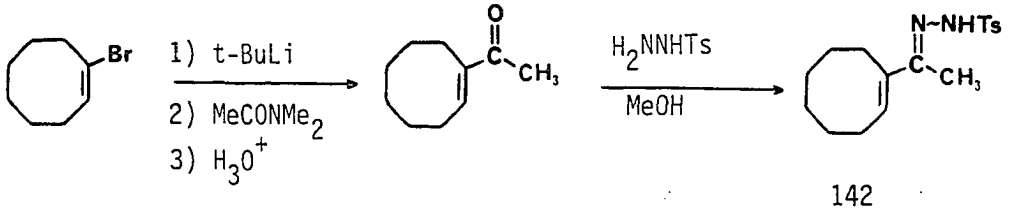
The deuterium isotope effect measured for the photorearrangement of 1,2-cyclononadiene (**8**) to bicyclo[6.1.0]non-1(9)-ene (84) suggested that hydrogen, rather than carbon, was migrating in the singlet photoreactions of **8**. The photolysis of 1-methyl-1,2-cyclononadiene (83) afforded an additional opportunity to determine if carbon migration is able to compete with hydrogen migration. In allene **83**, there are 4 potential 1,2-migrations (Scheme 47). These may lead to isomeric cyclopropenes **125** or **141**. If methyl or alkyl migration is able to compete with hydrogen migration, the presence of 9-methylbicyclo[6.1.0]non-1(9)-ene (**141**) in the photolysate would be expected, as closure of vinylcarbenes to cyclopropenes is almost invariably facile.

Scheme 47



A sample of 9-methylbicyclo[6.1.0]non-1(9)-ene (141) was conveniently obtained from the generation of vinylcarbene 140, via photolysis of the corresponding tosylhydrazone sodium salt. The tosylhydrazone precursor (142) was prepared as shown in Scheme 48.

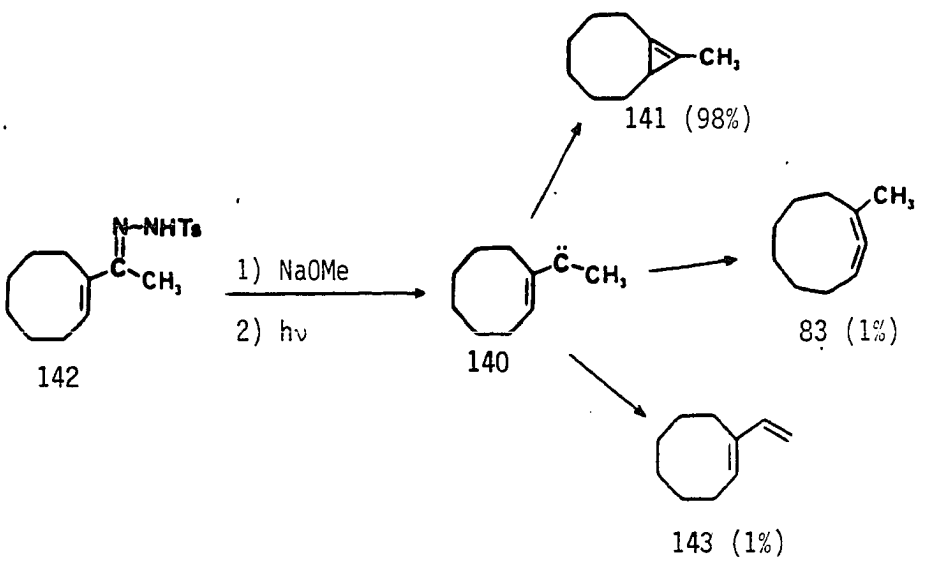
Scheme 48



142

Treatment of 1-acetylcyclooctene tosylhydrazone (**142**) in THF at -15°C with sodium methoxide, followed by irradiation through Pyrex, led in 51% yield to nearly pure (98%) cyclopropene **141**, with two minor isomeric products (m/e 136), as determined by GC-MS. Cyclopropene 141 was isolated by preparative scale GLC, and identified by comparison of its 300 MHz ^{1}H NMR spectrum with that reported.[27a] This was previously prepared by an entirely different route. The minor components, **83** and **143**, were identified by analysis of the 300 MHz ^{1}H NMR spectrum of the crude reaction mixture.

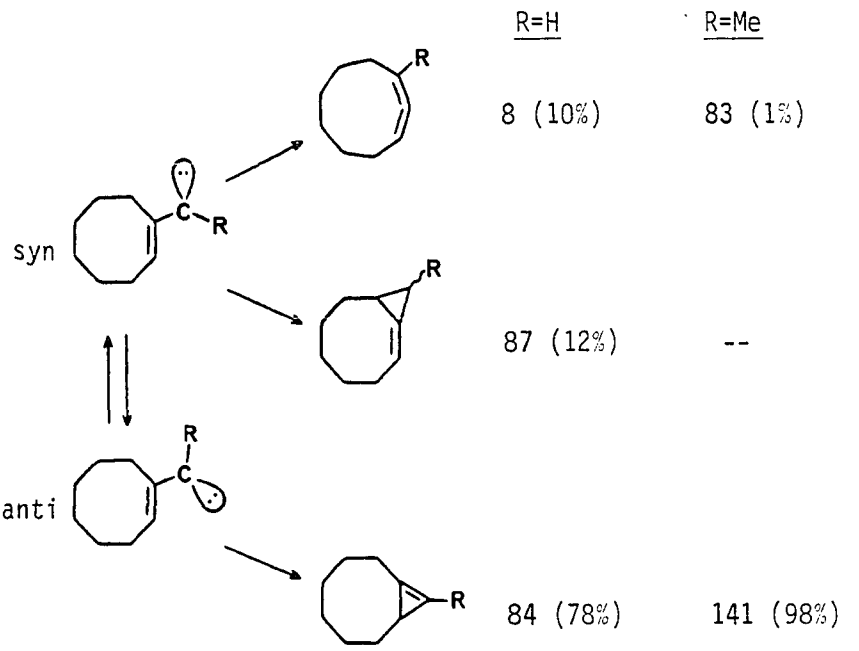
Scheme 49



Comparison of the behavior of vinylcarbene **140** with that of the unsubstituted analog, **109**, reveals that methyl substitution leads to the near exclusive formation of the cyclopropene product (Scheme 50). The significant amounts of allene **8** and methylenecyclopropane

87, which had been observed in the reaction of 109, are not paralleled in the reactions of 140. This behavior may be ascribed to differing chemistry of the possible syn and anti isomers for vinylcarbenes 109 and 140 (Scheme 50). The geometries of syn-109 and syn-140 appear to favor methylenecyclopropane formation via C-H insertion, and allene formation via 1,2-carbon migration. The geometries of anti-109 and anti-140 appear to favor cyclopropene formation via electrocyclic ring closure. Thus, methyl substitution may result in the preferential formation of anti-140 and lead to the near exclusive formation of cyclopropene product, as is observed. An alternative explanation is that the greater stability afforded vinylcarbene 140, due to its methyl substitution, may lead to greater selectivity in its reaction.

Scheme 50



With an authentic sample of 9-methylbicyclo[6.1.0]non-1(9)-ene (141) in hand, the photolysate from the irradiation of 1-methyl-1,2-cyclononadiene (83) was examined. No evidence for the presence of 141 could be observed by either capillary GLC analysis or 300 MHz ^{1}H NMR analysis of the mixture. This provides further evidence that carbon migration is not able to compete with hydrogen migration.

Discussion of 1-methyl-1,2-cyclononadiene singlet solution phase reaction mechanisms

In contrast to the solution phase singlet photoreaction of 1,2-cyclononadiene (8), where the rearrangement to cyclopropene 84 predominates and a concerted mechanism seems most likely, the solution phase singlet photoreaction of 1-methyl-1,2-cyclononadiene (83) appears to involve the intermediacy of 3-methylcyclonon-2-enylidene (132). This is evidenced by the observation of substantial amounts of the bicyclic olefins 126 and 127, in addition to cyclopropene 125, as primary photoproducts in the reaction of 83. These three products were formed in the independent generation of vinylcarbene 132, along with the 1,3-dienes 133 and 134. The 1,3-dienes 133 and 134 were not observed in the photoreaction of 83, however, their secondary photoreactions would be expected to be extremely facile. Indeed, upon irradiation of a pure sample of cis-trans-2-methyl-1,3-cyclononadiene (134), a very rapid conversion to the cis-cis isomer 135 was noted. The irradiation of a pure sample of cis-cis-1-methyl-1,3-cyclononadiene (135) also led to the formation of cis-cis-2-methyl-1,3-cyclo-

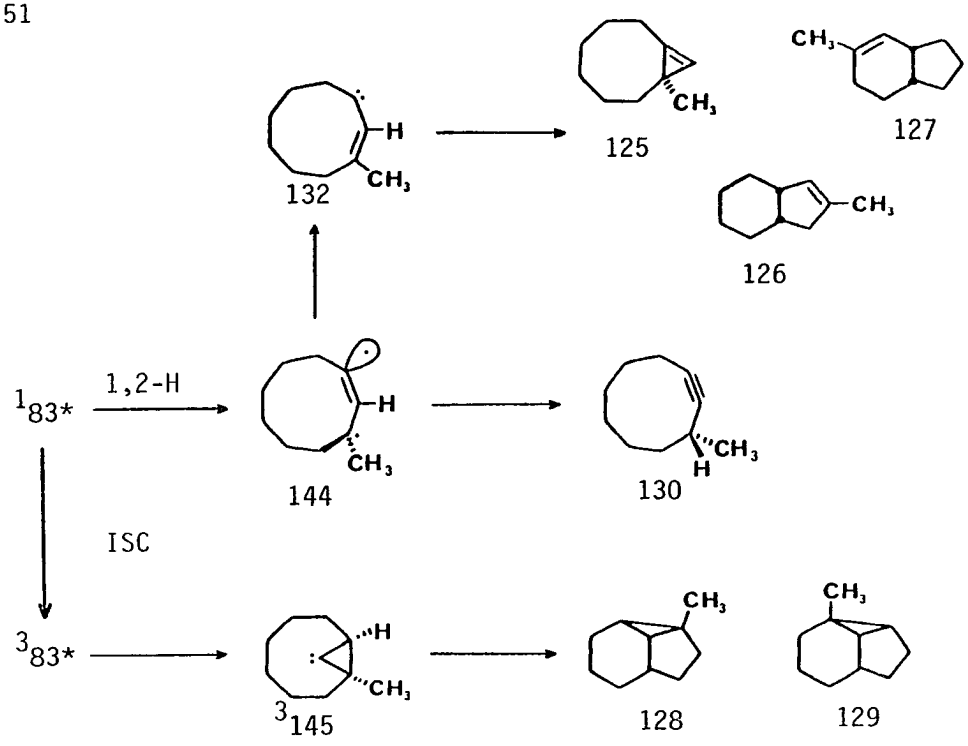
nonadiene (135) as the major product. cis-cis-2-Methyl-1,3-cyclononadiene (135) was observed as a secondary photoproduct in the reaction of 83, thus, it appears that all the products obtained in the independent generation of vinylcarbene 132 may also be formed in the photoreaction of 1-methyl-1,2-cyclononadiene (83).

The tricyclic products 128 and 129 may arise via triplet cyclopropylidene 145, in a process analogous to that postulated in the photoreaction of allene 8. The mechanism proposed for the formation of 3-methylcyclononyne (130) is also identical to that suggested in the photoreaction of allene 8. Scheme 51 shows the proposed pathways to the products observed upon irradiation of 1-methyl-1,2-cyclononadiene (83).

The vinylcarbene pathway proposed in the reaction of 83, and the concerted pathway proposed in the reaction of 8, must be closely related. This is clear from the significant changes induced by simple methyl substitution. One plausible explanation for this effect is that the stabilization afforded vinylcarbene 132 by methyl substitution, may favor the vinylcarbene pathway. Alternatively, methyl substitution may affect conformational changes in vinylcarbene intermediates, leading to the observed result.

The potential energy diagram depicting the observed reaction pathways (Figure 2), may perhaps be useful in rationalizing the effect of methyl substitution. The potential energy surfaces calculated would be expected to be highly dependent upon structure. Methyl substitution on the allene moiety may lead to a variation in the surfaces

Scheme 51



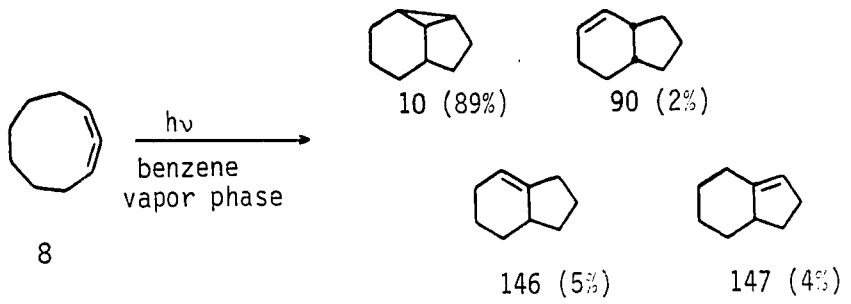
such that the minimum on the excited surface may be geometrically closer to the ground transition state **120**, leading to alkyne and vinylcarbene. This interpretation would also explain the observation of a much larger percentage of cycloalkyne product in the photoreaction of 1-methyl-1,2-cyclononadiene (**83**).

Triplet Vapor Phase Photochemistry of Cyclic Allenes

Benzene sensitized vapor phase irradiation of 1,2-cyclononadiene

Irradiation at 254 nm of a vapor phase mixture of 1,2-cyclononadiene (**8**) and benzene afforded predominantly tricyclo[4.3.0.$0^{2,9}$]nonane (**10**), as previously reported by Ward and Karafiath.[3] More careful scrutiny, however, reproducibly showed three minor isomeric (GC-MS) products to be present (Scheme 52). The ratio of these to tricyclic **10** was invariant from 3% to > 90% conversion of **8**, thus all are primary photoproducts. The four products were isolated by preparative scale GLC. Isomers **146** and **147** were identified by comparison of their ^{1}H and ^{13}C NMR spectra with those reported previously,[42] while isomer **90** was in hand from previous studies.

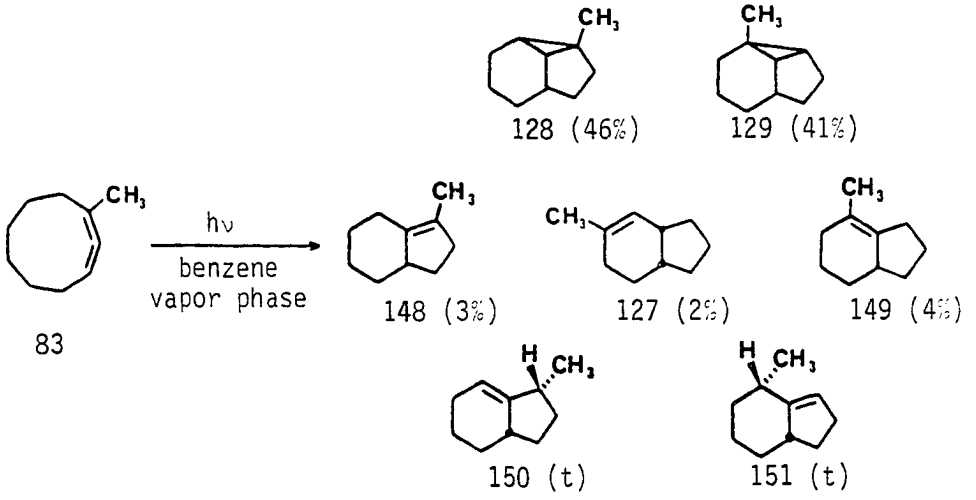
Scheme 52



Benzene-sensitized vapor-phase irradiation of 1-methyl-1,2-cyclononadiene

Irradiation at 254 nm of a vapor phase mixture of 1-methyl-1,2-cyclononadiene (**83**) and benzene resulted in the predominant formation of two products, identified as 9-methyltricyclo[4.3.0.$0^{2,9}$]nonane (**128**) and 2-methyltricyclo[4.3.0.$0^{2,9}$]nonane (**129**). As in the identical reaction of **8**, careful analysis of the product mixture revealed 5 minor isomeric (GC-MS) products were present in amounts varying from 2-4% (Scheme 53). Trace amounts of olefins 150 and 151 were also observed by 300 MHz ^{1}H NMR. The primary nature of the products shown in Scheme 53 was demonstrated by the examination of product ratios as a function of conversion (from 18% to 97%).

Scheme 53



Tricyclics **128** and **129** were isolated by preparative scale GLC and were characterized by their spectral data (^{1}H and ^{13}C NMR, IR, and HRMS). The 300 MHz ^{1}H NMR spectrum of each isomer was similar to that of the parent compound **10**. Each isomer, however, lacked one of the upfield resonances observed in **10**, which indicated that tricyclics **128** and **129** were formed. The assignment of these structures to the specific components isolated was made by comparison of their 300 MHz ^{1}H NMR spectra with those of tricyclo[4.4.0.$0^{2,10}$]decane (**152**)[43] and tricyclo[3.3.0.$0^{2,8}$]octane (**153**).[44] The two equivalent cyclopropyl protons in **152** are observed at δ 0.76, whereas in **153** they are observed at δ 1.27. Thus, structure **128** was assigned to the component displaying an upfield resonance at δ 0.70-0.64, while structure **129** was assigned to the component having no resonances in this region.

152 153

Figure 3. Related Tricyclic Structures

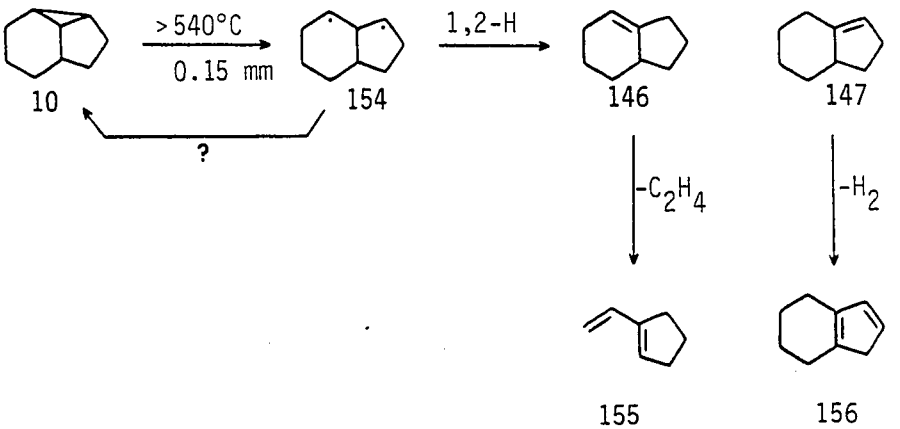
Confirmation of the tricyclic structure assignments was obtained from their thermolyses, which will be described later. Larger quantities of the bridgehead olefins **148**, **149**, **150**, and **151** were isolable from these thermolyses, and their characterization will also be described later. Two minor olefinic products (2-4% each) were not isolable in sufficient quantity and purity to permit their identification.

Independent generation of potential 1,3-diradical intermediates

1,2-Hydrogen migration from 1,3-diradicals to afford olefinic products is well-known. Therefore, 1,3-diradical **154** was believed to be the most likely precursor to olefins **146** and **147**, observed in the vapor phase benzene sensitized reaction of **8**. The flash vacuum thermolysis of tricyclic **10** offered a straightforward thermal route to **154**. Passage of **10** through a quartz tube at 540°C and 0.15 mm in standard fashion led cleanly to a 1:1 mixture of **146** and **147**, the result of homolysis of the most strained σ bond (Scheme 54). At higher temperatures, olefins **146** and **147** underwent secondary conversion to 1-vinylcyclopentene (**155**) and bicyclo[4.3.0]nona-1(6),7-

diene (156) via loss of ethylene and H_2, respectively. Both reactions are well-precedented. 1-Vinylcyclopentene (155) was characterized by its spectral data (MS, ^1H NMR), and bicyclo[4.3.0]nona-1(6),7-diene (156) was identified by comparison of its 300 MHz ^1H NMR spectrum with that reported.[45]

Scheme 54

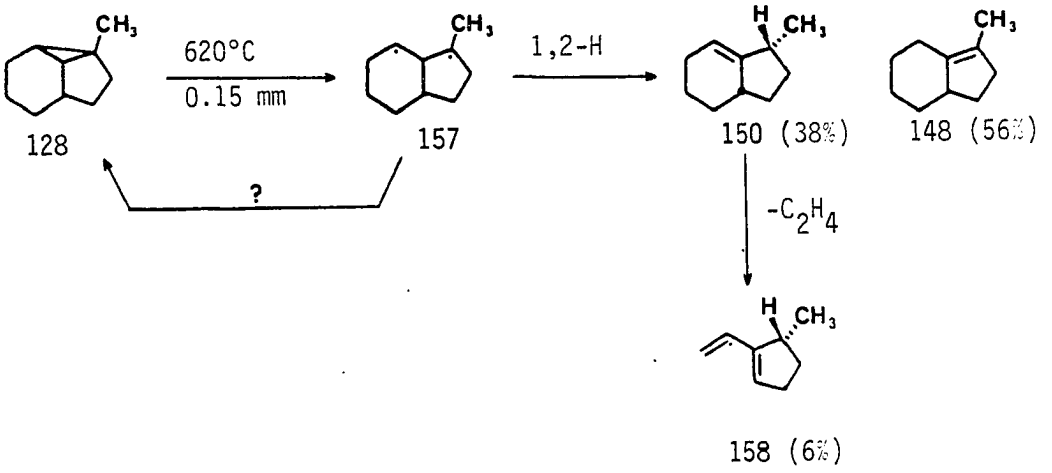


The formation of olefins 148, 149, 150, and 151 in the vapor phase benzene sensitized reaction of methyl derivative 83 is also suggestive of 1,3-diradical intermediates. The two potential precursors to these olefins, 1,3-diradicals 157 and 159, were generated by the same method used to obtain the parent 1,3-diradical 154, i.e., the flash vacuum thermolyses of pure samples of tricyclics 128 and 129.

Passage of 128 through a quartz tube at 620°C and 0.15 mm in standard fashion led to a mixture of three products identified as endo-9-methyl-bicyclo[4.3.0]non-1(2)-ene (150), 9-methylbicyclo-

[4.3.0]non-1(9)-ene (**148**), and 1-vinyl-5-methyl-cyclopentene (**158**), as shown in Scheme 55. Olefins **148** and **150** arise via 1,2-hydrogen migrations from 1,3-diradical **157**, while diene **158** undoubtedly is formed from secondary reaction of **150** in which ethylene is lost through a retro Diels-Alder reaction.

Scheme 55



The reaction products were identified by their spectral data (MS and ^{1}H NMR) and by analogy with the identical reaction of tricyclic **10**. Olefins **148** and **150** were demonstrated to be isomeric with tricyclic **128** by GC-MS analysis, while diene **158** resulted from loss of ethylene.

The 300 MHz ^{1}H NMR spectrum of **150** is consistent with the assigned structure. A broad singlet observed at δ 5.32 for one proton is similar in chemical shift and shape to the vinyl resonance observed

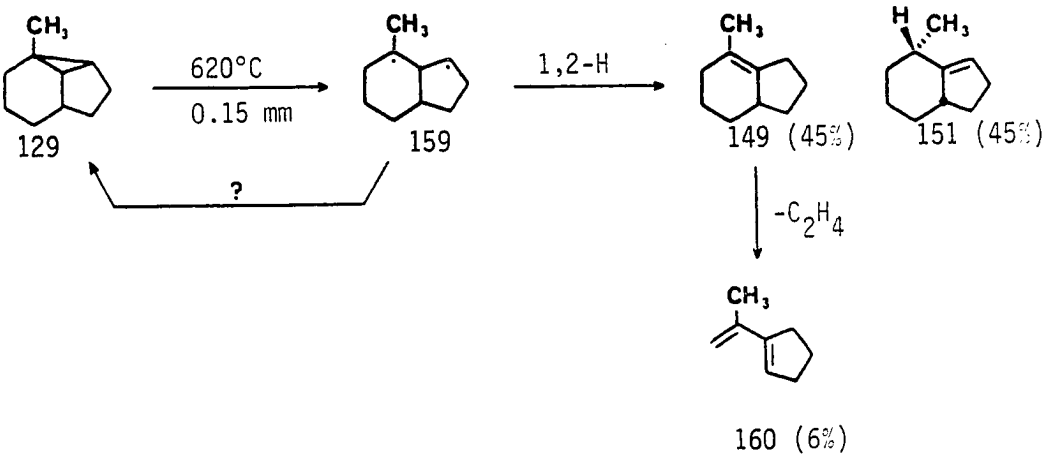
in the 300 MHz ^1H NMR spectrum of the parent compound **146**. The position of methyl substitution is specified by the structure determined for the retro Diels-Alder product **158**, and the proposed endo stereochemistry is based upon the suggested mechanism for the formation of **150** from **157**.

The 300 MHz ^1H NMR spectrum of **148** is very similar to that of the parent compound **147**. The lack of any vinyl resonance and the observed singlet at δ 1.60 for the methyl group supports the assigned structure.

Vinylcyclopentene **158** was also readily identified by its 300 MHz ^1H NMR spectrum. The observed vinyl resonances were very similar to those of the parent compound **155**. Allylic methyl substitution was deduced by the downfield shift of an allylic proton, and the specific assignment made is based upon the triplet observed for the vinyl cyclopentene proton.

Passage of **129** through a quartz tube, at 620°C and 0.15 mm, in standard fashion led to a mixture of three products identified as 2-methylbicyclo[4.3.0]non-1(2)-ene (**149**), and endo-2-methylbicyclo-[4.3.0]non-1(9)-ene (**151**) as shown in Scheme 56. As in the previous thermolyses, olefins **149** and **151** arise via 1,2-hydrogen migrations from 1,3-diradical **159**, and diene **160** is obtained from the retro Diels-Alder reaction of **149**.

Scheme 56



The reaction products were again isolated and identified by their spectral data (MS and ^{1}H NMR) and by analogy with the previously described thermolyses. GC-MS analysis of the mixture demonstrated olefins **149** and **151** were isomeric with tricyclic **129**, and that diene **160** resulted from loss of ethylene.

While the observed chemical shift for the methyl group (δ 1.57) in the 300 MHz ^{1}H NMR spectrum of **149** did not match the value reported in the literature (δ 2.10)[46], the spectrum obtained and the structure of the isolated retro Diels-Alder product **160** confirm the assignment. The 300 MHz ^{1}H NMR spectrum of **149** is very similar to that of the parent compound **146**. The lack of any vinyl resonance and the observed singlet at δ 1.57 for the methyl group provide support for the structure. It should be noted that the chemical shift for the methyl group is similar to that observed in the related compound **148**.

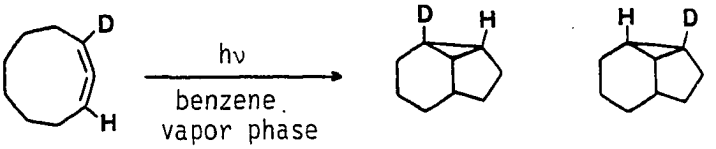
The 300 MHz ^1H NMR spectrum of **151** is very similar to that of the parent compound **147**. Perhaps most notable is the one proton triplet observed at δ 5.22, which is analogous to that observed in **147**. The proposed endo stereochemistry is again based upon the suggested mechanism for the formation of **151** from **159**.

Vinylcyclopentene **160** was readily identified by its 300 MHz ^1H NMR spectrum. The spectrum was very similar to that of the parent compound **155**, and the methyl substitution at the vinylic site was deduced by the absence of the downfield vinylic resonance, which was observed in **155**.

Deuterium kinetic isotope effect on the triplet photorearrangement of 1,2-cyclononadiene

Irradiation at 254 nm of a vapor phase mixture of benzene and 1-deuterio-1,2-cyclononadiene (**8-d**), prepared as described previously, afforded as the major product, tricyclic **10-d** (Scheme 57). This material was isolated by preparative scale GLC and analyzed by ^2H NMR. The spectrum displayed two cyclopropyl resonances at δ 1.27 and δ 0.78, of equal area, within experimental error. The assignment of the positions of deuterium substitution is based upon the arguments presented earlier for the characterization of the methyl-substituted tricyclics **128** and **129**.

Scheme 57



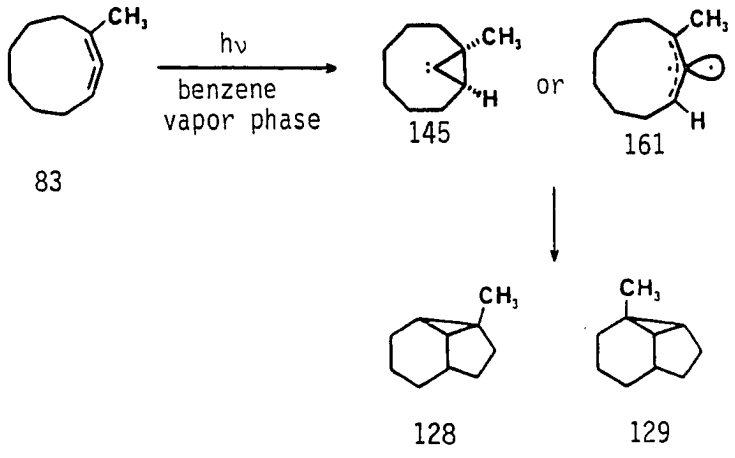
8-d 10-d (1:1)

Benzene sensitized vapor phase irradiation of optically active 1-methyl-1,2-cyclononadiene

The triplet vapor phase photorearrangement of allene 8 to tricyclic 10 has been proposed to proceed through a cyclopropylidene intermediate.[3] A planar triplet allene species may also lead to the observed tricyclic product, although this initially seemed less likely. Optically active 1-methyl-1,2-cyclononadiene (83) was prepared and irradiated in order to further probe the mechanism of the allene to tricyclic triplet vapor phase photorearrangement.

The two potential intermediates, which we consider may be directly formed from allene 83 and lead to the tricyclics 128 and 129, are shown in Scheme 58. Cyclopropylidene 145 is inherently chiral, while the planar biradical 161 is achiral. In principle, reaction via the cyclopropylidene pathway might transform optically active 83 into optically active 128 and 129, if stereospecific triplet closure occurs.

Scheme 58



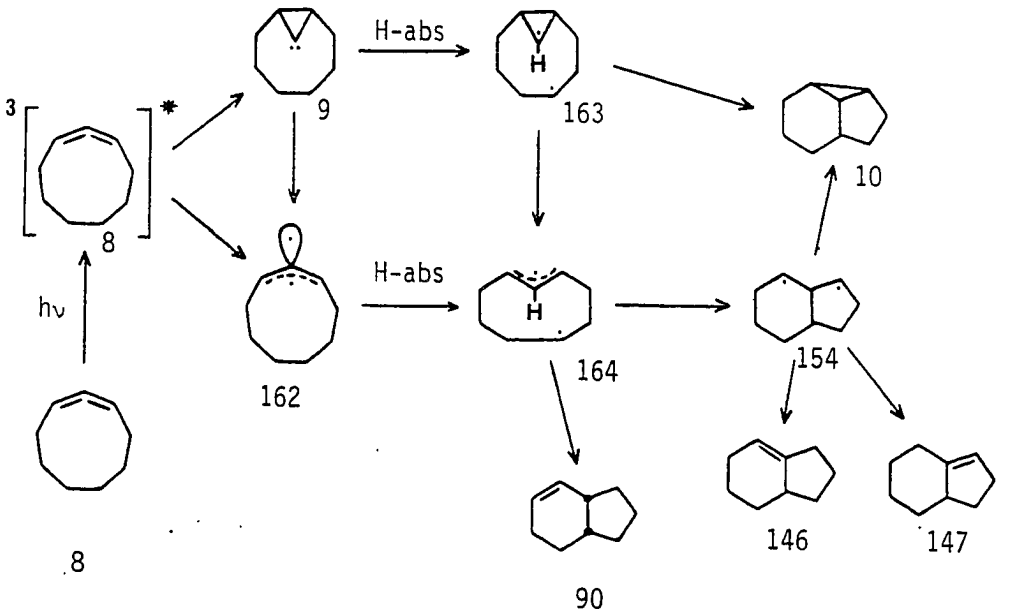
The procedure of Byrd and Caserio,[33] involving partial hydroboration with a chiral reagent, was employed (see Experimental Section) to obtain optically active 83 with $[\alpha]_D$ = +67° (ca. 2.5, $CDCl_3$). Although the optical purity of this allene is unknown, analogy to the parent allene suggests 15-30%. Irradiation at 254 nm of a vapor phase mixture of this material and benzene was followed by preparative scale GLC isolation of 128 and 129. Each tricyclic was found to be inactive within detection limits at the sodium D line. These measurements were made with ca. 30 mg of each tricyclic, which should be sufficient to observe a rotation of $[\alpha]_D > 0.7°$.

Discussion of cyclic allene triplet vapor phase photochemistry

In the vapor phase benzene sensitized photoreaction of 1,2-cyclononadiene (8), we considered two potential intermediates to be accessible directly from triplet excited 8: triplet cyclopropylidene

9 and planar triplet allene 162. Reaction pathways leading to all of the observed products may be drawn from either species (Scheme 59).

Scheme 59



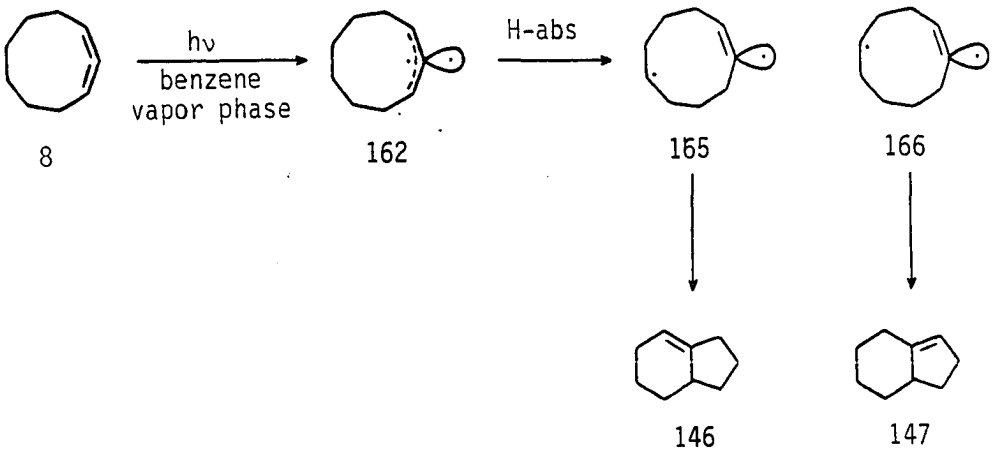
Along one pathway, triplet cyclopropylidene 9 may abstract a transannular hydrogen to afford 163, which may then close to tricyclic 10 following intersystem crossing, or ring open to give 164. Diradical 164 can close directly to 90, following intersystem crossing or, alternatively, may undergo bridging to the central carbon of the allyl radical to afford 1,3-diradical 154. At this point, three-ring closure or 1,2-hydrogen migration provide well-precedented routes to 10 or 146 and 147.

Planar triplet allene 162 may also explain the observed chemistry. Along this pathway, transannular hydrogen abstraction

would give diradical **164** from which all of the observed products may derive as previously mentioned.

An additional route to the bridgehead olefins **146** and **147** is via transannular hydrogen abstraction from planar triplet allene **162**, to afford vinyl diradicals **165** and **165** (Scheme 60). These diradicals may close directly to **146** and **147**, respectively, following intersystem crossing. Vinyl diradical **165** has been proposed as an intermediate in the photoreaction of cyclononyne (**85**), which gave **146** as the major product.[47]

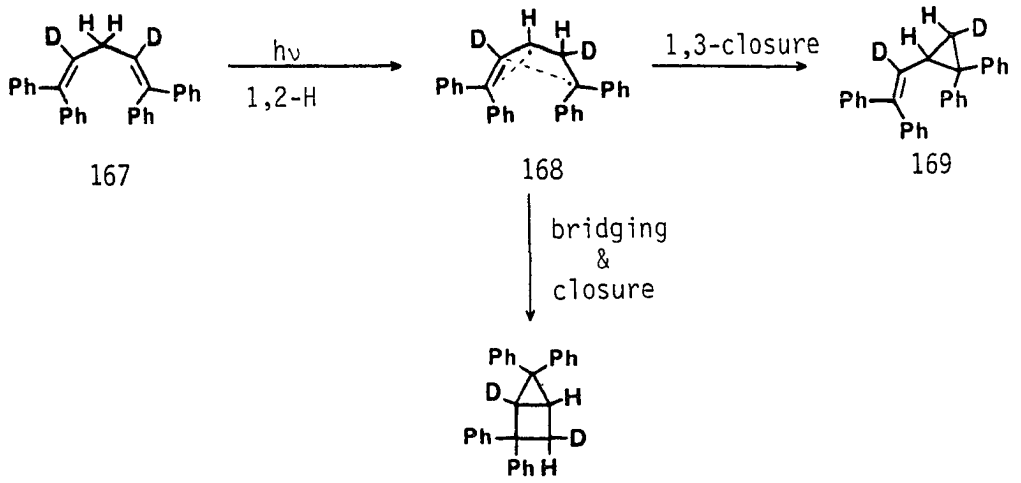
Scheme 60



Of the potential precursors to bridgehead olefins **146** and **147**, i.e. 1,3-diradical **154** or vinyl diradicals **165** and **166**, the former seems most likely. Indeed, the behavior of thermally generated **154**, especially the near-statistical product selectivity, corresponds very well with that postulated in Scheme 59. Moreover, the formation of allylic radical **164** from **162** would be expected to be favored over that of vinylic radicals **165** and **166**.

Perhaps the most difficulty encountered with the proposed intermediacy of **154** is its suggested formation from diradical **164**. Although coupling of an allyl radical at the central carbon is not generally expected, examination of models indicates that this process may be favored by proximity. Furthermore, there is literature precedence for such a process. In 1973, Zimmerman and Pincock described the photochemistry of 1,1,5,5-tetraphenyl-1,4-pentadiene (**167**).[48] The irradiation of deuterium labeled **167** suggested that 1,2-hydrogen migration was occurring. This was followed by either three ring closure to give vinylcyclopropane **169**, or bridging to the central carbon of the allyl radical to afford housane **170** (Scheme 61). Had the di-π-methane route to vinylcyclopropane **169** been operative, a different deuterium substitution in the product would have been observed.

Scheme 61



167 168 169

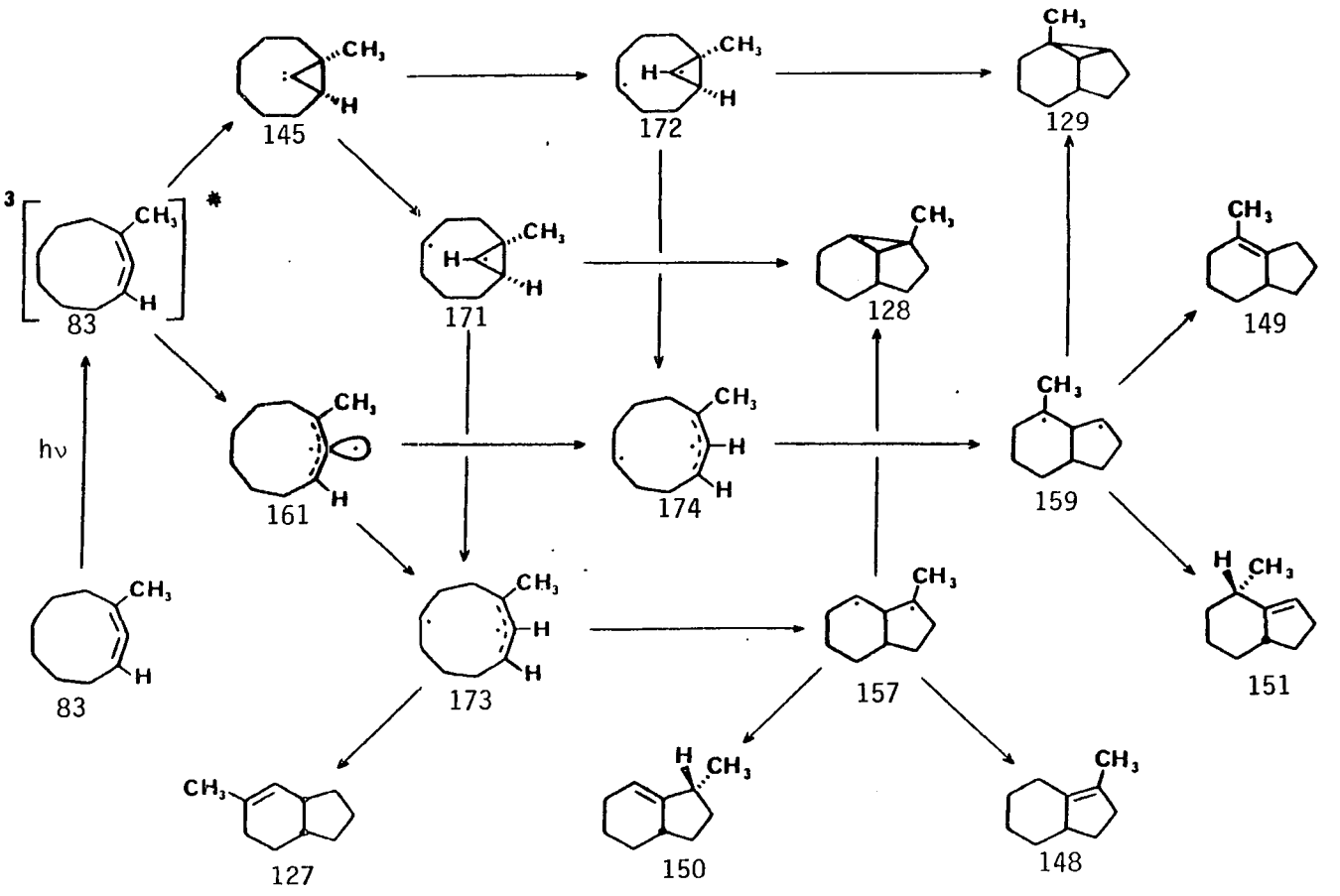
170

Although it appears that diradicals **154** and **164** are involved in the formation of the minor alkene products **90, 146** and **147**, the discussion presented thus far does not discriminate between their two possible origins. The lack of any observable deuterium isotope effects in the irradiation of 1-deuterio-1,2-cyclononadiene (8-d) implies a symmetrical intermediate, however, this result is also consistent with either pathway.

The benzene sensitized vapor phase photoreaction of 1-methyl-1,2-cyclononadiene (**83**) was very similar to that of **8**; tricyclic products accounted for ca. 87% of the isomeric mixture and corresponding minor olefinic products were identified. As in the reaction of **8**, planar triplet allene and triplet cyclopropylidene intermediates were considered to be accessible directly from triplet excited **83**. The pathways suggested in Scheme 62 are analogous to those presented earlier for the identical reaction of **8**.

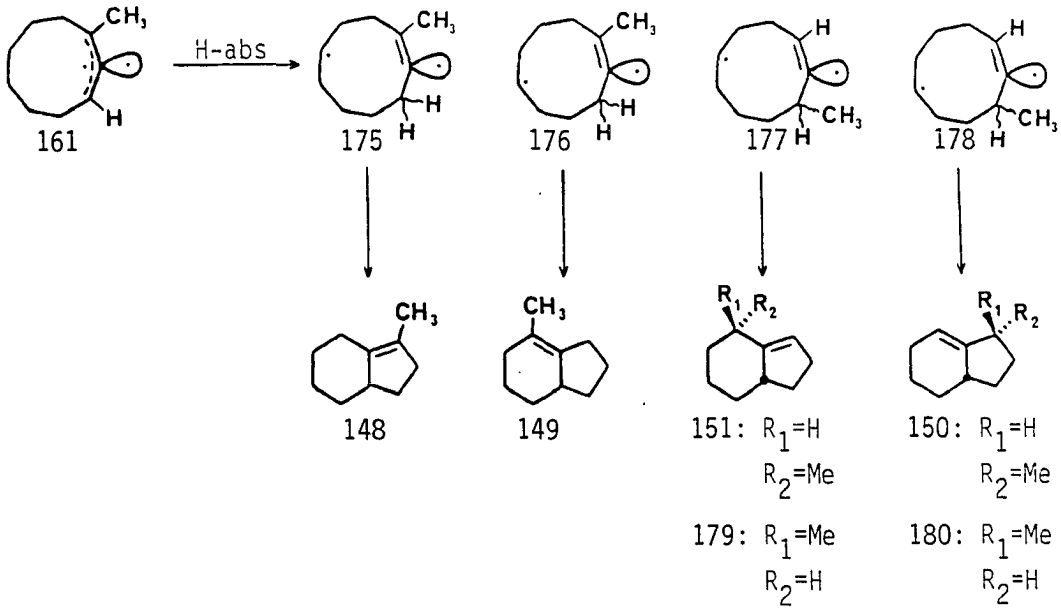
Also analogous to the reaction of the parent allene **8**, an alternative route to the bridgehead olefins **148, 149, 150,** and **151** is via transannular hydrogen abstraction from planar triplet allene **161**, to afford the vinyl radicals **175-178** (Scheme 63). As in the reaction of **8**, however, the intermediacy of 1,3-diradicals (**157** and **159**) seems more likely. The tetrasubstituted olefins **148** and **149** are formed in much larger amounts than the trisubstituted olefins **150** and **151**, a result which may be readily accounted for by preferential 1,2-hydrogen migration in 1,3-diradical species **157** and **159**. Although thermally generated **157** and **159** did not display this near exclusive selectivity,

Scheme 62


3
CH3
H
83
hν
83
145
171
161
172
174
173
129
128
159
149
151
157
127
150
148

in both cases the tetrasubstituted olefin formation was favored (ca. 56/44 and ca. 51/45). Under the conditions of the photolysis of **83**, diradicals **157** and **159** would be formed at much lower temperatures, and a greater selectivity would be expected.

Scheme 63



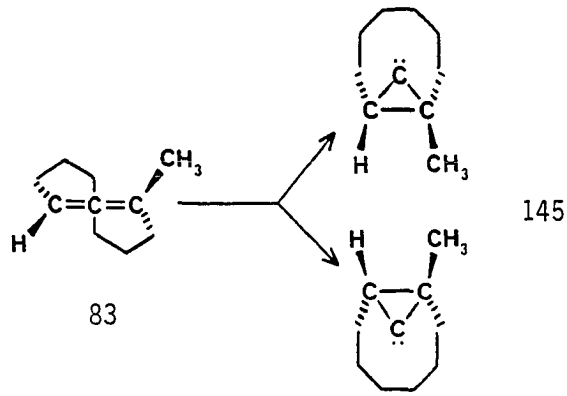
The formation of vinyl radicals **175-178** again seems unlikely, as the formation of allylic radicals **173** and **174** would be expected to be much more favorable. If these vinyl radicals were obtained, however, the selective formation of olefins **148** and **149** could be rationalized by suggesting the preferential formation of **175** and **176**. These vinyl radical species may be favored due to their methyl substitution. At any rate, if vinyl radicals **175-178** are intermediate, the exo isomers of **150** and **151** should also be observed. That only trace amounts of

150 and **151** were found, makes it difficult to determine if the exo isomers are formed. Authentic samples of each would be needed to rigorously exclude their formation.

While the irradiation of optically active **83** afforded an opportunity to distinguish between the two potential intermediates which may be formed directly from the allene, i.e., triplet cyclopropylidene **145** or planar triplet allene **161**, the results for this experiment were not definitive. The failure to detect any optical rotation in the isolated samples of **128** and **129** does not necessarily mitigate against **145**. This is because the allene may be rapidly racemizing and/or the triplet cyclopropylidene **145** may not be forming stereospecifically.

Racemization of the allene is undoubtedly a competitive reaction, however, if the quantum yield for tricyclic product formation is ca. 0.17 (as reported for the reaction of **8**[3]), then the tricyclic products may still have been expected to be optically active. If we examine one enantiomer of allene **83** and the mode of formation of cyclopropylidene **145**, we find that **145** may not be forming stereospecifically (Scheme 64). Moving the central carbon of the allene moiety up gives one enantiomer of **145**, while moving it down gives the other. The methyl substituent is the only factor present which might affect a preference for one motion over the other, and it may not be effective in doing so.

Scheme 64



83 145

Recent calculations and literature data allow the construction of a state correlation diagram for triplet allene (25) conversion to either triplet cyclopropylidene (37) or planar triplet allene (181), along C_2 bending and twisting coordinates (Figure 3). The relative energies (eV) listed are from ab initio studies, or from experiment. Geometries and energetics for the cyclopropylidene singlet and triplet states were calculated with a TCSCF (two-configuration SCF) wavefunction for the singlet ($^1A_1$) and ROHF (spin-restricted open shell Hartree-Fock) wavefunction for the triplet.[49] A split-valence 3-21G basis was augmented with a full set of polarization functions (d orbitals) at C_1. This general approach has proved satisfactory for most carbenes.[50] Using this basis set and level of calculation, total energies (hartrees) and relative energies (kcal/mol) for the singlet and triplet of cyclopropylidene are as follows: $^1A_1$ -115.17606 (0.0); $^3B_1$ -115.15250 (14.8). While the precise magnitude of this gap may change with higher level calculations, we believe the state ordering to be quite secure. Thus, in keeping with general ideas of energy vs.

bending angle in carbenes,[51] we predict cyclopropylidene to have a singlet ground state, ca. 0.6 eV below the triplet. Energies for cyclopropylidene relative to allene are not available from experiment. For the singlet, very high level ab initio calculations predict 2.7[36] or 2.8[52] eV, values significantly lower than previous predictions.[53] The triplet energy may be estimated from these energies and a singlet-triplet gap of 0.6 eV.

As a result of recent MCSCF calculations, it has been concluded that the singlet also should be the ground state of planar C_{2V} allene ($^1A_2 < {}^3A_2$).[54] This is a consequence of better electron correlation for the singlet; at the SCF level, the triplet is slightly favored.[54] Planar singlet allene was calculated to lie 2.01 eV above allene **25**, while planar triplet allene was calculated to lie 2.22 eV above **25**. The singlet energy corresponds to the allene ground state rotational barrier and is in good agreement with experiment (ca. 2.1 eV).[55]

For allene T_1 and T_2, relative energies of 4.28 and 4.89 eV were determined by electron-impact studies.[56] Ab initio studies yielded comparable values: 4.89 and 5.08 eV.[57] Finally, energies for upper triplets of planar allene (**181**) and cyclopropylidene (**37**) were roughly estimated from 3-21G triplet CI calculations.[49] Both were found to lie above the allene vertical triplet energies.

Interestingly, the two lowest lying vertical triplet states of allene ($^3A_1$ and $^3B_2$) cannot be produced by triplet benzene sensitization, as indicated by Figure 4. Nevertheless, two previous

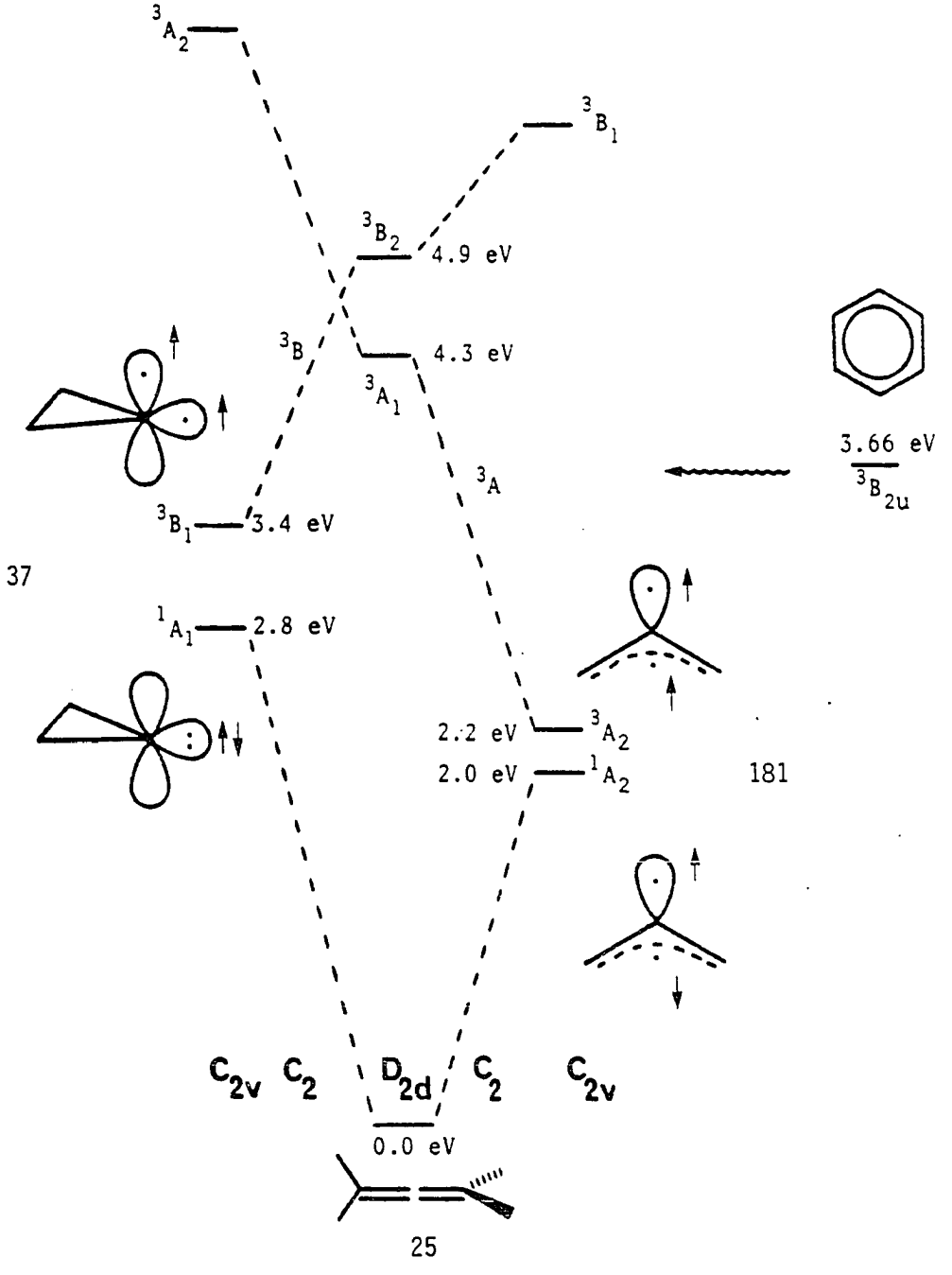


Figure 4. State Correlations for Allene

photophysical studies show allenes to efficiently quench benzene triplets.[21,58] A short-lived triplet exciplex provides a reasonable mechanism for this distinctly non-vertical energy transfer.

If we consider simple state correlations, we find that T_1 of allene formally correlates with the planar C_{2V} minimum **181**, while T_2 correlates with triplet cyclopropylidene **37**.[59] As allene triplets are usually generated from energy transfer, we conclude that, a priori, reaction might proceed to either triplet minimum if sufficient energy is available. Thus, energy transfer from triplet benzene (3.66 eV) can, in principle, lead to either a planar allene triplet (2.22 eV), or to the higher energy triplet cyclopropylidene (3.4 eV). Factors which determine the preference for these pathways remain unclear.

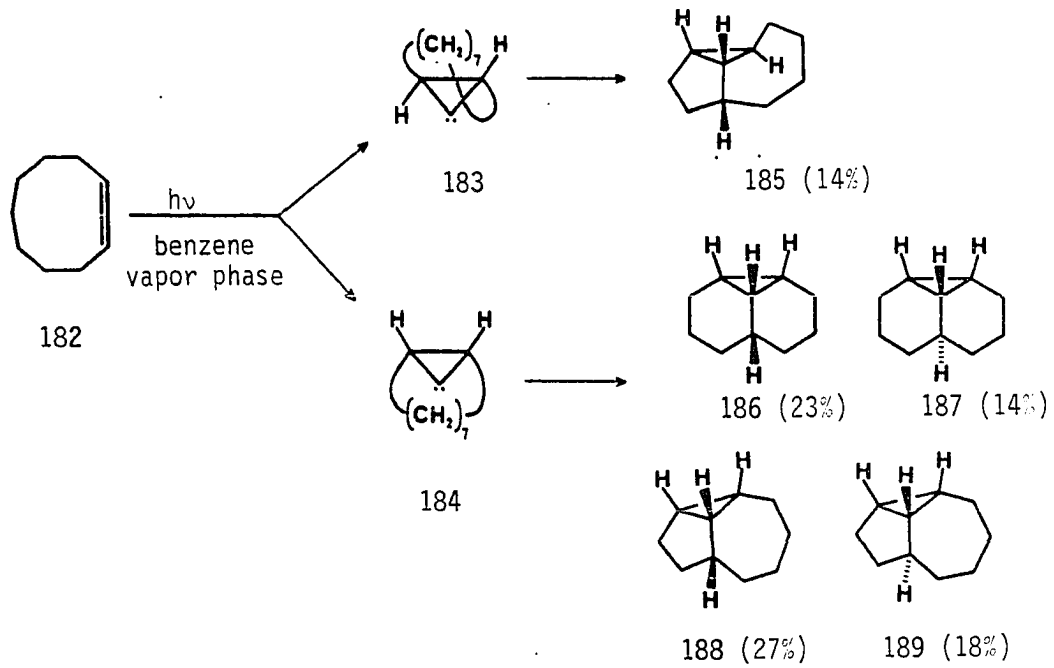
In summary, the triplet products from **8** and **83** can be accommodated through initial formation of planar triplet allene or triplet cyclopropylidene intermediates. Calculations indicate that, energetically, either may be obtained from triplet benzene sensitization. The observed minor olefinic products provide argument that bicyclic 1,3-diradicals and allylic radical species must be involved, but do not discriminate between the two previously mentioned origins.

The predominant formation of tricyclic products in each case appears to support the intermediacy of triplet cyclopropylidenes, as smaller amounts of these tricyclics would perhaps be expected to be obtained from the bicyclic 1,3-diradicals. Hydrogen abstraction by planar triplet allenes seems reasonable, however, and one cannot

completely exclude this possibility. Indeed, a duality of mechanisms may be operative, with the triplet cyclopropylidene pathway most likely predominating.

Perhaps the most compelling evidence favoring cyclopropylidene intermediates is obtained from the triplet vapor phase photoreaction of 1,2-cyclodecadiene (182), recently reported by Price and Johnson.[60] The large collection of three ring products observed (185-189), argues for the predominant formation of cis and trans cyclopropylidenes 183 and 184 (Scheme 65).

Scheme 65

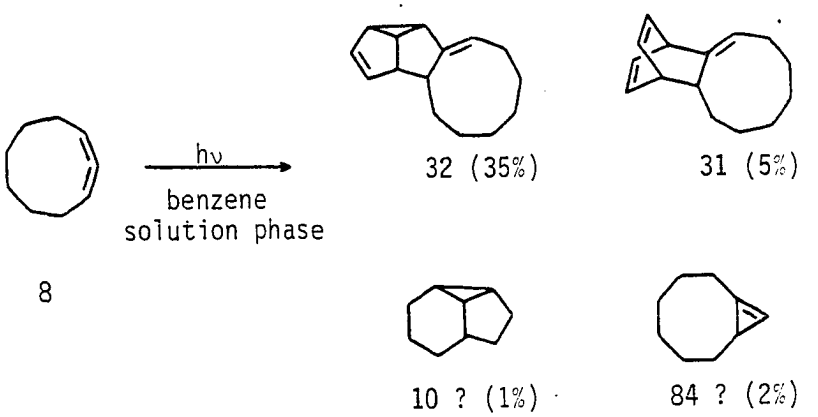


Triplet Solution Phase Photochemistry of 1,2-Cyclononadiene

Benzene sensitized solution phase irradiation of 1,2-cyclononadiene

Irradiation of 1,2-cyclononadiene (**8**) in benzene solution at 254 nm yielded mainly cycloadducts **31** and **32**, as previously reported by Bryce-Smith et al.[8] and Berridge et al.[9] These were accompanied by only small amounts of isomerization products, which are believed to be tricyclic **10** and cyclopropene **84** (Scheme 66). GLC analyses at varying conversions, using an internal standard, indicated that the isomeric products were primary and their yields were determined relative to reacted **8**.

Scheme 66



Cycloadducts **31** and **32** were identified by comparison of their 300 MHz ^{1}H NMR spectral data (from analysis of the crude reaction mixture) with those previously reported.[9] Our **31:32** ratio, which was reproducibly determined by 300 MHz ^{1}H NMR analysis of the crude

product, is exactly opposite to that reported.[9] The reason for this discrepancy is unclear, however, the reported ratio was determined by GLC analysis and some decomposition of the meta-cycloadduct may have occurred under these conditions. The preferred mode of cycloaddition for 8 was predicted to be meta,[9] and this appears to be what is happening.

The minor isomeric products, tricyclic 10 and cycloropene 84, were identified by comparison of their GLC retention times with those of authentic samples. Verification of their identities by 300 MHz ^1H NMR analysis of the crude mixture, however, was not possible.

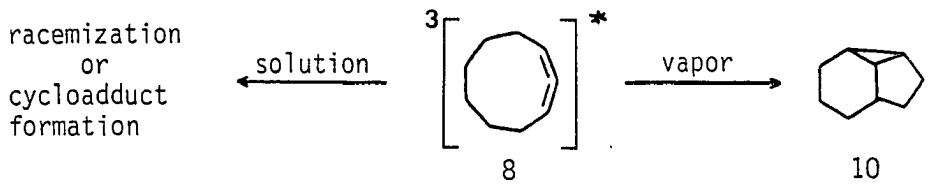
Benzene sensitized solution phase irradiation of optically active 1,2-cyclononadiene

The relative efficiency of triplet racemization of 8, to that of its other photoreactions, was determined by the irradiation at 254 nm of a benzene solution of an optically active sample, prepared as previously described. A plot of solution optical activity vs. loss of starting allene (relative to internal standard) according to equation 1 was linear (coorelation coefficient 0.99) and yielded $k_{racemization}/k_{reaction} = 60$. Thus, as in direct irradiation (presumably singlet), π bond rotation is the most facile triplet solution phase process.

Discussion of 1,2-cyclononadiene triplet solution phase photochemistry

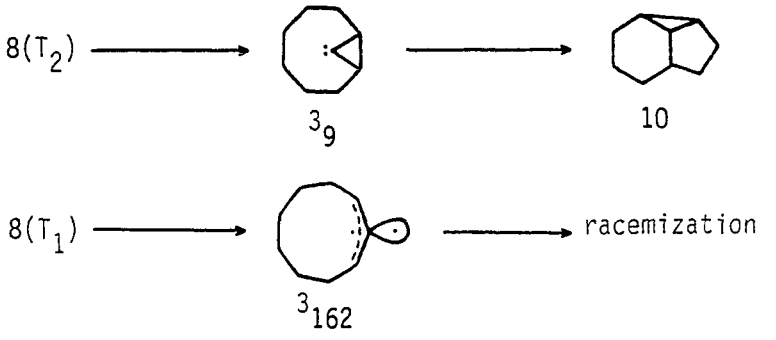
The benzene sensitized photoreaction of 1,2-cyclononadiene (8) was found to be highly phase specific. In the vapor phase irradiation tricyclo[4.3.0.$0^{2,9}$]nonane(10) is observed as the predominant photoproduct, while in solution only a small amount of 10 is observed. Although tricyclic 10 is not formed efficiently in benzene solution, energy transfer must occur since 8 is easily racemized. Thus, the observed phase specificity appears to derive from differing reactivities of triplet excited 8, depending upon the conditions under which it is obtained.

Scheme 67



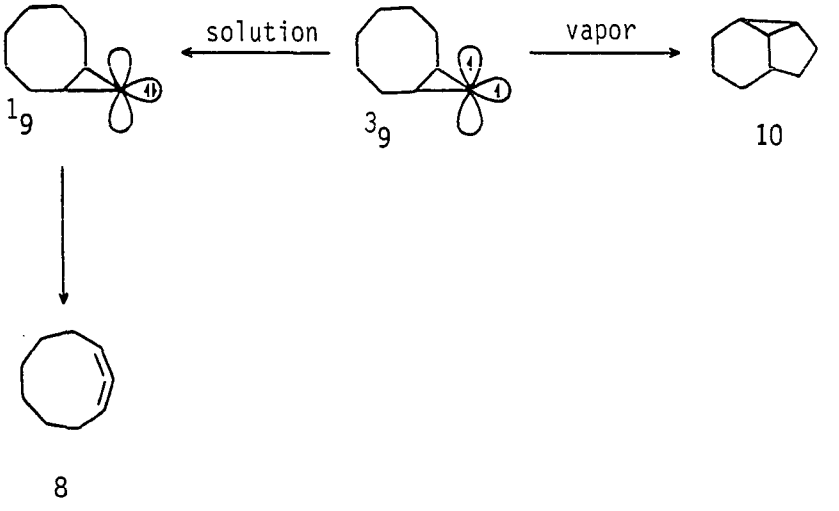
A plausible explanation for the observed medium effects can be presented based upon the state correlation diagram (Figure 4) for allene. If only the T_2 state of allene 8 leads to tricyclic 10, via cyclopropylidene 9, then one might expect to observe 10 only in the vapor phase reaction. In the vapor phase, closure to the cyclopropylidene may have a greater probability, since this requires dissipation of less energy. In solution, however, the more exothermic process should dominate, with the result that rotation to a planar allene is preferred and racemization of the allene is the predominant process observed.

Scheme 68



An alternative explanation is that the T_1 state of cyclopropylidene **9**, if formed in solution, may undergo rapid intersystem crossing to its S_0 state, which should rapidly open to starting allene **8**.

Scheme 69



The cycloaddition reaction observed in benzene solution probably involves exciplex formation between ground state 8 and singlet excited benzene, as discussed in the historical section.

CONCLUSION

The cyclic allenes examined in this study, 1,2-cyclononadiene (8) and 1-methyl-1,2-cyclononadiene (83), undergo a wide variety of fundamental photoreactions. The observed chemistry in strikingly dependent upon reaction conditions and structural variation. As expected, simple π bond rotation occurs from both singlet and triplet excited states, and is the most efficient reaction.

Photoisomerization of cyclic allenes to bicyclic cyclopropenes and cycloalkynes appears to be a general reaction, however, present evidence suggests that the mechanism is dependent upon structure. For 1,2-cyclononadiene (8), the cyclopropene product is formed almost exclusively and a concerted mechanism appears to be operative. This result contrasts with the similar photoreaction of linear phenyl allenes, where vinylcarbene intermediates have been implicated. The vinylcarbene and concerted pathways are closely related, and ring constraints in 8 may favor its effectively concerted rearrangement. Interestingly, the photoisomerization of 1-methyl-1,2-cyclononadiene (83) appears to proceed via a vinylcarbene intermediate. Why simple methyl substitution leads to the change in pathways is not yet clear.

Deuterium isotope effects observed here and in the reaction of triphenylallene, along with examination of the photoreaction of 83, indicate that 1,2-H migrations in allenes lead to the observed products. An initial 1,2-H migration in the allene singlet excited manifold may lead to cyclopropene directly in a concerted fashion or

to a vinylcarbene intermediate. A second 1,2-H migration from a bisected biradical geometry may lead to the observed alkyne products.

Only small amounts of tricyclic products are formed in the singlet photoreactions of 8 and 83. This contrasts with an earlier report, where tricyclic 10 was the sole product identified from the direct irradiation of 8.

Photoprotonation of 8 in methanol does not compete significantly with rearrangements, whereas the photoprotonation of phenyl allenes in methanol is the major process observed. Apparently, phenyl substitution increases the facility of photoprotonation of allenes.

β-Homolysis predominates in the vapor phase direct irradiation of 8 and appears to be an upper excited state reaction. A wide variety of products are observed and a discrete vinylcarbene intermediate may be involved, in contrast to the solution phase reaction.

Phase specific chemistry was also observed in the benzene sensitized reactions of 8. Benzene cycloaddition predominates in solution, whereas isomerization predominates in the vapor phase. The solution phase cycloaddition reaction most likely proceeds via a singlet exciplex.

In the vapor phase triplet manifold tricyclic products predominate, accompanied by small amounts of olefinic products. Triplet cyclopropylidene and planar triplet allene intermediates appear reasonable, however, the former seems most consistent with present data. Experiments with deuterated 8 and optically active 83 did not allow differentiation. The observed minor olefinic products suggest

that an interesting and unusual radical coupling to the central carbon of an allyl radical moiety is occurring.

EXPERIMENTAL

General

^{1}H NMR (300 MHz) spectra and ^{13}C NMR spectra were measured on either a Nicolet NT300 or a Bruker WM300 spectrometer. ^{1}H NMR (60 MHz) spectra were measured on a Varian EM360 spectrometer. All spectra were measured with $CDCl_3$ as solvent and TMS as reference.

Optical rotations were measured on either a Perkin-Elmer 141 or a Jasco ORD/CD spectropolarimeter.

Analytical gas chromatographic analyses were performed with a Hewlett-Packard 5793A instrument equipped with a flame ionization detector and an attached model 3390A integrator. The following columns were used: (A) Carbowax 20M capillary (25m at 60°C), (B) Dimethylsilicon capillary (25m at 100°C), (C) 10% Carbowax 20M (10' x 1/8" glass column at 100°C), and (D) 15% FFAP (6' x 1/8" stainless steel at 100°C).

Preparative gas chromatographic separations were performed on a Varian 920 gas chromatograph with a glass-lined injector. The following columns were used: (E) 15% Carbowax 20M (10' x 1/4" glass column at 100°C), (F) 10% SE-30 (10' x 3/8" stainless steel column at 60°C), (G) 20% SE-30 (10' x 3/8" glass column at 85°C), and (H) 15% Apiezon (10' x 1/4" stainless steel column at 120°C).

In all solution-phase photochemical experiments, spectroquality solvents were used. Argon was bubbled through the solution prior to and during irradiations. The light source was either a Rayonet RPR-

100 reactor, fitted with 185/254 nm, 254 nm, or 300 nm lamps, or a 450 W Conrad-Hanovia mercury lamp with a standard immersion-well apparatus.

Melting points are uncorrected.

1,2-Cyclononadiene (8)

1,2-Cyclononadiene (8) was prepared by the method of Skattebol and Soloman.[61] To a mechanically stirred slurry of cyclooctene (35.5 mL, 30 g, 027 mol) and potassium t-butoxide (45 g, 0.40 mol) in 150 mL pentane at 0°C was added dropwise a solution of bromoform (26.0 mL, 75 g, 0.30 mol) in 50 mL pentane. The mixture was then allowed to warm to room temperature and was stirred overnight. Water (200 mL) was added and the mixture was neutralized with 10% aqueous hydrochloric acid. The aqueous and organic layers were separated and the aqueous layer was extracted with pentane (2 x 100 mL). The pentane extracts were combined, washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Distillation yielded 9,9,dibromobicyclo[6.10]nonane (57.7 g, 0.205 mol, 76%) as a clear oil, B.P. 75-80°C at 0.025 mm (lit.[61] 62°C at 0.04 mm).

Methyllithium (55.0 mL of a 1.5 M sol'n, 83 mmol) was added dropwise to a solution of 9,9-dibromobicyclo[6.10]nonane (18.6 g, 66 mmol) in 100 mL dry ether maintained at -30°/-40°C. Stirring was continued for 30 min and then water (50 mL) was added carefully. The aqueous and organic layers were separated and the aqueous layer was extracted with ether (2 x 50 mL). The ether extracts were combined,

washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Distillation gave 7.0 g (57 mmol, 87%) of product as a clear oil, B.P. 52-53°C at 6 mm (lit.[61] 62-63°C at 16 mm). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.25 (quintet, 4.4 Hz, 2H), 2.29-2.17 (m, 4H), 1.85-1.34 (m,8H).

This material was found to be ca. 99.9% pure by capillary GLC analysis (column A). The retention time of the impurity present, 4.60 min, matches that of tricyclo[4.3.0.$0^{2,9}$]nonane (10).

Direct irradiation of 1,2-cyclononadiene (8) in pentane

A solution of 251 mg of 1,2-cyclononadiene (8) in 300 mL of pentane was irradiated for 9 h through a Vycor filter. The solution was concentrated under reduced pressure at 0° to give 240 mg of a clear oil. Capillary GLC (column A) and 300 MHz ^{1}H NMR analysis indicated 42% conversion to 11 products. These were isolated on a preparative scale (column E) and characterized by the identify of their capillary GLC (column A) retention times and ^{1}H NMR (300 MHz) spectra with those of authentic samples. GC-MS showed all components to be isomeric with starting material. Isolated products were as follows. **cis-Bicyclo[5.2.0]non-8-ene** (105, 2%, rt 3.07 min); **cis-Bicyclo[4.3.0]non-7-ene** (91, 18%, rt 3.07 min); **trans-Bicyclo[5.2.0]non-8-ene** (106, 4%, rt 3.17 min); **cis-Bicyclo[4.3.0]non-2-ene** (90, 14%, rt 3.70 min); **cis-Bicyclo[6.1.0]non-2-ene** (103, 2%, rt 4.00 min); **cis-cis-1,3-Cyclononadiene** (92, 2%, rt 4.07 min); **Bicyclo[6.1.0]non-1(9)-ene** (84, 36%, rt 4.45 min): ^{1}H NMR (300 MHz,

$CDCl_3$) δ 6.47 (br s, 1H), 2.71 (ddd, 14.5 Hz, 5.8 Hz, 3.8 Hz, 1H), 2.32 (dddd, 14.5 Hz, 10.8 Hz, 4.9 Hz, 1.9 Hz, 1H), 1.94-1.82 (m, 1H), 1.74-1.18 (m, 10H). ^{13}C NMR δ 126.6, 102.1, 33.2, 29.7, 26.7, 25.6, 25.5, 20.7, 16.7. IR (neat) 2920, 2850, 1780, 1460 cm^{-1}. UV (pentane) λ max < 185 nm. MS, m/e 121, 107, 93, 79, 67, high resolution MS (M^+ - H) 121.1012 (calculated 121.1017); Tricyclo-[4.3.0.$0^{2,9}$]nonane (10, 3%, rt 4.60 min); Bicyclo[6.1.0]non-1(2)-ene (87, 8%, rt 4.74 min); Unidentified (4%, rt 4.87 min); Cyclononyne (85, 7%, rt 8.68 min).

In other experiments, the reaction was monitored at low conversion (0.25-2%) and 84, 10, and 85 (ratio 94:3:3) were found to comprise > 95% of the primary products.

Irradiation of pentane solutions at 185 (+254) nm in the Rayonet apparatus did not alter the low conversion ratio.

Vapor phase direct irradiation of 1,2-cyclononadiene (8)

1,2-Cyclononadiene (5 μL) was placed into a 230 mL quartz tube, the tube was cooled to -78°C, and the system was degassed by evacuating to ca. 0.15 mm and backflushing with nitrogen several times. After evacuating to 0.15 mm, the tube was sealed, allowed to warm to room temperature and was irradiated in a Rayonet photoreactor fitted with 185/254 nm lamps for 30-60 min (10-20% conversion). 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 at 0°C

to ca. 0.25 mL. Capillary GLC (column A) analysis revealed a very complex mixture of over 12 components. Product ratios proved quite variable from run to run; typical values for the major components of the mixture are reported. All identifications are based upon both capillary GLC (column A) retention times, and 300 MHz ^{1}H NMR analysis of the crude mixture, with comparisons to authentic samples in hand. Products were as follows. **cis-Bicyclo[4.3.0]non-7-ene** (91, 3%, rt 3.04 min); **1,3,8-Nonatriene** (88, 30-40%, rt 3.09 min): mixture of cis and trans isomers (ca. 1:3); **cis-Bicyclo[4.3.0]non-2-ene** (90, 3%, rt 3.67 min); **cis-cis-1-3-Cyclononadiene** (92, 7%, rt 4.08 min); **Non-1-en-8-yne** (89, 0-35%, typically 7%, rt 4.22 min); **Bicyclo[6.1.0]non-1(9)-ene** (84, 15%, rt 4.37 min); **Tricyclo[4.3.0.$0^{2,9}$]nonane** (10, 9%, rt 4.58 min); **1-Vinylcycloheptene** (93, 5%, rt 4.68 min); **3-Methylenecyclooctene** (94, 4%, rt 4.81 min). **Cyclononyne** (85, 4%, rt 8.58 min).

Base catalyzed isomerization of bicyclo[6.1.0]non-1(9)-ene (84)

A solution of 30 mg of hydrocarbon mixture (containing 84, 87, and 8 in the ratio 6:1:1) in 5 mL dry DMSO was added to a stirring solution of 300 mg potassium t-butoxide in 5 mL dry DMSO at room temperature under nitrogen. The mixture was stirred for 30 min, poured into 30 mL water, and extracted with pentane (3 x 20 mL). The pentane extracts were combined, washed with water (3 x 20 mL), dried over magnesium sulfate, filtered, and concentrated under reduced pressure at 0°C to yield 17 mg of a clear oil. GLC (column E) and 60

MHz ^{1}H NMR analyses indicated two components in a ratio of 5:1, identified as bicyclo[6.1.0]non-1(2)-ene (87) and 1,2-cyclononadiene (8), respectively.

Diimide reduction of bicyclo[6.1.0]non-1(9)-ene (84)

Acetic acid (10 mL) was added very slowly to a stirring mixture of dipotassium azodicarboxylate (1.1 g) and 64 mg of hydrocarbon mixture (containing 84, 87, and 8 in the ratio 7:1:1) in 15 mL of methanol at room temperature under nitrogen. Stirring was continued overnight. The mixture was poured into 50 mL water and extracted with pentane (3 x 25 mL). The pentane extracts were combined, washed with sat'd $NaHCO_3$ (50 mL), and with water (3 x 50 mL), dried over magnesium sulfate, filtered, and concentrated under reduced pressure at 0°C to give 46 mg of a slightly yellow oil. GLC (column E) analysis and 60 MHz ^{1}H NMR analysis indicated one major component (ca. 80%) identified as cis-bicyclo[6.1.0]nonane (86) by comparison with an authentic sample.

Direct irradiation of bicyclo[6.1.0]non-1(9)-ene (84) in pentane.

A solution of 65 mg of bicyclo[6.1.0]non-1(9)-ene (84) in 300 mL of pentane was irradiated for 60 min through a Vycor filter. The solution was concentrated under reduced pressure at 0°C to give 75 mg of a clear oil. Capillary GLC (column A) and 300 MHz ^{1}H NMR analyses indicated 35% conversion to 10 products. All identifications are based upon both capillary GLC (column A) retention times and 300 MHz

^{1}H NMR analysis of the crude mixture, with comparisons to authentic samples in hand. GC-MS showed all components to be isomeric with starting material. Products were as follows. **cis-Bicyclo[5.2.0]non-8-ene** (**105**, 2%, rt 3.07 min); **cis-Bicyclo[4.3.0]non-7-ene** (**91**, 18%, rt 3.07 min); **trans-Bicyclo[5.2.0]non-8-ene** (**106**, 4%, rt 3.18 min); **cis-Bicyclo[4.3.0]non-2-ene** (**90**, 15%, rt 3.70 min); **cis-Bicyclo[6.1.0]non-2-ene** (**103**, 2%, rt 4.00 min); **cis-cis-1,3-Cyclononadiene** (**92**, 9%, rt 4.08 min); **Bicyclo[6.1.0]non-1(2)-ene** (**87**, 11%, rt 4.75 min); Unidentified (8%, rt 4.87 min); **cis-trans-1,3-Cyclononadiene** (**104**, 1%, rt 4.98 min); **1,2-Cyclononadiene** (**8**, 22%, rt 6.38 min); **Cyclononyne** (**85**, 7%, rt 8.66 min).

Capillary GLC analysis of the product mixture at low conversion (2%) indicated the cis- and trans-bicyclo[5.2.0]non-8-enes (**105** and **106**) to be secondary and derived from 1,3-cyclononadiene (**92**). The amounts of **105**, **106**, and **92** observed at 2% conversion are 0%, 0%, and 15%, with the amounts of all other products remaining constant.

1,3,8-Nonatriene (88)

Methyllithium (2.4 mL of a 1.5 M sol'n, 3.6 mmol) was added dropwise to a stirring slurry of allyltriphenylphosphonium bromide (1.51 g, 3.94 mmol) in 50 mL dry ether at 0°C. After 60 min, 5-hexen-1-al (0.310 g, 3.16 mmol) was added dropwise as a solution in 10 mL dry ether. The mixture was allowed to warm to room temperature and stirring was continued for 5 hours. Water (1 mL) was added and the mixture was poured into 150 mL pentane, dried over magnesium sulfate,

filtered through neutral alumina, and concentrated under reduced pressure at 0°C to afford 1,3,8-nonatriene (0.15 g, 1.23 mmol, 39%) as a clear oil. 300 MHz ^{1}H NMR analysis of the product indicated it was a mixture of the cis and trans isomers; present in a ratio of 43/57 respectively. **trans-1,3,8-Nonatriene:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.32 (dt, 16.8 Hz, 10.1 Hz, 1H), 6.06 (dd, 14.9 Hz, 10.1 Hz, 1H), 5.87-5.73 (m, 1H), 5.68 (dt, 14.9 Hz, 7.2 Hz, 1H), 5.08 (d, 16.8 Hz, 1H), 5.05-4.93 (m, 3H), 2.2-2.0 (m, 4H), 1.6-1.4 (m, 2H); **cis-1,3,8-Nonatriene:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.63 (dt, 16.8 Hz, 11.0 Hz, 1H), 5.45 (dt, 10.6 Hz, 7.7 Hz, 1H), 5.18 (d, 16.8 Hz, 1H).

Direct irradiation of cis-cis-1,3-cyclononadiene (92) in pentane

A solution of 44 mg of 1,3-cyclononadiene (92) in 50 mL of pentane was irradiated for 60 min with 254 nm lamps in the Rayonet apparatus. The rapid cis-trans photoequilibration was essentially complete in ca. 5 min (92/104 = ca. 11:1), after which time other products were observed to be formed. Capillary GLC (column A) and 300 MHz ^{1}H NMR analysis indicated ca. 16% conversion of the 1,3-cyclononadienes to 9 products. These were isolated on a preparative scale (column E) and identified as follows. **cis-Bicyclo[5.2.0]non-8-ene** (**105**, 20%, rt 3.04 min): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.08 (s, 2H), 2.95-2.85 (m, 2H), 1.8-1.1 (m, 10H); **cis-Bicyclo[4.3.0]non-7-ene** (**91**, 23%, rt 3.07 min); **trans-Bicyclo[5.2.0]non-8-ene** (**106**, 25%, rt 3.17 min): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.17 (s, 2H), 2.6-2.5 (m, 2H), 1.8-1.1 (m, 10H); **cis-Bicyclo[4.3.0]non-2-ene** (**90**, 2%, rt 3.70 min); cis-

Bicyclo[6.1.0]non-2-ene (103, 9%, rt 4.00 min); Bicyclo[6.1.0]non-1(9)-ene (84, 8%, rt 4.45 min); 3-Methylenecyclooctene (94, 8%, rt 4.81 min); 1,4-Cyclononadiene (107, 3%, rt 5.12 min); 1,2-Cyclononadiene (8, 1%, rt 6.38 min).

cis-Bicyclo[4.3.0]nonan-3-one (96)

5-Indanol (10.0 g, 74.5 mmol) was dissolved in 40 mL of 95% ethanol and platinum oxide (150 mg) along with 20 drops of concentrated hydrochloric acid was added. The mixture was agitated in a Parr hydrogenation apparatus under 50 psi of hydrogen for 8 hours. The mixture was then filtered through celite, poured into 100 mL water, and extracted with ether (3 x 50 mL). The ether extracts were combined, washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Distillation of the residue afforded two fractions. (I) The first fraction (4.0 g, 32 mmol, 43%), B.P. 35-40°C at 4.5 mm, was a mixture of hydrindanes (cis/trans = 91/9) as indicated by GLC analysis (column D) and by 300 MHz ^{1}H NMR analysis. (II) The second fraction (4.36 g, 31.1 mmol, 41%), B.P. 93-95°C at 4.5 mm, was a mixture of alcohols. ^{1}H NMR (300 MHz) analysis indicated two components, in a 3/1 ratio, which correspond to the two epimeric cis-bicyclo[4.3.0]nonan-3-ols expected. The major product had a multiplet at δ 3.60-3.47 (1H) and the minor product had a multiplet at δ 3.88-3.75 (1H).

The mixture of cis-bicyclo[4.3.0]nonan-3-ols (4.00 g, 28.5 mmol) was oxidized with Collins reagent prepared from chromium trioxide

(15.6 g, 156 mmol) and pyridine (25.2 mL, 24.6 g, 312 mmol) in 200 mL methylene chloride. The material obtained after standard work up was distilled under reduced pressure to afford cis-bicyclo[4.3.0]nonan-3-one (3.68 g, 26.6 mmol, 93%) as a clear oil, B.P. 87-89°C at 6 mm (lit.[62] 106°C at 13 mm). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.50-2.15 (m, 6H), 2.00-1.80 (m, 3H), 1.80-1.64 (m, 2H), 1.64-1.53 (m, 1H), 1.53-1.40 (m, 1H), 1.40-1.25 (m, 1H). IR (neat) 2940, 2880, 1715, 1460, 1425, 1230 cm^{-1}.

cis-Bicyclo[4.3.0]nonan-3-one tosylhydrazone

cis-Bicyclo[4.3.0]nonan-3-one (0.50 g, 3.6 mmol) was added to a stirring suspension of tosylhydrazide (0.67 g, 3.6 mmol) in 4 mL methanol. The tosylhydrazide was quickly taken up and precipitation of the tosylhydrazone followed. The mixture was stirred for 60 min at room temperature. After cooling, the crystals were collected, washed with cold methanol, and dried to give the desired tosylhydrazone (0.86 g, 78%) as white crystals melting at 161-162°C. ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.8-7.0 (m, 4H), 2.40 (s, 3H), 2.3-0.9 (m, 14H). IR (KBr) 3320, 2920, 2850, 1640, 1595, 1390, 1330, 1160, 1025 cm^{-1}. Anal. Calcd for $C_{16}H_{22}N_2O_2S$: C, 62.72; H, 7.24; N, 9.14. Found: C, 62.80; H, 7.15; N, 9.16.

cis-Bicyclo[4.3.0]non-2-ene (90)

Sodium methoxide (350 mg, 6.5 mmol) was added to a solution of cis-bicyclo[4.3.0]nonan-3-one tosylhydrazone (500 mg, 1.63 mmol) in 20

mL dry diglyme and the mixture was heated slowly while stirring under nitrogen. The mixture was heated to 165°C and stirred for 2 h. After cooling, 40 mL water was added and the product was extracted into pentane (2 x 25 mL). The pentane extracts were combined, washed with water (5 x 50 mL), dried over magnesium sulfate, filtered through neutral alumina, and concentrated under reduced pressure at 0°C to give a clear oil (177 mg, 89%). Capillary GLC (column A) analysis indicated two components in the ratio 76:24. These were isolated on a preparative scale (column E) and identified as follows. **cis-Bicyclo[4.3.0]non-2-ene** (76%, rt 3.67 min): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.66 (d, 1.5 Hz, 2H), 2.4-2.3 (m, 1H), 2.1-2.0 (m, 1H), 2.0-1.9 (m, 2H), 1.9-1.25 (m, 8H). ^{13}C NMR δ 131.1, 126.2, 39.4, 36.7, 32.4, 30.8, 25.9, 24.1, 23.3 IR (neat) 3020, 2940, 2870, 1650, 1450 cm^{-1}; **cis-Bicyclo[4.3.0]non-3-ene** (24%, rt 3.85 min): ^{1}H NMR δ 5.64 (t, 1.4 Hz, 2H), 2.2-2.05 (m, 2H), 2.05-1.9 (m, 2H), 1.9-1.75 (m, 2H), 1.75-1.50 (m, 4H), 1.45-1.32 (m, 2H).

cis-Bicyclo[4.3.0]nonan-8-one (98)

2-Indanone (2.50 g, 18.9 mmol) was hydrogenated as above. The material obtained, a mixture of the epimeric cis-alcohols and the saturated hydrindanes, was oxidized with Collins reagent prepared from chromium trioxide (7.06 g, 70.6 mmol) and pyridine (11.4 mL, 11.1 g, 141 mmol) in 100 mL methylene chloride. The material obtained after standard work up was distilled under reduced pressure to afford 1.47 g of cis-bicyclo[4.3.0]nonan-8-one containing ca. 20% of the sat'd

hydrindanes (corrected yield: 1.18 g, 8.5 mmol, 45%) as a clear oil, B.P. 82-86°C at 6 mm (lit.[63] 109°C at 23 mm). Spectral data were obtained on a sample purified by preparative GLC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40-2.05 (m, 6H), 1.67-1.30 (m, 8H). IR (neat) 2930, 2860, 1745, 1450, 1410, 1240, 1160.

cis-Bicyclo[4.3.0]nonan-8-one tosylhydrazone

cis-Bicyclo[4.3.0]nonan-8-one (0.50 g, 3.6 mmol) and tosylhydrazide (0.67 g, 3.6 mmol) were reacted as above to give the desired tosylhydrazone (0.79 g, 72%) as white crystals melting at 198-199°C. ^{1}H NMR (60 MHz, $CDCl_3$) δ 8.0-7.2 (m, 4H), 2.43 (s, 3H), 2.4-2.0 (m, 6H), 1.6-1.2 (m, 8H). IR (KBr) 3220, 2920, 2850, 1650, 1590, 1395, 1330, 1160 cm^{-1}. Anal. Calcd for $C_{16}H_{22}N_2O_2S$: C, 62.72; H, 7.24; N, 9.14. Found: C, 62.72; H, 7.11; N, 9.02.

cis-Bicyclo[4.3.0]non-7-ene (91)

Methyllithium (3.3 mL, 1.5 M, 4.95 mmol) was added dropwise to a stirring suspension of cis-bicyclo[4.3.0]nonan-8-one tosylhydrazone (503 mg, 1.64 mmol) in 20 mL dry ether under nitrogen at room temperature. The mixture was stirred for 2 h, cooled to 0°C, and 20 mL water was added carefully. The layers were separated and the organic layer washed with water (3 x 25 mL), dried over magnesium sulfate, filtered, and concentrated under reduced pressure at 0°C. The residue was taken up in pentane, filtered through neutral alumina, and concentrated under reduced pressure at 0°C to give cis-Bi-

cyclo[4.3.0]non-7-ene (125 mg, 62%) as a clear oil. ^{1}H NMR (300 MHz, $CDCl_3$ δ 5.70 (s, 2H), 2.58-2.48 (m, 1H), 2.27 (ddd, 14.9 Hz, 6.9 Hz, 1.7 Hz, 1H), 2.16 (sextet, 6.1 Hz, 1H), 2.01 (dd, 14.9 Hz, 5.1 Hz, 1H), 1.70-1.25 (m, 8H). I.R. (neat) 3060, 2920, 2840, 1600, 1450 cm^{-1}.

Thermolysis of 1,2-cyclononadiene (8)

Non-1-en-8-yne(**89**), trans-bicyclo[4.3.0]non-2-ene (**112**), and cis-bicyclo-[4.3.0]non-2-ene (**90**) were obtained from the thermolysis of 1,2-cyclononadiene (**8**) by the method of Crandall and Watkins.[28] cis-Bicyclo[4.3.0]non-2-ene (**90**) was incorrectly assigned in the literature report as cis-bicyclo[4.3.0]non-7-ene (**91**). 1,2-Cyclononadiene (0.61 g, 5.0 mmol) was passed slowly (30 min) through a horizontal quartz tube, packed with quartz chips, maintained at 650°C, and at a pressure of 0.20 mm. The product was collected in a cooled trap, rinsed out with pentane, and concentrated under reduced pressure at 0°C to give the product (0.40 g, 3.3 mmol, 65%) as a yellow oil.

GLC analysis (column F) indicated three major components which were isolated on a preparative scale (column F). **Non-1-en-8-yne** (89, ca. 61%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.81 (ddt, 17.0 Hz, 10.3 Hz, 6.7 Hz, 1H), 5.00 (d quartet, 17.0 Hz, 1.7 Hz, 1H), 4.94 (dd, 10.3 Hz, 0.8 Hz, 1H), 2.19 (td, 6.9 Hz, 2.6 Hz, 2H), 2.1-2.0 (m, 2H), 1.94 (t, 2.6 Hz, 1H), 1.6-1.4 (m, 6H); **trans-Bicyclo[4.3.0]non-2-ene** (112, ca. 11%) ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.84 (dd, 9.8 Hz, 1.4 Hz, 1H) 5.58 (d quartet, 9.8 Hz, 1H), 2.23-2.06 (m, 2H), 1.98-1.92 (m, 1H), 1.88-1.61

(m, 5H), 1.54-1.26 (m, 2H), 1.22-1.07 (m, 2H); **cis-Bicyclo[4.3.0]non-2-ene (90**, ca. 27%).

Base catalyzed isomerization of 1,2-cyclononadiene (8)

cis-cis-1,3-Cyclononadiene (92) and cis-cis-1,4-cyclononadiene (107) were obtained by the method of Vaidyanathaswamy and Devaprabhakara.[29] 1,2-Cyclononadiene (2.0 g, 16.4 mmol) was added to a solution of potassium t-butoxide (3.7 g, 33.0 mmol) in 20 mL dry DMSO (distilled from sodium hydroxide) and the mixture was warmed to 70°C and stirred for 60 min. After cooling, the mixture was poured into 40 mL water and extracted with pentane (3 x 50 mL). The pentane extracts were combined, washed with water, dried over magnesium sulfate, filtered through neutral alumina, and concentrated under reduced pressure at 0°C to afford the product (1.8 g, 14.7 mmol, 90%) as a clear oil. GLC analysis (column E) indicated two major components which were isolated on a preparative scale. **cis-cis-1,3-Cyclononadiene (92**, ca. 80%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.90 (d, 9.7 Hz, 2H), 5.71 (quartet, 9.7 Hz, 2H), 2.2-2.1 (m, 4H), 1.7-1.6 (m, 2H), 1.54-1.46 (m, 4H); **cis-cis-1,4-Cyclononadiene (107**, ca. 20%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.62-5.48 (m, 4H), 2.86 (t, J = 7.3 Hz, 2H), 2.30-2.23 (m, 4H), 1.59-1.54 (m, 4H).

Tricyclo[4.3.0.$0^{2,9}$]nonane (10)

Tricyclo[4.3.0.$0^{2,9}$]nonane (10) was prepared by the method of Cardenas et al.[64] A solution of bromoform (3.0 mL, 8.67 g, 34.3 mmol) in 5 mL pentane was added dropwise to a stirring slurry containing potassium t-butoxide (4.2 g, 37.4 mmol) and 1,3-cyclooctadiene (7.3 g, 67.5 mmol) in 40 mL pentane at 0°C. The mixture was then warmed to room temperature and stirred overnight. After standard work up, the crude pentane solution obtained was filtered through neutral alumina and concentrated under reduced pressure. The excess 1,3-cyclooctadiene was removed by distillation under reduced pressure and 9,9-dibromobicyclo[6.1.0]non-2-ene (4.75 g, 17.0 mmol, 45%) was obtained as a clear oil.

Methyllithium (20 mL of a 1.3 M sol'n, 26.0 mmol) was added dropwise to a solution of 9,9-dibromobicyclo[6.1.0]non-2-ene (3.7 g, 13.2 mmol) in 20 mL dry ether at -30/-40°C. After warming to room temperature, the reaction was worked up in the usual manner and the residue obtained after concentration under reduced pressure at 0°C was distilled to afford a mixture of tricyclo[4.3.0.$0^{2,9}$]nonenes (280 mg, 2.33 mmol, 18%) as a clear oil, B.P. 60-65°C at ca. 15 mm.

Acetic acid (15 mL, 260 mmol) was slowly added dropwise to a stirring slurry containing dipotassium azodicarboxylate (1.3 g, 6.7 mmol) and the tricyclo[4.3.0.$0^{2,9}$]nonenes mixture (200 mg, 1.66 mmol) in 15 mL methanol. After 3 days, the mixture was poured into water and extracted with pentane. The pentane extracts were combined,

washed with sat'd aqueous sodium bicarbonate, washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure at 0°C to give 220 mg of product as a slightly colored oil. GLC analysis (column E) indicated two major components, tricyclo[4.3.0.$0^{2,9}$]nonane (10), and unreacted tricyclo[4.3.0.$0^{2,9}$]non-3-ene, in a ratio of ca. 3.6/1 respectively. The sat'd product was isolated on a preparative scale (column E). Tricyclo[4.3.0.$0^{2,9}$]nonane (10): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.50-2.40 (m, 1H), 2.30-2.15 (m, 1H), 1.95-1.80 (m, 3H), 1.75-1.60 (m, 1H), 1.55-1.40 (m, 2H), 1.40-1.20 (m, 5H), 0.85-0.75 (m, 1H).

Bicyclo[6.1.0]non-1(2)-ene (87) and cis-bicyclo[6.1.0]non-2-ene (103)

Bicyclo[6.1.0]non-1(2)-ene (87) and cis-bicyclo[6.1.0]non-2-ene (103) were prepared from cis-9-bromobicyclo[6.1.0]nonane by the method of Osborn et al.[26] cis-9-Bromobicyclo[6.1.0]nonane (0.50 g, 2.5 mmol) was added to a stirring solution of potassium t-butoxide (1.4 g, 12.5 mmol) in 20 mL dry DMSO. After 7 hours, the mixture was poured into 80 mL water and extracted with pentane (3 x 50 mL). The pentane extracts were combined, washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure at 0°C to give the product as a clear oil. GLC analysis indicated the two expected products were present in a ratio of 2:1 and each was isolated on a preparative scale (column E). Bicyclo[6.1.0]non-1(2)-ene (87, major component): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.87 (br s, 1H), 2.40-2.24 (m, 2H), 2.09-1.84 (m, 3H), 1.71-1.13 (m, 5H), 0.88-0.78 (m, 1H), 0.62-

0.49 (m, 2H); **cis-Bicyclo[6.1.0]non-2-ene (103,** minor component) ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.7-5.6 (m, 1H), 5.41 (d, 10.8 Hz, 1H), 2.5-0.8 (m, 10H), 0.69 (td, 8.4 Hz, 4.2 Hz, 1H), -0.18 (td, 4.8 Hz, 4.2 Hz, 1H).

1-Vinylcycloheptene (93)

Methyllithium (3.0 mL of 1.5 M sol'n, 4.50 mmol) was added dropwise to a stirring slurry of methyltriphenylphosphonium bromide (1.80 g, 5.04 mmol) in 45 mL dry ether at 0°C. After 60 min, cycloheptene-1-carboxaldehyde (0.50 g, 4.03 mmol) was added dropwise as a solution in 5 mL dry ether. The mixture was stirred at 0°C for 60 min and then at room temperature for 60 min. Water (1 mL) was added and the mixture was poured into 100 mL pentane, dried over magnesium sulfate, filtered through neutral alumina, and concentrated under reduced pressure at 0°C to afford the product (0.33 g, 2.7 mmol, 67%) as a clear oil. GLC analysis (column C) indicated one major component which was isolated on the preparative scale (column E). **1-Vinylcycloheptene (93):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.32 (dd, 17.4 Hz, 10.7 Hz, 1HH), 5.89 (t, 6.7 Hz, 1H), 5.09 (d, 17.4 Hz, 1H), 4.90 (d, 10.7 Hz, 1H), 2.33-2.29 (m, 2H), 2.21 (dd, 11.2 Hz, 6.7 Hz, 2H), 1.79-1.73 (m, 2H), 1.55-1.49 (m, 4H).

3-Methylenecyclooctene (94)

3-Methylenecyclooctene (94) was prepared from cyclooct-2-en-1-one (0.50 g, 4.03 mmol) by the Wittig procedure described above. The product (0.388 g, 3.18 mmol, 79%) was obtained as a clear oil. GCC

analysis (column C) indicated one major component which was isolated on a preparative scale (column E). **3-Methylenecyclooctene (94):** ^1H NMR (300 MHz, $CDCl_3$) δ 6.24 (d, 11.7 Hz, 1H), 5.49 (dt, 11.7 Hz, 8.6 Hz, 1H), 4.92 (d, 2.3 Hz, 1H), 4.81 (s, 1H), 2.58 (t, 6.8 Hz, 2H), 2.5-2.4 (m, 2H), 1.7-1.5 (m, 6H).

cis-trans-1,3-Cyclononadiene (104)

A solution of cis-cis-1,3-cyclononadiene (0.155 g, 1.27 mmol) in 150 mL of pentane was irradiated with the 254 nm lamps in the Rayonet apparatus. After 4 min, the rapid cis/trans photoequilibration was near completion, while other products were minimal, and the reaction was stopped. The solution was concentrated under reduced pressure at 0°C to give a clear oil. GLC analysis (column C) indicated two major components in a ratio of 11:1. The major component corresponded to cis-cis-1,3-cyclononadiene and the minor component corresponded to cis-trans-1,3-cyclononadiene which was isolated on a preparative scale (column E). **cis-trans-1,3-Cyclononadiene (104):** ^1H NMR (300 MHz, $CDCl_3$) δ 6.14 (d, 10.5 Hz, 1H), 5.78 (dd, 10.5 Hz, 5.6 Hz, 1H), 5.70 (d, 18.1 Hz, 1H), 5.65-5.55 (m, 1H), 2.4-2.2 (m, 2H), 2.2-2.0 (m, 2H), 1.7-1.4 (m, 6H).

1,2-Cyclononadione-bis-tosylhydrazone

Cyclononadione[65] (0.80 g, 5.2 mmol) was added to a solution of tosylhydrazide (2.4 g, 12.9 mmol) in 30 mL glacial acetic acid. The mixture was stirred for two hours and the crystals were collected,

washed with water, and dried to give the desired bis-tosylhydrazone (1.85 g, 3.8 mmol, 73%) as white crystals, m.p. 162-163°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.8-7.2 (m, 10H), 2.4 (s, 6H), 2.5-2.35 (m, 4H), 1.4-0.6 (m, 10H).

Cyclononyne (85)

Cyclononyne (85) was prepared by the general procedure of Meier and Menzel.[66] 1,2-Cyclononadione-bis-tosylhydrazone (300 mg, 0.61 mmol) was dissolved in 220 mL dry THF, sodium methoxide (260 mg, 4.8 mmol) was added, and the mixture was degassed with Argon for 30 min. The mixture was then irradiated through Vycor for 90 min, poured into 400 mL water, and extracted with pentane (2 x 100 mL). The pentane extracts were combined, washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure at 0°C. The residue was taken up in pentane, filtered through neutral alumina, and concentrated as above to afford cyclononyne (33 mg, 0.27 mmol, 44%) as a clear oil. GLC analysis (column E at 130°C) indicated one major component which was isolated on a preparative scale. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.2-2.1 (m, 4H), 1.73-1.54 (m, 10H).

Cyclonon-2-en-1-ol

Cyclonon-2-en-1-ol was prepared by the method of Santelli et al.[67] 1,2-Cyclononadiene (51.4 g, 0.421 mol) was added to a solution of mercuric sulfate (4.3 g, 14.5 mmol) in 350 mL of 88% formic acid and the mixture was stirred overnight. The reaction mixture was then

carefully added to an ice cooled solution of potassium carbonate (900 g) in 2000 mL water and this mixture was extracted with ether (3 x 250 mL). The ether extracts were combined and washed with sat'd aqueous sodium bicarbonate (2 x 200 mL) and water (400 mL). The solution was dried over magnesium sulfate, filtered, and concentrated under reduced pressure.

The crude cyclonon-2-en-1-formate was added to a mixture of barium hydroxide (61.0 g, 0.19 mol) in 300 mL water and the mixture was refluxed for 2 hr. After cooling, the reaction mixture was filtered and the residue was rinsed with ether (150 mL). The aqueous and organic layers were separated and the aqueous layer was extracted with ether (2 x 150 mL). The ether layers were combined, washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Distillation gave 48.1 g (0.343 mol, 81%) of product as a clear oil, B.P. 105-108°C at 7 mm (lit.[67] 62°C at 0.5 mm). ^{1}H NMR (60 MHz, $CDCl_3$) δ 5.8-5.2 (m, 2H), 4.8-4.3 (m, 1H), 2.73 (s, 1H), 2.3-1.9 (m, 2H), 1.9-1.0 (m, 10H).

Cyclonon-2-en-1-one

Chromium trioxide (50.4 g, 0.504 mol) was added portionwise to a mechanically stirred solution of pyridine (82 mL, 80.2 g, 1.01 mol) in 1000 mL methylene chloride. After 90 min, the cyclonon-2-en-1-ol (17.6 g, 0.126 mol) was added and the mixture was stirred overnight. The reaction mixture was then filtered, and the filtrate was washed with 5% aqueous sodium hydroxide (3 x 400 mL), water (400 mL), 5%

aqueous hydrochloric acid (3 x 400 mL), water (400 mL), sat'd aqueous sodium bicarbonate (400 mL), and water (400 mL). The solution was then dried over sodium sulfate, filtered, and concentrated under reduced pressure. Distillation afforded 14.0 g (0.101 mol, 80%) of product as a clear oil, B.P. 50-55°C at 0.45 mm (lit.[67] 48-49°C at 0.5 mm). ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.5-5.8 (m, 2H), 2.8-2.2 (m, 4H), 2.2-1.3 (m, 8H).

Cyclonon-2-en-1-one tosylhydrazone (110)

Cyclonon-2-en-1-one (4.0 g, 29 mmol) was added to a solution of tosylhydrazide (5.2 g, 28 mmol) and pyridine (ca. 40 drops) in 60 mL methanol at 0°C. Stirring was continued for 60 min at 0°C and water (ca. 25 mL) was added to induce crystallization. The crystals were collected, washed with cold 75% aqueous methanol, and dried to yield the desired tosylhydrazone (1.6 g, 18%) as off-white crystals melting at 111°-114°C. (lit.[32b] 115°-117°C). ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.9-7.1 (m, 4H), 6.2-5.6 (m, 2H), 2.38 (s, 3H), 2.6-2.1 (m, 4H), δ 1.6-1.1 (m, 8H).

1-Bromocyclooctene

1-Bromocyclooctene was prepared by the method of Wittig and Dorsch.[68] To a solution of cyclooctene (60 mL, 51 g, 0.46 mol) in 100 mL carbon tetrachloride, cooled with an ice bath, was added dropwise a solution of bromine (24 mL, 75 g, 0.47 mol) in 75 mL carbon tetrachloride. After the addition, cyclooctene was added dropwise to

decolorize the solution. Morpholine (85 mL, 85 g, 0.97 mol) was then added to the crude dibromide solution and the reaction mixture was heated to reflux for 24 hours. After cooling, the mixture was filtered to remove the precipitated morpholine hydrobromide, and the filtrate was washed with 5% aqueous hydrochloric acid (3 x 200 mL), water (200 mL), sat'd aqueous sodium bicarbonate (200 mL), and water (200 mL). The solution was then dried over sodium sulfate, filtered, and concentrated under reduced pressure. Distillation gave 46.0 g (0.24 mol, 53%) of product was a clear oil, B.P. 78-80°C at 7 mm (lit.[68] 87-90°C at 15 mm). ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.00 (t, J = 8 Hz, 1H), 2.8-2.3 (m, 2H), 2.3-1.8 (m, 2H), 1.8-1.2 (m, 8H).

Cyclooctene-1-carboxaldehyde

Cyclooctene-1-carboxaldehyde was prepared by the method of Neumann and Seebach.[69] To a solution of 1-bromocyclooctene (29.5 g, 0.156 mol) in 100 mL dry THF, cooled to -78°C, was added dropwise a solution of t-butyllithium (184 mL of a 1.7M sol'n, 0.313 mol). Stirring was continued for 60 min, a solution of N,N-dimethylformamide (20.0 mL, 18.9 g, 0.258 mol) in 20 mL dry THF was then added dropwise, the mixture was allowed to warm slowly to room temperature, and stirring was continued overnight. Sat'd aqueous ammonium chloride (100 mL), followed by water (200 mL), was then added to the ice cooled mixture and the aqueous and organic layers were separated. The aqueous layer was extracted with pentane (2 x 100 mL) and the organic layers were combined, washed with water, dried over magnesium sulfate,

filtered, and concentrated under reduced pressure. Distillation afforded 17.1 g (0.124 mol, 79%) of product as a clear oil, B.P. 78-80°C at 4 mm (lit.[69] 100-110°C at 10 mm). ^{1}H NMR (60 MHz, $CDCl_3$) δ 9.37 (s, 1H), 6.67 (t, J = 8 Hz, 1H), 2.7-2.0 (m, 4H), 2.0-1.2 (m, 8H).

Cyclooctene-1-carboxaldehyde tosylhydrazone (111)

Cyclooctene-1-carboxaldehyde (2.0 g, 14.5 mmol) was added to a stirring suspension of tosylhydrazide (2.6 g, 14.0 mmol) in 20 mL benzene. The mixture was stirred at room temperature for 60 min, cooled to 0°C, and pentane (ca. 20 mL) was added to induce crystallization. The crystals were collected, washed with pentane, and dried to give the desired tosylhydrazone (4.4 g, 99%) was white crystals melting at 118.5-120°C (lit.[32a] 117-119°C). ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.9-7.2 (m, 5H), 5.92 (t, J = 8 Hz, 1H), 2.40 (s, 3H), 2.6-2.0 (m, 4H), 1.7-1.2 (m, 8H).

General procedure for vinylcarbene generation by photolysis of tosylhydrazone sodium salts

The tosylhydrazone was dissolved in dry THF (200-400 mL/g of tosylhydrazone), the solution was degassed with nitrogen for 30 min, and sodium methoxide (4 equivalents) was added. Irradiation through Pyrex quickly resulted in a red coloration (diazo intermediate) and the irradiation was continued until the color had completely faded (ca. 60 min). The mixture was poured into pentane, washed with water,

dried over magnesium sulfate, filtered, and concentrated under reduced pressure at 0°C. The residue was taken up in pentane, filtered through neutral alumina, and concentrated as above to afford the hydrocarbon products as a clear oil.

Photolysis of the sodium salt of cyclonon-2-en-1-one tosylhydrazone (110)

Reaction of cyclonon-2-en-1-one tosylhydrazone (500 mg, 1.6 mmol) as described above gave 140 mg (70%) of hydrocarbon product as a clear oil. Capillary GLC (column A) analysis indicated seven components. The 5 major components (**91**, **90**, **92**, **84**, **104**) were isolated on a preparative scale (column E) and were characterized by the identify of their capillary GLC (column A) retention times and 300 MHz ^1H NMR spectra with those of authentic samples. The 2 minor components (**112**, **8**) were assigned based upon comparison of their capillary GLC (column A) retention times with those of authentic samples. **cis-Bicyclo-[4.3.0]non-7-ene** (**91**, 6%, rt 3.04 min); **trans-Bicyclo[4.3.0]-non-2-ene** (**112**, 0.7%, rt 3.37 min); **cis-Bicyclo[4.3.0]non-2-ene** (**90**, 27%, rt 3.67 min); **cis-cis-1,3-Cyclononadiene** (**92**, 23%, rt 4.04 min); **Bicyclo-[6.1.0]non-1(9)-ene** (**84**, 40%, rt 4.38 min); **cis-trans-1,3-Cyclononadiene** (**104**, 3%, rt 4.94 min); **1,2-Cyclononadiene** (**8**, 0.3%, rt 6.32 min).

Photolysis of the sodium salt of cyclooctene-1-carboxaldehyde tosylhydrazone (111)

Reaction of cyclooctene-1-carboxaldehyde tosylhydrazone (1.5 g, 4.9 mmol) at 0°C and as described above gave 0.26 g (44%) of hydro-

carbon product as a clear oil. Capillary GLC (column A) analysis indicated three components. These were isolated on a preparative scale (column E) and were characterized by the identity of their capillary GLC (column A) retention times and 300 MHz ^{1}H NMR spectra with those of authentic samples. **cis-Bicyclo[6.1.0]non-1(9)-ene** (84, 78%, rt 4.38 min); **Bicyclo[6.1.0]non-1(2)-ene** (87, 12%, rt 4.75 min); **1,2-Cyclononadiene** (8, 10%, rt 6.32 min).

General procedure for vinylcarbene generation by thermolysis of tosylhydrazone sodium salts

The tosylhydrazone was dissolved in dry diglyme (10-20 mL/g of tosylhydrazone), sodium methoxide (4 equivalents) was added, and the mixture was stirred under nitrogen while heating slowly. After the reaction was completed, the mixture was cooled, water was added, and the product was extracted into ether. The ether extracts were combined, washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure at 0°C. The residue was taken up in pentane, filtered through neutral alumina, and concentrated as above to give the hydrocarbon product.

Thermolysis of the sodium (and lithium) salt of cyclonon-2-en-1-one tosylhydrazone (110)

Reaction of cyclonon-2-en-1-one tosylhydrazone (496 mg, 1.62 mmol) as described above gave 65 mg (33%) of product as a clear oil. During the reaction, a red coloration developed at ca. 80°C and had

completely faded by the time the mixture reached 120°C. The reaction was stopped at this point. Capillary GLC (column A) analysis indicated six isomeric C_9H_{14} products, identified by their capillary GLC (column A) retention times and by 300 MHz ^1H NMR analysis of the crude reaction mixture (with the exception of **112**, identified only by capillary (column A) retention time. **cis-Bicyclo[4.3.0]non-7-ene** (91, 10%, rt 3.04 min); **trans-Bicyclo[4.3.0]non-2-ene** (112, 0.5%, rt 3.38 min); **cis-Bicyclo[4.3.0]non-2-ene** (90, 58%, rt 3.67 min); **cis-Bicyclo[6.1.0]non-2-ene** (103, 14%, rt 3.97 min); **cis-cis-1,3-Cyclononadiene** (92, 15%, rt 4.04 min); **Bicyclo[6.1.0]non-1(9)-ene** (84, 3%, rt 4.38 min).

Similar reaction using 1 equivalent of n-butyllithium instead of the sodium methoxide gave 140 mg (70%) of product as a clear oil, with no change in the product ratios.

Thermolysis of the sodium salt of cyclooctene-1-carboxaldehyde tosylhydrazone (111)

Reaction of cyclooctene-1-carboxaldehyde tosylhydrazone (1.0 g, 3.3 mmol) for 2 h at reflux and as described above, but without filtering through neutral alumina, gave 0.61 g of crude product as a yellow oil. Capillary GLC analysis and 300 MHz ^1H NMR analysis indicated no C_9H_{14} products were present. The crude product was bulb to bulb distilled at a bath temperature of 170°C (0.15 mm) to give a clear oil which solidified upon standing and melted at 44-54°C. This was identified as 3,4-hexamethylenepyrazole, **117** (lit.[32a] m.p. 45-

46°C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.4 (br s, 1H), 7.27 (s, 1H), 2.78 (t, 6.3 Hz, 2H), 2.59 (t, 6.3 Hz, 2H), 1.8-1.3 (m, 8H).

Direct irradiation of 1,2-cyclononadiene (8) in methanol

A solution of 1,2-cyclononadiene (300 mg) in 300 mL of methanol was irradiated for 40 min through a Vycor filter. The methanol solution was diluted with 300 mL pentane, washed with water (3 x 400 mL), dried over magnesium sulfate, filtered, and concentrated under reduced pressure at 0°C to give 230 mg of a clear oil. Three 10 mL aliquots were taken at various times during the irradiation and worked up as described above. Capillary GLC (column A) analysis of these aliquots and the crude reaction product, along with 300 MHz ^{1}H NMR analysis of the crude product mixture, indicated conversion (1.4% at 40 min) to the 4 primary photoproducts described below (accounting for > 95% of the product mixture). Products were as follows. **Bicyclo-[6.1.0]non-1(9)-ene** (**84**, 90%, rt 4.37 min); **Tricyclo[4.3.0.0^{2,9}]nonane** (**10**, 3%, 45 4.58 min); **Cyclononyne** (**85**, 2%, rt 8.44 min); **cis-3-Methoxycyclononene** (**99**, 3%, rt 11.13 min).

The above data also indicated that no exo-9-methoxybicyclo-[6.1.0]nonane (**exo-102**) was formed in the irradiation (detection limit ca. 0.1%). This was demonstrated by coinjection of an authentic sample. Although an observed capillary GLC (column A) peak at rt 11.57 min (0.4%) matched that of cis-1-methoxycyclononene (**101**), this product is not obtained in the irradiation of **8** in methanol. In a larger conversion experiment (ca. 30%), the ether products from the

reaction were collected as a mixture, and 300 MHz ^{1}H NMR analysis demonstrated the absence of **101**. 1-(Methoxymethyl)cyclooctene (**100**), however, was observed at higher conversions, but corresponds to a secondary product as determined by plotting product ratios as a function of conversion.

cis-3-Methoxycyclononene (**99**)

A solution of cis-cyclonon-2-en-1-ol (2.0 g, 14.3 mmol) in 5 mL dry DME was added dropwise to a stirring slurry of rinsed sodium hydride (2.1 g of 50% in oil, 44 mmol) in 15 Ml dry DME at 0°C. The mixture was allowed to warm to room temperature and stirring was continued overnight. Iodomethane (3.4 mL, 7.75 g, 55 mmol) was then added dropwise at 0°C and the mixture was allowed to warm to room temperature. After 3 hours, the excess sodium hydride was quenched with 10 mL sat'd aqueous ammonium chloride. The mixture was poured into 50 mL water and extracted with ether (2 x 50 mL). The ether extracts were combined, washed with 10% aqueous sodium thiosulfate, washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Distillation of the residue afforded **cis-3-methoxycyclononene** (1.9 g, 12.3 mmol, 86%) as a clear oil, B.P. 76-77°C at 6 mm. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.70 (quartet, 9 Hz, 1H), 5.35 (dd, 11 Hz, 9 Hz, 1H), 4.20-4.10 (m, 1H), 3.29 (s, 3HO, 2.20-2.05 (m, 2H), 1.85-1.20 (m, 10H).

Cyclononanone

Cyclonon-2-en-1-ol (4.0 g, 28.5 mmol) was taken up in 25 mL ether, a catalytic amount of Pd on carbon was added, and the mixture was stirred under a hydrogen balloon. After 48 hours, GLC analysis (Carbowax 20 M capillary; 25 m, 160°C) indicated complete conversion of starting material to a mixture of cyclononanone and cyclononanol in a ratio of 64:36 respectively. A similar result was reported by Mehta in 1970.[70] The mixture was filtered through celite, concentrated under reduced pressure, and the residue was oxidized with Collins reagent prepared from chromium trioxide (7.8 g, 78 mmol) and pyridine (12.6 mL, 12.3 g, 156 mmol) in 200 mL methylene chloride. The material obtained after standard work up was distilled to afford cyclononanone (3.72 g, 26.5 mmol, 93%) as a clear oil, B.P. 81-83°C at 6 mm. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.47-2.43 (m, 4H), 1.91-1.83 (m, 4H), 1.65-1.53 (M, 4H), 1.45-1.35 (m, 4H).

cis-1-Methoxyclononene (101)

A solution containing cyclononanone (2.0 g, 14.3 mmol), trimethylorthoformate (1.6 mL, 14.6 mmol), and p-toluenesulfonic acid (ca. 50 mg) in 10 mL methanol was refluxed for 24 hours. After cooling, the mixture was made basic with sodium methoxide, poured into 50 mL water, and extracted with 50 mL pentane. The pentane extract was washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure at 0°C. Distillation afforded the dimethyl Ketal (1.80 g, 9.7 mmol, 68%) as a clear oil, B.P. 95-102°C at 6 mm.

A mixture of cyclononanone dimethyl ketal (1.50 g, 8.05 mmol) and ammonium dihydrogen phosphate (100 mg, 0.87 mmol) was heated slowly to 190°C and the methanol formed was collected by distillation. After methanol production stopped, the mixture was cooled and then distilled under reduced pressure to afford cis-1-methoxyclclononene (1.18 g, 7.65 mmol, 95%) as a clear oil, B.P. 76-78° C at 6 mm (lit.[71] 84-86°C at ca. 10 mm). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.46 (t, J = 8.5 Hz, 1H), 3.49 (s, 3H), 2.25-2.21 (m, 2H), 2.14-2.08 (m, 2H), 1.63-1.37 (m, 10H).

9-Methoxybicyclo[6.1.0]nonane (102)

The endo and exo isomers of 9-methoxybicyclo[6.1.0]nonane (102) were obtained by the method of Schollkopf and Paust.[72] Methyllithium (110 mL of 1.1 M, 121 mmol), prepared from methyl iodide, was added dropwife to a mechanically stirred mixture of cyclooctene (30 mL, 35.4 g, 230 mmol) and α,α-dichloromethyl methyl ether (4.0 mL, 5.08 g, 44.2 mmol). After 90 min, the mixture was cooled to 0°C and the excess methyllithium was quenched by the careful dropwise addition of 50 mL water. The aqueous and organic layers were separated and the organic layer was washed with water (4 x 50 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure at 0°C. The residue was distilled at reduced pressure to give 1.2 g (7.8 mmol, 18%) of a clear oil (after washing with sodium thiosulfate), B.P. 78-88°C at 7 mm (lit.[72] 98-100°C at 14 mm). GLC analysis (column C at 140°C) indicated two major components which were isolated on a preparative

scale (column E) and identified as follows. **exo-9-Methoxybicyclo[6.1.0]nonane** (exo-102, 27%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.31 (s, 3H), 2.61 (t, J = 2.5 Hz, 1H), 2.07-1.98 (m, 2H), 1.72-1.43 (m, 4H), 1.43-1.25 (m, 4H), 0.97-0.76 (m, 4H); **endo-9-Methoxybicyclo[6.1.0]nonane** (endo-102, 73%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.36 (s, 3H), 3.12 (t, J = 6.7 Hz, 1H), 1.85-1.72 (m, 2H), 1.72-1.52 (m, 4H), 1.46-1.28 (m, 6H), 0.68-0.54 (m, 2H).

1-(Methoxymethyl)cyclooctene (100)

Sodium borohydride (1.0 g, 26 mmol) was added in portions to a solution of cyclooctene-1-carboxaldehyde (2.0 g, 14.5 mmol) in 25 mL methanol at 0°C. After 30 min, the mixture was poured into 50 mL sat'd aqueous ammonium chloride and extracted with ether (2 x 50 mL). The ether extracts were combined, washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Distillation afforded cyclooctene-1-methanol (1.76 g, 12.6 mmol, 87%) as a clear oil, B.P. 60-61°C at 0.40 mm (lit.[73] 67.5-73°C at 0.5 mm).

1-(Methoxymethyl)cyclooctene was prepared from cyclooctene-1-methanol (1.5 g, 10.7 mmol), sodium hydride (1.5 g of 50% in oil, 31 mmol), and iodomethane (2.0 mL, 4.6 g, 32 mmol) by the procedure described above. 1-(Methoxymethyl)cyclooctene (1.39 g, 9.01 mmol, 84%) was obtained as a clear oil, B.P. 75-77°C at 6 mm. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.61 (t, J = 8.2 Hz, 1H), 3.81 (s, 2H), 3.29 (s, 3H), 2.20-2.11 (m, 4H), 1.60-1.40 (m, 8H).

1-Deuterio-1,2-cyclononadiene (8-d)

To a solution of 1-bromocyclooctene (9.4 g, 0.050 mol) in 50 mL dry THF, cooled to -78°C, was added dropwise a solution of t-butyllithium (48.0 mL of a 2.1 M sol'n, 0.101 mol). Stirring was continued for 60 min, a solution of D_2O (2.0 mL, 2.2 g, 0.11 mol) in 50 mL dry THF was then added dropwise, the mixture was warmed to room temperature, and stirring was continued an additional 120 min. The mixture was then diluted with 150 mL water and extracted with pentane (3 x 50 mL). The pentane extracts were combined, washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure at 0°C. Distillation afforded 1-deuteriocyclooctene (3.5 g, 0.031 mol, 63%) as a clear oil, B.P. 135-145°C. ^2H NMR analysis indicated that the deuterium was incorporated solely in the vinyl position, while ^1H NMR analysis indicated that there was ca. 100% deuterium incorporation at that site.

This material was converted to the deuterium substituted allene by the method described for the preparation of unlabeled 1,2-cyclononadiene (8). From 1-deuteriocyclooctene (3.4 g, 31 mmol) was obtained 1-deuterio-1,2-cyclononadiene (2.0 g, 16 mmol, 52% overall), B.P. 60-62°C at 10 mm. ^2H NMR analysis indicated that the deuterium was incorporated solely in the allenic position, while ^1H NMR analysis indicated that there was ca. 100% deuterium incorporation at that site.

Direct irradiation of 1-deuterio-1,2-cyclononadiene (8-d) in pentane

A solution of 201 mg of 1-deuterio-1,2-cyclononadiene (8-d) in 250 mL of pentane was irradiated for 120 min through a Vycor filter. The solution was concentrated under reduced pressure at 0°C to give 208 mg of a clear oil. GLC analysis (column E) indicated 3.3% conversion to bicyclo[6.1.0]non-1(9)-ene (84-d) with very little secondary chemistry observable (< 0.5%). ^{2}H NMR analysis of the crude product mixture indicated a ratio of 1.26:1 for the allylic cyclopropenyl signal (δ 1.43) to the vinylic signal (δ 6.45). The experiment was repeated an additional four times at slightly different conversions to give a mean value of 1.30 ± 0.06.

Partial resolution of 1,2-cyclononadiene (8)

Optically active 1,2-cyclononadiene (8) was prepared by the method of Byrd and Caserio.[33] Boron trifluoride etherate (9.0 mL, 10.4 g, 73 mmol) was added dropwise to a mixture of sodium borohydride (3.3 g, 87 mmol) and (+)α-pinene (23.2 mL, 20 g, 146 mmol), [α] = 46°, in 45 mL dry triglyme at 0°C. The mixture was stirred mechanically at 0°C for 20 hours. The suspension of sym-(+)-tetraisopinocampheyldiborane in triglyme was then cooled to -15°C and racemic 1,2-cyclononadiene (18.0 g, 147 mmol) was added rapidly. After 3 hours, the unreacted 1,2-cyclononadiene was recovered by distillation at reduced pressure (B.P. 55-85°C at 30 mm). The material obtained was taken up in pentane, washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure at 0°C. Distillation of the

residue afforded optically active 1,2-cyclononadiene (5.9 g, 48 mmol, 66%) containing a small amount of α-pinene. Pure samples of optically active 1,2-cyclononadiene were obtained by preparative scale GLC (column E) and had $[\alpha]_D$ = -23.7° (ca. 1.35, $CHCl_3$).

Irradiation of optically active 1,2-cyclononadiene (8)

A solution of 307 mg of 1,2-cyclononadiene, $[\alpha]_D$ = -23.7° (1.35, $CHCl_3$), in 300 mL of pentane was irradiated for 45 min through a Vycor filter. The solution was concentrated under reduced pressure at 0°C to give 320 mg of a slightly yellow oil. GLC analysis (column E) indicated 4% conversion to bicyclo(6.1.0)non-1(9)-ene (84). The cyclopropene and unreacted starting material were isolated on a preparative scale (column E) and their rotations were measured. Recovered 1,2-cyclononadiene (8) had a specific rotation, $[\alpha]_D$, of -3.2° (2.06, $CHCl_3$). No activity could be detected in the cyclopropene sample (ca. 10 mg/2 mL) down to 250 nm.

Several other experiments at different conversions of allene (1%-3%) gave similar results.

Singlet racemization of optically active 1,2-cyclononadiene (8)

A solution of 22 mg of 1,2-cyclononadiene, $[\alpha]_D$ = +29° (0.43, pentane), purified by preparative scale GLC (column E), in 5 mL of pentane was irradiated for 40 min through a Vycor filter. The rotation of the solution at 300 nm was monitored at 10 min intervals. The appearance of product (i.e., cyclopropene) was also

monitored at these intervals by GLC (column C) and the amount of 1 remaining was calculated. Data were plotted according to equation (1) in the text. A value of 70/1 (correlation coefficient = 0.99) was found for $k_{racemization}/k_{isomerization}$.

Benzene sensitized vapor phase irradiation of 1,2-cyclononadiene (8)

1,2-Cyclononadiene (180 mg) and benzene (260 mg) were placed into a 3.7 L Vycor tube, the bottom portion of the tube was cooled to -78°C, and the system was degassed by evacuating to ca. 0.15 mm and backflushing with nitrogen several times. After evacuating to 0.15 mm, the tube was allowed to warm to room temperature and was irradiated for 4.5 days in a Rayonet photoreactor fitted with 254 nm lamps. The reaction vessel was then cooled to -78°C, vented to nitrogen, and the product was collected with pentane. The pentane solution was filtered through neutral alumina and was concentrated under reduced pressure at 0°C to give 165 mg of a clear oil. Capillary GLC (column A) analysis indicated 97% conversion to 4 major products. These were isolated on a preparative scale (column E) and identified as follows. **Bicyclc[4.3.0]non-1(9)-ene** (147, 4%, rt 3.41 min): ^{1}H NMR δ 5.23 (t, 2.0 Hz, 1H), 2.5-2.4 (m, 1H), 2.4-2.3 (m, 1H), 2.3-2.2 (m, 2H), 2.15-2.0 (m, 1H), 2.0-1.85 (m, 2H), 1.8-1.7 (m, 2H), 1.4-1.1 (m, 3H), 0.94 (quartet d, 3.0 Hz, 9.0 Hz, 1H). ^{13}C NMR δ 146.4, 120.1, 45.6, 35.9, 31.1, 30.8, 30.0, 27.4, 26.2; **cis-Bicyclo[4.3.0]non-2-ene** (90, 2%, rt 3.67 min); **Bicyclo[4.3.0]non-1(2)-ene** (146, 5% rt 3.90 min): ^{1}H NMR δ 5.38 (br s, 1H), 2.4-1.4 (m,

11H), 1.1-0.9 (m, 2H). ^{13}C NMR δ 145.0, 116.9, 41.0, 33.6, 30.2, 29.2, 25.4, 23.3, 22.7; Tricyclo[4.3.0.$0^{2,9}$]nonane (10, 89%, rt 4.67 min).

In other experiments conducted at lower conversion (4%-36%), the ratio of photoproducts remained unchanged.

Benzene sensitized vapor phase irradiation of 1-deuterio-1,2-cyclononadiene (8-d)

1-Deuterio-1,2-cyclononadiene (15 ml) and benzene (10 ml) were placed into a 230 mL quartz tube and the system was cooled, degassed, and evacuated as above. After warming to room temperature, the mixture was irradiated for 60 min in a Rayonet photoreactor fitted with 254 nm lamps. The product was collected as above and concentrated under reduced pressure at 0°C to give 17 mg of a clear oil. GLC analysis (column E) indicated essentially complete reaction of starting material. The major product, tricyclo[4.3.0.$0^{2,9}$]nonane (10-d) was isolated on a preparative scale (column E). The ^{2}H NMR spectrum of isolated 10-d displayed two cyclopropyl resonances, at δ 1.27 and δ 0.78, of equal area within experimental error.

Thermolysis of tricyclo[4.3.0.$0^{2,9}$]nonane (10)

Tricyclo[4.3.0.$0^{2,9}$]nonane (120 mg) was passed slowly (45 min) through a horizontal quartz tube, packed with quartz chips, maintained at 660°C and at a pressure of 0.15 mm. The product was collected in a

cooled trap, rinsed out with pentane, and concentrated under reduced pressure at 0°C to give 130 mg of a yellow oil. Capillary GLC (column A) analysis indicated 66% conversion to 4 major products. These were isolated on a preparative scale (column E) and identified as follows. **1-Vinylcyclopentene** (**155**, 23%, rt 2.13 min): ^{1}H NMR δ 6.58 (dd, 17.1 Hz, 10.8 Hz, 1H), 5.72 (s, 1H), 5.05 (d, 17.1 Hz, 1H), 5.04 (d, 10.8 Hz, 1H), 2.42 (t, 7.4 Hz), 4H), 1.92 (quintet, 7.4 Hz, 2H); **Bicyclo[4.3.0]non-1(9)-ene** (**147**, 44%, rt 3.41 min); **Bicyclo[4.3.0]non-1(2)-ene** (**146**, 23%, rt 3.90 min); **Bicyclo[4.3.0]nona-1(6),7-diene** (**157**, 10%, rt 5.96 min): ^{1}H NMR δ 6.32 (dt, 5.3 Hz, 1.3 Hz, 1H), 6.22 (d, 5.3 Hz, 1H), 2.9-2.8 (m, 2H), 2.35-2.25 (m, 4H), 1.75-1.65 (m, 4H).

In experiments conducted at lower temperatures (540°C and 600°C), the proportions of 1-vinylcyclopentene (**155**) and bicyclo[4.3.0]nona-1(6),7-diene (**156**) were significantly decreased. At 540°C (0.15 mm), capillary GLC (column A) analysis indicated 4% conversion to bicyclo[4.3.0]non-1(9)-ene (**147**) and bicyclo[4.3.0]non-1(2)-ene (**146**) in a ratio of 1:1.

Benzene sensitized solution phase irradiation of 1,2-cyclononadiene (8)

A solution containing 177 mg of 1,2-cyclononadiene (**8**) and 157 mg of tetradecane (internal standard) in 300 mL of benzene was irradiated for 48 h through a Corex filter. GLC (column C, 100-125°C) analysis indicated 42% conversion of the allene at this time. GLC (column C, 100-125°C) analysis at various points throughout the irradiation

indicated the following isomeric products to be primary: **bicyclo-[6.1.0]non-1(9)-ene** (84, 2%) and **tricyclo[4.3.0.0^{2,9}]nonane** (10, 1%). A 20 mL aliquot of the crude reaction solution was concentrated under reduced pressure at ca. 5°C and the residue was analyzed by 300 MHz ^{1}H NMR. The following cycloadducts were observed: **meta-cycloadduct** (32, 35%); and **para-cycloadduct** (31, 6%). Spectral data (^{1}H NMR) were in agreement with those reported by Berridge et al.[9]

Triplet racemization of optically active 1,2-cyclononadiene (8)

A solution containing 23 mg of tetradecane (internal standard) and 22 mg of 1,2-cyclononadiene, $[\alpha]_D$ = +29° (0.43, pentane), purified by preparative scale GLC (column E), in 5 mL of benzene was irradiated for 60 min through a Corex filter. The rotation of the solution at 450 nm was monitored at 10 min intervals. The disappearance of starting material was also monitored by GLC (column C at 125°C) at these intervals. The data were plotted as before for the singlet. A value of 60/1 (correlation coefficient = 0.99) was found for k_{rac}/k_p. (This is the ratio of loss of rotation to reaction of starting allene.)

1-Methylcyclooctene

1-Methylcyclooctanol was prepared by the Grignard reaction of methylmagnesium iodide with cyclooctanone. From cyclooctanone (50.0 g, 0.40 mol), methyl iodide (50 mL, 0.80 mol), and magnesium (15 g, 0.62 mol) was obtained 1-methylcyclooctanol. The crude product was

taken up in 200 mL benzene, p-toluenesulfonic acid (ca. 200 mg) was added, the mixture was heated to reflux, and the water formed was removed using a Dean-Stark trap. After 5 hours, the solution was cooled, washed with saturated aqueous sodium bicarbonate, washed with water, dried over sodium sulfate, filtered, and the benzene was removed by distillation at atmospheric pressure. The residue was chromatographed over silica gel, eluting with hexane, to remove unreacted cyclooctanone present. Distillation afforded 1-methylcyclooctene (32.5 g, 0.26 mol, 65%) as a clear oil, B.P. 160-163°C. ^{1}H NMR (60 MHz, $CDCl_3$) δ 5.45 (t quartet, J=8Hz, J=1.5 Hz, 1H), 2.3-1.8 (m, 4H), 1.70 (d, J=1.5 Hz, 3H), 1.6-1.3 (m, 8H).

1-Methyl-1,2-cyclononadiene (83)

1-Methyl-1,2-cyclononadiene (**83**) was prepared by the method described for 1,2-cyclononadiene. From 1-methylcyclooctene (32.4g, 0.26 mol), bromoform (34.1 mL, 0.39 mol), and potassium t-butoxide (55.0 g, 0.49 mol) was obtained 1-methyl-9,9-dibromobicyclo[6.1.0]nonane (57.7 g, 0.19 mol, 75%) as a clear oil, B.P. 90-95°C at 0.10 mm.

Addition of methyllithium (110 mL of a 1.5 M solution, 0.165 mol) to a solution of the 1-methyl-9,9-dibromobicyclo[6.1.0]nonane (33.0 g, 0.111 mol) in dry ether at -30/-40°C and subsequent work up afforded 1-methyl-1,2-cyclononadiene (14.2 g, 0.104 mol, 94%) as a clear oil, B.P. 66-69°C at 7 mm (lit.[74] 66-67°C at 16 mm). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.17 (br s, 1H), 2.35-2.10 (m, 2H), 1.82-1.73 (m, 1H), 1.69 (d, J = 2.8 Hz, 3H), 1.65-1.45 (m, 7H), 1.45-1.25 (m, 2H).

Direct irradiation of 1-methyl-1,2-cyclononadiene (83) in pentane

A solution of 231 mg of 1-methyl-1,2-cyclononadiene (83) in 300 mL of pentane was irradiated for 5h through a Vycor filter. The solution was concentrated under reduced pressure at 0°C to give 246 mg of a clear oil. GLC (column C), capillary GLC (column B), and 300 MHz ^{1}H NMR analysis indicated 15% conversion to 10 products. These were isolated on a preparative scale (column G and column E) and the following were characterized by the identify of their capillary GLC (column B and column A) retention times and 300 MHz ^{1}H NMR spectra with those of authentic samples. The capillary GLC retention times listed are those observed on column B. **8-Methylbicyclo[6.1.0]non-1(9)-ene** (125, 21%, rt 6.73 min): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.54 (br s, 1H), 2.62 (dt, J=14.1 Hz, J=4.6 Hz, 1H), 2.29 (dddd, J=14.1 Hz, J=10.9 Hz, J=5.3 Hz, J=1.8 Hz, 1H), 1.88-1.76 (m, 1H), 1.63-1.23 (m, 8H), 1.13 (s, 3H), 1.10-0.96 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 132.2, 107.3, 37.4, 30.5, 27.1, 26.2, 25.8, 25.7, 25.0, 20.7. IR (GC-IR) 2935, 2866, 1771, 1454, 1373 cm^{-1}. MS, m/e 136, 121, 107, 93, 79, 67, **cis-8-Methylbicyclo[4.3.0]non-7-ene** (126, 31%, rt 7.21 min); **9-Methyltricyclo[4.3.0.0^{2,9}]nonane** (128, 2%, rt 7.53 min); **2-Methyltricyclo[4.3.0.0^{2,9}]nonane** (129, 2% rt 7.78 min); **cis-cis-2-Methyl-1,3-cyclononadiene** (135, 3%, rt 7.90 min); **cis-3-Methylbicyclo[4.3.0]non-2-ene** (127, 16%, rt 8.46 min); **3-Methylcyclononyne** (130, 19%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.55-2.45 (m, 1H), 2.18-2.12 (m, 2H), 1.83-1.73 (m, 1H), 1.73-1.32 (m, 9H), 1.07 (d, J=7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ

92.1, 86.6, 36.5, 30.3, 27.2, 26.9, 25.6, 24.0, 20,4, 19.2. IR (neat) 2964, 2930, 2860, 2231, 1456, 1373 cm^{-1}.

In other experiments, the reaction was monitored at low conversion (0.4-6%) and **125**, **127**, **128**, **129**, **127**, and **130** (ratio 26:22:3:4:10:24 at 0.4% conversion) were demonstrated to be primary products.

cis-8-Methylbicyclo[4.3.0]non-7-ene (126)

A solution of cis-bicyclo[4.3.0]nonan-8-one (0.50 g, 3.6 mmol) in 10 mL dry ether was added dropwise to a solution of methyllithium (5.0 mL of 1.6 M, 8.0 mmol) at room temperature. The reaction mixture was then heated to reflux and stirred for 60 min. After cooling, the mixture was carefully added to 25 mL saturated aqueous ammonium chloride, the aqueous and organic layers were separated, and the aqueous layer was extracted with ether (25 mL). The ether layers were combined, washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure to give cis-8-methylbicyclo[4.3.0]nonan-8-ol (0.53 g, 95%) as a clear oil.

A solution of the crude cis-8-methylbicyclo[4.3.0]nonan-8-ol (0.47 g, 3.0 mmol) in 3 mL dry DMSO was heated to 160°C and stirred for 24 hours. After cooling, the mixture was poured into 25 mL water and extracted with pentane (25 mL). The pentane extract was washed with water, dried over magnesium sulfate, filtered through neutral alumina, and concentrated under reduced pressure at 0°C to give **cis-8-Methylbicyclo[4.3.0]non-7-ene** (0.25 g, 1.8 mmol, 61%) as a clear oil. ^1H NMR (300 MHz, $CDCl_3$) δ 5.25 (t, J=4 Hz, 1H), 2.57-2.47 (m,

1H), 2.25-2.13 (m, 2H), 1.91 (dd, J=22 Hz, J=10 Hz, 1H), 1.71 (s, 3H), 1.65-1.20 (m, 8H).

cis-3-Methylbicyclo[4.3.0]non-2-ene (127)

Reaction of cis-bicyclo[4.3.0]nonan-3-one (0.50g, 3.6 mmol) with methyllithium (4.8 mL of a 1.5 M solution, 7.2 mmol) as described above gave cis-3-methylbicyclo[4.3.0]nonan-3-ol (0.54 g, 3.5 mmol, 97%) as a clear oil. GLC analysis (column D at 200°C) and 300 MHz ^{1}H NMR analysis indicated the product was a 50:50 mixture of the two potential epimeric alcohols.

A solution of the crude cis-3-methyl-bicyclo[4.3.0]nonan-3-ols (0.51 g, 3.31 mmol) in 5 mL dry DMSO was heated to 160°C and stirred for 24 hours. The reaction was worked up as above to give the product (0.28 g, 2.1 mmol, 63%) as a clear oil. Capillary GLC (column B) analysis indicated two components which were separated on a preparative scale (column E at 75°C) and identified as follows. **cis-3-Methylbicyclo[4.3.0]non-2-ene** (127, 81%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.34 (dd, J=1.7 Hz, J=1.4 Hz, 1H), 2.38-2.27 (m, 1H), 2.07-1.93 (m, 1H), 1.86 (t, J=6.1 Hz, 2H), 1.83-1.22 (m, 8H), 1.65 (s, 3H); **cis-3-Methylbicyclo[4.3.0]non-3-ene** (19%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.33 (br s, 1H), 2.15-1.87 (m, 4H), 1.87-1.55 (m, 6H), 1.65 (s, 3H), 1.45-1.30 (m, 2H).

Base catalyzed isomerization of 1-methyl-1,2-cyclononadiene (83)

1-Methyl-1,2-cyclononadiene (0.52 g, 3.8 mmol) was added to a solution of potassium t-butoxide (1.0 g, 8.9 mmol) in 5 mL dry DMSO. The mixture was stirred at room temperature for 21 hours, poured into 20 mL water, and extracted with pentane (30 mL). The pentane extract was washed with water, dried over magnesium sulfate, filtered through neutral alumina, and concentrated under reduced pressure at 0°C to afford the product mixture (0.403 g, 3.0 mmol, 78%) as a clear oil. GLC analysis (column C) indicated complete conversion of starting material to four products. The four components were isolated on a preparative scale (column E) and identified as follows. **cis-cis-2-Methyl-1,3-cyclononadiene (135, 28%):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.82 (d, J=10.7 Hz, 1H), 5.61 (dt, J=10.7 Hz, J=8.3 Hz, 1H), 5.37 (t, J=8.3 Hz, 1H), 2.09-2.00 (m, 4H), 1.70 (s, 3H), 1.65-1.55 (m, 2H), 1.47-1.37 (m, 4H); **cis-cis-1-Methyl-1,3-cyclononadiene (133,** 53%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.86 (d, J=10.7 Hz, 1H), 5.66 (dt, J=10.7 Hz, J=8.3 Hz, 1H), 5.59 (s, 1H), 2.13-2.04 (m, 4H), 1.74 (s, 3H), 1.60-1.40 (m, 6H); **cis-cis-2-Methyl-1,4-cyclononadiene (137,** 10%): ^{1}H NMR (300 MHz, $CDCl_3$) δ5.68 (dt, J=10.4 Hz, J=8.1 Hz, 1H), 5.53 (dt, J=10.4 Hz, J=8.4 Hz, 1H), 5.20 (t, J=8.3 Hz, 1H), 2.81 (d, J=8.1 Hz, 2H), 2.26-2.14 (m, 4H), 1.73 (s, 3H), 1.55-1.45 (m, 4H); **cis-cis-1-Methyl-1,4-cyclononadiene (136, 9%):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.60-5.44 (m, 2H), 5.27 (t, J=8.3 Hz, 1H), 2.78 (t, J=8.0 Hz, 2H), 2.28-2.15 (m, 4H), 1.67 (s, 3H), 1.65-1.45 (m, 4H).

1-Acetylcyclooctene

t-Butyllithium (92 mL of a 1.7 M solution, 0.156 mol) was added dropwise to a solution of 1-bromocyclooctene (14.7 g, 0.078 mol) in 40 mL dry THF at -78°C. After 60 min, a solution of N,N-dimethylacetamide (11 mL, 10.3 g, 0.12 mol) in 50 mL dry THF was added dropwise. The mixture was allowed to warm slowly to room temperature and stirring was continued overnight. Saturated aqueous ammonium chloride (100 mL) was added to the mixture at 0°C, the mixture was diluted with 100 mL pentane, and the aqueous and organic layers were separated. The organic layer was washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Distillation through 60 mm Vigreux column afforded 1-acetylcyclooctene (5.6 g, 0.037 mol, 47%) as a clear oil, B.P. 90-100°C at 5 mm (lit.[75] 105-107°C at 11 mm). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.87 (t, J=8.3 Hz, 1H), 2.46-2.42 (m, 2H), 2.38-2.30 (m, 2H), 2.31 (s, 3H), 1.67-1.57 (m, 2H), 1.57-1.38 (m, 6H).

1-Acetylcyclooctene tosylhydrazone (142)

1-Acetylcyclooctene (1.50 g, 9.85 mmol) was added to a stirring slurry of tosylhydrazide (1.84 g, 9.88 mmol) in 10 mL methanol. The mixture was stirred at room temperature for 60 min, cooled to 0°C, and the crystals were collected and washed with cold methanol. The filtrate (ca. 50 mL) was cooled at 0°C, water (ca. 10 mL) was added to induce crystallization, and a second crop of crystals were collected and washed with cold 75% aqueous methanol. The crystals were dried on

a vacuum line overnight with refluxing acetone warming. The desired tosylhydrazone (2.70 g, 8.43 mmol, 86%) was obtained as white crystals melting at 118-119°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, J=8.2 Hz, 2H), 7.52 (br s, 1H), 7.29 (d, J=8.2 Hz, 2H), 6.11 (t, J=8.2 Hz, 1H), 2.52-2.48 (m, 2H), 2.42 (s, 3H), 2.28-2.21 (m, 2H), 1.87 (s, 3H), 1.57-1.28 (m, 8H). IR (KBr) 3230, 3040, 2930, 2860, 1620, 1600, 1450, 1390, 1345, 1165, 920 cm^{-1}. Anal. Calcd. for $C_{17}H_{24}N_2O_2S$: C, 63.72; H, 7.55; N, 8.74. Found: C, 63.62; H, 7.54; N, 8.91.

Photolysis of the sodium salt of 1-acetylcyclooctene tosylhydrazone (142)

Reaction of 1-acetylcyclooctene tosylhydrazone (1.00 g, 3.12 mmol) at -15°C and as described above gave 0.218 g (1.60 mmol, 51%) of hydrocarbon product as a clear oil. Capillary GLC (column A) analysis indicated three components identified as follows. **9-Methylbicyclo[6.1.0]non-1(9)-ene** (141, 98%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.61 (ddd, J=14.4 Hz, J=5.7 Hz, J=3.9 Hz, 1H), 2.23-2.10 (m, 1H), 1.97 (d, J=2.0 Hz, 3H), 1.88-1.76 (m, 1H), 1.62-1.12 (m, 10H); **1-Methyl-1,2-cyclononadiene** (83, 1%); **1-Vinylcyclooctene** (143, 1%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.29 (dd, J=17.4 Hz, J=10.7 Hz, 1H), 5.71 (t, J=8.3 Hz, 1H), 5.11 (d, J=17.4 Hz, 1H), 4.91 (d, J=10.7 Hz, 1H).

3-Methylcyclonon-2-en-1-one

3-Methylcyclonon-2-en-1-one was prepared by the general procedure of Dauben and Michno.[76] Methyllithium (18 mL of a 1.5 M solution, 27 mmol) was added dropwise to a solution of cyclonon-2-en-1-one (3.07 g,

22.2 mmol) in 100 mL dry ether at -78°C. The mixture was allowed to warm to room temperature and stirred for 2 hours. Water (50 mL) was then added carefully at 0°C, the aqueous and organic layers were separated, and the aqueous layer was extracted with ether (25 mL). The ether layers were combined, washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure.

The crude 1-methylcyclonon-2-en-1-ol in 20 mL methylene chloride was added to a stirring slurry of pyridinium chlorochromate (9.6 g, 44.5 mmol) in 60 mL methylene chloride and the mixture was stirred at room temperature for 2 hours. The mixture was then diluted with 100 mL ether, the solution was decanted from the black residue, and the residue was washed with ether. The product solution was washed with 5% aqueous sodium hydroxide (2 x 200 mL), water (200 mL), 5% aqeous hydrochloric acid (2 x 200 mL), water (200 mL), saturated aqueous sodium bicarbonate (200 mL), and water (200 mL). The solution was then dried over sodium sulfate, filtered, and concentrated under reduced pressure. Capillary GLC (column B at 150°C) analysis indicated one major component (the desired product) and six minor components. The crude material was chromatographed over silica gel (3 cm x 60 cm column) eluting with 10% ether/hexanes and collecting fractions in 150 mL increments. Fractions 5-7 contained material with > 95% purity by capillary GLC (column B at 150°C) analysis. These fractions were combined, concentrated under reduced pressure, and distilled to give 3-methylcyclonon-2-en-1-one (0.68 g, 4.5 mmol, 20%) as a clear oil, B.P. 103-105°C at 4.8 mm. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.00 (s, 1H), 2.71-2.67

(m, 2H), 2.61-2.57 (m, 2H), 1.94 (t, J=1.3 Hz, 3H), 1.87-1.77 (m, 2H), 1.65-1.54 (m, 4H), 1.46-1.36 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 205.6, 153.4, 130.5, 40.9, 31.0, 28.7, 28.4, 27.2, 26.7, 24.3. IR (neat) 2920, 2860, 1640, 1470, 1440, 1225, 1165 cm^{-1}. MS, m/e 152, 137, 109, 95, 82, 67, high resolution MS (M^+) 152.1198 (calculated 152.1201).

3-Methylcyclonon-2-en-1-one tosylhydrazone (131)

3-Methylcyclonon-2-en-1-one (0.50 g, 3.3 mmol) was added to a stirring suspension of tosylhydrazide (0.61 g, 3.3 mmol) in 10 mL benzene. The mixture was stirred at room temperature for 60 min, cooled to 0°C, and pentane was added to induce crystallization. The crystals were collected, washed with pentane, and dried to give the desired tosylhydrazone (0.57 g, 1.8 mmol, 55%) as off-white crystals melting at 108-112°C. ^1H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, J=8.2 Hz, 2H), 7.62 (br s, 1H), 7.29 (d, J=8.2 Hz, 2H), 5.35 (d, J=1.2 Hz, 1H), 2.42 (s, 3H), 2.36-2.31 (m, 2H), 1.77 (d, J=1.2 Hz, 3H), 1.81-1.74 (m, 1H), 1.65-1.55 (m, 3H), 1.45-1.25 (m, 6H). IR (KBr) 3195, 2920, 2850, 1645, 1595, 1440, 1380, 1330, 1155, 1035 cm^{-1}. Anal. Calcd. for $C_{17}H_{24}N_2O_2S$: C, 63.72; H, 7.55; N, 8.74. Found: C, 63.44; H, 7.71; N, 8.85.

Photolysis of the sodium salt of 3-methylcyclonon-2-en-1-one tosylhyrazone (131)

Reaction of 3-methylcyclonon-2-en-1-one tosylhydrazone (250 mg, 0.78 mmol) as described above gave 87 mg (0.64 mmol, 82%) of hydro-

carbon product as a clear oil. Capillary GLC (column B) analysis indicated five components. These were isolated on a preparative scale (column G) and were characterized by the identify of their capillary GLC (column B) retention times and 300 MHz ^{1}H NMR spectra with those of authentic samples, with the exception of cis-trans-2-methyl-1,3-cyclononadiene. cis-trans-2-Methyl-1,3-cyclononadiene was characterized by its 300 MHz ^{1}H NMR spectrum, and by its facile photoisomerization to cis-cis-2-methyl-1,3-cyclononadiene, an authentic sample of which was in hand. Products were identified as follows. **8-Methylbicyclo[6.1.0]non-1(9)-ene** (125, 30%, 6.71 min); **cis-8-Methylbicyclo[4.3.0]non-7-ene** (126, 9%, 7.15 min); **cis-3-Methylbicyclo[4.3.0]non-2-ene** (127, 36%, 8.45 min); **cis-cis-1-Methyl-1,3-cyclononadiene** (133, 19%, 8.68 min); **cis-trans-2-Methyl-1,3-cyclononadiene** (134, 5%, 9.04 min): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.69 (d, J=16.3 Hz, 1H), 5.56-5.45 (m, 2H), 2.40-2.15 (m, 2H), 2.15-1.90 (m, 2H), 1.75-1.25 (m, 6H), 1.78 (s, 3H).

Direct irradiation of cis-cis-1-methyl-1,3-cyclononadiene (133)

A solution of 65 mg of cis-cis-1-methyl-1,3-cyclononadiene (133) in 300 mL of pentane was irradiated for 15 min through a Vycor filter. The solution was concentrated under reduced pressure at 0°C to give 73 mg of a clear oil. Capillary GLC (column B) and 300 MHz ^{1}H NMR analysis indicated 61% conversion to 3 major products. These were isolated on a preparative scale (column G at 95°C) and identified by their 300 MHz ^{1}H NMR spectra, with the exception of cis-cis-2-methyl-

1,3-cyclononadiene (135), which was characterized by the identity of its capillary GLC retention time and 300 MHz ^{1}H NMR spectrum with those of an authentic sample. Products were identified as follows. **cis-cis-5-Methyl-1,3-cyclononadiene** (12%, rt 7.34 min): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.86 (d, J=11.1 Hz, 1H), 5.78 (d, J=11.2 Hz, 1H), 5.73-5.63 (m, 1H), 5.33 (t, J=11 Hz, 1H), 2.53-2.43 (m, 1H), 2.23-2.10 (m, 1H), 2.10-1.95 (m, 1H), 1.80-1.15 (m, 6H), 0.93 (d, J=6.7 Hz, 3H); **cis-cis-2-Methyl-1,3-cyclononadiene** (135, 51%, rt 7.88 min); **trans-cis-1-Methyl-1,3-cyclononadiene** (23%, rt 9.36 min): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.21 (d, J=11.2 Hz, 1H), 5.77-5.68 (m, 1H), 5.66 (br s, 1H), 2.2-0.6 (m, 10H), 1.60 (s, 3H).

Vapor phase benzene sensitized irradiation of 1-methyl-1,2-cyclononadiene (83)

1-Methyl-1,2-cyclononadiene (350 ml) and benzene (500 ml) were placed into a 3.7 L Vycor tube, the system was degassed as described previously, and the vapor phase mixture was irradiated for 5 days in a Rayonet photoreactor fitted with 254 nm lamps. The reaction vessel was then cooled to -78°C, vented to nitrogen, and the product was collected in pentane. The pentane solution was filtered through neutral alumina and was concentrated under reduced pressure at 0°C to give 294 mg of a clear oil. Capillary GLC (column A) analysis indicated 97% conversion to 6 major products. These were isolated on a preparative scale (column E at 80°C) and identified as follows. **9-Methyltricyclo[4.3.0.0^{2,9}]nonane** (128, 46%, rt 3.91 min): ^{1}H NMR

(300 MHz, $CDCl_3$) δ 2.50-2.42 (m, 1H), 2.30-2.15 (m, 1H), 1.88-1.78 (m, 3H), 1.62-1.54 (m, 1H), 1.41-1.20 (m, 6H), 1.11 (s, 3H), 0.70-0.64 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 38.2, 33.8, 32.8, 31.3, 28.6, 28.0, 24.5, 23.9, 19.2, 17.2. IR (neat) 3020, 2990, 2940, 2870, 1480, 1450 cm^{-1}. high resolution MS (M^+) 136.1249 (calculated 136.1252); **2-Methyltricyclo[4.3.0.0^{2,9}]nonane** (129, 41%, rt 4.20 min): ^1H NMR (300 MHz, $CDCl_3$) δ 2.46-2.40 (m, 1H), 2.23-2.08 (m, 1H), 1.94-1.53 (m, 4H), 1.47-1.25 (m, 6H), 1.08 (td, J-7.4 Hz, J=2.0 Hz, 1H), 0.90 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 40.1, 33.8, 33.4, 31.3, 28.8, 28.7, 27.1, 26.9, 21.1, 18.3. IR (neat) 3020, 2940, 2880, 1480, 1450 cm^{-1}, high resolution MS (M^+) 136.1254 (calculated 136.1252); **Unidentified** (2%, rt 4.39 min): may correspond to cis-1-methylbicyclo[4.3.0]non-2-ene; **9-Methylbicyclo[4.3.0]non-1(9)-ene** (148, 3%, rt 4.59 min); **cis-3-Methylbicyclo[4.3.0]non-2-ene** (127, 2%, rt 4.75 min); **2-Methylbicyclo[4.3.0]non-1(2)-ene** (149, 4%, rt 5.39 min).

^1H NMR (300 MHz) analysis of the 9-methyltricyclo[4.3.0.0^{2,9}]-nonane (128) obtained by preparative scale GLC indicated that a minor product having two vinylic hydrogens was present. This unidentified olefinic product did not resolve from 128 by capillary GLC analysis (column A), however, 300 MHz ^1H NMR analysis of the crude reaction mixture indicated it is formed in ca. 2-4% yield. The percentage of 128 listed above is corrected for this impurity.

Trace amounts of endo-2-methylbicyclo[4.3.0]non-1(9)-ene (151) and endo-9-methylbicyclo[4.3.0]non-1(2)-ene (150) were observed in the

mixture by capillary GLC (column B) analysis and 300 MHz ^{1}H NMR analysis.

In other experiments conducted at lower conversion (18-40%), the ratio of photoproducts remained unchanged.

Thermolysis of 2-methyltricyclo[4.3.0.0^{2,9}]nonane (129)

Flash vacuum thermolysis of 2-methyl-tricyclo[4.3.0.0^{2,9}]nonane (35 mg) at 620°C and 0.15 mm, by the procedure described above, afforded 30 mg of a clear oil. Capillary GLC (column B) analysis indicated 64% conversion to 3 major products. These were isolated on a preparative scale (column E at 80°C) and identified as follows. **1-Isopropenylcyclopentene (160, 6%, rt 3.92 min):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.78-5.75 (m, 1H), 4.88 (d, J=6 Hz, 2H), 2.52-2.42 (m, 4H), 1.97-1.87 (m, 2H), 1.93 (s, 3H); **endo-2-Methylbicyclo[4.3.0]non-1(9)-ene (151, 45%, rt 7.88 min):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.22 (t, J=2.0 Hz, 1H), 2.48-2.32 (m, 1H), 2.32-2.23 (m, 2H), 2.17-1.88 (m, 3H), 1.78-1.67 (m, 2H), 1.49-1.31 (m, 2H), 1.08 (d, J=6.5 Hz, 3H), 1.00-0.82 (m, 2H); **2-Methylbicyclo[4.3.0]non-1(2)-ene (149, 45%, rt 9.25 min):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.27-2.15 (m, 2H), 2.15-2.01 (m, 1H), 2.01-1.65 (m, 6H), 1.57 (s, 3H), 1.53-1.40 (m, 2H), 1.05-0.90 (m, 2H).

Thermolysis of 9-methyltricyclo[4.3.0.0^{2,9}]nonane (128)

Flash vacuum thermolysis of 9-methyl-tricyclo[4.3.0.0^{2,9}]nonane (37 mg) at 620°C and 0.15 mm, by the procedure described above,

afforded 42 mg of a clear oil. Capillary GLC (column B) analysis indicated 51% conversion to 3 major products. These were isolated on a preparative scale (column G at 95°C) and identified as follows. **1-Vinyl-5-Methylcyclopentene** (158, 6%, rt 3.27 min): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.45 (dd, J=17.5 Hz, J=10.7 Hz, 1H), 5.66 (t, J=2.5 Hz, 1H), 5.13 (d, J=17.5 Hz, 1H), 5.04 (d, J=10.7 Hz, 1H), 2.95-2.85 (m, 1H), 2.50-2.05 (m, 3H), 1.65-1.57 (m, 1H), 1.07 (d, J=6.9 Hz, 3H); endo-**9-Methylbicyclo[4.3.0]non-1(2)-ene** (150, 38%, rt 8.26): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.32 (br s, 1H), 2.50-2.35 (m, 1H), 2.30-2.15 (m, 1H), 2.10-1.90 (m, 3H), 1.90-1.68 (m, 3H), 1.67-1.32 (m, 2H), 1.32-1.09 (m, 2H), 1.01 (d, J=6.8 Hz, 3H); **9-Methylbicyclo[4.3.0]non-1(9)-ene** (148, 56%, 8.38 min): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.53-2.43 (m, 1H), 2.43-2.33 (m, 1H), 2.30-2.17 (m, 2H), 2.07-1.95 (m, 1H), 1.95-1.85 (m, 1H), 1.82-1.65 (M, 3H), 1.60 (s, 3H), 1.40-1.22 (m, 2H), 1.22-1.06 (m, 1H), 1.0-0.85 (m, 1H).

Partial resolution of 1-methyl-1,2-cyclononadiene (83)

Optically active 1-methyl-1,2-cyclononadiene (83) was prepared by the same method used to resolve the parent allene, 1,2-cyclononadiene (8). From racemic 1-methyl-1,2-cyclononadiene (13.6 g, 0.100 mol), sodium borohydride (2.1 g, 0.055 mol), (+)-α-pinene with [α] = +46° (15.9 mL, 13.6 g, 0.100 mol), and boron trifluoride etherate (6.1 mL, 7.0 g, 0.050 mol) was obtained optically active 1-methyl-1,2-cyclononadiene (5.51 g, 0.040 mol, 81%) containing a small amount of α-pinene. A pure sample of optically active 1-methyl-1,2-cyclononadiene

(83), fraction 3 (B.P. 63-64°C at 7 mm) of the above product, had $[\alpha]_D$ = +66.8° (ca. 2.5, $CDCl_3$).

Benzene sensitized vapor phase irradiation of optically active 1-methyl-1,2-cyclononadiene (83)

A vapor phase mixture of optically active 1-methyl-1,2-cyclononadiene (150 µl) and benzene (750 µl) was irradiated as above for 16 hours. GLC analysis (column H) of the product mixture indicated near complete conversion to the two tricyclic products, 128 and 129, present as the major components. These were isolated on a preparative scale (column G) and analyzed for optical activity. No activity could be detected in either sample (ca. 30 mg/2mL) at 589 nm.

BIBLIOGRAPHY

1. Steinmetz, M.G.; Srinivasan, R.; Leigh, W.J. Rev. Chem. Intermed. 1984, 5, 57.

2. Johnson, R.P. Org. Photochem. 1985, 17, in press.

3. Ward, H.R.; Karafiath, E. J. Am. Chem. Soc. 1969, 91, 7475.

4. Ward, H.R.; Karafiath, E. J. Am. Chem. Soc. 1968, 90, 2193.

5. Ward, H.R.; Karafiath, E. J. Am. Chem. Soc. 1969, 91, 522.

6. Karan, H.I. J. Org. Chem. 1981, 46, 2186.

7. Collin, J.; Lossing, F.P. Can. J. Chem. 1957, 35, 778.

8. Bryce-Smith, D.; Foulger, B.E.; Gilbert, A. J. Chem. Soc., Chem. Commun. 1972, 664.

9. Berridge, J.C.; Forrester, J.; Foulger, B.E.; Gilbert, A. J. Chem. Soc. Perkin I 1980, 2425.

10. Morikawa, A.; Brownstein, S.; Cvetanović, R.J. J. Am. Chem. Soc. 1979, 92, 1471.

11. Wilzbach, K.E., Kaplan, L. J. Am. Chem. Soc. 1971, 93, 2073.

12. Feree, W.I.; Grutzner, J.B.; Morrison, H. J. Am. Chem. Soc. 1971, 93, 5502.

13. Doepker, R.D.; Hill, D.L. J. Phys. Chem. 1969, 73, 1313.

14. Diaz, Z., Doepker, R.D. J. Phys. Chem. 1977, 81, 1442.

15. Chapman, O.L. Pure Appl. Chem. 1975, 40, 511.

16. Steinmetz, M.G.; Mayes, R.T.; Yang, J.-C. J. Am. Chem. Soc. 1982, 104, 3518.

17. Klett, M.W.; Johnson, R.P. Tetrahedron Lett. 1983, 24, 2523.

18. Klett, M.W.; Johnson, R.P. J. Am. Chem. Soc., in press.

19. Steinmetz, M.G.; Stark, E.J.; Yen, Y.-P.; Mayes, R.T. J. Am. Chem. Soc. 1983, 105, 7209.

20. Borden, W.T. Ph.D. Dissertation, Harvard University, Cambridge, Mass., 1968.

21. Rodriguez, O.; Morrison, H. J. Chem. Soc., Chem. Commun. 1971, 679.

22. Hornback, J.M. "17th Annual Report on Research Under Sponsorship of the Petroleum Research Fund"; American Chemical Society: Washington, D.C., 1972; p. 121.

23. Fujita, K.; Matsui, K.; Shono, T. J. Am. Chem. Soc. 1975, 97, 6256.

24. Klett, M.W.; Johnson, R.P. Tetrahedron Lett. 1983, 24, 1107.

25. Rafizadeh, K.; Yates, K. J. Org. Chem. 1984, 49, 1500.

26. Osborn, C.L.; Shields, T.C.; Shoulders, B.A.; Krause, J.F.; Cortez, H.U.; Gardner, P.D. J. Am. Chem. Soc. 1965, 87, 3158.

27. a. Suda, M. Tetrahedron Lett. 1980, 21, 4355.
b. Baird, M.S.; Nethercott, W. Tetrahedron Lett. 1983, 24, 605.

28. Crandall, J.K.; Watkins, R.J. Tetrahedron Lett. 1970, 1251.

29. Vaidyanathaswamy, R.; Devaprabhakara, D. Indian J. Chem. 1975, 13, 873.

30. Stierman, T.J.; Johnson, R.P. J. Am. Chem. Soc. 1983, 105, 2492.

31. a. Shumate, K.M.; Neuman, P.N.; Fonken, G.J. J. Am. Chem. Soc. 1965, 87, 3996.
b. Shumate, K.M.; Fonken, G.J. J. Am. Chem. Soc. 1966, 88, 1073.

32. a. Bellesia, F.; Grandi, F.; Pagnoni, U.M. J. Chem. Res., Synop. 1981, 114.
b. Grandi, R.; Pagnoni, U.M.; Travej, R. J. Chem. Res., Synop. 1979, 246.

33. Byrd, L.R.; Caserio, M.C. J. Am. Chem. Soc. 1971, 93, 5758.

34. Wagner, P.J.; Kelso, P.A.; Zepp, R.G. J. Am. Chem. Soc. 1972, 94, 7480.

35. Kirmse, W.; Hellwig, G. Chem. Ber. 1982, 115, 2744.

36. Honjou, N.; Pacansky, J.; Yoshimine, M. J. Am. Chem. Soc. 1984, 106, 5361.

37. Steinmetz, M.G.; Yen, Y.-P.; Poch, G.C. J. Chem. Soc., Chem. Commun. 1983, 1504.

38. Davis, J.H.; Goddard, W.A.; Bergman, R.G. J. Am. Chem. Soc. 1977, 99, 2427.

39. Padwa, A. Org. Photochem. 1979, 4, 261.

40. Price, J.D.; Johnson, R.P. Tetrahedron Lett. 1985, in press.

41. Brun, P.; Casanova, J.; Hatem, J. Bull. Soc. Chim. Fr. 1977, 521.

42. Becker, K.B. Helv. Chim. Acta 1977, 60, 68.

43. Price, J.D. Masters Thesis, Iowa State University, Ames, Iowa, 1985.

44. Monti, S.A. J. Org. Chem. 1970, 35, 380.

45. Dane, L.M.; de Haan, J.W.; Kloosterziel, H. Tetrahedron Lett. 1970, 2755.

46. Balata, F.; Dello Jacono, A.R.; Gambacorta, A. J. Org. Chem. 1983, 48, 566.

47. Inoue, Y.; Ueda, Y.; Hakushi, T. J. Am. Chem. Soc. 1981, 103, 1806.

48. Zimmerman, H.E.; Pincock, J.A. J. Am. Chem. Soc. 1973, 95, 2957.

49. Dupuis, M.; Spangler, D.; Wendoloski, J.J. NRCC Software Catalog 1, Prog. No. QG01 (GAMESS), Lawrence Berkeley Laboratory, University of California, Berkeley, CA, 1980.

50. Davidson, E.R. "Diradicals"; Borden, W.T.; Editor; Wiley-Interscience: New York, 1982, Chapter 2, p. 73.

51. Baird, N.C.; Taylor, K.F. J. Am. Chem. Soc. 1978, 100, 1333.

52. Reudenberg, K.R.; Valtazanos, P., Department of Chemistry, Iowa State University, Ames, Iowa, to be published.

53. Bodor, N.; Dewar, M.J.S.; Wasson, J.S. J. Am. Chem. Soc. 1972, 94, 9095.

54. Angus, R.O., Jr.; Schmidt, M.W.; Johnson, R.P. J. Am. Chem. Soc. 1985, 107, 532.

55. Roth, W.R.; Ruf, G.; Ford, P.W. Chem. Ber. 1974, 107, 48.

56. Mosher, O.A.; Flicker, W.M.; Kuppermann, A. J. Chem. Phys. 1975, 62, 2600.

57. Schaad, L.J.; Burnelle, L.A.; Dressler, K.P. Theor. Chim. Acta 1969, 15, 91.

58. Schmidt, M.W.; Lee, E.K.C. J. Am. Chem. Soc. 1970, 92, 3579.

59. Borden, W.T. Tetrahedron Lett. 1967, 5, 447.

60. Price, J.D.; Johnson, R.P. J. Am. Chem. Soc. 1985, 107, 2187.

61. Skattebol, L.; Soloman, S. Org. Syn. 1973, coll. vol. 5, p. 306.

62. Granger, R.; Nau, P.; Nau, J. Bull. Soc. Chim. Fr. 1958, 531.

63. Huckel, W.; Friedrich, H. Justus Liebigs Ann. Chem. 1927, 451, 132.

64. Cardenas, C.G.; Shoulders, B.A.; Gardner, P.D. J. Org. Chem. 1967, 32, 1220.

65. Blomquist, A.T.; Liu, L.H.; Bohrer, J.C. J. Am. Chem. Soc. 1952, 74, 3643.

66. Meier, H.; Menzel, I. Synthesis 1971, 215.

67. Santelli, M.; Bertrand, M.; Ronco, M. Bull. Soc. Chim. Fr. 1964, 3273.

68. Wittig, G.; Dorsch, H.-L. Justus Liebigs Ann. Chem. 1968, 711, 46.

69. Neumann, H.; Seebach, D. Chem. Ber. 1978, 111, 2785.

70. Mehta, G. Org. Prep. & Proc. 1970, 2, 245.

71. Taskinen, E. Acta Chem. Scand., Ser. B 1980, B34, 643.

72. Schollkpft, U.; Paust, J. Chem. Ber. 1965, 98, 2221.

73. Cope, A.C.; Burton, P.E. J. Am. Chem. Soc. 1960, 82, 5439.

74. Moorthy, S.N.; Vaidyanathaswamy, R.; Devaprabhakara, D. Synthesis 1975, 194.

75. Olah, G.A.; Fung, A.P. Synthesis 1981, 473.

76. Dauben, W.G.; Michno, D.M. J. Org. Chem. 1977, 42, 682.

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